12-2002

Exciplex Tuning and Optical Memory Studies for Dicyanoargentate(1) and Dicyanoaurate(1) Ions Doped in Potassium Chloride Crystals Extension to Mixed Metal Gold and Silver Systems

Samanthika Ruvinie Hettiarachchi

Follow this and additional works at: http://digitalcommons.library.umaine.edu/etd

Recommended Citation
Hettiarachchi, Samanthika Ruvinie, "Exciplex Tuning and Optical Memory Studies for Dicyanoargentate(1) and Dicyanoaurate(1) Ions Doped in Potassium Chloride Crystals Extension to Mixed Metal Gold and Silver Systems" (2002). Electronic Theses and Dissertations. 204.
http://digitalcommons.library.umaine.edu/etd/204

This Open-Access Dissertation is brought to you for free and open access by DigitalCommons@UMaine. It has been accepted for inclusion in Electronic Theses and Dissertations by an authorized administrator of DigitalCommons@UMaine.
EXCIPEX TUNING AND OPTICAL MEMORY STUDIES FOR
DICYANOARGENTATE(I) AND DICYANOAURATE(I) IONS DOPED IN
POTASSIUM CHLORIDE CRYSTALS. EXTENSION TO MIXED METAL
GOLD AND SILVER SYSTEMS

By
Samanthika Ruvinie Hettiarachchi

B.Sc (Special Degree in Chemistry), University of Ruhuna, Sri Lanka, 1996

A THESIS
Submitted in Partial Fulfillment of the
Requirements for the Degree of
Doctor of Philosophy
(in Chemistry)

The Graduate School
The University of Maine
December, 2002

Advisory Committee:
Howard H. Patterson, Professor of Chemistry, Advisor
Carl P. Tripp, Associate Professor of Chemistry
François G. Amar, Associate Professor of Chemistry
Alice E. Bruce, Associate Professor of Chemistry
Alla Gamarnik, Assistant Professor of Chemistry
EXCIPLEX TUNING AND OPTICAL MEMORY STUDIES FOR
DICYANOARGENTATE(I) AND DICYANOAURATE(I) IONS DOPED IN
POTASSIUM CHLORIDE CRYSTALS. EXTENSION TO MIXED METAL
GOLD AND SILVER SYSTEMS

By Samanthika Ruvinie Hettiarachchi

Advisor: Dr. Howard H. Patterson

An Abstract of the Thesis Presented
in Partial Fulfillment of the Requirements for the
Degree of Doctor of Philosophy
(in Chemistry)
December, 2002

Exciplex tuning and optical memory behavior of [Ag(CN)2⁻] and [Au(CN)2⁻] ions
doped in KCl host crystals, pure KAg(CN)2, and pure KAu(CN)2 have been studied.
Additionally, d¹⁰⁻d¹⁰ (KAu(CN)2-KAg(CN)2) and d¹⁰⁻d⁸ (KAu(CN)2, KAg(CN)₂-K₂Pt(CN)₄)
mixed metal systems have been synthesized and characterized.

Several ultraviolet and visible emission bands are observed for [Ag(CN)2⁻] and
[Au(CN)2⁻] ions doped in KCl host crystals. Each emission band becomes dominant at a
characteristic excitation wavelength: that is the energy of the emission can be tuned by
site-selective spectroscopy. Luminescence, Raman and theoretical results suggest the
formation of Au-Au and Ag-Ag bonded excimers and exciplexes between adjacent
[Ag(CN)2⁻] and [Au(CN)2⁻] ions in the host lattice. The emission and Raman bands are
assigned to different [Ag(CN)$_2$]$^-$ and [Au(CN)$_2$]$^-$ exciplexes. These results give rise to a new optical phenomenon called "exciplex tuning".

When a single crystal of [Ag(CN)$_2$]/KCl at 77 K is irradiated with 266 nm laser light, the intensity of the high energy peak at 338 nm is increased with increasing exposure time and, concurrently, the intensity of the low energy peak at 415 nm is decreased. This process is reversible; that is, heating the crystal to room temperature restores the crystal to its original state. This phenomena of "optical memory" and erasure of the optical memory has been studied for both [Ag(CN)$_2$]$^-$ ions and [Au(CN)$_2$]$^-$ ions doped with varying concentrations in KCl as well as with pure KAg(CN)$_2$ and pure KAu(CN)$_2$ single crystals.

The d$^{10}$-d$^{10}$ mixed metal system (KAu(CN)$_2$-KAg(CN)$_2$) shows Ag-Au delocalization in the lowest energy excited electronic state. Observed luminescence in this d$^{10}$-d$^{10}$ mixed system is strongly tunable; that is, the emission energy of this system can be tuned by varying physical parameters such as excitation wavelength, temperature, and the Ag/Au ratio.

The d$^{10}$-d$^8$ mixed metal system (KAu(CN)$_2$, KAg(CN)$_2$-K$_2$Pt(CN)$_4$) represents an example of energy transfer between d$^{10}$ and d$^8$ systems. In other words, the lowest excited state energy of KAu(CN)$_2$ or KAg(CN)$_2$ can be transferred to the lowest excited state of K$_2$Pt(CN)$_4$. 
This thesis is dedicated to my loving husband, two daughters, parents, two sisters and brother.
ACKNOWLEDGMENTS

First and foremost, my utmost thank is to my loving husband, Jinasena, who stood behind me during the past six years. Without his encouragement, help and patience, I would not have come this far. My words are not sufficient to explain how my daughters, Nethmi, and Sithmi helped me to have an enjoyable life after having them. Specially, Nethmi’s adorable activities helped me to forget all the stress I had while in the laboratory. My life was further delighted after having Sithmi at the last moment of my thesis work. My family and Jinasena’s family members should deserve many thanks for their continuous support. Particularly, my mother must deserve special thanks for coming here twice to help me.

I would like to express my special thanks to my thesis advisor, Professor Howard H. Patterson for his guidance throughout my research career. His “typical behavior” of motivating students to work all the time, helped me to finish my research work on time.

It is immense pleasure to thank and express my indebtedness to Professor Alice E. Bruce who encouraged and helped me to get admission to the University of Maine. Her kind advice and patience helped me to overcome my difficulties ever since I came here. I would also like to thank her for serving on my committee. My sincere thanks are offered to Professor Carl P. Tripp for all his help and for serving on my committee. Specially, his help with the Raman instrument has been invaluable. Also, his useful discussions about my research made my work easier. My sincere thanks are extended to Professors Farçois G. Amar and Alla Gamarnik for their help and for serving on my committee.
always appreciate Professor Amar's great help and understanding given to me and Jinasena. Also, Professor Gamarnik's friendliness is very much appreciable.

Much of my research work would not have been possible without help from David Labrecque, the research associate and the instrumentation specialist in our department. Specially, his help with the lifetime and Raman instruments is greatly appreciated.

I would like to thank Professor Mitchell Bruce for his help whenever needed. My gratitude also goes to Professor Bruce Jensen for his help with the ATR/FTIR spectrometer even though I haven't include any data in this thesis. I would like to offer my special thanks to Professor Jayendran Rasaiah for his friendship. I would also like to offer my sincere gratitude to Robert Kirk for his help and friendship during teaching labs.

I would also like to express my sincere thanks to Dr. Sofian Kanan for all his help specially, with carrying out Raman experiments. I would also like to express my appreciation to Marsha Kanan for her friendship and help. Sincere thanks are also extended to Dr. Mohammad Omary for his advice, encouragement and help given to me. Thanks are also offered to Nattapong Srisook, a previous group member, who trained me how to use a fluorescence spectrophotometer.

I would like to thank specially to Julie Colis, a group member, for her help and friendship. I have always enjoyed having her as a close friend. I would also like to thank the rest of the group members, Eric Arehart, Bjorn Lake, as well as Manal Omary, Christie Larochelle, and Hank Tracy for their friendship. Also, my thanks are given to James Smaby and Catherine Talley for their friendship and help.
I will never forget Koneshan Sivapathasundram, Devanadan Loganathan and Doreen Thompson for their help given to us when we first came here. I would also like to thank Marybeth Judy, Diane Judy, Sukla Lakshman, Dilip Lakshman, Aparna Waghe, Anil Waghe, Ahmed Mohammad and Hanan Abdau for their friendship.

I would like to express my thanks to Cindy Commeau, Margaret Forbes, and Linda Maynard for their help and friendship. Thanks are also extended to all graduate students in the department of chemistry, specially, Scott Larkin who helped me moving liquid nitrogen tanks.

Last, but not the least, many thanks are offered to the University of Maine Chemistry Department for financial support and a teaching assistantship. I would also like to express my appreciation to the Petroleum Research Fund, administered by the American Chemical Society for a research assistantship during the last two years of my Ph.D program.
# TABLE OF CONTENTS

DEDICATION ........................................................................................................... ii

ACKNOWLEDGMENTS ............................................................................................... iii

LIST OF TABLES ........................................................................................................ xii

LIST OF FIGURES ........................................................................................................ xiv

Chapter

1. INTRODUCTION .................................................................................................... 1
   1.1. Closed Shell Metal-Metal Interactions .......................................................... 1
       1.1.1. d^{10} systems ......................................................................................... 2
           1.1.1.1. Copper(I) compounds .................................................................... 2
           1.1.1.2. Silver(I) compounds ...................................................................... 3
           1.1.1.3. Gold (I) compounds .................................................................... 5
       1.1.2. d^{8} systems ........................................................................................... 7
           1.1.2.1. Pd(II) compounds ......................................................................... 7
           1.1.2.2. Pt(II) compounds ......................................................................... 9
   1.2. Excimers and Exciplexes ............................................................................... 15
       1.2.1. Organic excimers/exciplexes ................................................................ 15
       1.2.2. Inorganic excimers/exciplexes ............................................................ 15
   1.3. Optical Memory .............................................................................................. 18
   1.4. Mixed Metal Systems ..................................................................................... 21
       1.4.1. d^{10} - d^{10} delocalized systems ....................................................... 21
       1.4.2. d^{10} - d^{8} delocalized systems ......................................................... 25
   1.5. Goal and Overview of Thesis ....................................................................... 28
1.6. References ................................................................................. 29

2. EXPERIMENTAL ........................................................................... 35
  2.1. Chemicals .................................................................................. 35
  2.2. Crystal Growing ......................................................................... 35
    2.2.1. Synthesis of Ag(CN)$_2$/KCl, Au(CN)$_2$/KCl, pure KAg(CN)$_2$,
           and pure KAu(CN)$_2$ crystals .................................................. 35
    2.2.2. Synthesis of mixed metal crystals ......................................... 36
  2.3. Atomic Absorption Measurements ............................................. 37
  2.4. Low Temperature Experiments ................................................ 38
  2.5. Steady-state Photoluminescence Spectroscopy .......................... 38
  2.6. Optical Memory Experiments ................................................... 39
  2.7. Lifetime Analysis ........................................................................ 40
  2.8. Raman Spectroscopy .................................................................. 40
  2.9. Computational Details ............................................................... 40
  2.10. References ............................................................................... 42

3. SPECTROSCOPIC STUDIES ON “EXCIPEX TUNING” FOR
      DICYANOAURATE(I) IONS DOPED IN POTASSIUM CHLORIDE

  3.1. Introduction ............................................................................... 43
  3.2. Experimental ............................................................................. 46
  3.3. Computational Details ............................................................... 47
  3.4. Results and Discussion ............................................................... 48
    3.4.1. Atomic absorption results .................................................. 48
5. OPTICAL MEMORY AND TEMPERATURE

DEPENDENT STUDIES ON DICYANOAURATE(I)

IONS DOPED IN POTASSIUM CHLORIDE CRYSTALS .............................................. 112

5.1. Introduction ........................................................................................................... 112

5.2. Experimental ....................................................................................................... 113

5.3. Results and Discussion ....................................................................................... 114

5.3.1. Atomic absorption and steady state photoluminescence data ................. 114

5.3.2. Assignment of luminescence bands ............................................................... 115

5.3.3. Optical memory studies ................................................................................. 118

5.3.4. Identification of products after 266 nm laser exposure ......................... 121

5.3.5. Optical memory studies at different temperatures ................................. 125

5.4. Conclusions ......................................................................................................... 135

5.5. References .......................................................................................................... 136

6. d^{10}-d^{10} and d^{10}-d^{8} MIXED METAL COMPOUNDS ........................................ 138

6.1. Introduction .......................................................................................................... 138

6.2. Experimental ....................................................................................................... 140

6.3. Computational Details ....................................................................................... 141

6.4. Results and Discussion ....................................................................................... 141

6.4.1. d^{10}-d^{10} mixed metal system ................................................................. 141

6.4.1.1. Atomic absorption measurements ......................................................... 141

6.4.1.2. Photoluminescence spectra of different d^{10} mixed samples and its temperature behavior ................................................. 142

6.4.1.3. Lifetime measurements ........................................................................... 152
6.4.1.4. Extended Hückel calculations ............................................. 157

6.4.2. d^{10}-d^8 system .................................................................. 169

6.4.2.1. Au-Pt sample .................................................................. 169

6.4.2.1.1. Steady-state photoluminescence data ......................... 169

6.4.2.1.2. Temperature dependent data ....................................... 173

6.4.2.2. Photoluminescence studies of KAg(CN)_2 - K_2Pt(CN)_4 sample ................................................................. 174

6.5. Conclusions ....................................................................... 183

6.6. References ........................................................................ 185

7. SUMMARY, CONCLUSIONS AND SUGGESTED FUTURE WORK ........ 187

7.1. Introduction ........................................................................ 187

7.2. Spectroscopic Studies of "Exciplex Tuning" for Dicyanoaurate(I) Ions Doped in Potassium Chloride Crystals ..................... 187

7.3. The Optical Memory Studies on Dicyanoargentate(I) and

Dicyanoaurate(I) Ions Doped in Potassium Chloride Crystals .......... 190

7.4. d^{10}-d^{10} and d^{10}-d^8 Mixed Metal Compounds ..................... 193

7.5. Suggested Future Work ......................................................... 196

BIBLIOGRAPHY ........................................................................ 199

APPENDIX A. OPTICAL MEMORY STUDIES ON

DICYANOARGENTATE(I) AND DICYANOAURATE(I)

IONS DOPED IN POTASSIUM CHLORIDE CRYSTALS ................. 210
APPENDIX B. SPECTROSCOPIC STUDIES ON K[Au(SCN)₂]
AND [Bu₄N]₂[Au(SCN)₂] ................................................................. 223
BIOGRAPHY OF THE AUTHOR ...................................................... 228
LIST OF TABLES

Table 1.1. Van der Waals radii of $d^{10}$ and $d^8$ atoms ......................................................... 2

Table 2.1. Amounts of $KAg(CN)_2$ and $KAu(CN)_2$ used to synthesize each $d^{10}$-$d^{10}$ mixed metal system ................................................................. 36

Table 2.2. Relativistic parameters used in the extended Hückel calculations ......................... 41

Table 3.1. Correlation of luminescence and Raman bands in various doped and pure crystals of the dicyanoaurates(I) and dicyanoargentates(I). Lifetime measurements were carried out at 77K ........................................ 53

Table 3.2. Summary of the results of EH calculations for the ground and first excited state of different oligomers of $[Au(CN)_2]^-$ (all with an eclipsed conformation) ................................................................. 63

Table 3.3. General qualitative assignment of the emission bands observed in solids and solutions of $Au(CN)_2^-$ species ........................................ 70

Table 3.4. Summary of the results of both ground and excited states of different $[Ag(CN)_2]^-$ using extended Hückel calculations ................... 82

Table 4.1. Assignments of the observed luminescence bands in the $[Ag(CN)_2^-]/KCl$ system ................................................................. 86

Table 4.2. Calculated activation energies ($E_a$) for $[Ag(CN)_2^-]/KCl$ batches 1 and 2 ........................................ 92

Table 4.3. Different slopes at different temperatures for batch 1 of $[Ag(CN)_2^-]/KCl$ ................................................................. 100

Table 4.5. Calculated kinetic parameters in $[Ag(CN)_2^-]/KCl$ system .................................. 107
Table 5.1. Assignments of the emission bands observed in different batches of KAu(CN)₂/KCl as well as in pure KAu(CN)₂.  

Table 5.2. Different values for (k₁ + k₂) at different temperatures for batch 1 of KAu(CN)₂/KCl.  

Table 5.3. Calculated kinetic parameters for the KAu(CN)₂/KCl system as well as pure KAu(CN)₂.  

Table 6.1. The initial Au:Ag molar ratio and the atomic absorption spectroscopic (AA'S) results for each sample.  

Table 6.2. Lifetime data for pure KAg(CN)₂ and KAu(CN)₂ as well as different emission bands observed in the d¹⁰ mixed sample with a 1:1.45 Au:Ag ratio at 4 K and 77 K.  

Table 6.3. Summary of the results of Extended Hückel calculations for the ground and first excited states of eclipsed dimeric species of \([\text{Au(CN)}₂⁻]\) and \([\text{Ag(CN)}₂⁻]\) units.  

Table 6.4. Summary of the results of Extended Hückel calculations for the ground and first excited states of eclipsed trimeric species of \([\text{Au(CN)}₂⁻]\) and \([\text{Ag(CN)}₂⁻]\) units.  

Table A.1. Atomic absorption spectroscopic (AA'S) results of each batch.  

Table B.1. Lifetime data for the observed luminescence bands in K[Au(SCN)₂] at 77K.
LIST OF FIGURES

Figure 1.1. The structure of \( \{ \text{Au(SpyH)(PPh}_2\text{py)}\}_2^{2+} \) ion ........................................... 6

Figure 1.2. The structure of \( \text{Pt}_2(\mu-\text{P}_2\text{O}_5\text{H}_2)_4^{4-} \) .................................................. 11

Figure 1.3. Schematic diagram of \( \text{Pt}_4(\text{acetate})_8 \) .......................................................... 12

Figure 1.4. A segment of the chain of compound 1 ................................................................. 24

Figure 1.5. Qualitative orbital diagram for the direct Pt-Au interaction of
\[ \text{[PEt}_3\text{]}_2(\text{C}_6\text{F}_5)\text{Pt}(\mu-H)\text{Au(PPh}_3\text{)}](\text{CF}_3\text{SO}_3) \] ........................................ 26

Figure 3.1. Emission spectra of a single crystal of \( \text{KAu(CN)}_2/\text{KCl} \) batch 1 at 77K with different excitation wavelengths .................................................. 50

Figure 3.2. Corrected excitation spectra of a single crystal of \( \text{KAu(CN)}_2/\text{KCl} \)
batch 1 at wavelengths corresponding to the emission maxima of bands II, III, and IV at 77K ................................................................. 51

Figure 3.3. Emission spectra of pure \( \text{KAu(CN)}_2 \) and three batches of
\( \text{KAu(CN)}_2/\text{KCl} \) crystals at 77K, when excited at 272 nm ........................................... 54

Figure 3.4. Emission spectra of pure \( \text{KAu(CN)}_2 \) and three batches of
\( \text{KAu(CN)}_2/\text{KCl} \) crystals at 77K, when excited at 315 nm ........................................... 55

Figure 3.5. Raman spectra of single crystals of pure \( \text{KAu(CN)}_2 \) and three
batches of \( \text{KAu(CN)}_2/\text{KCl} \) in the region of the cyanide stretching frequency ................................................................. 57

Figure 3.6. Emission spectra of pure \( \text{KAg(CN)}_2 \) and two batches of
\( \text{KAg(CN)}_2/\text{KCl} \) crystals at 77K, when excited at 245 nm ........................................... 59
Figure 3.7. Emission spectra of pure KAg(CN)$_2$ and two batches of KAg(CN)$_2$/KCl crystals at 77K, when excited at 275 nm.........................60

Figure 3.8. Raman spectra of single crystals of pure KAg(CN)$_2$ and two batches of KAg(CN)$_2$/KCl in the region of the cyanide stretching frequency........61

Figure 3.9. Ground and the first excited state potential energy curves for bent [Au(CN)$_2$]$_3$.................................................................65

Figure 3.10. Ground and the first excited state potential energy curves for linear [Au(CN)$_2$]$^-$..........................................................66

Figure 3.11. Exciplex tuning of the dicyanoaurate(I) emission in different media.................................................................69

Figure 4.1. Emission and corrected excitation spectra of a single crystal of [Ag(CN)$_2$]$^-$/KCl batch 1 at 77 K.................................80

Figure 4.2. Potential energy curves of the ground and the first excited state of linear [Ag(CN)$_2$]$^-$..........................................................83

Figure 4.3. Potential energy curves of the ground and the first excited state bent [Ag(CN)$_2$]$_3$...............................................................84

Figure 4.4. Potential energy curves of the ground and the first excited state of linear [Ag(CN)$_2$]$^-$..........................................................85

Figure 4.5. Emission spectra of a single crystal of [Ag(CN)$_2$]$^-$/KCl batch 1 variation with the temperature upon excitation at 265 nm...........87

Figure 4.6. A plot of logarithm of (I$_2$/I$_1$) versus 1/T for [Ag(CN)$_2$]$^-$/KCl batch 1..........90

Figure 4.7. A plot of logarithm of (I$_2$/I$_1$) versus 1/T for [Ag(CN)$_2$]$^-$/KCl batch 2..........91
Figure 4.8. [Ag(CN)₂]/KCl batch 1 HE and LE peak area variation with exposure time at 77 K .......................................................... 93

Figure 4.9. [Ag(CN)₂]/KCl batch 2 HE and LE peak area variation with the exposure time at 77 K ...................................................... 94

Figure 4.10. Pure KAg(CN)₂ HE and LE peak area variation with exposure time at 77 K .................................................................. 95

Figure 4.11. Emission spectra variation of a single crystal of pure KAg(CN)₂ with the exposure time as well as the recovery step at 77 K upon excitation at 275 nm ............................................................................ 97

Figure 4.12. A plot of the natural logarithm of \{[B]_{r}-[B]_{l}\} of [Ag(CN)₂]/KCl batch 1 with increasing exposure time at 77 K .................................................. 101

Figure 4.13. A plot of natural logarithm of \(k_1/T\) of [Ag(CN)₂]/KCl batch 1 versus 1/T .................................................................................. 104

Figure 4.14. A plot of natural logarithm of \(k_2/T\) of [Ag(CN)₂]/KCl batch 1 versus 1/T .................................................................................. 105

Figure 5.1. Emission and corrected excitation spectra of KAu(CN)₂/KCl batch 1 at 77 K ............................................................................ 116

Figure 5.2. Emission spectra of different batches of KAu(CN)₂/KCl as well as pure KAu(CN)₂ at 77 K upon excitation at 275 nm .................. 117

Figure 5.3. KAu(CN)₂/KCl different batches as well as pure KAu(CN)₂ em 390 nm peak area variation with exposure time at 77 K .......... 119

Figure 5.4. KAu(CN)₂/KCl batch 1 emission spectra (ex 275 nm) variation with the exposure time and the recovery step at 77 K ............ 120
Figure 5.5. Emission spectra of AuCN powder and a single crystal of KAu(CN)$_2$/KCl batch 1 after laser exposure upon excitation at 337 nm at 77 K

Figure 5.6. A plot of the natural logarithm of $\{[A]_t-[A]_e\}$ of KAu(CN)$_2$/KCl batch 1 with increasing exposure time at 4 K

Figure 5.7. A plot of natural logarithm of $k_1/T$ for KAu(CN)$_2$/KCl batch 1

Figure 5.8. A plot of natural logarithm of $k_2/T$ for KAu(CN)$_2$/KCl batch 1

Figure 6.1. Emission spectra variation with the Au:Ag ratio at 77 K upon excitation at 275 nm

Figure 6.2. Emission spectra variation with the molar ratio of Au:Ag at 77 K upon excitation at 265 nm

Figure 6.3. Emission spectra of single crystals of different $d^{10}$ mixed samples at 4 K upon excitation at 265 nm

Figure 6.4. Emission spectra of a single crystal of a $d^{10}$ mixed sample with a Au:Ag 1:1.45 upon excitation at 265 nm as a function of temperature

Figure 6.5. Emission spectra of a single crystal of a $d^{10}$ mixed metal sample with a Au:Ag ratio of 1:1.45 upon excitation at 275 nm

Figure 6.6. Excitation spectra of a single crystal of a $d^{10}$ mixed sample with a Au:Ag ratio of 1:1.45 at 77 K
Figure 6.7. Emission spectra of a single crystal of a $d^{10}$ mixed sample with a Au:Ag ratio of 1:1.45 at 77 K as a function of the excitation wavelength.

Figure 6.8. Emission spectra of a single crystal of a $d^{10}$ mixed sample with a Au:Ag ratio of 1:1 as a function of excitation wavelength at 4 K.

Figure 6.9. Excitation spectra of a single crystal of a $d^{10}$ mixed sample with a Au:Ag ratio of 1:1.45 at 4 K.

Figure 6.10. Potential energy curves of the ground and the first excited state for eclipsed $[\text{Ag(CN)}_2]^2$.

Figure 6.11. Potential energy curves of the ground and the first excited state for eclipsed $[\text{Au(CN)}_2]^2$.

Figure 6.12. Potential energy curves of the ground and the first excited state for eclipsed $[\text{Ag(CN)}_2\text{Au(CN)}_2]^2$ dimer.

Figure 6.13. Ground and the first excited state potential energy curves for linear $[\text{Au(CN)}_2]$.$3$.

Figure 6.14. Ground and the first excited state potential energy curves for linear $[\text{Ag(CN)}_2]$.$3$.

Figure 6.15. Potential energy curves of the ground and the first excited state for linear $[\text{Ag}_2\text{Au(CN)}_6]^3$ trimer.

Figure 6.16. Potential energy curves of the ground and the first excited state for linear $[\text{Au}_2\text{Ag(CN)}_6]^3$ trimer.
Figure 6.17. Emission spectra of single crystals of pure K$_2$Pt(CN)$_4$, pure KAu(CN)$_2$, and 1 mole of KAu(CN)$_2$ : 1 mole of K$_2$Pt(CN)$_4$

at 77 K upon excitation at 275 nm........................................170

Figure 6.18. Emission spectra of a single crystal of 1 mole of KAu(CN)$_2$

1 mole of K$_2$Pt(CN)$_4$ at 77 K when excited at 275 and 380 nm ............171

Figure 6.19. Excitation spectra of a single crystal of 1 mole of

KAu(CN)$_2$: 1 mole of K$_2$Pt(CN)$_4$ at wavelengths corresponding to the emission maxima of emission

bands at 77K........................................................................172

Figure 6.20. Emission spectra of single crystals of 1 mole of KAu(CN)$_2$

1 mole of K$_2$Pt(CN)$_4$, pure KAu(CN)$_2$, and pure K$_2$Pt(CN)$_4$

at 4 K upon excitation at 275 nm at 4 K........................................175

Figure 6.21. Emission spectra of a single crystal of 1 mole of

KAu(CN)$_2$: 1 mole of K$_2$Pt(CN)$_4$ at different temperatures upon excitation at 275 nm..................................................176

Figure 6.22. Emission spectra of a single crystal of 1 mole of KAu(CN)$_2$

1 mole of K$_2$Pt(CN)$_4$ at 77 K and room temperature upon excitation at 275 nm.............................................................177

Figure 6.23. Emission spectra of single crystals of pure KAg(CN)$_2$, pure K$_2$Pt(CN)$_4$ and 1 mole of KAg(CN)$_2$: 1 mole of K$_2$Pt(CN)$_4$

at 77 K upon excitation at 265 nm..........................................178
Figure 6.24. Emission spectra of a single crystal of 1 mole of
KAg(CN)₂ : 1 mole of K₂Pt(CN)₄ upon excitation at
265 nm at 77 K and room temperature...............................180

Figure 6.25. Excitation spectra of a single crystal of 1 mole of KAg(CN)₂:
1 mole of K₂Pt(CN)₄ at wavelengths corresponding to the
emission maxima at 77 ..............................................181

Figure 6.26. Emission spectra of single crystals of pure KAg(CN)₂, pure
K₂Pt(CN)₄ and 1 mole of KAg(CN)₂ : 1 mole of
K₂Pt(CN)₄ at 4 K upon excitation at 265 nm........................182

Figure A1. Emission spectra of single crystals of four batches of
KAg(CN)₂:KAu(CN)₂ (1:1 molar)/KCl at 77 K upon
excitation at 275 nm..................................................211

Figure A2. Emission spectra of single crystals of four batches of
KAg(CN)₂:KAu(CN)₂ (1:1 molar)/KCl at 77 K upon
excitation at 245 nm..................................................212

Figure A3. Emission spectra of a single crystal of KAg(CN)₂:KAu(CN)₂
(1:1 molar)/KCl batch 4 at 77 K as a function of excitation
wavelength............................................................213

Figure A4. Excitation spectra of a single crystal of KAg(CN)₂:KAu(CN)₂
(1:1 molar)/KCl batch 4 at 77 K as a function of emission
wavelength............................................................214
Figure A5. Raman spectra of single crystals of four batches of
KAg(CN)2:KAu(CN)2 (1:1 molar)/KCl in the region of the
cyanide stretching frequency ................................................... 215

Figure A6. Raman spectra of single crystals of four batches of
KAg(CN)2:KAu(CN)2 (1:1 molar)/KCl in the region of the
cyanide bending frequency ................................................... 216

Figure A7. KAg(CN)2:KAu(CN)2 (1:1 molar)/KCl batch 1 386 and
430 nm emission peak area variation (ex 275 nm) with 266 nm
laser exposure time at 77 K ................................................... 217

Figure A8. KAg(CN)2:KAu(CN)2 (1:1 molar)/KCl batch 2 386 and 430 nm
emission peak area variation (ex 275 nm) with 266 nm laser
exposure time at 77 K ................................................... 218

Figure A9. KAg(CN)2:KAu(CN)2 (1:1 molar)/KCl batch 3 386 and 430 nm
emission peak area variation (ex 275 nm) with 266 nm laser
exposure time at 77 K ................................................... 219

Figure A10. KAg(CN)2:KAu(CN)2 (1:1 molar)/KCl batch 4 386 and 430 nm
emission peak area variation (ex 275 nm) with 266 nm laser
exposure time at 77 K ................................................... 220

Figure A11. KAg(CN)2:KAu(CN)2 (1:1 molar)/KCl batch 2 emission
spectra variation (ex 275 nm) before and after laser exposure
as well as the recovery step at 77 K ................................................... 221
Figure A12. KAg(CN)$_2$·KAu(CN)$_2$ (1:1 molar)/KCl batch 4 emission spectra variation (ex 275 nm) before and after laser exposure as well as the recovery step at 77 K.................................................................222

Figure B1. Emission and excitation spectra of K[Au(SCN)$_2$] at 4 K..........................223

Figure B2. K[Au(SCN)$_2$] emission spectra (ex 320 nm) variation with the temperature.................................................................224

Figure B3. Emission and excitation spectra of [Bu$_4$N]$_2$[{Au(SCN)$_2$}]$_2$ at 4 K.........226

Figure B4. [Bu$_4$N]$_2$[{Au(SCN)$_2$}]$_2$ emission spectra (ex 365 nm) variation with the temperature.................................................................227
INTRODUCTION

1.1. Closed Shell Metal-Metal Interactions

Despite the repulsion expected between two closed shell metal cations, there are numerous examples of $d^{10}$ Cu(I), Ag(I), and Au(I) coordination compounds with short metal-metal bond lengths that have been structurally characterized, ranging from dimers to polymers. Other than $d^{10}$ coordination compounds, many examples of $d^{8}$ compounds including Pd(II) and Pt(II) have been reported with short metal-metal bond distances. When the crystal field splitting energies are large, coordination compounds with $d^{8}$ metal atoms are considered to be closed shell systems. Crystal field splitting is large for second and third row transition metal cations like Pd(II) and Pt(II).

Metal-metal interactions in closed shell systems seem to occur only when the separation between two interacting metal atoms is less than the sum of the Van der Waals radii of the two metal atoms. Table 1.1 summarizes Van der Waals radii of $d^{10}$ and $d^{8}$ atoms. The luminescence properties of these $d^{10}$ and $d^{8}$ compounds has been interpreted on the basis of these metal-metal interactions depending on the degree of metal-metal bonding in the system being studied.
Table 1.1. Van der Waals radii of \(d^{10}\) and \(d^8\) atoms.\(^1\)

<table>
<thead>
<tr>
<th>Atom</th>
<th>Van der Waals radii, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu ((d^{10}))</td>
<td>1.40</td>
</tr>
<tr>
<td>Ag ((d^{10}))</td>
<td>1.70</td>
</tr>
<tr>
<td>Au((d^{10}))</td>
<td>1.70</td>
</tr>
<tr>
<td>Pd ((d^8))</td>
<td>1.60</td>
</tr>
<tr>
<td>Pt ((d^8))</td>
<td>1.70 - 1.80</td>
</tr>
</tbody>
</table>

1.1.1. \(d^{10}\) systems

1.1.1.1. Copper(I) compounds

Cu(I) compounds have been intensively studied because of their efficient luminescence properties. Particularly, the luminescence of these compounds has been ascribed to metal-to-ligand charge transfer (MLCT), where the electron is transferred from the copper(I) center to the unoccupied \(\pi^*\) orbital of the ligand,\(^2\)-\(^4\) or to charge transfer to solvent (CTTS), where the electronic charge moves to the solvent molecule from the central atom.\(^5\),\(^6\) On the other hand, as another source of light emission, metal-centered transitions of the types \(3d^{10} \rightarrow 3d^94s\) and \(3d^{10} \rightarrow 3d^94p\) on Cu(I) were also studied.\(^7\),\(^8\) The rich luminescence properties observed for Cu(I) compounds have been considered for many potential applications such as tunable solid state lasers,\(^9\) photocatalysts,\(^10\) and photosensitizers for water splitting.\(^11\)

Most studies of Cu(I) compounds have been carried out for tetranuclear Cu(I) clusters of the type \(Cu_4X_4L_4\) (where \(X = \) halogen, and \(L = \) pyridine, amine, or phosphate).\(^12\),\(^13\) Also, many investigations have focused on synthesizing highly
luminescent Cu(I)-phenanthroline complexes because of their possible practical applications including energy conversion and storage. For example, Felder et al. have recently studied the rich luminescent properties of six different phenanthroline complexes of Cu(I). In this study, four complexes displayed relatively intense metal-to-ligand charge transfer (MLCT) emission bands with maxima around 720 nm at ambient temperature. From this study, they have noticed that complexes bearing long alkyl chains in the 2,9 positions and methyl residues in the 3,8 positions of the phenanthroline ring displayed strong luminescence both in fluid and rigid media.

On the other hand, Horváth and Stevenson have investigated the excited-state interaction of [Cu(CN)₂]⁻ with halide ions. In this case, the emitting species was an exciplex. Excited state trimers and longer oligomers are referred as exciplexes. The luminescent species was explained by a mechanism involving both ground and excited state equilibrium reactions. The association of the halo ligand with the excited state dicyanocuprate(I) complex was 10 times higher than the ground state association. Therefore, Horváth et al. have concluded that the emitting species was an exciplex.

The best example for cuprophilicity, or Cu-Cu interactions, has been reported in tetrameric haloamine clusters of Cu(I). A Cu-Cu bond distance of 3.12 Å was observed in this study providing an explanation for the low-energy luminescence of this Cu(I) cluster compound.

1.1.1.2. Silver(I) compounds

Ag(I) compounds have been used as photographic materials, photoconductors and photocatalysts for NO decomposition. Although Ag(I) compounds have many
potential applications, very few examples have been reported for the luminescence properties of Ag(I) coordination compounds.\textsuperscript{25-28} The first study was reported by Vogler and Kunkely in 1989.\textsuperscript{26} There are numerous examples of Ag(I) compounds with Ag-Ag interactions or argentophilic interactions that have been structurally characterized.\textsuperscript{29-34} In the majority of these compounds, the Ag-Ag interactions are assisted by the presence of bridging or capping ligands.\textsuperscript{30-32,34} Our research group has previously reported the crystal structure, electronic structure, and temperature dependent Raman spectra of Tl[Ag(CN)\textsubscript{2}] as the first example of ligand-unsupported argentophilic interactions.\textsuperscript{29} The crystal structure of Tl[Ag(CN)\textsubscript{2}] showed a Ag-Ag bond distance of 3.11 Å. Raman spectra showed $\nu_{\text{Ag-Ag}}$ at 75-125 cm\textsuperscript{-1}, which also gave a clear indication of the presence of Ag-Ag interactions.

Binuclear Ag(I) complexes have been investigated extensively.\textsuperscript{30-32} For example, four different binuclear Ag(I) complexes supported by aliphatic phosphine ligands have been studied recently.\textsuperscript{32} Crystal structures of the four compounds namely, [Ag(PC\textsubscript{y}3)(O\textsubscript{2}CCF\textsubscript{3})\textsubscript{2}], [Ag\textsubscript{2}(\mu-dcpm)\textsubscript{2}][CF\textsubscript{3}SO\textsubscript{2}]\textsubscript{2}, [Ag\textsubscript{2}(\mu-dcpm)\textsubscript{2}][PF\textsubscript{6}], and [Ag\textsubscript{2}(\mu-dcpm)(\mu-O\textsubscript{2}CCF\textsubscript{3})\textsubscript{2}], (where dcpm = bis(dicyclohexylphosphino)methane), and PC\textsubscript{y}3 = tricyclohexylphosphine), showed Ag-Ag bond distances of 3.10, 2.95, 2.92, and 2.89 Å respectively. The appearance of the Ag-Ag fundamental stretch (80 cm\textsuperscript{-1}) and overtone bands in the Raman spectra gave a further indication of the existence of Ag-Ag interactions. Also, a UV-visible absorption band at 261 nm for these compounds was assigned to a $4d\sigma^* \rightarrow 5p\sigma$ transition originating from Ag-Ag interactions.

Examples in the literature that look at Ag-Ag interactions of trinuclear, tetranuclear as well as polymeric Ag(I) compounds are mostly based on X-Ray
crystallographic data. For instance, ligand-unsupported Ag-Ag interactions in the trinuclear Ag(I) compound, \([\text{Ag}_3(2-(3(5)-\text{pz})\text{py})_3]_2\cdot2\text{py}\), (where py = pyridine, and pz = pyrazole), showed a Ag-Ag bond distance of 3.65 Å.  

1.1.1.3. Gold (I) compounds

The study of Au(I) compounds has been facilitated by their potential applications in a variety of areas including medicinal chemistry, chemical sensitizers of photographic emulsions, and luminescent based sensors. In particular, \([\text{Au(CN)}_2]^-\) has been exploited in the extraction of gold from its ores, gold electroplating applications, and antiarthritis drugs. Many researchers have studied the electronic structure of Au(I) compounds. These Au(I) compounds have a tendency to aggregate via Au-Au or aurophilic interactions to form dimers, and longer oligomers. These aurophilic interactions can be enhanced by relativistic effects because these effects are more pronounced in Au(I) than Ag(I). Relativistic effects basically stabilize the 6s and 6p orbitals but destabilize the 5d orbitals of gold atoms. As a result, the 5d-6s energy separation gets smaller and the 6s-6p separation gets larger. This leads to the mixing of orbitals and finally some bonding between gold atoms.

The synthesis and structural characterization of many Au(I) mononuclear compounds have been reported. Recently, our research group has reported a study of the photoluminescence and electronic structure of \(\text{Tl}[\text{Au(CN)}_2]\). The electronic structure calculations clearly demonstrated the covalency of both Tl-Au and Au-Au interactions in \(\text{Tl}[\text{Au(CN)}_2]\) and revealed specific orbital contributions responsible for these interactions. Fischer et al. have also reported pressure dependence studies of
Tl[Au(CN)₂] by neutron powder diffraction and optical studies.²³ The structural results indicated that the change in luminescence energy with pressure was due to a change in Tl-Au as well as the Au-Au interatomic separations. Many examples in the literature exist of ligand supported aurophilic interactions.²²,²⁴-²⁸ However, the aurophilic interactions present in Tl[Au(CN)₂] are the best example of ligand-unsupported interactions.

Among binuclear and polynuclear Au(I) compounds, Hao et al. have reported the formation of binuclear and cluster compounds from the mononuclear Au(I) compound, Au(Spy)(PPh₂py), (where py = pyridine, and Ph₂ = diphenyl).²⁵ Protonation of the pyridyl groups of Au(Spy)(PPh₂py) leads to the formation of the H-bonded dimer \( \{Au(SpyH)(PPh₂py)\}_2(PF_6)_2 \) having strong aurophilic interactions with a Au-Au bond distance of 2.98 Å.

![Diagram](image)

**Figure 1.1.** The structure of \( \{Au(SpyH)(PPh₂py)\}_2(PF_6)_2 \)²⁵ ion.
They have also synthesized two heterobimetallic compounds, [{AuCu-(μ-Spy)(μ-PPh2py)}2](PF6)2 and [AuCu(P(η-tolyl)3)2(μ-Spy)(μ-PPh2py)2](NO3) which show strong Au-Cu interactions. Three different emission bands at 470, 635, and 510 nm were observed for solutions of both binuclear and heterobinuclear compounds at room temperature. The shift of emission maxima may be due to the influence of H bonding or Cu(I) coordination to the filled thiolate orbital energy or the effect of metal-metal interactions of the Au(I) acceptor orbital energy. Based on their previous studies of Au(I) thiolate phosphine complexes, the emitting state was assigned to a S(π*) → Au ligand to metal charge transfer (LMCT) transition.

1.1.2. \textit{d}^8 \textit{systems}

1.1.2.1. Pd(II) compounds

Very few investigations have been reported of the luminescence properties of Pd(II) compounds in the literature. Craig \textit{et al.} have studied the photophysical properties of Pd(II) complexes containing the ortho-metalating ligand, 2-phenylpyridinate (ppy·). They have studied four different ortho-metalated Pd(II) compounds namely, [Pd(II)(ppy)Cl]2 (1), [Pd(II)(ppy)(bpy)Cl] (2), [Pd(II)(ppy)(en)Cl] (3), and [Pd(II)(ppy)(CO)Cl] (4), (where bpy = 2,2'-bipyridine, and en = ethylenediammine). UV-vis absorption and low temperature luminescence results for these four Pd(II) ortho-metalated compounds indicated that large contributions to the excited states were due to transitions localized on the 2-phenylpyridinate ligand. The observed high energy absorption transitions within the range of 240-340 nm were intraligand π-π* transitions localized on the 2-phenylpyridinate ligand. The low energy absorption transition that
was observed around 350 nm was also assigned to ligand-localized \( \pi-\pi^* \) transitions of the 2-phenylpyridinate ligand. All four Pd(II) compounds did not show luminescence at room temperature. The emission energies at 77 K for the four different Pd(II) compounds were very similar indicating that the ligand trans to the ortho-metalated ligand has very little influence on the luminescence properties.

Photophysical descriptions of several Pd(II) orthometalated azobenzene complexes of the type \((\text{Azb}')(\text{PdBr}(L))\), (where \(\text{Azb}' = \text{orthometallated 4-methoxy-azobenzene, and L = cis or trans-4-stilbazole, pyridine or 3-methylpyridine}\)), have been reported. These studies indicated that the photophysics of these compounds were predominantly ligand-localized in character. Luminescence lifetimes of these complexes in solution were short (<1 ns) at room temperature and were characterized as singlet-singlet intraligand fluorescence emissions.

Harrison et al. have reported the optical spectra of \(\text{PdBr}_4^{2-}\) ion doped in \(\text{Cs}_2\text{ZrCl}_6\) at 2 K. An electronic band observed between 19185 and 21836 cm\(^{-1}\) with sharp vibrational structure has been assigned as the d-d transition, \(\Gamma_1(1A_{1g}) \rightarrow \Gamma_2(1A_{2g})\). The possible presence of a Jahn-Teller effect for the \(\Gamma_1(1A_{1g}) \rightarrow \Gamma_5(1E_g)\) transition for \(\text{PdBr}_4^{2-}\) ion doped in \(\text{Cs}_2\text{ZrCl}_6\) has been examined. A laser excited luminescence and absorption study of \(\text{Pd(CN)}_4^{2-}\) ions doped in NaCl, NaCN, and KCN has also been reported. The luminescence spectra of \(\text{Pd(CN)}_4^{2-}\) ions doped in alkali halide and alkali cyanide crystals showed lifetimes and energies very similar to the luminescence of previously reported pure \(\text{BaPd(CN)}_4\) crystals. After comparison of the luminescence spectra of these two systems, the authors have concluded that different palladium clusters
were responsible for observed luminescence in $\text{Pd(CN)}_4^{2-}$ ions doped in alkali halide and alkali cyanide crystals.

Ellenson et al. have reported a laser excited luminescence study of $\text{BaPd(CN)}_4\cdot4\text{H}_2\text{O}$. Luminescence studies of single crystals of $\text{BaPd(CN)}_4\cdot4\text{H}_2\text{O}$ within the range of 5 to 296 K showed the presence of a short-lived component (<10 ns) centered at 26,000 cm$^{-1}$ and a long lived component (2 μs) at 19,000 cm$^{-1}$. The 26,000 cm$^{-1}$ transition showed a strong temperature dependence resulting from the changing Pd-Pd separation with temperature.

Kunkely et al. have investigated the photoluminescence properties of trimeric Pd(II) acetate in solution (glacial acetic acid or benzene). The UV-vis absorption band that appeared at 399 nm has been attributed to a ligand-to-metal charge transfer (LMCT) transition. Considering the molecular orbital scheme of $\text{Pd}_3(\text{acetate})_6$, it is also reasonable to assign this 399 nm absorption to the $d\sigma^* \rightarrow p\sigma$ transition of the (PdII)$_3$ moiety. This trimeric Pd(II) compound is luminescent at room temperature. The emission spectrum of this compound in benzene showed a strong band at 475 nm and a weak band at 595 nm. This 475 nm emission band has been assigned as phosphorescence; whereas the 595 nm emission band is assigned as fluorescence. All observed emission bands originated from a $d\sigma^* \rightarrow p\sigma$ excited state which involved Pd-Pd interactions in the triangular [Pd(II)]$_3$ moiety.

1.1.2.2. Pt(II) compounds

It is well known that the majority of mononuclear Pt(II) compounds with low energy metal-centered excited states are not luminescent in solution at room
A possible explanation for this would be that the presence of low-energy ligand-field excited states mediate a radiationless deactivation. However, for some mononuclear Pt(II) compounds low-energy intraligand, metal-to-ligand charge transfer, and ligand-to-ligand charge transfer states are emissive in solution. In addition to mononuclear Pt(II) compounds, a variety of bi- and polynuclear Pt(II) compounds have been shown to have luminescence under ambient conditions. In these cases, emission does not originate from metal-centered excited states. Instead, the emission originates from excited states that are characterized by strong metal-metal bonding.

Lai et al. have recently investigated the synthesis and characterization of a series of mononuclear cyclometalated Pt(II) complexes namely, [Pt(L)Cl], (where L = 4-(aryl)-6-phenyl-2,2'-bipyridine if aryl = H (1), phenyl (2), 4-chlorophenyl (3), 4-tolyl (4), 4-methoxyphenyl (5), 3,4,5-trimethoxyphenyl (6)), and [Pt(L)E]+ (where E = py (7), PPh3 (8)). These mononuclear Pt(II) complexes are emissive in solution as well as in the solid state. The observed emission around 560 nm of compounds 1-6 in CH2Cl2 at room temperature was assigned to be 3MLCT in nature. This assignment was made because the variation in the emission energy maxima was small (ranging from 562 to 568 nm) and no trends were apparent for the different para substituents. The lack of trend may be due to limited electronic communication between the 4-aryl group and the planar 6-phenyl-2,2'-bipyridine moiety. For compounds 7 and 8, a blue shift in the emission maxima was observed. This could be due to an increase of the charge on the Pt(II) center, causing an enhancement in the energy of the 3MLCT transition. The solid state emission band around 600 nm for compounds 1-6 was basically due to intermolecular metal-metal and ligand-ligand interactions which yield low energy [dσ* → π*] transitions.
The most widely studied binuclear Pt(II) compound is Pt$_2$(µ-P$_2$O$_5$H$_2$)$_4$$^4$ commonly named "platinum pop". Figure 1.2 shows the structure of "platinum pop".

![Structure of Pt$_2$(µ-P$_2$O$_5$H$_2$)$_4$$^4$.](image)

**Figure 1.2.** The structure of Pt$_2$(µ-P$_2$O$_5$H$_2$)$_4$$^4$.69

The single crystal X-ray structure of K$_4$[Pt$_2$(µ-P$_2$O$_5$H$_2$)$_4$]:2H$_2$O showed the anion with an eclipsed "lantern" structure having planar Pt(II) centers linked by µ-P$_2$O$_5$H$_2$$^2$- groups. The anion has a Pt-Pt separation of 2.925(1) Å with no ligand bonded to the axial sites.73

The excited state chemistry of Pt$_2$(µ-P$_2$O$_5$H$_2$)$_4$$^4$ is probably the richest of all d$^8$-d$^8$ complexes. An aqueous solution of this compound showed an intense green emission at 514 nm accompanied by emission at 407 nm at room temperature.59 This 514 nm emission band was assigned as phosphorescence having a lifetime of ~9 µs whereas the 407 nm band was assigned as fluorescence since it had a lifetime of 8-40 ps.74,75 Extended spectroscopic investigations on this compound allowed for the elucidation of the dσ* → po excited states.74-76
Pt(II) compounds have several potential applications. Among these, Pt\textsubscript{2}(\textmu-P\textsubscript{2}O\textsubscript{3}H\textsubscript{2})\textsubscript{4}\textsuperscript{+} has been used for the trace detection of platinum.\textsuperscript{77} Since the intensity of the 514 nm emission band was linear with concentration, emission was detected at 77 K from solutions containing only 4 parts per trillion platinum.

The synthesis and characterization of a luminescent Pt(II) cyclic trimer, [Pt(thpy)(bzim)]\textsubscript{3} where thpy = 2-(2'-thienyl)pyridine, and bzim = 7,8-benzoquinoline) has been reported.\textsuperscript{71} When dissolved in CH\textsubscript{2}Cl\textsubscript{2}, this compound is emissive at room temperature with peak maxima at 560 nm and 606 nm. A small blue shift was observed (from 560 to 557 nm and from 606 to 601 nm) upon cooling to 77 K. These emissions were assigned as metal-to-ligand charge transfer transitions with ligand center character. In the crystalline form, multiple emissions at 571, 617, and 664 nm were observed at room temperature (RT). The crystal showed a red shift in the emission band that first appeared at 606 nm (77 K) and then showed up at 664 nm (RT) and was assigned as due to excimeric emission arising from $\pi$-stacking in the solid state.

Kunkely et al. have studied the photoluminescence properties of tetrameric Pt(II) acetate, Pt\textsubscript{4}(acetate)\textsubscript{8}, in solution.\textsuperscript{78} The structure of Pt\textsubscript{4}(acetate)\textsubscript{8} is show in figure 1.3.

![Figure 1.3. Schematic diagram of Pt\textsubscript{4}(acetate)\textsubscript{8}.\textsuperscript{78}](image)
This compound consists of a $[\text{Pt}^{2+}]_4$ square which is held together by Pt-Pt bonds and bridging acetate ligands. Therefore, each Pt(II) ion is in an octahedral environment having Pt-Pt bonds. The $\text{Pt}_4(\text{acetate})_8$ solution showed two emission maxima at 510 nm and 630 nm upon excitation at 420 nm at room temperature. Green emission at 510 nm was assumed to be fluorescence because of its short lifetime (5 ns). The red emission at 630 nm corresponded to phosphorescence because it had a longer lifetime (1.8 μs). Extended Hückel molecular orbital calculations have shown that the Pt-Pt interaction was mainly based on two d orbitals at each Pt$^{2+}$ ion that overlap in the Pt$_4$ square. The overlapping of these d orbitals resulted in generation of four bonding and four antibonding molecular orbitals. The bonding molecular orbitals were filled because each Pt$^{2+}$ provided two electrons. Therefore, the $[\text{Pt}^{2+}]_4$ moiety was held together by four Pt-Pt bonds but only one bonding molecular orbital was strongly stabilized. The lowest unoccupied molecular orbital (LUMO) was metal-metal antibonding in nature and the highest occupied molecular orbital (HOMO) was weakly bonding in nature. According to this, Voglar et al. have assigned the absorption band at 405 nm to a metal centered type transition.

Among oligomeric and polymeric Pt(II) compounds, the tetracyanoplatinates have been well known for more than one hundred years. For example, one of the extensively studied tetracyanoplatinate compounds abbreviated as KCP and having the formula of $\text{K}_2\text{Pt(CN)}_4\text{Br}_{0.3}\cdot3\text{H}_2\text{O}$, consists of a columnar stacked array of planar $[\text{Pt(CN)}_4]$ units that form a chain of Pt atoms with a short Pt-Pt bond separation of 2.894 Å. In this compound, the $\text{Br}^-$ occupies 60% of the sites in the center of the unit cell. Water molecules form a hydrogen-bonded network between the CN$^-$ ligands and the K$^+$ ions and
effectively cross-link the [Pt(CN)₄] chains. The importance of the water molecule in the lattice has been emphasized by the fact that small changes in the degree of hydration can produce very large differences in the specific conductivity in the platinum atom chain direction. This compound has a metallic-type anisotropic electrical conductivity at room temperature, which provided the motivation to study [Pt(CN)₄]²⁻ chain type compounds in the solid state.

Yersin et al. have studied low temperature emission from various salts of [Pt(CN)₄]²⁻. From their investigations, they have concluded that the stacking which occurs in the crystal leads to a splitting of the platinum orbitals located on the z axis. Therefore, the emission properties of these crystals strongly depend on the Pt-Pt bond distance. Detailed absorption and emission studies of K₂Pt(CN)₄ and BaPt(CN)₄ in aqueous solution have been reported. The emission spectra of aqueous K₂Pt(CN)₄ showed a quite complex behavior and it was also concentration dependent. From that, Yersin et al. have concluded that the emission was associated with the formation of oligomers.

Our research group has reported the energy transfer from a Pt-Ni excited state to Pt(II) clusters in quasi-one-dimensional Ba(Pt,Ni)(CN)₄.nH₂O crystals. The authors have found that at higher temperatures, the emission was from a Pt-Ni state. Therefore, at higher temperatures (250 K), the hopping rate of excitation energy was quite fast and was trapped by clusters of Pt(II) ions. Upon decreasing the temperature, the energy transfer rate was gradually decreased.
1.2. Excimers and Exciplexes

The formation of excimers and exciplexes is a well-established phenomenon in organic literature, but is less common in inorganic literature. From this point on, excited state dimers will be referred to excimers while excited state trimers and longer oligomers will be referred to as exciplexes.

1.2.1. Organic excimers/exciplexes

Förster et al. have reported the first example of excimer formation in the organic literature. Upon increasing the concentration of pyrene in n-heptane, the intensity of the monomer emission band at 125 nm started decreasing while the intensity of the excimer emission band at 157 nm started increasing. This occurrence indicated the formation of stable, pyrene dimeric species in the excited state.

Among recent examples, Zachariasse et al. have studied the chain length dependence of intramolecular excimer formation with 1,n-Bis(1-pyrenylcarboxy) alkanes for n = 1-16, 22 and 32. Intramolecular excimer fluorescence was observed for all compounds except the n = 1 compound. Based on their study, the scientists have concluded that the presence of methylene hydrogens next to the pyrenyl moieties of these compounds was important for observing excimer formation.

1.2.2. Inorganic excimers/exciplexes

Among examples of inorganic excimers and exciplexes in the literature, only a few are metal-metal bonded. For instance, exciplex formation between [Cu(CN)$_2$] and halide ligands has been reported. In this system, association was also found in the ground state, which had a stepwise formation constant that was an order of magnitude
smaller than in the excited state. The 10-fold higher association of the halo-ligand with the excited dicyanocuprate(I) complex compared to the ground state association, led scientists to believe that the emitting species was an exciplex. The rate of the formation of $^1[Cu(CN)_2X]^2-$ exciplexes decreased in the order of Cl > Br > I.

Zink et al. have reported excimer formation for Ag$^+$ and Cu$^+$ doped β-alumina.$^{86}$ $^*[Cu-Ag]^{2+}$ and $^*[Cu-Cu]^{2+}$ are the two excimers formed in that system. The authors have observed emission bands at 640, 550, and 400-450 nm originating from $^*[Cu-Ag]^{2+}$ excimers, $^*[Cu-Cu]^{2+}$ excimers, and Cu monomers, respectively.

Excimer formation in [Pt(4,7-diphenyl-1,10-phenanthroline)(CN)$_2$] has been reported as an example showing that excimer formation required a relatively high concentration of the monomer.$^{87}$ The photoluminescence spectrum of a low concentration of this Pt(II) compound in CH$_2$Cl$_2$ showed a green emission at 520 nm (monomer emission) at room temperature. As the concentration increased, a red emission at 615 nm (dimer emission) appeared and grew at the expense of the green emission. In dilute solution, the intraligand ππ$^*$ state of the monomer was deactivated by emission and nonradiative deactivation. As the concentration increased, the association of monomers led to the formation of excimers.

Nagle et al. have reported exciplex formation between d$^{10}$-s$^2$ systems.$^{88}$ The interaction between the lowest energy triplet excited state of Pt$_2$(P$_2$O$_5$H$_2$)$_4^{4+}$ and Tl$^+$ in aqueous solution at room temperature gave two phosphorescent triplet exciplexes, ($^3$Pt$_2$Tl) and ($^3$Pt$_2$Tl$_2$), as a result of Pt-Pt-Tl bonding. Both exciplexes had lifetimes of 10 μs.
Only one example has been reported for exciplex formation in d\textsuperscript{10}-d\textsuperscript{8} systems.\textsuperscript{89} Luminescent exciplex formation was found to occur between Pt(II) and Au(I) coordination compounds for mixtures of Au(CN)\textsubscript{2}\textsuperscript{-} and Pt\textsubscript{2}(P\textsubscript{2}O\textsubscript{5}H\textsubscript{2})\textsubscript{4}\textsuperscript{4+} in aqueous solution. The emission spectrum of Pt\textsubscript{2}(P\textsubscript{2}O\textsubscript{5}H\textsubscript{2})\textsubscript{4}\textsuperscript{4+} showed fluorescent and phosphorescent luminescence bands at 400 and 514 nm, respectively. The addition of Au(CN)\textsubscript{2}\textsuperscript{-} in the aqueous solution resulted in the formation of two new bands at 440 and 571 nm. The band at 440 nm has been assigned to fluorescence from an excited [Pt\textsubscript{2}(P\textsubscript{2}O\textsubscript{5}H\textsubscript{2})\textsubscript{4}\textsuperscript{4+}- Au(CN)\textsubscript{2}\textsuperscript{-}] ground state pair. The 571 nm band was attributed to a phosphorescent exciplex of formula [Pt\textsubscript{2}(P\textsubscript{2}O\textsubscript{5}H\textsubscript{2})\textsubscript{4}\textsuperscript{4+}- Au(CN)\textsubscript{2}\textsuperscript{-}]. By analogy to the exciplexes involving Tl\textsuperscript{+},\textsuperscript{88} this exciplex should involve direct Pt(II)-Au(I) interactions at the axial Pt-Pt sites. The authors stated that additional spectroscopic and lifetime measurements would be needed to characterize the [Pt\textsubscript{2}(P\textsubscript{2}O\textsubscript{5}H\textsubscript{2})\textsubscript{4}\textsuperscript{4+}- Au(CN)\textsubscript{2}\textsuperscript{-}] exciplex.

Recently, exciplex formation for [Ag(CN)\textsubscript{2}\textsuperscript{-}]\textsuperscript{n} ions doped in KCl as well as in zeolite A have been reported.\textsuperscript{90,91} The scientists have noticed that different exciplexes were due to the formation of different excited state oligomers, \textsuperscript{n}[Ag(CN)\textsubscript{2}\textsuperscript{-}], in the doped systems. For [Ag(CN)\textsubscript{2}\textsuperscript{-}] ions doped in KCl system, the formation of Ag-Ag bonded excimers and exciplexes gave rise to the different luminescence bands observed over the 285-610 nm range.\textsuperscript{90} These luminescence bands can be tuned by varying the excitation wavelength or by varying the dopant concentration. The authors were able to observe tunability of 18,000 cm\textsuperscript{-1} in the UV and visible wavelength for a single crystal of [Ag(CN)\textsubscript{2}\textsuperscript{-}] ion doped in KCl by changing the excitation wavelength.
1.3. Optical Memory

Optical memory is a phenomenon that is analogous to a process that is written, read, and erased. Crystals can be written by irradiating them at low temperature, read by detecting the luminescence, and erased by heating the crystal back up to room temperature. Zink et al. have reported excellent examples showing optical memory in Cu\(^+\), and Cu\(^+\)/Ag\(^+\) doped β-alumina.\(^{86}\) The framework of β-alumina consists of closed packed "spinal blocks" separated by open regions containing mobile cations called "conduction planes". These "spinal blocks" contain Al, Mg, and O atoms.

The emission spectra of Cu\(^+\) doped β-alumina showed blue emission at 440 nm and green emission at 540 nm at 10 K.\(^{86b}\) The blue emission was assigned to isolated monomers whereas the green emission was assigned to [Cu-Cu]\(^{2+}\) dimers. When a small portion of the crystal was irradiated under UV light (351 nm) at 10 K, the blue emission decreased in intensity while the green emission intensity significantly increased. On the other hand, in the unirradiated portion of the crystal there was no change in the emission intensity of both peaks, indicating that the crystal remembered which part of it was irradiated. When the crystal was warmed back to room temperature, the blue emission was reformed in the irradiated portion and the emission spectrum represented both blue and green emission as unirradiated portions of the crystal. So, the optical memory can be erased by heating. During the writing process, dimers were formed and stayed together when the sample was left in the dark at low temperature.

Zink et al. have also reported similar optical memory behavior in Cu\(^+\)/Ag\(^+\) doped β-alumina.\(^{86a}\) The emission of Cu\(^+\)/Ag\(^+\) doped β-alumina was due to the formation of excimers and exciplexes. Three major emission bands at 640, 550, and 400-450 nm were
originated from [Cu-Ag]^{2+}, [Cu-Cu]^{2+}, and Cu^{+} monomers respectively. When a small portion of a crystal was irradiated under UV light at 10 K, the emission spectrum of that portion represented orange emission (640 nm) originating from [Cu-Ag]^{2+}, while the emission spectrum of the unirradiated portion represented green emission (550 nm) due to [Cu-Cu]^{2+}. When the crystal was warmed to room temperature, the memory was erased.

Optical memory studies of Pb[Au(CN)_{2}]_{2} have been reported. Upon excitation at 399 nm, the emission spectrum showed two bands at 463 nm (high energy (HE) band) and 547 nm (low energy (LE) band) at 78 K. The HE band has been assigned to a Pb^{2+} (6p \rightarrow 6s) transition and the LE band to a [Au(CN)_{2}]^{-} transition. Upon exposure to a 337 nm laser, the intensity of both the HE and LE emission bands decreased indicating the formation of non-luminescent species. Since the HE band assigned to Pb(II) decayed along with the LE band assigned to an Au(I) transition, both the Au(I) and the Pb(II) species were being changed to non-luminescent species. The mechanism proposed for the decrease in intensity with exposure to the 337 nm laser showed that Pb^{2+} had been oxidized to form Pb^{4+} while Au(I) had been reduced to form Au. Equations 1-3 show the reactions that led to the formation of Pb^{4+} and Au.

\[
[Au(CN)_{2}]^{-} + h\nu (337 \text{ nm}) \rightarrow [Au(CN)_{2}]^{k} \quad (1)
\]

\[
2 [Au(CN)_{2}]^{k} + Pb^{2+} \rightarrow 2 [Au(CN)_{2}]^{2-} + Pb^{4+} \quad (2)
\]

\[
[Au(CN)_{2}]^{2-} \rightarrow \text{Au} + 2CN^{-} \quad (3)
\]
Once again, when the crystal was heated to room temperature the original Pb[Au(CN)$_2$]$_2$ species was recovered. Extended Hückel molecular orbital calculations have been carried out for the linear Au-Pb-Au geometrical form of Pb[Au(CN)$_2$]$_2$. These calculations indicated that the formation of weak covalent Pb-Au interactions in Pb[Au(CN)$_2$]$_2$.

Recently, optical memory studies of TlAg(CN)$_2$ have been reported. When the crystal was excited at 318 nm, the emission spectrum showed a single peak at 412 nm at 77 K. This emission band was assigned to the excited [Ag(CN)$_2$]$^{3-}$ trimer. When the crystal was irradiated by 318 nm light at 77 K, the 412 nm emission band decreased in intensity. This decay in the luminescence intensity with exposure to the 318 nm suggested that a photochemical reaction occurred which resulted in a non-luminescent species. Initially the authors proposed a mechanism that is shown in Equation 4, assuming that the [Au(CN)$_2$]$^+$ monomer was the primary photoreactive species responsible for this process. The excited monomer has been considered a strong oxidizing agent to convert Tl$^+$ to Tl$^{3+}$.

$$2[Ag(CN)_2]^{2-} + Tl^+ \rightarrow 2[Ag(CN)_2]^{2-} + Tl^{3+} \quad (4)$$

The scientists thought that the energy released from the oxidation/reduction reaction in Equation 4 would be sufficient to break the Ag-C bond so that the luminescence would be quenched (see Equation 5).

$$[Ag(CN)_2]^{2-} \rightarrow Ag + 2CN^{-} \quad (5)$$
After calculating the Ag-C bond strength for the \([\text{Ag(CN)}_2]^{2-}\) dianion using ab initio calculations, the authors have concluded that the cleavage of the Ag-C bond (Equation 5) was possible. This mechanism was modified to a \([\text{Ag(CN)}_2]^{3-}\) trimer. In this modification, the Ag-Ag bond cleavage takes place rather than Ag-C bond cleavage. The excited state of the \([\text{Ag(CN)}_2]^{3-}\) trimer was expected to be an oxidizing agent, but weaker than the monomer. The Ag-Ag bond length in the \([\text{Ag(CN)}_2]^{4+}\) anion was thought to be longer than the sum of the Van der Waals radii of two Ag atoms so that this \([\text{Ag(CN)}_2]^{4+}\) species was not expected to show luminescence. The initial luminescence intensity was recovered by heating the crystal to room temperature so that the original \([\text{Ag(CN)}_2]^{3-}\) trimer was recovered.

1.4. Mixed Metal Systems

Several attempts have been made by different investigators to understand the nature of mixed metal systems. One would expect that excited state delocalization occurs upon forming mixed metals. Examples of mixed metal systems have also shown that the metal-metal bond distance for a particular mixed metal compound is less than the sum of the Van der Waals radii of the two interacting metal atoms.\(^{94-98}\)

1.4.1. \(d^{10}-d^{10}\) delocalized systems

Coordination compounds of group 11 with Au-Au interactions (aurophilic interactions), Ag-Ag interactions (argentophilic interactions) as well as Cu-Cu interactions (cuprophilic interactions) are well-known.\(^{12,29,52}\) On the other hand, mixed metal heterometallic compounds with Ag-Au, Ag-Cu, or Cu-Au interactions are rare.\(^{94-99}\)
This may be due to the fact that interacting metals need to satisfy conditions like being coordinated to identical ligands, and having identical coordination number, geometry, counterions in ionic compounds, and space group.

Most examples involving mixed metal systems have been based on X-ray crystallographic data.  

For example, Braunstein et al. have reported the crystal structure of \([\text{CuPt}_3(\mu-\text{CO})_3(\text{PPh}_3)_2]\text{BF}_4\) as an example of cluster formation between Cu(I) and Pt(0). The crystal structure consists of a distorted tetrahedral geometry with the Cu(PPh₃) group capping the Pt₃ face, with one Pt atom being bound to two PPh₃ ligands. The Cu-Pt bond distance of this compound was 2.650 Å.

Argentophilic-aurophilic bonding in the heterobimetallic organosulfur complex, AgAu(MTP)₂ (where MTP = diphenylmethylenethiophosphinate) has been synthesized, characterized and compared with homobimetallic Au₂(MTP)₂ and Ag₂(MTP)₂. Using X-ray crystallography, the intramolecular Ag-Au bond distance in AgAu(MTP)₂ was found to be 2.912 Å. This distance was very short compared to the metal-metal distance in Au₂(MTP)₂ and Ag₂(MTP)₂ (it was ~3.0 Å for both). The absorption spectra of very dilute solutions of all these three compounds showed similar spectra having maximum around 275 nm at room temperature. Since the absorption band position was not dependent on the metal, this absorption band was assigned to an intraligand transition. At a concentration near the saturation point, the absorption edges were gradually red shifted at room temperature. Absorption edges were at 335, 350, and 450 nm for compounds Ag₂(MTP)₂, AuAg(MTP)₂, and Au₂(MTP)₂ respectively. The shift in the absorption edge for each compound in the concentrated solutions to lower energy indicated that the molecular aggregation increased as the concentration increased. The authors have carried
out density functional theory (DFT) calculations for dimer and trimer models of these three compounds and the values of the HOMO-LUMO gap followed the same order for the absorption edges for the three compounds providing good agreement with the observed experimental results.

Fernández et al. have studied the optical properties of $[\text{Au}_2\text{Ag}_2 (\text{C}_6\text{F}_5)_4(\text{OCMe}_2)_2]_n$ in solution as well as in the solid state. This compound showed Au-Ag distances of 2.7903(9) Å and 2.7829 Å for the two silver atoms in the main unit bonded to two gold atoms. The photoluminescence spectrum of this solid compound at 77 K showed an emission band at 554 nm, which was a result of metal-centered $(d\sigma^*)(p\sigma)$ or $d\delta^*-p\sigma$ excited states. None of the precursor gold(I) compounds or Ag(I) compounds showed emission at 554 nm at 77 K indicating that this emission resulted in interactions between the two metal centers. On the other hand, this compound in acetone solution showed an emission band at 405 nm which was assigned to a pentafluorophenyl localized $\pi^*\pi$ excited state or $\pi$-metal-to-metal charge transfer transition. DFT calculations agreed with experimental results and showed the nature of the orbitals involved in each transition.

Luminescent chains formed from triangular gold complexes sandwiching Ag(I) and Tl(I) have been reported as examples involving $d^{10}$-$d^{10}$ and $d^{10}$-$s^2$ systems, respectively. Structures of $\{\text{Ag}([\mu-\text{C, N-bzim}])_3\}_2\text{BF}_4\cdot\text{CH}_2\text{Cl}_2$ (1), $\{\text{Tl}([\mu-\text{C, N-bzim}])_3\}_2\text{PF}_6\cdot0.5\text{THF}$ (2) (where bzim = 1-Benzylimidazolate), and $\{\text{Tl}([\mu-\text{C(OET)=N C}_6\text{H}_4\text{CH}_3])_3\}_2\text{PF}_6\cdot\text{THF}$ (3) have been synthesized and characterized. As shown in Figure 1.4, each Ag(I) is bonded to six Au(I) atoms forming a distorted Ag(I) centered trigonal prism of the Au(I) atoms. This compound showed Ag-Au bond distances ranging from 2.731(2) to 2.922(2) Å indicating considerable metal-metal
interactions. Compound 1 was the first example in which a naked Ag(I) ion was bonded to Au(I) atoms.

![Diagram of compound 1 chain](image)

**Figure 1.4.** A segment of the chain of compound 1. The benzyl groups are not shown.

The molecular structure of compound 2 was nearly analogous to compound 1, where the central Tl(I) atom of the cluster was bonded to six Au(I) atoms forming a distorted Tl(I)-centered trigonal prism with Tl-Au bond distances ranging from 2.9711(7) to 3.0448(7) Å. On the other hand, compound 3 had Tl-Au bond distances ranging from 3.0673(4) to 3.1075(4) Å.

These three compounds showed low energy visible emissions at room temperature. Also, the three compounds exhibited luminescence thermochromism, as shown by red shifts in the emission maxima, which was caused by cooling the crystal to
77 K. Observed luminescence bands were associated with excited states that were delocalized along the crystallographic axis of the chain.

1.4.2. $d^{10}$-$d^8$ delocalized systems

For $d^{10}$-$d^8$ systems, a number of structurally characterized compounds which show metalophilic attractions are known. Among those, Balch et al. have reported many examples that include Au(I) and Ir(II). The authors studied the first luminescent heteronuclear compound, $[\text{AuIr(CO)Cl(\mu-dpm)}_2][\text{PF}_6]$ (where dpm = bis(diphenylphosphino)methane), containing a $d^{10}$-$d^8$ pair. This compound had a Au-Ir bond distance of 2.986(1) Å. The absorption spectrum of $[\text{AuIr(CO)Cl(\mu-dpm)}_2][\text{PF}_6]$ in dichloromethane showed a strong band at 440 nm which was assigned to a spin-allowed $d_{\sigma^*} \rightarrow p_z$ transition in which the $z$ axis was along the Ir-Au bond. The weaker band at 518 nm may be the spin-forbidden counterpart of this transition. The absorption energy of this compound ($\lambda_{\text{max}} = 440$ nm) was in between $[\text{Ir}_2(\text{CO})\text{Cl}_2(\mu-dpm)_2]$ ($\lambda_{\text{max}} = 518$ nm) and $\text{Au}_2(\text{CO})(\mu-dpm)_2^{2+}$ ($\lambda_{\text{max}} = 518$ nm) indicating that the transition involved predominantly metal orbitals. The emission spectrum upon excitation at 430 nm consisted of two bands at 498 and 570 nm at 77 K. The emission band at 498 nm was due to fluorescence and the 570 nm band was due to phosphorescence. At room temperature, both emission bands were present but the 570 nm band was less intense. This can be explained by the temperature dependent quenching of phosphorescence.

The X-ray crystal structure of the heteronuclear hydrido-bridged gold compound, $[\text{PEt}_3]^2(\text{C}_6\text{F}_3)\text{Pt(}\mu-\text{H})\text{Au(PPH}_3\text{)}][\text{CF}_3\text{SO}_3]$, containing Au(I)-Pt(II) has been studied. The structure consisted of square planar trans-[PtH-(C$_6$F$_3$)(PEt$_3$)$_2$] and nearly linear
"AuH(PEt₃)" units sharing the hydride ligand. The Pt-Au bond distance of this compound was found to be 2.714(1) Å. A possible qualitative orbital interaction scheme for the \([\text{PEt}_3]_2(\text{C}_6\text{F}_5)\text{Pt}(\mu-\text{H})\text{Au(PPPh}_3])\)\((\text{CF}_3\text{SO}_3)\) compound is shown in Figure 1.5.

![Figure 1.5](image)

**Figure 1.5.** Qualitative orbital diagram for the direct Pt-Au interaction of \([\text{PEt}_3]_2(\text{C}_6\text{F}_5)\text{Pt}(\mu-\text{H})\text{Au(PPPh}_3])\)\((\text{CF}_3\text{SO}_3)\).²⁹

Crespo et al. have reported experimental and theoretical studies of \([\text{AuCl(Ph}_2\text{PCH}_2\text{SPh})_2\text{PdCl}_2]\) as the first example showing Au(I)-Pd(II) interactions.¹⁰⁶ The crystal structure of this compound had a Au(I)-Pd(II) bond distance of 3.140 Å. Theoretical calculations were carried out using second-order Møller-Plesset (MP2) level and showed that the major contribution for Au(I)-Pd(II) interaction was dispersion. There were also some ionic contributions that led to Au(I)-Pd(II) interactions in \([\text{AuCl(Ph}_2\text{PCH}_2\text{SPh})_2\text{PdCl}_2]\).

The synthesis and structural characterization of the luminescent tetranuclear mixed metal Pt(II)-Cu(I) complex, \([\text{Pt}_2(\text{dppm})_2(\text{C}≡\text{CPh})_4(\text{Cu(MeCN)})_2](\text{PF}_6)_2\) has been studied recently.¹⁰⁷ The scientists have compared the crystal structure of this compound
with its precursor compound, [Pt₂(dppm)₂(C=CPPh)₄] and found that the Pt-Pt distance of the Pt(II)-Cu(I) mixed metal compound was significantly shorter than the precursor compound. The Pt-Pt bond distance of the mixed metal compound was 3.0124(9) Å and the corresponding value for the precursor compound was 3.437(1) Å. The shortening of the Pt-Pt bond distance in the mixed metal compound was ascribed to the encapsulation of the Cu(I) ion by two adjacent alkyl ligands. This process pulls the platinum atoms closer together as a result of the reduced donor strength of the alkyl ligands upon copper(I) coordination. Therefore, metal-metal interactions occur by pulling metal centers closer due to the reduced electron density of the platinum centers in the mixed metal compound. Upon excitation at 350 nm, both the mixed metal and the precursor compounds showed strong luminescence at 77 K as well as at room temperature. At 77 K, both solid compounds showed two emission bands at around 460-495 nm (HE band) and 540-600 nm (LE band). The emission bands of the mixed metal compound were lower in energy than those of the precursor compound. This may be due to the reduced Pt-Pt separation in the mixed metal compound which resulted in a larger dσ-dσ* splitting. This would also increase the dσ* orbital energy in the mixed metal compound upon coordination of Cu(I) ions. The HE band was assigned to intraligand phosphorescence of the bridging diphosphine ligands and the LE band was ascribed to phosphorescence derived from the metal-metal-to-ligand charge transfer state.
1.5. Goal and Overview of Thesis

The purpose of this thesis is to elucidate three unresolved issues for dicyanoargentate(I) and dicyanoaurate(I) coordination compounds. Exciplex tuning, optical memory and mixed metal system interactions are the three fundamental issues that have been focused on in this work.

The chapters in the thesis have been arranged as follows. Chapter 1 discusses background information and gives a literature review of topics that are relevant to this study. All experimental and theoretical methods used in this thesis are presented in Chapter 2. Chapter 3 discusses spectroscopic studies of "exciplex tuning" for dicyanoaurate(I) ions doped in potassium chloride crystals. Chapters 4 and 5 discuss the optical memory and temperature dependent studies for dicyanoargentate(I) and dicyanoaurate(I) ions doped in potassium chloride crystals. In chapter 6, d^{10}-d^{10} and d^{10}-d^{8} mixed metal compounds are discussed. Finally, Chapter 7 summarizes the thesis, gives conclusions and proposes future research work.
1.6. References


Chapter 2

EXPERIMENTAL

2.1. Chemicals

Potassium dicyanoargentate(I), potassium dicyanoaurate(I), potassium tetracyanoplatinate(II), potassium tetracyanopalladate(II), and potassium chloride were purchased from Alfa-Aesar Company. Puro-graphic™ calibration standards (998 μg/ml gold in 5% HCl, and 995 μg/ml silver in 5% HNO₃) for the atomic absorption measurements were purchased from the Cole-Parmer Company.

2.2. Crystal Growing

2.2.1. Synthesis of Ag(CN)₂/KCl, Au(CN)₂/KCl, pure KAg(CN)₂, and pure KAu(CN)₂ crystals

Ag(CN)₂/KCl crystals were synthesized using 3.75 g of KCl, 0.25 g of KAg(CN)₂ and ~15 ml of distilled water. Upon slow evaporation at room temperature, the first set of crystals was formed after 24 hours. The first set of crystals was harvested as batch 1 and the remaining mother solution was allowed to evaporate longer. After nine days and just before the solution was dry, the second set of crystals was harvested as batch 2.

Au(CN)₂/KCl crystals were synthesized using 5 g of KCl, 0.2 g of KAu(CN)₂ and ~15 ml of distilled water. After slow evaporation of mother solution at room temperature, three batches (batch 1, batch 2, and batch 3) were harvested after four, six, and twenty days. Pure KAg(CN)₂ crystals were synthesized from 0.4 g of KAg(CN)₂ and
~5 ml of distilled water. On the other hand, pure KAu(CN)₂ crystals were synthesized using 0.3 g of KAu(CN)₂ and ~4 ml distilled water.

2.2.2. Synthesis of mixed metal crystals

1 mole Ag(CN)₂: 1 mole Au(CN)₂ doped in KCl were synthesized as follows: In a clean beaker, 0.375 g of KCl and 0.25 g of pure KAg(CN)₂ were dissolved in ~15 ml of distilled and deionized water. In a separate beaker, 5 g of KCl and 0.2 g of KAu(CN)₂ were dissolved in ~15 ml of distilled and deionized water. The two solutions were poured together and allowed to evaporate slowly at room temperature. The first set of crystals was harvested after one day. The remaining mother solution was evaporated longer and a second set of crystals was harvested after 4 days. Again, the remaining mother solution was evaporated slowly and then the third and fourth sets of crystals were harvested after 9 and 15 days, respectively.

For the synthesis of d¹⁰-d¹⁰ mixed metal crystals with different Ag and Au ratios, different amounts of KAg(CN)₂ and KAu(CN)₂ were used as shown in Table 2.1.

Table 2.1. Amounts of KAg(CN)₂, and KAu(CN)₂ used to synthesize each d¹⁰-d¹⁰ mixed metal system.

<table>
<thead>
<tr>
<th>Ag:Au mole ratio</th>
<th>Mass of KAg(CN)₂ (g)</th>
<th>Mass of KAu(CN)₂ (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1.11</td>
<td>0.17</td>
<td>0.25</td>
</tr>
<tr>
<td>1:0.31</td>
<td>0.09</td>
<td>0.38</td>
</tr>
<tr>
<td>1:3.10</td>
<td>0.52</td>
<td>0.25</td>
</tr>
<tr>
<td>1:6.11</td>
<td>0.51</td>
<td>0.13</td>
</tr>
</tbody>
</table>
After preparing saturated aqueous solutions of each mixture in Table 2.1, the solutions were evaporated slowly at room temperature. Crystals were harvested after 3 - 5 days.

Two types of d^{10}-d^{8} systems were synthesized. The first type was a Ag-Pt system and the second type was a Au-Pt system. The first type of crystals were synthesized using KAg(CN)_{2} as a d^{10} compound. The 1:1 molar ratio of Pt-Ag mixed crystals were synthesized after slow evaporation a mother solution containing 0.47 g of K_{2}[Pt(CN)_{4}], 0.25 g of KAg(CN)_{2} and ~6 ml of distilled water at room temperature. The 1:1 molar ratio of Pt-Ag mixed crystals was grown using 0.33 g of K_{2}[Pt(CN)_{4}], 0.25 g of KAu(CN)_{2} and ~5 ml of distilled water. Pure K_{2}[Pt(CN)_{4}] crystals were grown using 0.4 g of K_{2}[Pt(CN)_{4}] and ~4 ml of distilled water. All crystals were harvested after 4-5 days.

2.3. Atomic Absorption Measurements

Atomic absorption measurements were carried out using a Model 857-Smith-Hieftje 11/12 spectrophotometer. For the KAu(CN)_{2}/KCl crystals, standard solutions (1-30 ppm) were prepared using puro-graphic	m calibration standards (998 μg/ml gold in 5% HCl) from the Cole-Parmer Company. In order to analyze the %Au of each batch of KAu(CN)_{2}/KCl single crystals, very dilute aqueous solutions were prepared. For example, 10 ml of KAu(CN)_{2}/KCl batch 1 solution was prepared using 0.0128 g of KAu(CN)_{2}/KCl batch 1. The wavelength of the lamp source was 267 nm.

On the other hand, for the silver samples, puro-graphic	m calibration standards (995 μg/ml silver in 5% HNO_{3}) were used to prepare standard solutions (1-30 ppm) and the wavelength of the lamp source was 328 nm.
2.4. Low Temperature Experiments

Two types of continuous flow cryostats were used in order to achieve low temperatures. A model Lt-3-110 Heli-Tran cryogenic liquid transfer system including T-type thermocouple and Omega model CN132 temperature process controller was used to achieve temperatures between 77 K and room temperature with an accuracy of ± 1 K. Liquid nitrogen was used as a coolant in this setup. The second type was a Janis model ST-100 cryostat including a silicon diode thermocouple, a digital voltmeter with a serial bus interface, a 25 Ω heater coil, and a computer program that converted the voltage from the silicon diode into temperature in degrees Kelvin. Using this cryostat, the temperature could reach as low as 4 K with an accuracy of 0.5 K. Liquid helium was used as a coolant in this set up.

2.5. Steady-state Photoluminescence Spectroscopy

Steady-state photoluminescence spectra were recorded using a Photon Technology International (PTI) Model QuantaMaster-1046 spectrophotometer. This instrument is equipped with two excitation monochromators, a single emission monochromator and a 75 W xenon lamp. The excitation and emission slit widths were varied depending on the experiment. The sample was mounted on a copper holder using Cry-Con grease, composed of high vacuum grease and a small amount of copper dust. This copper-grease mixture was used because it did not show luminescence in the areas where the crystals displayed their luminescence properties. The shroud that covered the sample had two perpendicular quartz windows, which allowed the incident beam of light to reach the sample as well as the emitted light beam to reach the detector. This
spectrophotometer is connected to a computer and controlled by the PTI Instrument Control Program, OSCAR, and recorded emission and excitation spectra. All excitation spectra were corrected using the quantum counter rhodamine B for the spectral variations of the lamp. For this correction, the raw excitation spectrum is divided by the excitation spectrum of rhodamine B.

2.6. Optical Memory Experiments

In order to carry out optical memory experiments, the crystal of interest was mounted on a copper holder using Cry-Con grease. Then, the crystal was cooled to 77 K or various other temperatures and allowed to reach equilibrium over a period of 30 minutes. In the initial step, the emission and excitation spectra were recorded. Then, the shutter of the fluorescence spectrometer was closed and the crystal was irradiated with a 266 nm laser for five minutes. After 5 minutes, the 266 nm laser was turned off and the shutter of the fluorescence spectrometer was opened and the emission and excitation spectra were recorded. It is worth mentioning here that the whole crystal was covered by 266 nm laser because of its small size. The irradiation and spectra recording processes were repeated using 5-minute increments for 1.5 hours. Then, the crystal was warmed up to room temperature in the dark for two hours and recooled down to the previous temperature. After waiting 30 minutes for the system to reach equilibrium, the emission and excitation spectra were recorded for the recovery step.

In order to calculate kinetic parameters, optical memory experiments were carried out at different temperatures. In the kinetic analysis, the following assumption was
made: the integrated peak area was proportional to the concentration of the luminescent species.

2.7. Lifetime Analysis

Lifetime measurements were carried out using a Nanolase diode-pumped solid state laser. This laser gives an output of 0.43 ns and pulses at 266 nm with a repetition rate of 8.1 kHz. The detection system includes a McPherson Model 2025 monochromator, a Hamamatsu R1463 photomultiplier, and a Princeton Applied Research model 115 Wide Band Preamplifier. A Lecroy 9310 400 MHz digital oscilloscope was used to collect data. All decays were averaged over 1000 sweeps.

2.8. Raman Spectroscopy

Raman spectra were obtained using a Raman Imaging Microscope System 1000 equipped with a diode laser operating at $\lambda_{ex} = 785$ nm. All measurements were carried out at room temperature for the same single crystals used in the luminescence measurements.

2.9. Computational Details

Ground and first excited state calculations were carried out using the FORTICON 8 program (QCMP011). The relativistic parameters used for all atoms are as shown in Table 2.2.

Ground and first excited state calculations were carried out for free monomers, dimers, trimers, and tetramers. Details of the calculations for the free oligomers have
been described earlier.\textsuperscript{2} Ground state calculations were carried out for the monomer, dimer, and trimer units of [Au(CN)$_2$] ions doped in a KCl lattice. Upon doping [Au(CN)$_2$]$_n$ oligomers in the KCl lattice, the Au$^+$ ions replace the K$^+$ ions and the CN$^-$ ions replace the Cl$^-$ ions. A [Au(CN)$_2$] ion doped in the KCl lattice was modeled by a layer containing a Au$^+$ ion occupying the site of a K$^+$ ion with four neighboring Cl$^-$ ions separated by 3.19 Å and four neighboring K$^+$ ions separated by 4.51 Å.\textsuperscript{3} The two CN$^-$ ions were in the perpendicular axis to the plane of the layer.

Ground and first excited calculations for the d$^{10}$-d$^{10}$ mixed metal system were carried out for the eclipsed [Au(CN)$_2$]$_2$ dimer, eclipsed [Ag(CN)$_2$]$_2$ dimer, eclipsed [AgAu(CN)$_4$]$^{2-}$ dimer, linear [Au(CN)$_2$]$_3$ trimer, linear [Ag(CN)$_2$]$_3$ trimer, linear [AgAu$_2$(CN)$_6$]$^{3-}$ trimer and linear [AuAg$_2$(CN)$_6$]$^{3-}$ trimer units.

\textbf{Table 2.2.} Relativistic parameters used in the extended Hückel calculations.\textsuperscript{1}

<table>
<thead>
<tr>
<th>Atom</th>
<th>Orbital</th>
<th>Hij(eV)</th>
<th>Slater Exponent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>6s</td>
<td>-7.937</td>
<td>2.124</td>
</tr>
<tr>
<td></td>
<td>6p</td>
<td>-3.466</td>
<td>1.496</td>
</tr>
<tr>
<td></td>
<td>5d</td>
<td>-12.37</td>
<td>3.471</td>
</tr>
<tr>
<td>Ag</td>
<td>5s</td>
<td>-6.453</td>
<td>1.594</td>
</tr>
<tr>
<td></td>
<td>5p</td>
<td>-3.289</td>
<td>1.17</td>
</tr>
<tr>
<td></td>
<td>4d</td>
<td>-13.91</td>
<td>3.248</td>
</tr>
<tr>
<td>C</td>
<td>2s</td>
<td>-19.39</td>
<td>1.577</td>
</tr>
<tr>
<td></td>
<td>2p</td>
<td>-11.07</td>
<td>1.434</td>
</tr>
<tr>
<td>N</td>
<td>2s</td>
<td>-26.25</td>
<td>1.886</td>
</tr>
</tbody>
</table>
2.10. References


Chapter 3

SPECTROSCOPIC STUDIES OF “EXCIPEX TUNING” FOR DICYANOAUARATE(I) IONS DOPED IN POTASSIUM CHLORIDE CRYSTALS

3.1. Introduction

Bonding in compounds of closed shell $d^{10}$ atoms such as gold(I) has attracted the interest of experimental and theoretical chemists because of the remarkable tendency of these compounds to form supramolecular aggregates owing to Au-Au aurophilic bonding. A variety of structures showing gold(I) compounds aggregate as dimers, oligomers, and polymers have been reported. Che and his coworkers have reported a Resonance Raman investigation of Au$_2$[bis(dicyclohexylphosphine)methane]$_2$(ClO$_4$)$_2$, which showed Au(I)-Au(I) single bond formation in the excited state. A further study by the same group has shown that analogous Ag(I) species also give rise to Ag-Ag single bond formation in the excited state. Our group has recently reported a comparison between Ag-Ag and Au-Au interactions in the ground and excited states of dicyano complexes.

---

The contents of this chapter have been based on a paper has been published in *J. Phys. Chem. B*. 2002, 106 (39), 10058-10064. (Samanthika R. Hettiarachchi, Manal A. Rawashdeh-Omary, Sofian M. Kanan, Mohammad, A. Omary, Howard H. Patterson and Carl P. Tripp. Spectroscopic Studies of “Exciplex Tuning” for Dicyanoaurate(I) Ions Doped in Potassium Chloride Crystals.)
Monovalent gold complexes have been shown to have a variety of applications. For example, \([\text{Au}(\text{CN})_2]^-\) ions play an important role in medicinal chemistry.\(^{11}\) The modern day use of \([\text{Au}(\text{CN})_2]^-\) ions for medicinal purposes originated from Robert Koch's discovery, that \([\text{Au}(\text{CN})_2]^-\) ions have bacteriostatic properties.\(^ {12}\) It has also been reported that \([\text{Au}(\text{CN})_2]^-\) is a common metabolite of injectable gold drugs such as auranofin for the treatment of rheumatoid arthritis.\(^ {13}\) Other potential applications of Au(I) compounds such as in optical sensors,\(^ {14}\) bio-sensors,\(^ {15}\) and photocatalysts\(^ {16}\) provide a strong motivation to study monovalent Au(I) compounds.

Our recent studies of cyano complexes of Au(I) and Ag(I) relate the photoluminescence properties to the formation of metal-metal bonded excimers and exciplexes. Although luminescent exciplexes are well-known molecular entities in the photochemistry and photophysics of organic systems,\(^ {17}\) the field is less common in the inorganic literature and most reported inorganic exciplexes are not luminescent.\(^ {18}\) Metal-metal bonded excimers and exciplexes are the only class of luminescent inorganic exciplexes. Members of this class include homoatomic and heteroatomic exciplexes involving closed shell metal ions, mostly \(d^8\) and \(d^{10}\) systems. Examples include those reported by Zink \textit{et al.} involving *[Cu\(^+\)-Ag\(^-\)]\(^*\) and *[Cu\(^+\)-Cu\(^+\)]\(^*\) simple ions in doped \(\beta\)" alumina,\(^ {19,20}\) also Nagle \textit{et al.} have reported the existence of Ti\(^+\) bonding to Pt(II) in aqueous solutions of tetrakis(\(\mu\)-diphosphito)diplatinate(II) and thallium(I),\(^ {21a,b}\) and the formation of Pt(II)-Au(I) bonds in aqueous solutions of \([\text{Au}(\text{CN})_2]^-\) and Pt\(_2\)(P\(_2\)O\(_5\)H\(_2\))\(_4\).\(^ {22}\)

We contributed to this field by introducing the optical phenomenon of "exciplex tuning", which describes the tuning of the emission in \([\text{Ag}(\text{CN})_2]^-\)-doped alkali halide crystals to various bands in the ultraviolet and visible regions with each band due to a different
oligomeric \([\text{Ag(CN)}_2]_n\) excimer or exciplex.\(^{23-26}\) Tuning the excited state properties is extremely important in a variety of optoelectronic applications in relation to some fundamental scientific issues such as excitonic energy transfer.\(^{27-30}\) Examples illustrating the significance of exciplex tuning in \(d^{10}\) complexes in scientific and practical applications have been reported by some of us regarding tunable energy transfer to lanthanide ions,\(^{31}\) the photocatalytic action of \(\text{Ag(I)}\)-doped ZSM-5 zeolites in the decomposition of nitric oxide,\(^{32}\) and \(\text{Ag(I)}\)-catalyzed photodecomposition of pesticides.\(^{33,34}\)

Our group has previously reported luminescence and X-ray measurements versus temperature for pure \(\text{KAu(CN)}_2\).\(^{35}\) These results demonstrated the sensitivity of the emission energy to changes in Au-Au separation. Very recently, we have reported the ground and excited state aurophilic and argentophilic interactions of \(\text{[Au(CN)}_2]_n\) and \(\text{[Ag(CN)}_2]_n\) oligomers in solution.\(^{10,36}\) We report here the first example of exciplex tuning for \(\text{[Au(CN)}_2]_n\) ions doped in KCl single crystals. Tuning of the luminescence is studied by site-selective excitation and varying the dopant concentration. By varying the dopant concentration, we have observed from our spectroscopic data an unusual trend: as the dopant concentration increases, the size of the oligomers increases and this is accompanied by a shorter Au-Au bond distance. At the highest dopant concentration, the Au-Au bond distance is shorter than that found in the pure \(\text{KAu(CN)}_2\) crystal. In contrast, at the highest doping level of the \(\text{[Ag(CN)}_2]_n/\text{KCl}\) system, the Ag-Ag bond distance is similar to the same bond length as the corresponding pure crystal. Correlation between the luminescence and Raman bands is made for \(\text{M(CN)}_2^+/\text{KCl}\) (\(\text{M}=\text{Au, Ag}\)) doped crystals with varying M content as well as pure crystals of \(\text{KM(CN)}_2\).
3.2. Experimental

Single crystals of KAu(CN)$_2$/KCl were grown by slow evaporation of a saturated aqueous solution containing 5g of KCl and 0.2g of KAu(CN)$_2$ at ambient temperature. The first batch of KAu(CN)$_2$/KCl crystals was harvested after four days of slow evaporation. After harvesting the first batch of crystals (henceforth referred to as "batch 1"), the remaining solution (mother liquor) was allowed to evaporate under ambient conditions. The second batch of KAu(CN)$_2$/KCl crystals (batch 2) was harvested after six days. The remaining solution was allowed to evaporate to just before dryness (twenty days) at which point, the last batch of crystals (batch 3) was harvested. Pure KAu(CN)$_2$ single crystals were grown from a nearly saturated aqueous solution of KAu(CN)$_2$ and the crystals were harvested after fourteen days. Single crystals of KAg(CN)$_2$/KCl were grown using a similar synthetic procedure but using 7.5g of KCl and 0.5g of KAg(CN)$_2$. After slow evaporation, the first batch of KAg(CN)$_2$/KCl crystals was harvested after one day. The remaining solution was allowed to evaporate longer and, just before dryness, the second batch of KAg(CN)$_2$/KCl crystals was harvested after thirteen days.

The metal content of the different batches of doped crystals was determined using atomic absorption spectroscopy. Atomic absorption measurements were carried out using a Model 857-Smith-Hieftje 11/12 spectrophotometer. In order to determined the gold content of the different batches of KAu(CN)$_2$/KCl, puro-graphic™ calibration standards (998 μg/ml gold in 5% HCl) from the Cole-Parmer Company were used as the standard. The crystal growing process was repeated a second time and atomic absorption, luminescence and Raman analyses gave reproducible data. Atomic
absorption analyses for different batches of KAg(CN)$_2$/KCl were carried out using purigraphic$^\text{TM}$ calibration standards (995 $\mu$g/ml silver in 5% HNO$_3$).

Raman spectra were obtained using a Raman Imaging Microscope System 1000 equipped with a diode laser operating at $\lambda_{ex} = 785$ nm. All measurements were carried out at room temperature for the same single crystals used in the luminescence measurements.

Steady-state photoluminescence spectra were collected using a Photon Technology International Model QuantaMaster-1046 spectrophotometer equipped with a 75 W xenon lamp. Wavelengths were selected with two excitation monochromators and a single emission monochromator. All spectra were recorded at 77K. Excitation spectra were corrected for spectral variation of the lamp using rhodamine B as a quantum counter. Liquid nitrogen was used as the coolant in a Model LT-3-110 Heli-Tran cryogenic liquid transfer system.

Lifetime measurements were recorded using a Nanolaser diode-pumped solid-state laser that pulses at 266 nm with a repetition rate of 8.1 kHz. A 400 MHz LeCroy 9310 digital oscilloscope was used to collect data. The decays were averaged over 1000 sweeps on the oscilloscope. All lifetime measurements were carried out at 77K.

3.3. Computational Details

Ground and first excited state calculations were carried out using the FORTICON 8 program (QCMP011). Relativistic parameters used for all atoms have been reported previously.$^{37}$ Ground and first excited state calculations were carried out for free
monomers, dimers, trimers, and tetramers. Details of the calculations for the free oligomers have been described earlier.\textsuperscript{36}

Ground state calculations were carried out for monomer and eclipsed dimer units of [Au(CN)\textsubscript{2}]\textsuperscript{−} ions doped in a KCl lattice. Upon doping [Au(CN)\textsubscript{2}]\textsubscript{n} (n = 1, 2) in the KCl lattice, the Au\textsuperscript{+} ions replace the K\textsuperscript{+} ions and the CN\textsuperscript{−} ions replace the Cl\textsuperscript{−} ions. A [Au(CN)\textsubscript{2}]\textsuperscript{−} ion doped in a KCl lattice was modeled by a layer containing a Au\textsuperscript{+} ion occupying the site of a K\textsuperscript{+} ion with four neighboring Cl\textsuperscript{−} ions separated by 3.19 Å and four neighboring K\textsuperscript{+} ions separated by 4.51 Å.\textsuperscript{38} The two CN\textsuperscript{−} ions were in the perpendicular axis to the plane of the layer described hitherto.

3.4. Results and Discussion

3.4.1. Atomic absorption results

Pure KAu(CN)\textsubscript{2} and three batches isolated from a mixture of KAu(CN)\textsubscript{2} and KCl have been studied. Atomic absorption spectroscopy analysis has shown that the values of % Au (by wt) are 0.45, 1.38, and 2.20 for KAu(CN)\textsubscript{2}/KCl crystals referred to herein as batches 1, 2, and 3, respectively. The variation of Au content among the KAu(CN)\textsubscript{2}/KCl batches can be explained by the synthetic procedure. The crystals formed in the early stage of slow evaporation of the starting KCl solution contained a low concentration of [Au(CN)\textsubscript{2}]\textsuperscript{−} ions. Therefore, batch 1 has the lowest Au content. After harvesting the first batch of crystals (batch 1), the remaining mother liquor contains a higher concentration of [Au(CN)\textsubscript{2}]\textsuperscript{−} than the starting solution. This leads to KCl crystals grown with a higher gold content in batch 2. Batch 3 has the highest gold content because it is harvested from the most concentrated mother liquor after harvesting batches 1 and 2. Similar arguments
also apply for the analogous silver doped system that we are studying in this paper. Atomic absorption analyses of KAg(CN)$_2$/KCl batches 1 and 2 gave 1.21 and 2.23 %Ag (wt), respectively.

3.4.2. Steady-state photoluminescence spectroscopy

Figure 3.1 shows the emission spectra of KAu(CN)$_2$/KCl batch 1 at 77K. Three emission bands at 335, 390, and 425 nm are observed by varying the excitation wavelength in the excitation range 270-350 nm, as illustrated in Figure 3.1. No other emission bands are observed by varying the excitation wavelength (the two bumps at ~495 and ~512 nm are artifacts from the lamp source). The emissions at 335, 390 and 425 nm are henceforth referred to as II, III, and IV, respectively (as shown in Table 3.3, only KAu(CN)$_2$ solutions shows emission band I).

The corrected excitation spectra of KAu(CN)$_2$/KCl batch 1 at 77K are shown in Figure 3.2. Each emission band observed in Figure 3.1 has a characteristic excitation maximum. Therefore, various emission bands can be resolved by selecting the excitation wavelength. The absorption spectra of infinitesimally dilute aqueous solutions of KAu(CN)$_2$ show a structured profile with $\lambda_{\text{max}} \leq 250$ nm. All observed excitation bands in the doped KAu(CN)$_2$/KCl (see Figure 3.2) are at wavelengths longer than 250 nm; this red shift is presumably due to metal-metal interactions. Doped [Ag(CN)$_2$]/KCl systems show excitation and emission bands, the low energy of which has been attributed to metal-metal interactions in different aggregations and orientations of [Ag(CN)$_2$] units. Solutions with high concentrations of [Au(CN)$_2$]$^-$ and [Ag(CN)$_2$]$^-$ also show similar red shifts in the absorption and emission energies due to oligomerization.
Figure 3.1. Emission spectra of a single crystal of KAu(CN)$_2$/KCl batch 1 at 77K with different excitation wavelengths.
Figure 3.2. Corrected excitation spectra of a single crystal of KAu(CN)$_2$/KCl batch 1 at wavelengths corresponding to the emission maxima of bands II, III, and IV at 77K.
Figure 3.3 shows the emission spectra of batches 1-3 as well as pure KAu(CN)$_2$ at 77 K upon excitation at 272 nm. According to Figure 3, batches 1 and 3 show the three aforementioned bands II and III, and IV. On the other hand, batch 2 and pure KAu(CN)$_2$ show only band III. Upon excitation at 315 nm, both batches 1 and 3 show bands III and IV whereas batch 2 and pure KAu(CN)$_2$ show only band III (Figure 3.4). These results indicate the presence of three emission sites in the mixed crystals with the lowest and highest Au content while the crystals with intermediate Au content have only one emission site, similar to the situation in pure KAu(CN)$_2$ crystals. This trend was verified with a complete new set of crystals.

Lifetime measurements for the observed luminescence bands present in three batches of KAu(CN)$_2$/KCl and pure KAu(CN)$_2$ at 77K are summarized in Table 3.1. The observed microsecond scale lifetimes for emission bands III and IV in each system suggests that these emissions are due to phosphorescent transitions, which are enhanced due to the large spin-orbit coupling of gold (spin-orbit coupling constant, $\zeta$, for the 5d orbital of Au(I) is 5,100 cm$^{-1}$). It was not feasible to measure the lifetime for band II because of its very weak intensity with 266 nm laser excitation.

3.4.3. Raman spectroscopy

Figure 3.5 shows the Raman spectra of the three batches of KAu(CN)$_2$/KCl as well as pure KAu(CN)$_2$ in the cyanide stretching frequency region. Batch 2 and pure KAu(CN)$_2$ have only one strong peak at $\sim$2176 cm$^{-1}$ (traces c and a, respectively). Meanwhile, batch 1 (trace d) has two resolved peaks at $\sim$2169 and $\sim$2176 cm$^{-1}$ whereas
Table 3.1. Correlation of luminescence and Raman bands in various doped and pure crystals of the dicyanoaurates(I) and dicyanoargentates(I). Lifetime measurements were carried out at 77K.\(^a\)

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Emission (excitation) bands, nm</th>
<th>Raman peaks, cm(^{-1})</th>
<th>(\tau) (390 nm), (\mu)s</th>
<th>(\tau) (425 nm), (\mu)s</th>
<th>Emission (excitation) bands, nm</th>
<th>Raman peaks, cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch 1</td>
<td>335 (272), 390 (315), 425 (337)</td>
<td>2169, 2176</td>
<td>0.42 ±0.01</td>
<td>0.92 ±0.01</td>
<td>296 (245), 338 (275), 415 (265)</td>
<td>2118, 2124</td>
</tr>
<tr>
<td>Batch 2</td>
<td>390 (315)</td>
<td>2176</td>
<td>0.38 ±0.01</td>
<td>-</td>
<td>296 (245), 338 (275), 415 (265)</td>
<td>2118, 2124, 2159</td>
</tr>
<tr>
<td>Batch 3</td>
<td>335 (272), 390 (315), 425 (337)</td>
<td>2169, 2176, 2189</td>
<td>0.65 ±0.02</td>
<td>1.00 ±0.03</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pure</td>
<td>390 (315)</td>
<td>2176</td>
<td>0.34 ±0.01</td>
<td>-</td>
<td>415 (265)</td>
<td>2159</td>
</tr>
</tbody>
</table>

\(\mu\)s range.

\(^a\): Lifetime measurements for doped \([Ag(CN)\_2]\)/KCl crystals were reported in references 23-26 and also were in the \(\mu\)s range.
Figure 3.3. Emission spectra of pure KAu(CN)$_2$ and three batches of KAu(CN)$_2$/KCl crystals at 77K, when excited at 272 nm. The spectra are shown for single crystals on going from batch 3 to batch 1 to batch 2 to pure KAu(CN)$_2$. 
Figure 3.4. Emission spectra of pure KAu(CN)$_2$ and three batches of KAu(CN)$_2$/KCl crystals at 77K, when excited at 315 nm. The spectra are shown for single crystals on going from batch 3 to batch 1 to batch 2 to pure KAu(CN)$_2$. 
batch 3 (trace b) has an additional peak at $\sim 2189 \text{ cm}^{-1}$. The appearance of the $2169 \text{ cm}^{-1}$ peak for batches 1 and 3 (but not for batch 2 or pure KAu(CN)$_2$) is consistent with the appearance of the high-energy luminescence peak, II, only for these two batches (Figure 3.3).

There is a clear correlation between the Raman bands obtained for each sample and the corresponding photoluminescence spectra. Batch 2 and pure KAu(CN)$_2$ have virtually identical photoluminescence spectra and the Raman spectra of the two samples show a single $\text{CN}$ peak at the same frequency (2176 cm$^{-1}$). The presence of more than one peak other than 2176 cm$^{-1}$ band in the $\text{CN}$ region indicates different sites for [Au(CN)$_2$]$_n$ ions in the KCl lattice. Therefore, the peaks at 2169, 2176, and 2189 cm$^{-1}$ in Figure 3.5 are due to different [Au(CN)$_2$]$_n$ clusters present in the studied crystals. Gold-gold interactions are expected to strongly influence the C-N stretching vibration. On going from batch 1 $\rightarrow$ 2 $\rightarrow$ 3, the relative intensity of the Raman peaks with higher $\text{CN}$ values increases, which is consistent with increased Au-Au interactions in the same direction. However, it is unusual that batch 3 has a Raman peak at a higher frequency (2189 cm$^{-1}$) than the 2176 cm$^{-1}$ peak for pure KAu(CN)$_2$. An increase in gold-gold interactions leads to a decrease in back bonding from gold to the antibonding $\pi^*$ LUMO for the cyano group, hence a higher $\text{CN}$ value. This may result from either an increase in oligomerization (e.g., from dimers to trimers), or a shortening of the Au-Au distance in a given oligomer. The higher $\text{CN}$ value for batch 3 than for pure KAu(CN)$_2$ is likely due to a shorter Au-Au distance in the oligomer responsible for the dominant 2189 cm$^{-1}$ band in batch 3 compared to the Au-Au distance between [Au(CN)$_2$] species in the infinite layers of the pure compound. A somewhat similar situation has been encountered
Figure 3.5. Raman spectra of single crystals of pure KAu(CN)$_2$ and three batches of KAu(CN)$_2$/KCl in the region of the cyanide stretching frequency. The spectra are shown for single crystals of pure KAu(CN)$_2$ (a), batch 3 (b), batch 2 (c), and batch 1 (d) respectively.
in a structural study by Schmidbaur et al. for various haloisonitrilegold(I) complexes.\textsuperscript{41} It was found that compounds with infinite linear chain structures (i.e., polymers) showed longer Au-Au distances than those in more sterically encumbered compounds, which had oligomeric structures with shorter Au-Au distances.

To further validate the correspondence between the Raman and photoluminescence bands, single crystals of two batches of [Ag(CN)\textsubscript{2}]\textsuperscript{-}/KCl as well as pure KAg(CN)\textsubscript{2} were also synthesized and spectroscopically analyzed. Upon excitation at 245 nm (Figures 3.6) and 275 nm (Figure 3.7), three different luminescence bands are observed for the [Ag(CN)\textsubscript{2}]\textsuperscript{-}/KCl system. The relative intensities of these luminescence bands vary between the [Ag(CN)\textsubscript{2}]\textsuperscript{-}/KCl batches and the results here reproduce the trends we reported previously for this doped system.\textsuperscript{23-26} Pure KAg(CN)\textsubscript{2} shows only band C. The Raman spectra of these three samples are shown in Figure 3.8. Batch 1 shows 2 peaks at \textasciitilde2118 and \textasciitilde2124 cm\textsuperscript{-1}. Interestingly, the Raman spectrum of batch 2 (Figure 3.8b) shows an additional peak at \textasciitilde2159 cm\textsuperscript{-1} along with 2 peaks observed for batch 1. Pure KAg(CN)\textsubscript{2} shows only one Raman peak at \textasciitilde2159 cm\textsuperscript{-1}, which clearly correlates with band C in the luminescence spectra shown in Figure 3.6 and 3.7. Therefore the observed additional Raman peak at \textasciitilde2159 cm\textsuperscript{-1} in batch 2 is assigned to the same species giving rise to luminescence band C. After comparison of Figures 3.6, 3.7 and 3.8, the Raman bands observed at \textasciitilde2118 and \textasciitilde2124 cm\textsuperscript{-1} correlate with the observed luminescence bands A and B, respectively. Based on our discussion earlier that the stronger the metal-metal interactions the higher the frequencies in the Raman spectra and based on our luminescence bands assignment in Table 3.3 (vide infra), it is reasonable to assign bands A and B to dimers and bent trimers, respectively. Since bent trimers have
Figure 3.6. Emission spectra of pure KAg(CN)$_2$ and two batches of KAg(CN)$_2$/KCl crystals at 77K, when excited at 245 nm. The spectra are shown for single crystals of pure KAg(CN)$_2$ (a), batch 2 (b), and batch 1 (c) respectively.
Figure 3.7. Emission spectra of pure KAg(CN)$_2$ and two batches of KAg(CN)$_2$/KCl crystals at 77K, when excited at 275 nm. The spectra are shown for single crystals of pure KAg(CN)$_2$ (a), batch 2 (b), and batch 1 (c) respectively.
Figure 3.8. Raman spectra of single crystals of pure KAg(CN)2 and two batches of KAg(CN)2/KCl in the region of the cyanide stretching frequency. The spectra are shown for single crystals of pure KAg(CN)2 (a), batch 2 (b), and batch 1 (c) respectively.
stronger metal-metal interactions than dimers (as shown in Table 3.2, the bent trimer has a lower HOMO-LUMO gap than the dimer in both the ground and first excited states), Raman peaks due to bent trimers should appear at higher frequencies. Therefore, the Raman peaks at \(-2124\) and \(2118\) cm\(^{-1}\) are due to a bent trimer and a dimer, respectively. Luminescence band C is assigned to a linear trimer and correlates with the Raman band at \(-2159\) cm\(^{-1}\).

Table 3.1 shows the correlation between the luminescence and Raman bands for pure and doped crystals containing the dicyanoaurate(I) and dicyanoargentate(I) ions.

3.4.4. Extended Hückel (EH) calculations

The preceding luminescence and Raman results clearly suggest the presence of multiple emission centers in solid-state systems of the dicyanoaurates(I). We believe that these centers are due to ground- and excited-state oligomers of \([\text{Au(CN)}_2^-]\). In order to characterize Au-Au interactions in relation to our experimental results, we have carried out EH calculations for different \([\text{Au(CN)}_2^-]_n\) oligomers \((n=1-4, \text{ eclipsed conformations})\). The results are summarized in Table 3.2 for free and doped oligomers. We shall discuss first the ground state and first excited state calculations for free oligomers of \([\text{Au(CN)}_2^-]\) units. The data indicate that the aurophilic bonding and the electronic transition energies are both sensitive to the number of ions \((n)\) in the oligomers as well as the geometry and conformation of the ions in the oligomer. For example, ground state calculations for linear eclipsed oligomers reveal that as "\(n\)" increases from \(2 \rightarrow 3 \rightarrow 4\), the binding energy increases from \(0.13 \rightarrow 0.30 \rightarrow 0.44\) eV,
Table 3.2. Summary of the results of EH calculations for ground and first excited states of different oligomers of \([\text{Au(CN)}_2^-]_n\) (all with an eclipsed conformation).\(^a\)

<table>
<thead>
<tr>
<th>Species</th>
<th>([\text{Au}])</th>
<th>([\text{Au}]/\text{KCl})</th>
<th>([\text{Au}]_2/\text{KCl})</th>
<th>([\text{Au}]_2)</th>
<th>([\text{Au}]_3) (bent)</th>
<th>([\text{Au}]_3) (lin)</th>
<th>([\text{Au}]_3) (lin)</th>
<th>([\text{Au}]_4) (lin)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(d_{\text{Au-Au}}) (^0)</td>
<td>-</td>
<td>-</td>
<td>4.51</td>
<td>3.48</td>
<td>3.00</td>
<td>3.48</td>
<td>3.15</td>
<td>3.44</td>
</tr>
<tr>
<td>B.E., eV</td>
<td>-</td>
<td>-</td>
<td>5.1</td>
<td>0.13</td>
<td>0.88</td>
<td>0.266</td>
<td>0.877</td>
<td>0.30</td>
</tr>
<tr>
<td>O.P.</td>
<td>-</td>
<td>-</td>
<td>-0.0279</td>
<td>0.0226</td>
<td>0.0734</td>
<td>0.0203</td>
<td>0.0679</td>
<td>0.0116</td>
</tr>
</tbody>
</table>

\(^a\)Notation: \([\text{Au}]_{2,3,4} = [\text{Au(CN)}_2]_{2,3,4}\), *\([\text{Au}]_{2,3}: \text{excimer/exciplex, lin= linear, B.E. = Au-Au binding energy,}

and the HOMO-LUMO gap decreases from $3.78 \rightarrow 3.43 \rightarrow 3.34$ eV. Table 3.2 also shows that bent and linear trimers gave significantly different results, suggesting that different geometries in a given oligomer lead to differences in Au-Au bonding and electronic energies.

Table 3.2 also shows that for any given $[\text{Au(CN)}_2]_n$ oligomer, the excited state has a deeper potential well (higher binding energy), higher Au-Au overlap population, shorter Au-Au equilibrium distance than the corresponding ground state. For example, a ground state dimer has a binding energy of 0.13 eV while the corresponding value for the excited state is 0.88 eV. It is therefore concluded that, for all $[\text{Au(CN)}_2]_n$ oligomers, Au-Au bonding is stronger in the first excited state than in the corresponding ground state. Stronger Au-Au bonding in the first excited state than in the ground state is an indication of the formation of $[\text{Au(CN)}_2]_n$ excimers and exciplexes. The examples shown in Figures 3.9 and 3.10 illustrate the strong Au-Au bonding and low electronic energy for exciplexes compared to ground-state oligomers. The low energies, large Stokes shifts, and structureless features of the emission bands (even at cryogenic temperatures in doped single crystals) are consistent with the exciplex assignment for the emission bands of the systems described here, which the aforementioned calculations reinforce. Supporting evidence of this assignment, including characterization of the bonding in the triplet excimer in staggered $[\text{Au(CN)}_2]_2$ by modern UHF/MP2 calculations, has been published elsewhere.10

Ground state EH calculations have also been performed for the monomers, and eclipsed dimers doped in a modeled KCl lattice. Results of these calculations are summarized in Table 3.2. Comparison of the free $[\text{Au(CN)}_2^-]$ monomer versus the doped
Figure 3.9 Ground and the first excited state potential energy curves for bent \([\text{Au(CN)}_2]_3\).
Figure 3.10. Ground and the first excited state potential energy curves for linear \([\text{Au(CN)}_2]^3\).
monomer in Table 3.2 shows that both the HOMO and LUMO undergo destabilization by doping the monomer in the KCl lattice. This is likely due to the crystal field of the Cl ions in the KCl lattice. According to Table 3.2, doping the [Au(CN)2] monomer in the KCl lattice results in a reduction of the energy difference between the HOMO and the LUMO. This gives a possible explanation for observing lower energy excitation bands in the doped system compared to the lowest energy absorption band observed in dilute aqueous KAu(CN)2 solutions. Table 3.2 also shows that as one proceeds from [Au(CN)2]+ → [Au(CN)2]2-, the HOMO-LUMO gap decreases from 4.09 → 4.04 eV due to the presence of ground state interactions. Accurate information about the extent of Au-Au bonding and optical energies among various doped oligomers were not possible because of the very large lattice energy of the KCl crystal, which masks the much weaker Au-Au interactions in the EH calculations.

3.5. Exciplex Tuning

A given doped crystal of [Au(CN)2]/KCl exhibits multiple emission bands. For example, a single crystal from batch 1 displays three emission bands that span an emission range of more than 11,000 cm⁻¹ (Figure 3.1). Because these bands are due to metal-metal bonded exciplexes, the results here represent further examples of the "exciplex tuning" phenomenon, which was described earlier for doped crystals of [Ag(CN)2]/KCl and solutions of both K[Au(CN)2] and K[Ag(CN)2]. Exciplex tuning in a doped crystal of [Au(CN)2]/KCl can be achieved by site-selective excitation (Figure 3.1) and by varying the dopant concentration (Figure 3.3) in a similar manner to that described for doped crystals of [Ag(CN)2]/KCl. Site-selective excitation is used
to resolve the different emission bands from one another (Figures 3.1 and 3.2) while varying the dopant concentration is used to maximize the relative intensity of a given exciplex band (Figures 3.3). For example, \([\text{Au(CN)}_2^-]/\text{KCl} \) crystals with the highest Au content (batch 3) show three emission bands at 335, 390 and 425 nm upon excitation at 272 and 315 nm while crystals with a lower Au content (batch 2) show only one band at 390 nm regardless of the excitation wavelength.

Exciplex tuning of the dicyanoaurate(I) emission is seen in various doped crystals, pure crystals, and solutions. The tuning action is achieved by varying the excitation wavelength and temperature in any of these media, the dopant concentration and host alkali halide crystal in doped crystals, the counter ion in pure crystals, and concentration and solvent in solutions. While effective tuning can be achieved in any of these systems alone, the tuning range can be expanded over a wider emission energy range if one combines the results of the various media. To illustrate, we show in Figure 3.11 selected emission spectra of various dicyanoaurate(I) species at different conditions. Several exciplex emission bands are obtained from regions in the far UV (~270 nm) to the orange (~660 nm), i.e. spanning an energy range of ~22,000 cm\(^{-1}\) with this approach. Similar tuning was achieved for the dicyanoargentate(I) emission.

The various emission bands seen in Figure 3.11 are assigned to \([\text{Au(CN)}_2^-]_n\) exciplexes with different "n", configuration, and/or geometry. The exact identity of each exciplex cannot be determined with a great certainty. A reasonable assignment is suggested in Table 3.3 based on correlating the trends of luminescence energies seen in various dicyanoaurate(I) species (solutions with various concentrations, doped crystals with different dopant concentrations, and pure crystals), the Raman data and the trends of
Figure 3.11. Exciplex tuning of the [Au(CN)2-] emission in different media. Band I, 1.00x10⁻⁵ M KAu(CN)2 frozen solution in methanol (77 K, \( \lambda_{ex}=250 \text{nm} \)); II, 1.00x10⁻⁴ M KAu(CN)2 frozen solution in methanol (77 K, \( \lambda_{ex}=260 \text{nm} \)); III, KAu(CN)2/KCl doped crystal (11 K, \( \lambda_{ex}=265 \text{nm} \)); IV, KAu(CN)2/KCl doped crystal (120 K, \( \lambda_{ex}=350 \text{nm} \)); V, 0.200 M KAu(CN)2 aqueous solution (RT, \( \lambda_{ex}=320 \text{nm} \)); and VI, KAu(CN)2 pure crystal (RT, \( \lambda_{ex}=330 \text{nm} \)).
electronic energies for various [Au(CN)]\(_n^2\) oligomers obtained from the electronic structure calculations described above.

**Table 3.3.** General qualitative assignment of the emission bands observed in solids and solutions of Au(CN)\(_2^\) species.

<table>
<thead>
<tr>
<th>Band</th>
<th>Solids, (\lambda_{\text{max}}^{\text{em}}, \text{nm})</th>
<th>Solutions, (\lambda_{\text{max}}^{\text{em}}, \text{nm})</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td></td>
<td>275-285</td>
<td>([\text{Au(CN)}_2^-]_2)</td>
</tr>
<tr>
<td>II</td>
<td>320-355</td>
<td>320-350</td>
<td>bent ([\text{Au(CN)}_2^-]_3)</td>
</tr>
<tr>
<td>III</td>
<td>370-395</td>
<td>380-390</td>
<td>linear ([\text{Au(CN)}_2^-]_3)</td>
</tr>
<tr>
<td>IV</td>
<td>420-450</td>
<td>420-440</td>
<td>([\text{Au(CN)}_2^-]_4)</td>
</tr>
<tr>
<td>V</td>
<td></td>
<td>455-490</td>
<td>([\text{Au(CN)}_2^-]_n^a)</td>
</tr>
<tr>
<td>VI</td>
<td>600-640</td>
<td></td>
<td>([\text{Au(CN)}_2^-]_n^a)</td>
</tr>
</tbody>
</table>

\(^a\) \([\text{Au(CN)}_2^-]_n\) represents delocalized exciplexes

We are aware of three literature precedents in which the emission energies of the same or similar complexes have been tuned significantly. Efficient tuning of the emission of the tetracyanoplatinate (II) is achieved by a combination of chemical substitution (changing the counter ion) and application of high pressure in order to significantly change the Pt-Pt distances. Another example involves Pt(diimine)(dithiolate) complexes, whose charge transfer emission energies have been tuned by 7400 cm\(^{-1}\) by varying the ligands and their substituents. More recently, Balch and co-workers have described an example in which the emission energy for frozen solutions of the complex \([\text{Au}\{\text{C(NHMe)}_2\}_2]\)\(^7\) has been tuned to different visible colors by variation of the solvent and counter ion. The tuning we achieve for the dicyanoaurate(I)
and dicyanoargentate(I) ions, as described above, competes favorably with all these examples and spans a wider emission energy range.

3.6. Conclusions

This study illustrates interesting luminescence behavior of dicyanoaurates(I) doped in a KCl host lattice. Three luminescence bands are observed in the [Au(CN)$_2^-$]/KCl system while only one band is observed in the pure KAu(CN)$_2$ system excited with the same wavelengths. The luminescence in the [Au(CN)$_2^-$]/KCl system can be tuned by varying the excitation wavelength or by varying the dopant concentration. By increasing the dopant concentration of [Au(CN)$_2^-$], our spectroscopic data predict that the oligomer size increases. At the highest dopant concentration, the Au-Au bond distance is shorter than the corresponding value for the pure KAu(CN)$_2$. On the other hand, in the [Ag(CN)$_2^-$]/KCl system, the oligomer size increases with increasing dopant concentration of [Ag(CN)$_2^-$] and at the highest dopant levels, the Ag-Ag bond distance is similar to the value of pure KAg(CN)$_2$. We demonstrate efficient tunability of ~ 22,000 cm$^{-1}$ in various Au(CN)$_2^-$ systems.

Since observed luminescence bands are due to different orientations and different aggregations of [Au(CN)$_2^-$] units, Raman spectroscopy can be correlated with the measured photoluminescence spectra. Three emission bands observed for a single crystal of batch 3 of the [Au(CN)$_2^-$]/KCl system shows three peaks in the $\nu_{CN}$ region of the Raman spectrum giving a reasonable correlation among Raman and luminescence spectroscopic results. Extended Hückel calculation predictions give good agreement with the observed experimental results.
3.7. References


42. The calculated binding energy for $[\text{Au(CN)}_2]^-$ in KCl is 5.1 eV (Table 3.2). This value is too large to be attributed to Au-Au interactions because such interactions are typically 0.2-0.5 eV. Therefore, the extremely high binding energy of $[\text{Au(CN)}_2]^-$ dimer in KCl cannot be explained based on Au-Au interactions. The calculated Au-Au equilibrium distance for $[\text{Au(CN)}_2]^-$ dimer in KCl is 4.5 Å, which corresponds to the intercationic distance in the KCl lattice. The large stabilization of the $[\text{Au(CN)}_2^-]^2$ dimer in the KCl lattice is, therefore, mostly due to the lattice energy of the ionic...


44. The limits are based on emission energies at half maxima for bands I and VI in figure 3.11.


4.1. Introduction

The photochemistry of $^{d^{10}}$Ag(I) complexes has attracted a great deal of attention over the past few years.\(^1\textsuperscript{-9}\) There are numerous examples of Ag(I) coordination compounds with short Ag-Ag contacts that have been structurally characterized, ranging from dimers to infinite clusters. In a vast majority of these compounds, the Ag-Ag interactions (argentophilic interactions) are assisted by the presence of bridging or capping ligands. Only a few examples of ligand unsupported Ag(I) aggregates have been reported.\(^6\textsuperscript{,}10\textsuperscript{-13}\) Among these, our research group has reported the crystal structure, electronic structure and temperature dependent Raman spectra of Tl[Ag(CN)\(_2\)] as an example of ligand unsupported argentophilic interactions.\(^6\)

The molecular structure of silver dicyano compounds, M[Ag(CN)\(_2\)] where M = K\(^+\), Na\(^+\), Rb\(^+\), Cd\(^{2+}\) consist of layers of [Ag(CN)\(_2\)] ions alternating with layers of counterions.\(^14\textsuperscript{,}15\) In these compounds, metal ions bond directly to the cyanide ligands and/or to water molecules in hydrated compounds. Our group has reported excimer and exciplex formation for [Ag(CN)\(_2\)] ions doped in KCl as the first example of homoatomic metal-metal bonded exciplexes.\(^8\) Four different emission bands have been observed at 296 (band A), 327, 345 (band B), 417 (band C), and 548 nm (band D) by selecting...
excitation wavelengths as 226, 270, 280, 260, and 315 nm respectively. The studied crystals exhibited extremely large tunability of excited state energies over 18,000 cm⁻¹. By varying the excitation wavelength, different [Ag(CN)_2]_n oligomers can be excited and thus, different emission energies can be observed. These emission bands can also be tuned by varying the dopant concentration or by varying the temperature (luminescence thermochromism). Different dopant concentrations allow one to increase the statistical probability of longer oligomers so that stronger emissions can be observed at longer wavelengths. At different temperatures, different energy transfer pathways are responsible for observing different emission energies.

The purpose of this study is to elucidate the optical memory phenomenon in the [Ag(CN)_2]/KCl system. Two different dopant concentrations of [Ag(CN)_2] crystals were synthesized, studied and compared with the results for pure KAg(CN)_2. Extended Hückel calculations were carried out to assign observed luminescence bands and interpret optical memory results. In order to calculate the kinetic parameters for each system, temperature dependent studies have been carried out in the presence of 266 nm laser light at different temperatures.

4.2. Experimental

Pure KAg(CN)_2 as well as two different dopant concentrations of [Ag(CN)_2] crystals were synthesized and analyzed spectroscopically. The synthesis of single crystals of KAg(CN)_2 and [Ag(CN)_2] doped in KCl has been discussed in details in Chapter 2. The silver content of doped crystals was determined by atomic absorption spectroscopy using a Model 857-Smith-Hieftje 11/12 spectrophotometer. Emission and
excitation spectra were collected using a Photon Technology International Model QuantaMaster-1046 spectrophotometer. This instrument is equipped with a 75 W xenon lamp, two excitation monochromators, emission monochromator, and a detector. Emission and excitation spectra were recorded at different temperatures. All excitation spectra were corrected for the spectral variation in the lamp using Rhodamine B.

Optical memory experiments have been carried out for two different dopant crystals as well as pure KAg(CN)₂. Initially, a single crystal was mounted on a copper holder and cooled down to 77 K. Emission and excitation spectra were recorded after 30 minutes for its equilibrium. Then, the crystal was exposed to 266 nm laser for 5 minutes and emission and excitation spectra were recorded. It should be noted that the sample was not moved during the whole experiment. Laser exposure and spectra recording were repeated every 5 minutes for 1.5 hours. After that, the crystal was warmed up to room temperature for 2 hours and recooled down to 77 K. As the recovery step, emission and excitation spectra were recorded after 30 minutes of its equilibrium at 77 K. This optical memory experiment was repeated for batch 2 as well as for pure KAg(CN)₂ at 77 K to see the effect of doping. Experiments were also carried out for each sample at different temperatures in order to calculate kinetic parameters.

4.3. Computational Details

Extended Hückel calculations were carried out using FORTICON 8 (QCMP011) program. Relativistic parameters used for these calculations are tabulated in Chapter 2. Ground and the first excited state calculations have been carried out for the different
oligomers of \([\text{Ag(CN)}_2^-]\) units in order to assign luminescence bands and interpret optical memory results. Details of these calculations are discussed earlier.\textsuperscript{17}

4.4. Results and Discussion

4.4.1. Atomic absorption and steady state photoluminescence data

The silver content of \([\text{Ag(CN)}_2^-]/\text{KCl}\) crystals were determined by atomic absorption spectroscopy. Batch 1 of \([\text{Ag(CN)}_2^-]/\text{KCl}\) single crystals had 1.21% Ag by wt whereas batch 2 had 2.23% Ag by wt. As mentioned in Chapter 3, at 77 K, single crystals of these doped crystals showed three major luminescence bands, A, B, and C at 296, 338, and 415 nm respectively. Each emission band became dominant at a characteristic excitation wavelength. On the other hand, a single crystal of pure \(\text{KAg(CN)}_2\) showed only one emission band at 415 nm regardless of excitation wavelength. Figure 4.1 shows the emission as well as the excitation spectra of a single crystal of \([\text{Ag(CN)}_2^-]/\text{KCl}\) batch 1 at 77 K. Upon excitation at 275 nm, single crystals of batches 1 and 2 of \([\text{Ag(CN)}_2^-]/\text{KCl}\) showed two emission bands at 338 (HE), and 415 (LE) nm while a single crystal of pure \(\text{KAg(CN)}_2\) showed only one emission band at 415 nm (Chapter 3, Figure 3.7).

4.4.2. Extended Hückel calculation results

In order to assign observed luminescence bands, extended Hückel calculations were carried out for different oligomers of \([\text{Ag(CN)}_2^-]\) units \((n = 1 \text{ to } 3, \text{ eclipsed forms})\). From these calculations, correlation has been made between luminescence data and Ag-
Figure 4.1. Emission and corrected excitation spectra of a single crystal of [Ag(CN)$_2$]/KCl batch 1 at 77 K.
Ag interactions. These calculations were carried out for both ground and excited states and results are summarized in table 4.1. The absorption spectra of a very dilute solution of [Ag(CN)$_2$] shows only one absorption band at 196 nm. This absorption has been assigned as a metal to ligand charge transfer (MLCT) transition. All observed luminescence bands in the [Ag(CN)$_2$]/KCl system at 296, 338, and 415 nm, are strongly red shifted from the absorption band of a very dilute solution of [Ag(CN)$_2$]. Therefore, none of the luminescence bands can be assigned as monomers. The Ag-Ag interactions should be the reason to observe low energy luminescence bands. Based on the ground state calculation results, the Ag-Ag interactions that are present in the [Ag(CN)$_2$]/KCl system (HOMO-LUMO gap decreases in the direction of monomer → dimer → trimer). On the other hand, these interactions are very weak due to smaller relativistic effects compare to gold systems. Cotton et.al have reported that little or no bonding occurs between Ag(I) centers in the ground state even for the compounds with a Ag-Ag distance of 2.70 Å. Therefore, excited state interactions must be the reason to observe different low energy emission bands.

Extended Hückel calculation results also showed that excimer/exciplex formation occurs in the first excited state. The first excited state has a shorter Ag-Ag equilibrium distance, higher binding energy and greater overlap population compared to the ground state (figures 4.2, 4.3, 4.4). Excited state dimers are referred as excimers while excited state trimers and longer oligomers are referred as exciplexes. The HOMO-LUMO gaps for the excited dimer, bent trimer, and linear trimer are 3.98, 3.83, 3.55 eV respectively. Therefore the observed luminescence bands in the [Ag(CN)$_2$]/KCl system can be assigned as in table 4.2.
Table 4.1. Summary of the results of both ground and excited states of different [Ag(CN)$_2$]$_n$ using extended Hückel calculations.$^a$

<table>
<thead>
<tr>
<th>Species</th>
<th>[Ag]</th>
<th>[Ag]$_2$</th>
<th>[Ag]$_3$</th>
<th>Bent [Ag]$_3$</th>
<th>Bent [Ag]$_3$</th>
<th>Linear [Ag]$_3$</th>
<th>*Linear [Ag]$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>d$_{Ag-Ag}$ Å</td>
<td>8.00</td>
<td>3.58</td>
<td>3.00</td>
<td>3.54</td>
<td>3.15</td>
<td>3.49</td>
<td>3.09</td>
</tr>
<tr>
<td>B.E., eV</td>
<td>0.00</td>
<td>0.13</td>
<td>1.12</td>
<td>0.29</td>
<td>1.10</td>
<td>0.33</td>
<td>1.47</td>
</tr>
<tr>
<td>H-L gap, eV</td>
<td>4.95</td>
<td>4.37</td>
<td>3.98</td>
<td>4.17</td>
<td>3.83</td>
<td>4.00</td>
<td>3.55</td>
</tr>
<tr>
<td>O.P. (Ag-Ag)</td>
<td>0.00</td>
<td>0.003</td>
<td>0.034</td>
<td>0.003</td>
<td>0.0477</td>
<td>-0.008</td>
<td>0.027</td>
</tr>
</tbody>
</table>

$^a$Notation: [Ag]$_{2,3,4} = [Ag(CN)_2]_{2,3}$, $^* [Ag]_{2,3}$: excimer/exciplex, B.E. = Ag-Ag binding energy, H-L gap = HOMO-LUMO gap, O.P = overlap population.
Figure 4.2. Potential energy curves of the ground and the first excited state of linear $[\text{Ag(CN)}_2]^-$.
Figure 4.3: Potential energy curves of the ground and the first excited state for bent $[\text{Ag(CN)}_2]^-$.
Figure 4.4. Potential energy curves of the ground and the first excited state of linear $[Ag(CN)_2]_3$. 
Table 4.2. Assignments of the observed luminescence bands in the [Ag(CN)$_2$]/KCl system.

<table>
<thead>
<tr>
<th>Observed $\lambda_{\text{max}}^{\text{em}}$, nm</th>
<th>Calculated HOMO-LUMO gap, eV</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>296</td>
<td>3.98</td>
<td>$^\text{B}[\text{Ag(CN)}_2]_2$</td>
</tr>
<tr>
<td>338</td>
<td>3.83</td>
<td>Bent $^\text{B}[\text{Ag(CN)}_2]_3$</td>
</tr>
<tr>
<td>415</td>
<td>3.55</td>
<td>Linear $^\text{B}[\text{Ag(CN)}_2]_3$</td>
</tr>
</tbody>
</table>

4.4.3. Temperature dependent photoluminescence data (in the absence of laser)

Figure 4.5 shows the emission spectra of a single crystal of [Ag(CN)$_2$]/KCl batch 1 as a function of temperature upon excitation at 265 nm. According to figure 4.5, as the temperature increases, the 338 nm emission band decreases as the 415 nm emission band intensity increases. This temperature dependent behavior is an energy transfer process between excitons corresponding to the 338 nm ($^\text{B}$) and 415 ($^\text{C}$) bands.

$^\text{B} \rightarrow ^\text{C}$

where $^\text{B} = $ bent trimer exciton; $^\text{C} = $ linear trimer exciton

This temperature dependent behavior can be explained using scheme 4.1. According to scheme 4.1, excited state bent trimers can fall to their lowest excited energy state and emit light. Also, if the activation energy (Ea) is small, the lowest excited energy of bent trimers can be transferred to an excited state of the linear trimers and emit light.
Figure 4.5. Emission spectra of a single crystal of $[\text{Ag(CN)}_2^-]/\text{KCl}$ batch 1 variation with the temperature upon excitation at 265 nm.
**Scheme 4.1.** Schematic representation of energy transfer pathway between bent and linear trimers.

- **Notation:**
  - $T_1$ = bent trimers, $T_2$ = linear trimers, $E_{S_H}$ = highest excited state, $E_{S_L}$ = lowest excited state, $A$ = Excitation, $BT_1$ = bent trimer emission, $BT_2$ = linear trimer emission, curvy line = non-radiative energy transfer pathway.

The molar concentration of a reactant or product is directly proportional to the physical property of a reactant or product. Therefore, as a physical property, the luminescence intensity can be used. The activation energy can be calculated using the following equation.

$$\frac{I_2}{I_1} = Ae^{-Ea/RT}$$

(1)

Where

- $I_2$ = intensity of 415 nm emission band
- $I_1$ = intensity of 338 nm emission band
- $A$ = pre-exponential factor
- $Ea$ = activation energy
- $R$ = gas constant with value of 8.314 JK$^{-1}$mol$^{-1}$
- $T$ = Temperature in Kelvin
Taking the natural logarithm of equation 1 gives

\[ \ln \left( \frac{I_2}{I_1} \right) = -\left( \frac{E_a}{R} \right) \frac{1}{T} + \ln A \]  

(2)

According to equation 2, a plot of \( \ln \left( \frac{I_2}{I_1} \right) \) versus \( \frac{1}{T} \) should be linear. As shown in figure 4.6, after plotting \( \ln \left( \frac{I_2}{I_1} \right) \) versus \( \frac{1}{T} \) for \([\text{Ag(CN)}_2^-]/\text{KCl}\) batch 1, the activation energy, \( E_a \) can be calculated as follows.

\[ \text{Slope} = -31.38 \]

\[ -\frac{E_a}{R} = -31.38 \]

\[ E_a = 260.79 \pm 0.04 \text{ J mol}^{-1} \]

Ea value for the \([\text{Ag(CN)}_2^-]/\text{KCl}\) batch 1 (1.21 %Ag) is 260.79 ± 0.04 J mol\(^{-1}\). A similar experiment has been carried out for \([\text{Ag(CN)}_2^-]/\text{KCl}\) batch 2 (2.23 %Ag) at different temperatures. After plotting \( \ln \left( \frac{I_2}{I_1} \right) \) versus \( \frac{1}{T} \) for \([\text{Ag(CN)}_2^-]/\text{KCl}\) batch 2 (figure 4.7), an \( E_a \) value was calculated. Calculated \( E_a \) values for \([\text{Ag(CN)}_2^-]/\text{KCl}\) batches 1 and 2 are summarized in table 4.3. Pure KAg(CN)\(_2\) has not been considered in the study of energy transfer because at most temperatures (above ~ 20K) only the luminescence band C at 415 nm is present.

According to table 4.3, the calculated \( E_a \) value for \([\text{Ag(CN)}_2^-]/\text{KCl}\) batch 1 is smaller than the corresponding value for batch 2. Therefore, the energy transfer from 338 nm emission band to 415 nm emission band should be faster in batch 1 compared to batch.
Figure 4.6. A plot of logarithm of \((I_2/I_1)\) versus \(1/T\) for \([Ag(CN)_2]/KCl\) batch 1.
Figure 4.7. A plot of logarithm of $(I_2/I_1)$ versus $1/T$ for $[\text{Ag(CN)}_2]^+/\text{KCl}$ batch 2.
2. Experimentally, in a particular temperature, the change in 338 nm emission band to 415 nm emission band is greater in batch 1 compared to batch 2 of \([\text{Ag(CN)}_2^-]/\text{KCl}\).

<table>
<thead>
<tr>
<th>System</th>
<th>Ea, J mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch 1</td>
<td></td>
</tr>
<tr>
<td>(1.21 % Ag)</td>
<td>260.79 (\pm) 0.04</td>
</tr>
<tr>
<td>Batch 2</td>
<td></td>
</tr>
<tr>
<td>(2.23 % Ag)</td>
<td>1437.55 (\pm) 0.01</td>
</tr>
</tbody>
</table>

4.4.4. Optical memory phenomenon

The emission spectrum of a single crystal of \([\text{Ag(CN)}_2^-]/\text{KCl}\) batch 1 at 77 K showed two emission bands at 338 nm (HE) and 415 nm (LE) upon excitation at 275 nm. As shown in figure 4.8, with exposure to a 266 nm laser, the intensity of HE band increased concurrently as the intensity of LE band decreased and after 50 minutes both bands plateau. A similar trend was observed for batch 2 of \([\text{Ag(CN)}_2^-]/\text{KCl}\) (figure 4.9) and pure \(\text{KAg(CN)}_2\) (figure 4.10) but the change in the intensity of HE and LE bands decreases on going from batch 1 \(\rightarrow\) batch 2 \(\rightarrow\) pure \(\text{KAg(CN)}_2\). It is worth mentioning here that the pure \(\text{KAg(CN)}_2\) had only the LE band at 77 K but upon exposure to 266 nm laser, the HE band appeared and started growing. The change in HE and LE with the dopant concentration can be explained as follows: by increasing the dopant concentration of \([\text{Ag(CN)}_2^-]\), the strain of the KCl lattice becomes larger (Ionic radii of \(\text{K}^+\) and \(\text{Ag}^+\) are 1.33 and 1.26 Å, respectively\(^{20}\)). Therefore, the rate of changing linear trimers \(\rightarrow\) bent
Figure 4.8: \([\text{Ag(CN)}_2]^+/\text{KCl}\) batch HE and LE peak area variation with exposure time at 77 K.
Figure 4.9. [Ag(CN)$_2$]$^-$/KCl batch 2 HE and LE peak area variation with the exposure time at 77 K.
Figure 4.10. Pure KAg(CN)$_2$ HE and LE peak area variation with exposure time at 77 K.
trimers is slower in higher doped crystals (batch 2 with 2.23% Ag) compared to lower
doped crystals (batch 1 with 1.21% Ag).

After exposure to 266 nm laser for 1.5h, the crystal was warmed up to room
temperature in the dark for 2 hours and recooled down up to 77 K. After waiting 30
minutes to achieve equilibrium, the emission and excitation spectra were recorded as the
recovery step. The percent recovery of batch 1 of [Ag(CN)2]/KCl (both HE and LE
bands) was 98 %, and the corresponding values for batch 2 and pure KAg(CN)2 were 76,
and 90 % respectively. The optical memory experiments for each batch were repeated
three times (three cycles). For example, the percent recovery for the second and third
cycles of [Ag(CN)2]/KCl batch 1 were 97, and 95% respectively.

With the exposure to 266 nm laser at 77 K, the intensity of the HE band increases
along with a decrease in the intensity in LE band. After warming up the crystal to room
temperature and cooling down to 77 K, the intensity of both bands returns to their
original values (Figure 4.11). Therefore, by exposing to 266 nm laser, the memory has
been stored, and the heating the crystal back to room temperature, the memory has been
erased.

During the optical memory studies, only the conformational change (linear
trimers ↔ bent trimers) takes place. While exposing to 266 nm laser at 77 K, the
forward reaction (linear trimers → bent trimers) occurs while warming crystals back to
room temperature results in the reverse reaction (bent trimers → linear trimers) taking
place.
Figure 4.11. Emission spectra variation of a single crystal of pure KAg(CN)$_2$ with the exposure time as well as the recovery step at 77K upon excitation at 275 nm.
4.4.5. Optical memory studies at different temperatures

In order to calculate the kinetic parameters in the $[\text{Ag(CN)}_2^-]/\text{KCl}$ system, optical memory experiments for batch 1, 2, and pure $\text{KAg(CN)}_2$ were carried out at different temperatures ranging from 4 K to 77 K. It should be noted that above 77 K, no change was observed for both the HE and LE bands. The mechanism involves in optical memory phenomenon can be expressed as a reversible first order reaction upon and represented as follows.

$$A \leftrightarrow B \quad (3)$$

Where

$A = \text{linear trimer (reactant)}$

$B = \text{bent trimer (product)}$

The rate expression can be represented as follows.

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] \quad (4)$$

Where

$$\frac{d[B]}{dt} = \text{rate of formation of B}$$

$k_1 = \text{the rate constant for the forward reaction}$

$k_2 = \text{the rate constant for the reverse reaction}$

Also, the mass balance is given by

$$[A]_0 + [B]_0 = [A]_t + [B]_t = [A]_0 + [B]_0 \quad (5)$$

Where

$[A]_0$ and $[B]_0 = \text{the initial concentrations of A and B}$

$[A]_t$ and $[B]_t = \text{the concentrations of A and B at time, t}$
At equilibrium,

\[
\frac{d[B]}{dt} = 0 = k_1[A]_e - k_2[B]_e
\] (6)

\[
\frac{[B]_e}{[A]_e} = \frac{k_1}{k_2} = K_e
\] (7)

where \( K_e \) is the equilibrium constant

To obtain the rate law in terms of \( B \), equation (5) and (6) can be rearranged to obtain the following expression as

\[
[A]_t = [B]_e - \frac{[B]_e k_2}{k_1} - [B]_t
\] (8)

Substitution for \([A]_t\) from equation (8) into equation (4) gives

\[
\frac{d[B]}{dt} = k_1[B]_e + k_2[B]_e - k_1[B]_t - k_2[B]_t
\] (9)

\[
\frac{d[B]}{dt} = (k_1 + k_2) ([B]_e - [B]_t)
\] (10)

This equation can be rearranged and integrated over the limits \([B]_t = [B]_0\) to \([B]_t\) and \( t = 0 \) to \( t \) to obtain

\[
\ln([B]_e - [B]_t) = -(k_1 + k_2)t + \ln([B]_e - [B]_0)
\] (11)

The molar concentration of a reactant or product is directly proportional to the physical property of a reactant or product. Therefore, as a physical property, the integrated peak area of luminescence band \( B \) can be used. As shown in figure 4.12, after plotting \( \ln([B]_e \)
- [B] versus t for the batch 1 of [Ag(CN)\textsubscript{2}]\textsuperscript{-}/KCl at 77 K, the slope was obtained as 0.057. Therefore,

\[
-0.057 = -(k_1 + k_2)
\]  

(12)

Table 4.4 summarizes different slopes obtained at different temperatures for the batch 1 of [Ag(CN)\textsubscript{2}]\textsuperscript{-}/KCl.

**Table 4.4.** Different slopes at different temperatures for batch 1 of [Ag(CN)\textsubscript{2}]\textsuperscript{-}/KCl.

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>Slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>77</td>
<td>-0.057</td>
</tr>
<tr>
<td>75</td>
<td>-0.0479</td>
</tr>
<tr>
<td>60</td>
<td>-0.0442</td>
</tr>
<tr>
<td>44</td>
<td>-0.0330</td>
</tr>
<tr>
<td>28</td>
<td>-0.0343</td>
</tr>
<tr>
<td>4</td>
<td>-0.0485</td>
</tr>
</tbody>
</table>

The assumption has been made that at higher temperatures (above 60 K), the forward reaction \((k_1)\) dominates and the lower temperatures (below 60 K), the reverse reaction \((k_2)\) dominates.

In order to calculate the change of entropy of activation and the change of enthalpy of activation, transition state theory has been used.

\[
k_{\text{rate}} = \frac{k_B T}{h} \exp \frac{\Delta S^*}{R} \exp \frac{-\Delta H^*}{RT}
\]  

(13)
Figure 4.12. A plot of natural logarithm of \( \{B_e - B_h\} \) of [Ag(CN)₂]²⁻/KCl batch 1 with increasing exposure time at 77 K.
where

\[ k_{\text{rate}} = \text{the rate constant} \]

\[ k_B = \text{Boltzmann's constant} \]

\[ h = \text{Planck constant} \]

\[ \Delta S^* = \text{change of entropy of activation} \]

\[ \Delta H^* = \text{change of enthalpy of activation} \]

Dividing both sides of the equation 13 by \( T \) gives

\[
\frac{k_{\text{rate}}}{T} = \frac{k_B}{h} \exp \frac{\Delta S^*}{R} \exp \frac{-\Delta H^*}{RT}
\]  

Taking the natural logarithm of equation 14 gives

\[
\ln \left( \frac{k_{\text{rate}}}{T} \right) = \frac{-\Delta H^*}{R} \cdot \frac{1}{T} + \left\{ \ln \frac{k_B}{h} + \frac{\Delta S^*}{R} \right\}
\]

Applying equation 15 to \( k_1 \) (forward) and \( k_2 \) (reverse) rate constants results in

\[
\ln \left( \frac{k_1}{T} \right) = \frac{-\Delta H_1^*}{R} \cdot \frac{1}{T} + \left\{ \ln \frac{k_B}{h} + \frac{\Delta S_1^*}{R} \right\}
\]

\[
\ln \left( \frac{k_2}{T} \right) = \frac{-\Delta H_2^*}{R} \cdot \frac{1}{T} + \left\{ \ln \frac{k_B}{h} + \frac{\Delta S_2^*}{R} \right\}
\]

As shown in figures 4.13 and 4.14, after plotting \( \ln \left( \frac{k_1}{T} \right) \) versus \( \frac{1}{T} \) and \( \ln \left( \frac{k_2}{T} \right) \) versus \( \frac{1}{T} \), \( \Delta H_1^* \) and \( \Delta H_2^* \) can be calculated from slope values. From the intercepts, \( \Delta S_1^* \) and \( \Delta S_2^* \) can be calculated as follows.
From figure 4.13,

\[ \text{Slope} = 20.99 = \frac{-\Delta H_1^*}{R} \]

\[ \Delta H_1^* = -20.99 \times 8.31 \text{ J mol}^{-1} \]

\[ \Delta H_1^* = -174.43 \text{ J mol}^{-1} \]

From the intercept,

\[ \text{Intercept} = -7.63 = \ln \frac{k_B}{h} + \frac{\Delta S_1^*}{R} \]

\[ \Delta S_1^* = -260.93 \text{ J mol}^{-1}K^{-1} \]

Similarly from figure 4.14,

\[ \text{Slope} = 11.57 = \frac{-\Delta H_2^*}{R} \]

\[ \Delta H_2^* = -11.57 \times 8.31 \text{ J mol}^{-1} \]

\[ \Delta H_2^* = -96.15 \text{ J mol}^{-1} \]

From the intercept,

\[ \text{Intercept} = -7.30 = \ln \frac{k_B}{h} + \frac{\Delta S_2^*}{R} \]

\[ \Delta S_2^* = -258.19 \text{ J mol}^{-1}K^{-1} \]

Using the difference between the forward and reverse reactions, the change of enthalpy of activation (\(\Delta H^*\)) and the change of entropy of activation (\(\Delta S^*\)) can be calculated.
Figure 4.13. A plot of natural logarithm of $k_1/T$ versus $1/T$ for KAg(CN)$_2$/KCl batch 1.
Figure 4.14. A plot of natural logarithm of $k_2/T$ versus $1/T$ for KAg(CN)$_2$/KCl batch 1.
\[ \Delta H^* = \Delta H_1^* - \Delta H_2^* \]
\[ \Delta H^* = (-174.43) - (-96.15) \]
\[ \Delta H^* = -78.28 \pm 0.51 \text{ J mol}^{-1} \]

Also,
\[ \Delta S^* = \Delta S_1^* - \Delta S_2^* \]
\[ \Delta S^* = (-260.93) - (-258.19) \]
\[ \Delta S^* = -2.74 \pm 0.11 \text{ J mol}^{-1} \text{K}^{-1} \]

From the values of \( \Delta H^* \), \( \Delta S^* \), and \( \Delta G^* \) can be calculated as follows.

\[ \Delta G^* = \Delta H^* - T \Delta S^* \]

At 77 K,
\[ \Delta G^* = -78.28 - (77 \times (-2.74)) \]
\[ \Delta G^* = 132.70 \pm 1.14 \text{ J mol}^{-1} \]

Similar temperature dependent experiments were carried out for batch 2 of \([\text{Ag(CN)}_2^-]/\text{KCl}\) and pure \(\text{KAg(CN)}_2\). Table 4.5 summarizes the calculated values for \( \Delta H^* \), \( \Delta S^* \), and \( \Delta G^* \) for each studied system. The negative \( \Delta H^* \) values indicate that the activated complex is more stable compared to reactants. It has been reported in the literature that the negative, small \( \Delta H^* \) value can be regarded as an evidence of exciplex formation.\(^{21,22}\)

Also, the calculated negative \( \Delta S^* \) values give an indication of having more ordered activated complex. According to table 4.5, at 77 K, the \( \Delta G^* \) values for the \([\text{Ag(CN)}_2^-]/\text{KCl}\) batch 1 (1.21 %Ag), batch 2 (2.23 %Ag), and pure \(\text{KAg(CN)}_2\) are \(+132.70 \pm 1.14\), \(+380.50 \pm 0.98\), and \(+1466.52 \pm 1.23 \text{ J mol}^{-1}\) respectively. In other words, the forward reaction is non-spontaneous at 77 K. However, the forward reaction can occur if the
energy from 266 nm light (449.64 KJ mol\(^{-1}\)) is provided. Experimentally, the rate of conformational change (linear trimers → bent trimers) in above three systems follows the order of batch 1 > batch 2 > pure KAg(CN)\(_2\). In the absence of 266 nm laser, the positive \(\Delta G^*\) value of batch 1 is smaller compared to the corresponding value of batch 2. Therefore, with the additional energy of a 266 nm laser, the reaction (linear trimers → bent trimers) should be faster in batch 1 than batch 2. Pure KAg(CN)\(_2\) has the slowest rate for the conformational change and this correlates with this system having the largest positive \(\Delta G^*\) value without 266 nm laser.

**Table 4.5. Calculated kinetic parameters in [Ag(CN)\(_2\)]/KCl system.**

<table>
<thead>
<tr>
<th>System</th>
<th>(\Delta H^*), J mol(^{-1})</th>
<th>(\Delta S^*), J mol(^{-1}) K(^{-1})</th>
<th>(\Delta G^*) at 77 K, J mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ag(CN)(_2)]/KCl batch 1 (1.21 %Ag)</td>
<td>-78.28 ± 0.51</td>
<td>-2.74 ± 0.11</td>
<td>132.70 ± 1.14</td>
</tr>
<tr>
<td>[Ag(CN)(_2)]/KCl batch 2 (2.23 %Ag)</td>
<td>-881.53 ± 1.32</td>
<td>-16.39 ± 0.02</td>
<td>380.50 ± 1.43</td>
</tr>
<tr>
<td>Pure KAg(CN)(_2)</td>
<td>-1269.77 ± 1.54</td>
<td>-35.54 ± 0.53</td>
<td>1466.81 ± 2.09</td>
</tr>
</tbody>
</table>
4.5. Conclusions

This study demonstrates the presence of optical memory for \([\text{Ag(CN)}_2^−]\) doped in KCl with various dopant concentrations as well as in pure KAg(CN)_2. Two batches of \([\text{Ag(CN)}_2^−]/\text{KCl}\) with different dopant concentrations, batch 1 (1.21 \% Ag) and 2 (2.23 \% Ag) were synthesized and studied spectroscopically. Extended Hückel calculations were carried out to assign observed luminescence bands. According to these calculations, the 296 nm emission band is assigned as excited dimers while 338 and 415 nm emission bands are assigned as excited bent and linear trimers, respectively. Upon 266 nm laser irradiation of a single crystal at 77 K, the luminescence band at 338 nm increases along with the decrease in 415 nm luminescence band. In other words, linear trimers change to bent trimers with the laser exposure at 77 K. It is worth mentioning here that the luminescence band at 296 nm doesn’t change with the 266 nm laser exposure. The rate of changing the conformation changes with the dopant concentration. It follows the order of batch 1 > batch 2 > pure KAg(CN)_2. Warming the crystal back to room temperature, the reverse reaction takes place. By exposing to 266 nm laser, the memory has been stored, upon heating the crystal back to room temperature, the memory has been erased.

Temperature dependent studies for batches 1 and 2 of \([\text{Ag(CN)}_2^−]/\text{KCl}\) demonstrated that the energy transfer from 338 nm emission band to 415 nm emission band takes place at higher temperatures.

The temperature dependent studies for batches 1 and 2 of \([\text{Ag(CN)}_2^−]/\text{KCl}\) as well as pure KAg(CN)_2 have been carried out in the presence of a 266 nm laser. The calculated positive \(\Delta G^*\) values without the 266 nm laser at 77 K indicated that the forward reaction (linear trimers \(\rightarrow\) bent trimers) is not spontaneous at 77 K. But the
forward reaction can occur if the energy from 266 nm (449.64 KJ mol\(^{-1}\)) photon is provided. In the absence of a 266 nm laser, the positive \(\Delta G^*\) value of batch 1 is smaller compared to the corresponding value of batch 2. Therefore, in the presence of 266 nm laser, the reaction (linear trimer \(\rightarrow\) bent trimer) should be faster in batch 1 compared to batch 2 of \([\text{Ag(CN)}_2^-]/\text{KCl}\). For pure \(\text{KAg(CN)}_2\), in the absence of 266 nm laser \(\Delta G^*\) value is the most positive compared to doped system, therefore the rate should be the slowest in pure \(\text{KAg(CN)}_2\).
4.6. References


Chapter 5

OPTICAL MEMORY AND TEMPERATURE DEPENDENT STUDIES ON DICYANOAUURATE(I) IONS DOPED IN POTASSIUM CHLORIDE CRYSTALS

5.1. Introduction

In past few decades a great deal of attention has been paid to luminescent $d^{10}$ gold(I) compounds, and in particular those with intramolecular gold-gold interactions. Extensive photoluminescence experiments have been carried out on this class of compounds, and in many examples the relationship between aurophilicity (gold-gold bonding) and the emission energies has been established. Recent interest has been paid to study two dimensional $d^{10}$ gold(I) layered dicyano compounds, $\text{M[Au(CN)\textsubscript{2}]}$ (where $\text{M=Cs}^+$, $\text{K}^+$, and $\text{Tl}^+$). These compounds have crystal structures consisting of layers of cations alternating with layers of linear $\text{Au(CN)}\textsubscript{2}^-$ ions. The distance between gold atoms within the layer changes with the cation. In 1959, Rosenzweig et al. have reported the crystal structure of $\text{KAu(CN)\textsubscript{2}}$. In this compound, gold atoms are separated by 3.64 Å at room temperature. Our research group has reported a study of the laser emission and X-ray measurements versus temperature for $\text{KAu(CN)\textsubscript{2}}$. These results have demonstrated the sensitivity of the emission energy to change in Au-Au separation.

Optical memory is a phenomenon analogous to write, read and erase processes. Zink et al. have reported the optical memory studied on Cu$^+$ and Ag$^+$ ions doped $\beta''$-alumina. Our research group has reported optical memory in $\text{Pb[Au(CN)\textsubscript{2}]}$ and $\text{Tl[Ag(CN)\textsubscript{2}]}$. In the $\text{Pb[Au(CN)\textsubscript{2}]}$ system, light induced electron transfer in which
Au(I) was reduced to Au(CN)$_2^{2-}$ was assigned as the principal process responsible for the observed luminescence change. In the Tl[Ag(CN)$_2$] system, it was proposed that a photochemical reaction occurred with a light induced electron transfer mechanism in which the [Ag(CN)$_2$]$_3^{3-}$ was reduced to a [Ag(CN)$_2$]$_3^{4+}$ by Tl$^+$. By warming the crystal back to room temperature, the original [Ag(CN)$_2$]$_3^{3-}$ was reformed.

In Chapter 3, the luminescence properties of KAu(CN)$_2$/KCl crystals have been discussed. Three emission bands were observed at 335, 390, and 425 nm by selecting suitable excitation wavelengths. Different emission bands have been assigned to different excimers and exciplexes. These excimers and exciplexes can be tuned by varying the excitation wavelength or by varying the dopant concentration.

The purpose of this study is to investigate the presence of optical memory for crystals of [Au(CN)$_2^-$] ions doped in KCl. Three different dopant concentrations of crystals were used for this study. The optical memory of these three different dopant crystals are compared herein with that of pure KAu(CN)$_2$ crystals. Extended Hückel calculations have been carried out to assign the observed luminescence bands. Time dependent studies at different temperatures were carried out to calculate kinetic parameters. In order to predict photodecomposition products and propose a mechanism, different control experiments such as photoluminescence and photodecomposition experiments for AuCN were carried out.

### 5.2. Experimental

Single crystals of three different batches of KAu(CN)$_2$/KCl (0.45, 1.38, and 2.20 % Au for batch 1, 2, and 3 respectively) and pure KAu(CN)$_2$ were synthesized. Details
of the crystal growing have been discussed in Chapter 2. The gold content of the
different batches of KAu(CN)$_2$/KCl was determined by atomic absorption spectroscopy
using a Model 857-Smith-Hieftje 11/12 spectrophotometer. Photoluminescence spectra
were recorded using a Photon Technology International Model QuantaMaster-1046
spectrometer equipped with a 75 W xenon lamp. The emission and the excitation spectra
were recorded at different temperatures ranging from 4 K to 160 K using liquid helium or
liquid nitrogen as coolants. All excitation spectra were corrected for the variation of the
lamp intensity using Rhodamine B.

Optical memory experiments were carried out as follows: The crystal was
mounted on a copper holder using Cry-Con grease. Then the crystal was cooled down to
77 K and waited 30 minutes to reach equilibrium. Emission and excitation spectra were
recorded as an initial step. The crystal was exposed to 266 nm laser for 5 minutes and
emission and excitation spectra were recorded. Laser exposure and spectra recording
processes were repeated every 5 minutes for 1.5 hours. Then, the crystal was warmed up
to room temperature in the dark for 90 minutes and recooled down to 77 K. After waiting
for 30 minutes for equilibrium to be reached, the emission and excitation spectra were
recorded as the recovery step. This whole process was repeated at 4, 28, 44, 77, 120, and
160 K to calculate kinetic parameters.

5.3. Results and Discussion
5.3.1. Atomic absorption and steady state photoluminescence data

Atomic absorption spectroscopy analysis has shown that the values of % Au (by
wt) are 0.45, 1.38, and 2.20 for KAu(CN)$_2$/KCl crystals referred to herein as batches 1, 2,
and 3, respectively. Figure 5.1 shows the emission and excitation spectra of a single crystal of KAu(CN)$_2$/KCl batch 1 at 77 K. Upon excitation at 275 nm, the emission spectrum of a single crystal of batch 1 shows three bands at 335, 390, and 425 nm at 77 K. With the excitation at 315 nm, two emission bands at 390 and 425 nm have been observed for KAu(CN)$_2$/KCl batch 1 at 77 K. Figure 5.2 shows the emission spectra of single crystals of three different batches of KAu(CN)$_2$/KCl as well as pure KAu(CN)$_2$ when excited at 275 nm at 77 K. As shown in figure 5.2, both batches 1 and 3 show three emission bands at 335, 390, and 425 nm whereas batch 2 and pure KAu(CN)$_2$ show only one band at 390 nm.

5.3.2. Assignment of luminescence bands

As mentioned in Chapter 3, extended Hückel calculations were carried out for different [Au(CN)$_2$]$_n$ oligomers. These calculations were performed for both ground and the first excited states. Based on these calculations, the assignment of observed luminescence bands for different batches of KAu(CN)$_2$/KCl as well as for pure KAu(CN)$_2$ are shown in table 5.1. According to the luminescence band assignments in table 5.1, bent [Au(CN)$_2$]$_3$, linear [Au(CN)$_2$]$_3$, and linear [Au(CN)$_2$]$_4$ units are present both batch 1 and 3 of KAu(CN)$_2$/KCl whereas only linear [Au(CN)$_2$]$_3$ is present in batch 2 and pure KAu(CN)$_2$. 

115
Figure 5.1. Emission and corrected excitation spectra of KAu(CN)$_2$/KCl batch 1 at 77 K.
Figure 5.2. Emission spectra of different batches of KAu(CN)$_2$/KCl as well as pure KAu(CN)$_2$ at 77 K upon excitation at 275 nm.
Table 5.1. Assignments of the emission bands observed in different batches of KAu(CN)$_2$/KCl as well as in pure KAu(CN)$_2$.

<table>
<thead>
<tr>
<th>Luminescence band, nm</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>335</td>
<td>Bent $[^1]$[Au(CN)$_2$]$_3$</td>
</tr>
<tr>
<td>390</td>
<td>Linear $[^1]$[Au(CN)$_2$]$_3$</td>
</tr>
<tr>
<td>425</td>
<td>$[^2]$[Au(CN)$_2$]$_4$</td>
</tr>
</tbody>
</table>

5.3.3. Optical memory studies

As mentioned before, the emission spectra of a single crystal of KAu(CN)$_2$/KCl batch 1 shows three emission bands at 335, 390, and 425 nm when excited at 275 nm at 77 K. With the exposure to a 266 nm laser for 5 minutes, the intensity of all three emission bands decreased in intensity. Although the intensities of the three emission bands showed a significant change with laser exposure, the intensity change of 390 nm emission band was dramatic. Since the biggest emission intensity change was observed upon excitation at 275 nm, this 275 nm excitation wavelength was selected to monitor the change in emission intensity. Laser exposure as well as emission and excitation spectra recording were repeated every 5 minutes for 1.5 hours. Figure 5.3 shows how the emission energy at 390 nm (em 390 nm peak area) changes with laser exposure time. According to figure 5.3, with continuous laser exposure, the intensity of 390 nm emission band decreases up to 60 minutes and then plateau. Then the crystal was warmed up to room temperature in dark and waited for 2 hours. The same crystal was recooled down to 77 K, and waited 30 minutes for equilibrium to occur. After that, emission and excitation
Figure 5.3. KAu(CN)$_2$/KCl different batches as well as pure KAu(CN)$_2$ em 390 nm peak area variation with the exposure time at 77 K.
Figure 5.4. KAu(CN)$_2$/KCl batch 1 emission spectra (ex 275 nm) variation with the exposure time and the recovery step at 77 K.
spectra were recorded as the recovery step. After comparison of initial ($2.96 \times 10^7$ counts per second) and recovery emission intensities ($2.49 \times 10^7$ counts per second), the recovery was 84% from its initial intensity (figure 5.4). This optical memory experiment was repeated for KAu(CN)$_2$/KCl batch 1 for the second and the third time and the recovery for the second and third cycles were 82 and 81% respectively.

This optical memory experiment was repeated for batches 2, 3, and pure KAu(CN)$_2$. Figure 5.3 shows the 390 nm emission peak area variation with exposure time for each system. According to figure 5.3, it is obvious that the photodecomposition rate follows the order of batch 1 < batch 3 < batch 2 < pure KAu(CN)$_2$. In order to explain this trend let's consider the luminescence band assignment. Batch 2 of KAu(CN)$_2$/KCl and pure KAu(CN)$_2$ have only linear trimers whereas batches 1 and 3 have additional oligomers such as bent trimers and tetramers. Therefore, the decomposition of the linear trimer is faster in batch 2 and pure KAu(CN)$_2$ compared to batches 1 and 3.

After laser exposure, the crystals of batches 2, 3, and pure KAu(CN)$_2$ were warmed up to room temperature and recooled down to 77 K. Then, the emission and excitation spectra were recorded as the recovery step. The percent recovery was 67%, 81%, and 91% for batches 2, 3, and pure KAu(CN)$_2$ respectively.

5.3.4. Identification of products after 266 nm laser exposure

Since all emission bands at 335, 390, and 425 nm decreased their intensity with increasing 266 nm laser exposure, non-luminescence species should form as products. As discussed before, there are three types of oligomers, bent trimers, linear trimers, and
tetramers present in these systems. With the exposure to 266 nm laser three different pathways are possible for these oligomers.

1. $[\text{Au(CN)}_2^-]_n \rightarrow n[\text{Au(CN)}_2^-]$

Oligomers can be broken apart to form $[\text{Au(CN)}_2^-]$ monomers. However, monomers of $[\text{Au(CN)}_2^-]$ luminesce at 275 nm upon excitation at 250 nm at 77 K. During laser exposure experiments at 77 K, there was no evidence of a peak at 275 nm growing upon excitation at 250 nm. Therefore, this possibility can be eliminated.

2. $[\text{Au(CN)}_2^-] \rightarrow \text{AuCN} + \text{CN}^-$

As shown in figure 5.5, at 77 K, pure AuCN shows strong luminescence at 625 nm upon excitation at 337 nm. Also, figure 5.5 shows the emission spectra of a single crystal of KAu(CN)$_2$/KCl batch 1 after exposure to 266 nm laser for 90 minutes when excited at 337 nm. Comparing these two spectra, it is obvious that there is no evidence for the formation of AuCN in a single crystal of KAu(CN)$_2$/KCl batch 1 during 266 nm laser exposure. Therefore, this possibility can be eliminated.

3. $3[\text{Au(CN)}_2^-] \rightarrow 2\text{Au}(0) + \text{Au(CN)}_4^- + 2\text{CN}^-$

Disproportionation of $[\text{Au(CN)}_2^-]$ into Au(0), CN$^-$ and Au(CN)$_4^-$ is another possible mechanism. In order to explain this possibility, let's consider the following mechanism.

\[
\begin{align*}
3[\text{Au(CN)}_2^-] + \text{hv}(266 \text{ nm}) & \rightarrow 3[\text{Au(CN)}_2^-]^* \\
2[\text{Au(CN)}_2^-]^* + 2e^- & \rightarrow 2\text{Au}(0) + 4\text{CN}^- \\
[\text{Au(CN)}_2^-]^* + 2\text{CN}^- & \rightarrow \text{Au(CN)}_4^- + 2e^-
\end{align*}
\]
Figure 5.5. Emission spectra of AuCN powder and a single crystal of KAu(CN)$_2$/KCl batch 1 after laser exposure upon excitation at 337 nm at 77K.
The standard reduction potential of $[\text{Au(CN)}_2^-]/\text{Au}(0)$ is $-0.60\text{V}$. Many examples have been reported in the literature regarding the reduction of $\text{Au(CN)}_4^-$ into $[\text{Au(CN)}_2^-]$ in acidic media. For example, in very dilute $\text{H}_2\text{SO}_4$ solution, the $E^0$ value for the following reaction was estimated as $+1.41\text{V}$.

$$[\text{Au(CN)}_4^-] + 2\text{H}^+ + 2e \rightarrow [\text{Au(CN)}_2^-] + 2\text{HCN} \quad (4)$$

The authors stated that the $\text{Au(CN)}_4^-$ ion would presumably exchange cyanide with aqueous cyanide, but this has not yet been demonstrated.

The assumption has been made that the $E^0$ value for equation 4 is close to the $E^0$ value for the reduction of $\text{Au(CN)}_4^-$ into $[\text{Au(CN)}_2^-]$ in the $[\text{Au(CN)}_2^-]/\text{KCl}$ system. Therefore, in equation 3, the reduction potential of $\text{Au(CN)}_4^-/[\text{Au(CN)}_2^-]$ is $\sim -1.41\text{V}$. Without 266 nm laser, the $E^0$ value for the $3[\text{Au(CN)}_2^-] \rightarrow 2\text{Au}(0) + \text{Au(CN)}_4^- + 2\text{CN}^-$ reaction is $\sim -2.01\text{V}$ ($-0.60\text{V} + (-1.41\text{V})$. Therefore, the $\Delta G^0$ value will be positive ($\Delta G^0 = -nE^0F$) without 266 nm laser light. In other words, the $3[\text{Au(CN)}_2^-] \rightarrow 2\text{Au}(0) + \text{Au(CN)}_4^- + 2\text{CN}^-$ reaction will not be possible without 266 nm laser light.

Upon excitation at 266 nm laser light (266 nm = 4.66 eV), excited $[\text{Au(CN)}_2^-]$ ([Au(CN)$_2^-$]$^*$) acts as a strong oxidizing agent. In the presence of 266 nm laser, the $E^0$ value for the $3[\text{Au(CN)}_2^-] \rightarrow 2\text{Au}(0) + \text{Au(CN)}_4^- + 2\text{CN}^-$ reaction is $\sim +2.65\text{V}$ ($+4.66\text{V} +(-0.60\text{V}) + (-1.41\text{V})$. Therefore, the $\Delta G^0$ value will be negative ($\Delta G^0 = -nE^0F$) in the presence of 266 nm laser light. So that the $3[\text{Au(CN)}_2^-] \rightarrow 2\text{Au}(0) + \text{Au(CN)}_4^- + 2\text{CN}^-$ reaction is spontaneous in the presence of 266 nm laser light.

Experimental evidence gives good agreement with this mechanism. According to figure 5.3, the rate of decreasing intensity of 390 nm emission band follows the order of batch 1 $<$ batch 3 $<$ batch 2 $<$ pure KAu(CN)$_2$. According to the luminescence band
assignments, batch 2 and pure KAu(CN)$_2$ represent only linear trimers whereas batch 1 and 3 represent bent trimers and tetramers other than linear trimers. The rate of decreasing emission intensity of 390 nm band in batch 2 and pure KAu(CN)$_2$ is much faster compared to batches 1 and 3. For the $3[\text{Au(CN)}_2^-] \rightarrow 2\text{Au}(0) + \text{Au(CN)}_4^- + 2\text{CN}^-$ reaction, the reactant is $3[\text{Au(CN)}_2^-]$ (or trimer) so that the reaction is faster in the presence of only trimers in comparison to tetramers. Therefore, according to this mechanism, one should expect the fastest rate for batch 2 compared to batch 3 and batch 1 since batch 2 represents only linear trimers.

5.3.5. Optical memory studies at different temperatures

Optical memory studies for three batches of KAu(CN)$_2$/KCl as well as pure KAu(CN)$_2$ have been carried out at different temperatures ranging from 4 K to 160 K in order to calculate kinetic parameters. First, let's assume that the disproportionation reaction ($3[\text{Au(CN)}_2^-] \leftrightarrow 2\text{Au}(0) + 2\text{CN}^- + \text{Au(CN)}_4^-$) follows the first order kinetics. For the simplicity, reaction can be written as follows.

$$A \leftrightarrow B$$

Where

$A = \text{reactant}$

$B = \text{product}$

The rate expression can be represented as follows.

$$- \frac{d[A]}{dt} = k_1[A] - k_2[B]$$  \hspace{1cm} (5)

Where

$$- \frac{d[A]}{dt} = \text{rate of disappearance of } A$$
\[ k_1 = \text{the rate constant for the forward reaction} \]
\[ k_2 = \text{the rate constant for the reverse reaction} \]

Also, the mass balance is given by

\[ [A]_0 + [B]_0 = [A]_t + [B]_t = [A]_e + [B]_e \quad (6) \]

Where

\[ [A]_0 \text{ and } [B]_0 = \text{the initial concentrations of A and B} \]
\[ [A]_t \text{ and } [B]_t = \text{the concentrations of A and B at time, } t \]
\[ [A]_e \text{ and } [B]_e = \text{the concentrations of A and B at equilibrium} \]

At equilibrium,

\[ -\frac{d[A]}{dt} = 0 = k_1[A]_e - k_2[B]_e \quad (7) \]

\[ \frac{[B]_e}{[A]_e} = \frac{k_1}{k_2} = K_e \quad (8) \]

where \( K_e \) is the equilibrium constant

Equations (6) and (7) can be rearranged to obtain the following expression as

\[ [B]_t = [A]_e + \frac{[A]_e k_1}{k_2} - [A]_t \quad (9) \]

Substitution for \([B]_t\) from equation (9) into equation (5) gives

\[ -\frac{d[A]}{dt} = k_1[A]_t - k_2[A]_e - k_1[A]_e + k_2[A]_t \quad (10) \]

\[ -\frac{d[A]}{dt} = (k_1 + k_2) ([A]_t - [A]_e) \quad (11) \]
This equation can be rearranged and integrated over the limits $[\text{A}]_t = [\text{A}]_0$ to $[\text{A}]_t$ and $t = 0$ to $t$ to obtain

$$\ln([\text{A}]_t - [\text{A}]_c) = -(k_1 + k_2)t + \ln([\text{A}]_0 - [\text{A}]_c)$$

(12)

The molar concentration of a reactant or product is directly proportional to the physical property of a reactant or product. Therefore, as a physical property, the integrated peak area of luminescence band A can be used. After plotting $\ln([\text{A}]_t - [\text{A}]_c)$ versus $t$ for the batch 1 of KAu(CN)$_2$/KCl at 4 K, the slope was obtained as 0.0564. According to figure 5.6,

$$\text{Slope} = -0.0564 = -(k_1 + k_2)$$

After plotting $\ln([\text{A}]_t - [\text{A}]_c)$ versus $t$ for the batch 1 of KAu(CN)$_2$/KCl at other temperatures, the values for $(k_1 + k_2)$ can be obtained from slopes of each graphs. Table 5.2 summarizes the values for $(k_1 + k_2)$ at different temperatures.

Table 5.2. Different values for $(k_1 + k_2)$ at different temperatures for batch 1 of KAu(CN)$_2$/KCl.

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>$(k_1 + k_2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.0564</td>
</tr>
<tr>
<td>7</td>
<td>0.0571</td>
</tr>
<tr>
<td>28</td>
<td>0.0754</td>
</tr>
<tr>
<td>44</td>
<td>0.1232</td>
</tr>
<tr>
<td>81</td>
<td>0.0421</td>
</tr>
<tr>
<td>120</td>
<td>0.0363</td>
</tr>
<tr>
<td>160</td>
<td>0.0331</td>
</tr>
</tbody>
</table>
Figure 5.6. A plot of natural logarithm of ([A]_r-[A]_e) of KAu(CN)₉/KCl batch 1 with increasing exposure time at 4 K.
Transition state theory has been utilized to calculate the change of entropy of activation and the change of enthalpy of activation.

\[
k_{\text{rate}} = \frac{k_B T}{h} \exp \left( \frac{\Delta S^*}{R} \right) \exp \left( -\frac{\Delta H^*}{RT} \right)
\]

where

- \(k_{\text{rate}}\) = the rate constant
- \(k_B\) = Boltzmann's constant
- \(h\) = Planck constant
- \(\Delta S^*\) = change of entropy of activation
- \(\Delta H^*\) = change of enthalpy of activation

Dividing both sides of the equation by \(T\) gives

\[
\frac{k_{\text{rate}}}{T} = \frac{k_B}{h} \exp \left( \frac{\Delta S^*}{R} \right) \exp \left( -\frac{\Delta H^*}{RT} \right)
\]

Taking the natural logarithm of equation gives

\[
\ln \left( \frac{k_{\text{rate}}}{T} \right) = -\frac{\Delta H^*}{R} \cdot \frac{1}{T} + \left( \ln \frac{k_B}{h} + \frac{\Delta S^*}{R} \right)
\]

Applying equation to \(k_1\) (forward) and \(k_2\) (reverse) rate constants results in

\[
\ln \left( \frac{k_1}{T} \right) = -\frac{\Delta H_1^*}{R} \cdot \frac{1}{T} + \left( \ln \frac{k_B}{h} + \frac{\Delta S_1^*}{R} \right)
\]

\[
\ln \left( \frac{k_2}{T} \right) = -\frac{\Delta H_2^*}{R} \cdot \frac{1}{T} + \left( \ln \frac{k_B}{h} + \frac{\Delta S_2^*}{R} \right)
\]

The assumption has been made that at higher temperatures (above 77 K), the forward reaction \((k_1)\) dominates and the lower temperatures (below 77 K), the reverse reaction \((k_2)\) dominates.
For example, at 120 K,

\[(k_1 + k_2) = 0.0363 \approx k_1\]

At 4 K,

\[(k_1 + k_2) = 0.0564 \approx k_2\]

As shown in figures 5.7 and 5.8, after plotting \(\ln \left( \frac{k_1}{T} \right)\) versus \(\frac{1}{T}\) and \(\ln \left( \frac{k_2}{T} \right)\) versus \(\frac{1}{T}\), \(\Delta H_1^*\) and \(\Delta H_2^*\) can be calculated from slopes. From intercepts, \(\Delta S_1^*\) and \(\Delta S_2^*\) can be calculated as follows.

From figure 5.7,

\[
\text{Slope} = -156.85 = \frac{-\Delta H_1^*}{R}
\]

\[
\Delta H_1^* = -156.85 \times 8.31 \text{ J mol}^{-1}
\]

\[
\Delta H_1^* = -1303.42 \text{ J mol}^{-1}
\]

From the intercept,

\[
\text{Intercept} = -9.4539 = \left\{ \text{ln} \left[ \frac{k_B}{h} + \frac{\Delta S_1^*}{R} \right] \right\}
\]

\[
\Delta S_1^* = -276.09 \text{ J mol}^{-1}\text{K}^{-1}
\]

Similarly from figure 5.8,

\[
\text{Slope} = 7.6401 = \frac{-\Delta H_2^*}{R}
\]

\[
\Delta H_2^* = -7.6401 \times 8.31 \text{ J mol}^{-1}
\]

\[
\Delta H_2^* = -63.49 \text{ J mol}^{-1}
\]
Figure 5.7. A plot of natural logarithm of $k_1/T$ versus $1/T$ for KAu(CN)$_2$/KCl batch 1.
Figure 5.8. A plot of natural logarithm of $k_2/T$ versus $1/T$ for KAu(CN)$_2$/KCl batch 1.
From the intercept,

\[
\text{Intercept} = -6.1691 = \left\{ \ln \frac{k_B}{h} + \frac{\Delta S_*^2}{R} \right\}
\]

\[
\Delta S_*^2 = -248.79 \text{ J mol}^{-1}\text{K}^{-1}
\]

Using the difference between the forward and reverse reactions, the change of enthalpy of activation (\(\Delta H^*\)) and the change of entropy of activation (\(\Delta S^*\)) can be calculated.

\[
\Delta H^* = \Delta H_1^* - \Delta H_2^*
\]

\[
\Delta H^* = (-1303.42) - (-63.49)
\]

\[
\Delta H^* = -1239.93 \pm 0.08 \text{ J mol}^{-1}
\]

Also,

\[
\Delta S^* = \Delta S_1^* - \Delta S_2^*
\]

\[
\Delta S^* = (-276.09) - (-248.79)
\]

\[
\Delta S^* = -27.30 \pm 0.04 \text{ J mol}^{-1}\text{K}^{-1}
\]

From the values of \(\Delta H^*\), \(\Delta S^*\), and \(\Delta G^*\) can be calculated as follows.

\[
\Delta G^* = \Delta H^* - T \Delta S^*
\]

At 77 K,

\[
\Delta G^* = -1239.93 - (77 \times -27.30)
\]

\[
\Delta G^* = 862.17 \pm 0.02 \text{ J mol}^{-1}
\]

Similar temperature dependent experiments were carried out for the batch 2, and 3 of KAu(CN)\(_2\)/KCl and pure KAu(CN)\(_2\). Table 5.3 summarizes the calculated values for \(\Delta H^*\), \(\Delta S^*\), and \(\Delta G^*\) for each studied KAu(CN)\(_2\)/KCl system.
Table 5.3. Calculated kinetic parameters for the KAu(CN)$_2$/KCl system as well as pure KAu(CN)$_2$.

<table>
<thead>
<tr>
<th>System</th>
<th>$\Delta H^*$, J mol$^{-1}$</th>
<th>$\Delta S^*$, J mol$^{-1}$ K$^{-1}$</th>
<th>$\Delta G^*$ at 77 K, J mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>KAu(CN)$_2$/KCl batch 1</td>
<td>-1239.93 ± 0.08</td>
<td>-27.30 ± 0.04</td>
<td>+862.17 ± 0.02</td>
</tr>
<tr>
<td>KAu(CN)$_2$/KCl batch 2</td>
<td>-1083.39 ± 0.06</td>
<td>-19.96 ± 0.02</td>
<td>+453.80 ± 0.04</td>
</tr>
<tr>
<td>KAu(CN)$_2$/KCl batch 3</td>
<td>-1568.5 ± 0.09</td>
<td>-30.64 ± 0.01</td>
<td>+790.77 ± 0.03</td>
</tr>
<tr>
<td>Pure KAu(CN)$_2$</td>
<td>-1202.79 ± 0.01</td>
<td>-15.38 ± 0.05</td>
<td>+18.53 ± 0.05</td>
</tr>
</tbody>
</table>

According to table 5.3, the negative $\Delta H^*$ values indicate that the activated complex is more stable compared to reactants. Also, the calculated negative $\Delta S^*$ values give an indication of having more ordered activated complex. At 77 K, the $\Delta G^*$ values for the KAu(CN)$_2$/KCl batch 1, 2, 3, and pure KAu(CN)$_2$ in the absence of 266 nm laser are +862.17 ± 0.02, +453.80 ± 0.04, +790.77 ± 0.03 and +18.53 ± 0.05 J mol$^{-1}$ respectively. Positive $\Delta G^*$ values indicate that the disproportionation reaction is not spontaneous at 77 K without exposing to 266 nm laser. But the forward reaction can occur if the energy from 266 nm (449.64 KJ mol$^{-1}$) is provided. As mentioned before (figure 5.3), at 77 K, the disproportionation reaction rate follows the order of batch 1 < batch 3 < batch 2 < pure KAu(CN)$_2$. According to these calculations, the disproportionation reaction rate at 77 K should be faster in pure KAu(CN)$_2$ than the doped systems.
5.4. Conclusions

The study of the optical memory phenomenon in three different concentrations of [Au(CN)₂⁻] ions doped in KCl as well as pure KAu(CN)₂ have been discussed. At 77 K, upon excitation at 275 nm, both batches 1 (0.45 % Au) and 3 (2.20 % Au) of KAu(CN)₂⁻ /KCl showed three emission bands at 335, 390, and 425 nm whereas batch 2 (1.38 % Au) of KAu(CN)₂⁻ /KCl and pure KAu(CN)₂ showed only one emission band at 390 nm. With exposure to 266 nm laser, the intensity of all these three emission bands went down with the change in the 390 nm emission band the most dramatic. The change in the 390 nm emission peak area with laser exposure follows the order of batch 1 < batch 3 < batch 2 < pure KAu(CN)₂.

From extended Hückel calculations, the 335 nm emission band is assigned as excited bent trimers while the 390 and 425 nm emission bands are assigned as excited linear trimers and tetramers, respectively. With laser exposure, the disproportionation of [Au(CN)₂⁻] takes place: 3[Au(CN)₂⁻] → 2Au(0) + Au(CN)₄⁺ + 2CN⁻.

Warming exposed crystals back to room temperature and recooling down to 77 K, results in the intensities of emission bands going back to their original value. For these crystals, by exposing to 266 nm laser at low temperatures, the memory can be stored. Also, by warming the crystal back to room temperature and recooling down to low temperature, the memory can be erased.

Optical memory experiments for all three batches of KAu(CN)₂⁻ /KCl and pure KAu(CN)₂ were carried out at different temperatures to calculate kinetic parameters. These calculation results indicate that the disproportionation reaction is spontaneous if the energy from 266 nm (449.64 KJ mol⁻¹) is provided.
5.5. References


Chapter 6

d^{10}-d^{10} and d^{10}-d^{8} MIXED METAL COMPOUNDS

6.1. Introduction

Examples of group 11 homometallic closed shell interactions have been known for many years. Among these, Cu-Cu interactions or cuprophilic interactions have been studied extensively.\textsuperscript{1,2} X-Ray crystallographic results show that the Cu-Cu distances of these compounds are shorter than the sum of the Van der Waals radii of two copper atoms. Analogous Ag-Ag interactions or argentophilic interactions have also been studied using X-Ray crystallography as well as other spectroscopic methods such as luminescence, and Raman spectroscopy.\textsuperscript{3,4} There are also a large number of spectroscopic as well as theoretical studies that have been reported for the Au(I) coordination compounds having Au-Au interactions or aurophilic interactions.\textsuperscript{5,6}

Other than group 11 compounds, there are examples reported in the literature about group 9 coordination compounds showing homometallic closed shell interactions.\textsuperscript{7-10} For example, trimeric Pd(II) acetate in acetic acid or benzene shows Pd-Pd interactions.\textsuperscript{7} There are also few examples of bi and poly Pt(II) compounds have shown strong Pt-Pt interactions in the excited state.\textsuperscript{8-10}

Compared to homometallic coordination compounds, few examples have been reported in the literature about heterometallic coordination compounds.\textsuperscript{11-14} Among these examples, Rawashdeh-Omary \textit{et al.} have reported about a new type of heterobimetallic compound, AgAu(MTP)\textsubscript{2} (where MTP = diphenylmethylenethiophosphinenate) which shows argento-aurophilic bonding interactions.\textsuperscript{13} This heterobimetallic compound forms
an extended one dimensional chain structure in the solid state. From X-Ray crystallography, the intramolecular Ag-Au separation of this AgAu(MTP)₂ compound was found to be 2.912 Å. The absorption spectra of solutions of AgAu(MTP)₂, Ag₂(MTP)₂, and Au₂(MTP)₂ showed that the energies of the absorption edge followed the order of Au₂(MTP)₂ < AgAu(MTP)₂ < Ag₂(MTP)₂.

In the 1980's, our research group reported the absorption and luminescence properties of quasi-one-dimensional mixed metal compounds, Ba(Pt,Pd)(CN)₄ and Ba(Pt,Ni)(CN)₄ and compared with pure systems.¹⁴ The authors have concluded that the excited states of these compounds are delocalized over the Pt-Pd and Pt-Ni centers. One recent group member has studied the mixed metal compound of the type La[AgₓAu₁₋ₓ(CN)₂]₃ and the preliminary results indicated that the results were similar to Ba(Pt,Pd)(CN)₄ and Ba(Pt,Ni)(CN)₄.¹⁵ In these Ba(Pt,Pd)(CN)₄, Ba(Pt,Ni)(CN)₄ or La[AgₓAu₁₋ₓ(CN)₂]₃ systems, emission bands were observed in between the energies of the two pure systems.

The goal of this chapter is to discuss the synthesis and characterization of two types of mixed metal systems. The first type is a d¹⁰-d¹⁰ mixed metal system using KAu(CN)₂ and KAg(CN)₂ and to compare the results with the pure system results. Photoluminescence spectroscopy has been used as the major tool to study this system. Lifetime measurements helped to interpret observed luminescence bands as to whether they originated from a triplet excited state or a singlet excited state. Atomic absorption measurements have been carried out to evaluate the actual gold and silver ratio incorporated in the crystals. Extended Hückel calculations have been performed for
different combinations of $[\text{Au(CN)}_2]$ and $[\text{Ag(CN)}_2^-]$ units in order to explain observed experimental results.

The second type of mixed metal system involved $d^{10}$-$d^8$ ions using $\text{KAu(CN)}_2$, or $\text{KAg(CN)}_2$ and $\text{K}_2\text{Pt(CN)}_4$. Steady state photoluminescence spectroscopy as well as temperature dependent photoluminescence spectroscopy has been carried out to study these systems.

6.2. Experimental

Different Ag:Au ratios of $d^{10}$-$d^{10}$ mixed metals, 1 mole $\text{KAg(CN)}_2$ : 1 mole $\text{KAu(CN)}_2$ ($d^{10}$ mixed # 1), 1 mole $\text{KAg(CN)}_2$ : 3 mole $\text{KAu(CN)}_2$ ($d^{10}$ mixed # 2), 3 mole $\text{KAg(CN)}_2$ : 1 mole $\text{KAu(CN)}_2$ ($d^{10}$ mixed # 3), and 6 mole $\text{KAg(CN)}_2$ : 1 mole $\text{KAu(CN)}_2$ ($d^{10}$ mixed # 4), were synthesized. Details of the crystal growing have been discussed in Chapter 2. The silver and gold content of each sample were determined using atomic absorption spectroscopy. Atomic absorption measurements were carried out using a Model 857-Smith-Hieftje 11/12 spectrophotometer. Puro-graphic$^\text{TM}$ calibration standards (998 $\mu g/ml$ gold in 5% HCl) from the Cole-Parmer Company were used as the standard to analyze gold samples. On the other hand, puro-graphic$^\text{TM}$ calibration standards (995 $\mu g/ml$ silver in 5% HNO$_3$) were used for the silver samples.

For the $d^{10}$-$d^8$ mixed crystals, 1 mole of $\text{KAg(CN)}_2$ : 1 mole of $\text{K}_2\text{Pt(CN)}_4$ (Ag-Pt sample), and 1 mole of $\text{KAu(CN)}_2$ : 1 mole of $\text{K}_2\text{Pt(CN)}_4$ (Au-Pt sample) were synthesized according to the procedure described in Chapter 2.

Photoluminescence spectra were obtained using a Photon Technology International Model QuantaMaster-1046 spectrophotometer. This instrument is equipped .
with a 75 W xenon lamp, an emission monochromator, and two excitation monochromators. The emission and excitation spectra were recorded at different temperatures ranging from 4 K to room temperature using liquid helium and liquid nitrogen as coolants. All excitation spectra were corrected for the variation of the lamp background using Rhodamine B. Lifetime measurements were performed using a Nanolase diode-pumped solid-state laser pulses at 266 nm with a repetition rate of 8.1 kHz. The decays were averaged over 1000 sweeps on the oscilloscope. All measurements were carried out at room temperature for the same single crystals used in the luminescence measurements.

6.3. Computational Details

Extended Hückel calculations were carried out using FORTICON 8 (QCMP011) program. Relativistic parameters used for these calculations are tabulated in Chapter 2. Ground and the first excited state calculations have been carried out for the eclipsed $[\text{Au(CN)}_2]^2_2$ dimer, $[\text{Ag(CN)}_2]^2_2$ dimer, $[\text{AgAu(CN)}_4^{2-}]$ dimer, $[\text{Au(CN)}_2]^3_3$ trimer, $[\text{Ag(CN)}_2]^3_3$ trimer, $[\text{AgAu}_2(\text{CN})_6^{3-}]$ trimer and $[\text{AuAg}_2(\text{CN})_6^{3-}]$ trimer units in order to explain experimental results.

6.4. Results and Discussion

6.4.1. $d^{10}-d^{10}$ mixed metal system

6.4.1.1. Atomic absorption measurements

Atomic absorption measurements were carried out for different $d^{10}$ mixed samples and results are summarized in table 6.1. The results shown in table 6.1 reveal that the
ratio of Au:Ag incorporated in the crystal is different from the starting Au:Ag ratio. For example, the $d^{10}$ mixed # 4 sample has a Au:Ag molar ratio of 1 : 6.11 as the starting ratio but actually inside the crystal it was 1 : 1.45. This would mislead the analysis of other experiments in this research. Therefore, the atomic absorption analysis of the actual Au:Ag ratio inside the crystal is a very important part of this study. In order to verify these unexpected results, the crystal growing, atomic absorption measurements, and the luminescence experiments were repeated.

Table 6.1. The initial Au:Ag molar ratio and the atomic absorption spectroscopic (AA’S) results for each sample.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Started Au:Ag Ratio</th>
<th>Measured Au:Ag Ratio by AA’S</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d^{10}$ mixed # 1</td>
<td>1:0.31</td>
<td>1:0.09</td>
</tr>
<tr>
<td>$d^{10}$ mixed # 2</td>
<td>1:1.11</td>
<td>1:0.30</td>
</tr>
<tr>
<td>$d^{10}$ mixed # 3</td>
<td>1:3.10</td>
<td>1:0.61</td>
</tr>
<tr>
<td>$d^{10}$ mixed # 4</td>
<td>1:6.11</td>
<td>1:1.45</td>
</tr>
</tbody>
</table>

6.4.1.2. Photoluminescence spectra of different $d^{10}$ mixed samples and its temperature behavior

The photoluminescence spectra of single crystals of four different $d^{10}$ mixed samples are strongly dependent on the Au:Ag ratio, the temperature as well as the excitation wavelength. Figure 6.1 shows the emission spectra of single crystals of different $d^{10}$ mixed samples at 77 K upon excitation at 275 nm. As shown in figure 6.1, the emission spectra is strongly depend on the Au:Ag ratio. Single crystals of pure
Figure 6.1. Emission spectra variation with the Au:Ag ratio at 77 K upon excitation at 275 nm.
KAg(CN)$_2$ and pure KAu(CN)$_2$ show single emission bands at 415 and 390 nm, respectively, at 77 K regardless of the excitation wavelength. As the Au:Ag ratio increases from 1:0.09 to 1:0.30 to 1:0.61 to 1:1.45, instead of seeing two emission bands due to pure KAu(CN)$_2$ and KAg(CN)$_2$, two other emission shoulders appear at 343 nm and 372 nm. The sample having Au:Ag ratio of 1:0.09 shows basically one emission band at 390 nm similar to pure KAu(CN)$_2$. Actually this result is not surprising because this d$^{10}$ mixed sample has much more Au compared to Ag. Figures 6.2 and 6.3 show the emission spectra of single crystals of four different d$^{10}$ mixed samples when excited at 265 nm at 77 and 4 K respectively. These figures indicate that the emission spectra very much depend on the temperature. Even for the pure KAg(CN)$_2$, at 77 K, the emission spectrum shows one emission band at 415 nm while at 4 K it shows an additional peak at 312 nm upon excitation at 265 nm. According to figure 6.3, when the Au:Ag ratio increases, the emission bands due to mixed metals lie in between peaks due to pure systems. In other words, pure KAg(CN)$_2$ shows two emission bands at 312 and 415 nm at 4 K when excited at 265 nm. Also, pure KAu(CN)$_2$ shows one emission band at 390 nm. The d$^{10}$ mixed samples with Au:Ag ratios of 1:0.61 and 1:1.45 show two other emission bands at 343 and 372 nm in addition to emission peaks due to emission bands at 312, 386, and 425 nm. This gives an indication of having delocalized excited states in these mixed metal samples. The d$^{10}$ mixed sample having a Au:Ag ratio of 1:1.45 exhibits this delocalized behavior better than other d$^{10}$ mixed samples. Therefore, this d$^{10}$ mixed sample has been studied in detail. It is worth mentioning here that, the emission peak due to pure KAg(CN)$_2$ (415 nm) is red shifted (~10 nm) in the d$^{10}$ mixed metal system while the emission peak due to pure KAu(CN)$_2$ (390 nm) is blue shifted (~4 nm).
Figure 6.2. Emission spectra variation with the molar ratio of Au:Ag at 77 K upon excitation at 265 nm.
Figure 6.3. Emission spectra of single crystals of different $d^{10}$ mixed samples at 4 K upon excitation at 265 nm.
The delocalization occurs in $^{10}$ mixed samples and its temperature dependent behavior can be explained using scheme 6.1. At 4 K, all emissive states (312, 343, 372, 386, and 425 nm) can be excited and emit energies. Therefore, the emission spectrum of a single crystal of a $^{10}$ mixed sample with a Au:Ag ratio of 1:1.45 shows emission bands at 312, 343, 372, 386, and 425 nm. On the other hand, at 77 K, the emission spectrum of the same sample shows emission bands at 343, 372, 386, and 425 nm. In other words, the 312 nm emission band is quenched at 77 K. This is because as shown in scheme 6.1, the radiationless energy transfer occurs from 312 nm to 343 nm emissive state at 77 K. Radiationless energy transfer pathways become dominant at higher temperatures.

In order to explain the temperature behavior of $^{10}$ mixed samples in detail, the emission spectra were recorded at different temperatures ranging from 4 K to 145 K. Figure 6.4 shows the emission spectra of a single crystal of a $^{10}$ mixed sample with a Au:Ag 1:1.45 ratio for $\lambda_{ex} = 265$ nm as a function of temperature. As the temperature increases, radiationless energy transfer pathways become dominant. As a result, at higher temperatures, the higher energy emission bands quench and lower energy bands become dominant. For example, according to figure 6.4, when the temperature increases from 4 K to 79 K, the emission bands at 312, 343, and 372 decrease in intensity and the emission bands at 386 and 425 nm increase in intensity. Actually the intensity of the emission at 425 nm shows significant enhancement. This is due to energy transfer from other emissive states to the 425 nm emissive state. Further, upon increasing the temperature from 79 K to 130 and 145 K, the intensity of 386 and 425 nm emission bands decreases due to the quenching process. As shown in figure 6.5, at room temperature only one emission band has been observed at 375 nm. At room temperature, the 415 nm emission
Scheme 6.1. Schematic representation of different energy emission as well as energy transfer pathways of d^{10} mixed sample having 1:1.45 Au:Ag ratio.

Notation: A = direct excitation of 312 nm emission band, B, C, D, E, and F = emission from 312, 343, 372, 386, and 425 nm emission bands respectively, G = radiationless energy transfer pathway between 312 and 343 nm emission bands.

At a certain temperature, the emission bands observed in each d^{10} system are strongly dependent on the excited wavelength. For example, figure 6.6 shows the emission spectra of single crystal of d^{10} mixed emission spectra of single crystal of d^{10} mixed sample with Au:Ag ratio of 1:1.45 at 77 K as a function of the excitation wavelength. As shown in figure 6.6, different emission bands can be tuned by selecting
Figure 6.4. Emission spectra of a single crystal of a d^{10} mixed sample with a Au:Ag 1:1.45 upon excitation at 265 nm as a function of temperature.
Figure 6.5. Emission spectra of a single crystal of a $d^{10}$ mixed metal sample with a Au:Ag ratio of 1:1.45 upon excitation at 275 nm.
Figure 6.6. Excitation spectra of a single crystal of a $d^{10}$ mixed sample with a Au:Ag ratio of 1:1.45 at 77 K.
the excitation wavelength. As an example, upon excitation at 275 nm, the emission spectrum shows four emission bands at 343, 372, 386, and 425 nm whereas the excitation at 315 nm basically shows one emission band at 386 nm.

The corrected excitation spectra of a single crystal of a $d^{10}$ mixed sample with a Au:Ag ratio of 1:1.45 at 77 K are shown in figure 6.7. Each emission band observed in figure 6.6 has characteristic excitation maxima. This gives the opportunity to resolve various emission bands by selecting the excitation wavelength.

On the other hand, figure 6.8 shows the emission spectra of a single crystal of $d^{10}$ mixed metal sample with a Au:Ag ratio of 1:1.45 at 4 K as a function of excitation wavelength. At 4 K, various emission bands can be tuned by selecting the excitation wavelength. For example, upon excitation at 265 nm, the emission spectra show five emission bands at 312, 343, 372, 386, and 425 nm while the excitation at 285 nm shows only four emission bands at 343, 372, 386, and 425 nm. Figure 6.9 shows the corrected excitation spectra of a single crystal of a $d^{10}$ mixed metal sample with a Au:Ag ratio of 1:1.45 at 4 K. As shown in figure 6.8, each emission band has characteristic excitation maxima giving the opportunity to resolve different emission bands.

6.4.1.3. Lifetime measurements

Lifetime measurements for the observed luminescence bands present in a $d^{10}$ mixed sample having a Au:Ag ratio of 1:1.45 were carried out at 4 K and 77 K. The lifetime value of the 312 nm emission band was not detectable because of the filter used to protect the detector. Table 6.2 summarizes all other lifetime data obtained at 4 K and 77 K. According to table 6.2, observed lifetime data of the different emission bands
Figure 6.7. Emission spectra of a single crystal of a d$^{10}$ mixed sample with a Au:Ag ratio of 1:1.45 at 77 K as a function of the excitation wavelength.
Figure 6.8. Emission spectra of a single crystal of a d^{10} mixed sample with a Au:Ag ratio of 1:1.45 as a function of excitation wavelength at 4 K.
Figure 6.9. Excitation spectra of a single crystal of a $d^{10}$ mixed sample with a Au:Ag ratio of 1:1.45 at 4 K.
of the d\textsuperscript{10} mixed sample with a Au:Ag ratio of 1:1.45 show microsecond scale lifetimes at 77 K. These emission bands are the result of decay from triplet states (phosphorescence).

Table 6.2. Lifetime data for pure KAg(CN)\textsubscript{2} and KAu(CN)\textsubscript{2} as well as different emission bands observed in the d\textsuperscript{10} mixed sample with a 1:1.45 Au:Ag ratio at 4 K and 77 K.

<table>
<thead>
<tr>
<th>Emission band, nm</th>
<th>Lifetime at 4 K, (\mu s)</th>
<th>Lifetime at 77 K, (\mu s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>343 of mixed Ag-Au sample</td>
<td>0.076 (\pm) 0.001</td>
<td>2.20 (\pm) 0.02</td>
</tr>
<tr>
<td>372 of mixed Ag-Au sample</td>
<td>1.38 (\pm) 0.02</td>
<td>2.27 (\pm) 0.01</td>
</tr>
<tr>
<td>386 of mixed Ag-Au sample</td>
<td>3.00 (\pm) 0.01</td>
<td>3.03 (\pm) 0.01</td>
</tr>
<tr>
<td>425 of mixed Ag-Au sample</td>
<td>4.15 (\pm) 0.01</td>
<td>20.05 (\pm) 0.03</td>
</tr>
<tr>
<td>415 of pure KAg(CN)\textsubscript{2}</td>
<td>47.16 (\pm) 0.02</td>
<td>44.63 (\pm) 0.03</td>
</tr>
<tr>
<td>390 of pure KAu(CN)\textsubscript{2}</td>
<td>12.90 (\pm) 0.01</td>
<td>0.34 (\pm) 0.01</td>
</tr>
</tbody>
</table>

On the other hand, at 4 K, the 343 nm emission band shows a nanosecond scale lifetime indicating that this is the result of decay from a singlet state (fluorescence) while other emission bands show microsecond scale lifetimes (phosphorescence). Both pure KAg(CN)\textsubscript{2} and KAu(CN)\textsubscript{2} show microsecond scale lifetimes at 77 K as well as at 4 K indicating that these transitions are from triplet states (phosphorescence).

At 4 K, the lifetime value of the 386 (gold emission) and the 425 (silver emission) nm emission bands in the d\textsuperscript{10} mixed sample with a Au:Ag ratio of 1:1.45 are 3.00 and 4.15 \(\mu s\) respectively. Pure KAu(CN)\textsubscript{2} and KAg(CN)\textsubscript{2} have lifetime values of 12.90 and 30.94 \(\mu s\) at 4 K. The shorter lifetime values in the mixed Ag-Au system can be explained as follows.
\[
\tau = \frac{1}{k_{\text{rad}} + k_{\text{non-rad}} + k_{\text{mixed}}}
\]  

(1)

where,

\( \tau \) = lifetime value

\( k_{\text{rad}} \) = rate constant of radiative energy transfer pathway

\( k_{\text{non-rad}} \) = rate constant of non-radiative energy transfer pathway

\( k_{\text{mixed}} \) = rate constants in the mixed metal system

According to equation 1, when the value of \( k_{\text{mixed}} \) increases, the lifetime value, \( \tau \) should decrease. After comparison of the pure system results versus the mixed system, it is clear that in the mixed system because of the value of \( k_{\text{mixed}} \) in the denominator, the lifetime value should get smaller compared to the pure system.

As shown in table 6.2, it is also obvious that the lifetime value for a given emission band increases with the temperature. For example, at 4 K, the lifetime value for 425 nm emission band in the mixed sample is 4.15 \( \mu s \) and the corresponding value at 77 K is 20.05 \( \mu s \). This is because at higher temperatures the \( k_{\text{mixed}} \) value gets smaller. In other words, the mixed metal delocalization decreases with increasing temperature. Therefore at higher temperatures, the lifetime value should get larger.

6.4.1.4. Extended Hückel calculations

In order to make sense of experimental data, extended Hückel calculations were carried out for the ground and the first excited states of the eclipsed \([\text{Ag(CN)}_2]_2\) dimer, eclipsed \([\text{Au(CN)}_2]_2\) dimer, eclipsed \([\text{Ag(CN)}_2\text{Au(CN)}_2]^2\) dimer, linear \([\text{Au(CN)}_2]_3\) trimer, linear \([\text{Ag(CN)}_3^-]_3\) trimer, linear \([\text{AgAu}_2(\text{CN})_6]^{3-}\) trimer and linear \([\text{AuAg}_2(\text{CN})_6]^{3-}\)
trimer units. Results of these calculations are summarized in table 6.3 and 6.4. Figures 6.10, 6.11, and 6.12 show the ground and the first excited state potential energy diagrams for the eclipsed \([\text{Ag(CN)}_2^-]_2\) dimer, \([\text{Au(CN)}_2^-]_2\) dimer, and \([\text{Ag(CN)}_2\text{Au(CN)}_2]^{2-}\) dimer units. Let's first consider the ground state results of the eclipsed forms of \([\text{Ag(CN)}_2^-]_2\) dimer, \([\text{Au(CN)}_2^-]_2\) dimer, and \([\text{Ag(CN)}_2\text{Au(CN)}_2]^{2-}\) dimer. According to table 6.3, the equilibrium distance for the \([\text{Ag(CN)}_2^-]_2\) dimer is 3.58 Å whereas the corresponding value for the \([\text{Au(CN)}_2^-]_2\) dimer is 3.48 Å. On the other hand, the \([\text{Ag(CN)}_2\text{Au(CN)}_2]^{2-}\) dimer has an equilibrium distance of 3.51 Å which lies in between the values of the \([\text{Au(CN)}_2^-]_2\) and \([\text{Ag(CN)}_2^-]_2\) dimers.

A similar trend is for the HOMO-LUMO gap: the ground state HOMO-LUMO gap for the \([\text{Ag(CN)}_2\text{Au(CN)}_2]^{2-}\) dimer is 4.01 eV which lies in between the corresponding values for the \([\text{Au(CN)}_2^-]_2\) and \([\text{Ag(CN)}_2^-]_2\) dimers (4.37 eV and 3.78 eV respectively).

As shown in figures 6.10, 6.11, and 6.12, for a given dimeric unit, the first excited state has a deeper potential well, shorter metal-metal distance, and higher overlap population compared to the ground state indicating that the stronger metal-metal interactions are present (excimer/exciplex formation) in the first excited state. Also, in the first excited state, the equilibrium distance as well as the HOMO-LUMO gap for the excited \([\text{AgAu(CN)}_4]^{2-}\) dimer lies in between corresponding values for excited \([\text{Au(CN)}_2^-]_2\) and \([\text{Ag(CN)}_2^-]_2\) dimers. For example, in the first excited state the HOMO-LUMO gap for the excited \([\text{Ag(CN)}_2\text{Au(CN)}_2]^{2-}\) dimer is 3.71 eV which is in between the corresponding values for excited \([\text{Au(CN)}_2^-]_2\) and \([\text{Ag(CN)}_2^-]_2\) dimers (3.41 eV and 3.98 eV respectively). This agrees with the experimental data: at 4 K, the emission energy of
Table 6.3. Summary of the results of Extended Hückel calculations for the ground and first excited states of eclipsed dimeric species of [Au(CN)₂⁻] and [Ag(CN)₂⁻] units. *

<table>
<thead>
<tr>
<th>Species</th>
<th>[Au]₂</th>
<th>[⁎Au]₂</th>
<th>[Ag]₂</th>
<th>[⁎Ag]₂</th>
<th>[Au][Ag]</th>
<th>[⁎Au][Ag]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eq.Distance Å</td>
<td>3.48</td>
<td>3.00</td>
<td>3.58</td>
<td>3.00</td>
<td>3.51</td>
<td>3.03</td>
</tr>
<tr>
<td>B.E., eV</td>
<td>0.13</td>
<td>0.86</td>
<td>0.13</td>
<td>1.09</td>
<td>0.16</td>
<td>0.70</td>
</tr>
<tr>
<td>H-L gap, eV</td>
<td>3.78</td>
<td>3.41</td>
<td>4.37</td>
<td>3.98</td>
<td>4.01</td>
<td>3.71</td>
</tr>
<tr>
<td>O.P.</td>
<td>0.0226</td>
<td>0.0734</td>
<td>0.0032</td>
<td>0.0342</td>
<td>0.0112</td>
<td>0.0496</td>
</tr>
</tbody>
</table>

*Notation: [Au] = [Au(CN)₂⁻], [Ag] = [Ag(CN)₂⁻], [⁎Au]₂, [⁎Ag]₂: excimers, B.E. = binding energy, H-L gap= HOMO-LUMO gap, O.P = overlap population.
Figure 6.10. Potential energy curves of the ground and the first excited states for eclipsed [Ag(CN)₂]₂⁻.
Figure 6.11. Potential energy curves of the ground and the first excited states for eclipsed $[\text{Au(CN)}_2]^-$.
Figure 6.12. Potential energy curves of the ground and the first excited states for eclipsed $[\text{Ag(CN)}_2\text{Au(CN)}_2]^2-$ dimer.
d^{10}-d^{10} mixed metal bands (343, and 372 nm) lies in between emission energies of pure KAg(CN)₂ (312 and 415 nm) and pure KAu(CN)₂ (390 nm). Therefore, the emission energies of d^{10}-d^{10} mixed metal systems with Ag(CN)₂⁻ and Au(CN)₂⁻ arise from the delocalization of Ag and Au emissive states.

Table 6.4 summarizes the results of extended Hückel calculations for the linear [Au(CN)₂]₃ trimer, linear [Ag(CN)₂]₃ trimer, linear [AgAu₂(CN)₆]³⁻ trimer and linear [AuAg₂(CN)₆]³⁻ trimer units. Also, figures 6.13, 6.14, 6.15, and 6.16 show the potential energy diagrams for the ground and the first excited states of above trimeric units. In the same as for the dimeric units of [Au(CN)₄]²⁻, [Ag(CN)₄]²⁻, and [AgAu(CN)₄]²⁻, the potential energy diagrams of the trimeric units ([Au(CN)₂]₃, [AgAu(CN)₆]³⁻ trimer etc.) show a much deeper potential well, shorter Au-Au, Ag-Ag or Ag-Au distances, higher overlap population in the first excited state compared to the ground state. This gives an indication of stronger Au-Au, Ag-Ag, or Au-Ag interactions (the formation of excimer/exciplexes) in the first excited state.

As shown in table 6.4, it should be noted that by comparing of [Au₂Ag(CN)₆]³⁻ trimer versus [Ag₂Au(CN)₆]³⁻ trimer, the [Ag₂Au(CN)₆]³⁻ trimer has a higher Au-Ag overlap population than the corresponding value for the [Au₂Ag(CN)₆]³⁻ trimer. For example, in the first excited state, the overlap population for the [Ag₂Au(CN)₆]³⁻ trimer is 0.0401 eV which is higher than the corresponding value 0.0355 eV for the [Au₂Ag(CN)₆]³⁻ trimer. This gives a possible explanation for the experimental data showing more d^{10}-d^{10} mixed metal delocalization for the sample of having Au:Ag ratio of 1:1.45 ([Ag₂Au(CN)₆]³⁻ trimer) than Au:Ag the ratio of 1:0.51 ([Au₂Ag(CN)₆]³⁻ trimer).
Table 6.4. Summary of the results of Extended Hückel calculations for the ground and first excited states of eclipsed trimeric species of $[\text{Au(CN)}_2]$ and $[\text{Ag(CN)}_2]$ units.

<table>
<thead>
<tr>
<th>Species</th>
<th>$[\text{Au}]_3$</th>
<th>$^*,[\text{Au}]_3$</th>
<th>$[\text{Ag}]_3$</th>
<th>$^*,[\text{Ag}]_3$</th>
<th>$[\text{Ag}][\text{Au}]$</th>
<th>$^*,[\text{Ag}][\text{Au}]$</th>
<th>$[\text{Au}][\text{Ag}]$</th>
<th>$^*,[\text{Au}][\text{Ag}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eq. Distance, Å$^0$</td>
<td>3.44</td>
<td>3.08</td>
<td>3.54</td>
<td>3.15</td>
<td>3.48</td>
<td>3.10</td>
<td>3.42</td>
<td>3.09</td>
</tr>
<tr>
<td>B.E., eV</td>
<td>0.30</td>
<td>1.21</td>
<td>0.29</td>
<td>1.14</td>
<td>0.31</td>
<td>0.73</td>
<td>0.40</td>
<td>0.77</td>
</tr>
<tr>
<td>O.P.</td>
<td>0.0116</td>
<td>0.0569</td>
<td>0.003</td>
<td>0.048</td>
<td>0.0023</td>
<td>0.0401</td>
<td>0.0336</td>
<td>0.0355</td>
</tr>
</tbody>
</table>

Notation: $[\text{Au}] = [\text{Au(CN)}_2]$, $[\text{Ag}] = [\text{Ag(CN)}_2]$, $^*\,[\text{Au}]_3$, $^*\,[\text{Ag}]_3$: exciplexes. B.E. = binding energy, H-L gap = HOMO-LUMO gap, O.P. = overlap population.
Figure 6.13. Ground and the first excited state potential energy curves for linear $[\text{Au(CN)}_2]_3$. 
Figure 6.14. Ground and first excited state potential energy curves for linear \([\text{Ag(CN)}_2]\)_3.
Figure 6.15. Potential energy curves of the ground and the first excited states for a linear $[\text{Ag}_2\text{Au(CN)}_6]^+$ trimer.
Figure 6.16. Potential energy curves of the ground and the first excited states for a linear [Au₂Ag(CN)₆]⁺ trimer.
It is also worth mentioning here that each calculation carried out for the mixed metals showed considerable Au-Au or Ag-Ag overlap populations other than Au-Ag overlap populations in both ground and the first excited states. This gives a possible explanation of seeing emission bands correspond to pure KAu(CN)$_2$ and pure KAg(CN)$_2$ other than the bands due to delocalized excited states in the emission spectra of d$^{10}$-d$^{10}$ mixed metal samples.

6.4.2. d$^{10}$-d$^8$ system

Two types of d$^{10}$-d$^8$ systems were studied. First type was a Au-Pt sample synthesized from a 1:1 molar ratio of KAu(CN)$_2$ and K$_2$Pt(CN)$_4$ and the second type was a Ag-Pt sample using 1:1 molar ratio of KAg(CN)$_2$ and K$_2$Pt(CN)$_4$.

6.4.2.1. KAu(CN)$_2$ - K$_2$Pt(CN)$_4$ co-doped sample

6.4.2.1.1. Steady-state photoluminescence data

As shown in figure 6.17, photoluminescence spectra of a single crystal of KAu(CN)$_2$ - K$_2$Pt(CN)$_4$ sample at 77 K showed two emission bands at 390 and 458 nm when excited at 275 nm. On the other hand at 77 K, a single crystal of pure KAu(CN)$_2$ showed only one peak at 390 and pure K$_2$Pt(CN)$_4$ showed only one peak at 463 nm upon excitation at 275 nm. Comparing these three systems, there is no evidence for the formation of a d$^{10}$-d$^8$ delocalized state in the KAu(CN)$_2$ - K$_2$Pt(CN)$_4$ sample. The 463 nm emission band was little blue shifted (~ 5 nm) in the Au-Pt sample compared to pure K$_2$Pt(CN)$_4$ indicating that Pt-Pt bond distance gets shorter in the Au-Pt sample due to some kind of Au-Pt orbital mixing.
**Figure 6.17.** Emission spectra of single crystals of pure $\text{K}_2\text{Pt(CN)}_4$, pure $\text{KAu(CN)}_2$, and 1 mole of $\text{KAu(CN)}_2 : 1$ mole of $\text{K}_2\text{Pt(CN)}_4$ at 77 K upon excitation at 275 nm.
Figure 6.18. Emission spectra of a single crystal of 1 mole of KAu(CN)$_2$ : 1 mole of K$_2$Pt(CN)$_4$ at 77 K when excited at 275 and 380 nm.
Figure 6.19. Excitation spectra of a single crystal of 1 mole of KAu(CN)$_2$: 1 mole of K$_2$Pt(CN)$_4$ at wavelengths corresponding to the emission maxima of emission bands at 77K.
Figure 6.18 shows the emission spectra of a single crystal of KAu(CN)$_2$ - K$_2$Pt(CN)$_4$ sample upon excitation at different wavelengths at 77 K. According to figure 6.18, two emission bands are observed at 390 and 458 nm in the Au:Pt sample. Also, figure 6.19 shows the excitation spectra of a single crystal of Au:Pt sample at 77 K upon monitoring the excitation for the maximum emission observed in figure 6.18. From these figures, it is clear that depending on the excitation wavelength, emission can be observed only from Pt lowest excited states or from both Au and Pt lowest excited states. Scheme 6.2 represents these different energy emission and energy transfer pathways observed in the Au-Pt sample. According to scheme 6.2, upon excitation of the emissive state of Au, energy can be emitted from both Au and Pt lowest excited states because of the energy transfer from the lowest excited state of Au to Pt. On the other hand, upon excitation of a Pt emissive state, emission can be observed only from the lowest excited state of Pt.

6.4.2.1.2. Temperature dependent data

Figure 6.20 shows the emission spectra of single crystals of KAu(CN)$_2$ - K$_2$Pt(CN)$_4$ sample, pure KAu(CN)$_2$ and pure K$_2$Pt(CN)$_4$ at 4 K when excited at 275 nm. At 4 K, pure K$_2$Pt(CN)$_4$ shows two emission bands at 410 and 463 nm where as pure KAu(CN)$_2$ shows an emission band at 390 nm. On the other hand, the emission spectrum of the Au:Pt sample shows two emission bands at 410 and 463 nm when excited at 275 nm at 4 K. Emission and excitation spectra were recorded for the Au:Pt sample at different temperatures ranging from 4 K to room temperature to investigate the temperature dependent behavior of Au:Pt sample. Figures 6.21 and 22 demonstrate the emission spectra of a single crystal of a Au:Pt sample at different temperatures when
6.4.2.2. Photoluminescence studies of KAg(CN)$_2$ - K$_2$Pt(CN)$_4$ sample

According to figure 6.23, the emission spectra of a single crystal of Ag-Pt sample at 77 K shows two emission bands at 415 and 463 nm when excited at 265 nm. On the other hand, single crystals of pure KAg(CN)$_2$ and pure K$_2$Pt(CN)$_4$ show emission bands
Figure 6.20. Emission spectra of single crystals of 1 mole of KAu(CN)$_2$ : 1 mole of K$_2$Pt(CN)$_4$, pure KAu(CN)$_2$, and pure K$_2$Pt(CN)$_4$ at 4 K upon excitation at 275 nm at 4 K.
Figure 6.21. Emission spectra of a single crystal of 1 mole of KAu(CN)$_2$: 1 mole of K$_2$Pt(CN)$_4$ at different temperatures upon excitation at 275 nm.
Figure 6.22. Emission spectra of a single crystal of 1 mole of KAu(CN)$_2$ 1 mole of K$_2$Pt(CN)$_4$ at 77 K and room temperature upon excitation at 275 nm.
Figure 6.23. Emission spectra of single crystals of pure KAg(CN)$_2$, pure K$_2$Pt(CN)$_4$ and 1 mole of KAg(CN)$_2$ : 1 mole of K$_2$Pt(CN)$_4$ at 77 K upon excitation at 265 nm.
at 415 and 463 nm respectively. Similar to the Au:Pt system, there is no indication for the formation of any delocalized state. But, interesting enough to observe emission bands due to both KAg(CN)₂ and K₂Pt(CN)₄ in one system. As shown in figure 6.24, by increasing the temperature up to room temperature results in quenching of the 415 nm emission band and blue shifting the 463 nm band. The observed blue shift may be due to shorter Pt-Pt bond distances at higher temperatures.

Figure 6.25 shows the excitation spectra of a single crystal of Ag:Pt sample at 77 K upon monitoring the emission maxima observed in figure 6.23. At 4 K, the emission spectrum of this sample shows three emission bands at 310, 415, and 463 nm (figure 6.26). A single crystal of pure KAg(CN)₂ shows two emission bands at 310 and 415 nm at 4 K. As mentioned before at 4 K, the emission spectrum of a single crystal of K₂Pt(CN)₄ shows two emission bands at 410 and 463 nm. Once again, even at 4 K, there is no evidence for the formation of any delocalized state in this Ag-Pt system. But the significance of this system is that emissions due to both Ag and Pt can be observed in one system.
Figure 6.24. Emission spectra of a single crystal of 1 mole of KAg(CN)$_2$ : 1 mole of K$_2$Pt(CN)$_4$ upon excitation at 265 nm at 77 K and room temperature.
Figure 6.25. Excitation spectra of a single crystal of 1 mole of $\text{KAg(CN)}_2$ : 1 mole of $\text{K}_2\text{Pt(CN)}_4$ at wavelengths corresponding to the emission maxima at 77 K.
Figure 6.26. Emission spectra of single crystals of pure $\text{KAg(CN)}_2$ pure $\text{K}_2\text{Pt(CN)}_4$ and 1 mole of $\text{KAg(CN)}_2 : 1$ mole of $\text{K}_2\text{Pt(CN)}_4$ at 4 K upon excitation at 265 nm.
Figure 6.26. Emission spectra of single crystals of pure KAg(CN)$_2$, pure K$_2$Pt(CN)$_4$ and 1 mole of KAg(CN)$_2$: 1 mole of K$_2$Pt(CN)$_4$ at 4 K upon excitation at 265 nm.
6.5. Conclusions

Two types of mixed metal systems, $d^{10} - d^{10}$ (KAu(CN)$_2$-KAg(CN)$_2$) and $d^{10} - d^8$ (KAu(CN)$_2$:K$_2$Pt(CN)$_4$, KAg(CN)$_2$:K$_2$Pt(CN)$_4$) have been synthesized and characterized.

In the $d^{10} - d^{10}$ system, four different $d^{10} - d^{10}$ (KAu(CN)$_2$-KAg(CN)$_2$) mixed metal samples with different Au:Ag ratios have been studied. In the $d^{10} - d^{10}$ mixed sample having a Au:Ag ratio of 1:1.45, significant delocalization due to mixed metals was observed. For example, at 4 K, the emission spectrum of a single crystal of this mixed metal sample showed five emission bands at 310, 342, 372, 387, and 415 nm. The emission spectra of a single crystal of pure KAu(CN)$_2$ showed a single peak at 390 nm and pure KAg(CN)$_2$ showed two emission bands at 310 and 415 nm at 4 K. After comparison of these pure systems versus the 1:1.45 KAu(CN)$_2$:KAg(CN)$_2$ mixed sample, it is clear that emission bands at 343, 372 nm are due to Au-Ag delocalized states.

Different emission bands observed in a $d^{10} - d^{10}$ (KAu(CN)$_2$-KAg(CN)$_2$) mixed sample with a 1:1.45 Au:Ag ratio at 4 K as well as at 77 K can be tuned by varying the excitation wavelength or site selective excitation. Also, the observed emission bands are strongly dependent on the Au:Ag ratio and the temperature. At higher temperatures, energy transfer between different emissive states, a decrease in emission intensity due to quenching processes, and a blue shift in emission energy maxima were observed.

Lifetime values of a single crystal of $d^{10} - d^{10}$ (KAu(CN)$_2$-KAg(CN)$_2$) mixed sample with Au:Ag ratio of 1:1.45 at 77 K are of microsecond scale showing that the emission bands observed at 77 K originated from triplet excited states. On the other hand, at 4 K, 343 nm emission band showed nanosecond scale lifetime indicating that this emission originated from a singlet excited state. At 4 K, all other emission bands showed
 microsecond scale lifetimes. Lifetime values of emission bands in a single crystal of d\textsuperscript{10}-
d\textsuperscript{10} (KAu(CN)\textsubscript{2}-KAg(CN)\textsubscript{2}) mixed sample having Au:Ag ratio of 1:1.45 increases with the temperature.

Extended Hückel calculation results gave excellent agreement with observed experimental data. Calculation results indicated that the Au-Ag overlap population was higher in [Ag\textsubscript{2}Au(CN)\textsubscript{6}]\textsuperscript{3-} trimer than [Ag\textsubscript{2}Au(CN)\textsubscript{6}]\textsuperscript{3-} trimer. This gives very good agreement with observed experimental data. More d\textsuperscript{10}-d\textsuperscript{10} mixed metal delocalization was observed for the sample of having a Au:Ag ratio of 1:1.45 ([Ag\textsubscript{2}Au(CN)\textsubscript{6}]\textsuperscript{3-} trimer) than Au:Ag the ratio of 1:0.51 ([Au\textsubscript{2}Ag(CN)\textsubscript{6}]\textsuperscript{3-} trimer).

As examples for d\textsuperscript{10}-d\textsuperscript{8} systems, two types of systems have been studied. Two types involved KAu(CN)\textsubscript{2}:K\textsubscript{2}Pt(CN)\textsubscript{4} (Au-Pt sample) and KAg(CN)\textsubscript{2}:K\textsubscript{2}Pt(CN)\textsubscript{4} (Ag-Pt sample). In these systems, there are no evidence for the formation of delocalized excited states but interestingly, energy transfer between KAu(CN)\textsubscript{2} or KAg(CN)\textsubscript{2} (d\textsuperscript{10}) and K\textsubscript{2}Pt(CN)\textsubscript{4} (d\textsuperscript{8}) has been observed. In these samples, emissions due to both Au and Pt (also Ag and Pt) are observed. Also, observed emission bands are tunable: that is, different emission bands can be observed by varying the excitation wavelength.
6.6. References


Chapter 7

SUMMARY, CONCLUSIONS AND SUGGESTED FUTURE WORK

7.1. Introduction

This chapter summarizes what has been achieved in this thesis. Three major projects have been studied for this research. The first project is about spectroscopic studies of "exciplex tuning" for dicyanoaurate(I) ions doped in potassium chloride crystals. The second project is about an optical memory study for dicyanoargentate(I) and dicyanoaurate(I) ions doped in potassium chloride crystals. The third project is a study of d^{10}-d^{10} and d^{10}-d^{8} mixed metal systems. The following sections provide a summary of important findings in this thesis. Also, some suggested future research work is discussed.

7.2. Spectroscopic Studies of "Exciplex Tuning" for Dicyanoaurate(I) Ions Doped in Potassium Chloride Crystals

Three different concentrations of single crystals of [Au(CN)_2] doped in KCl host lattice were synthesized and studied spectroscopically. Single crystals of pure KAu(CN)_2 were also synthesized to compare with doped crystals. Atomic absorption spectroscopic measurements show that batch 1 of [Au(CN)_2]/KCl has 0.45% Au by weight while batches 2 and 3 have 1.38 and 2.20% Au by weight.

Steady state photoluminescence spectroscopic measurements have been carried out at 77 K for single crystals of three batches of [Au(CN)_2]/KCl as well as pure KAu(CN)_2. In the emission spectra of a single crystal of [Au(CN)_2]/KCl batch 1, three
emission bands at 335, 390, and 425 nm have been observed by varying the excitation wavelength in the excitation range 270-350 nm. Each emission band observed in batch 1 has a characteristic excitation maximum. Therefore, various emission bands can be resolved by selecting the excitation wavelength.

The emission spectra of single crystals of batches 1 and 3 of $[\text{Au(CN)}_2^-]/\text{KCl}$ at 77 K show three major emission bands at 335, 390, and 425 nm while batch 2 of $[\text{Au(CN)}_2^-]/\text{KCl}$ and pure $\text{KAu(CN)}_2$ show only one emission band upon excitation at 272 nm. Upon excitation at 315 nm, both batches 1 and 3 show emission bands at 390 and 425 nm whereas batch 2 and pure $\text{KAu(CN)}_2$ show only one emission band at 390 nm. These results indicate the presence of three emission sites in the mixed crystals with the lowest and highest Au content while the crystals with intermediate Au content have only one emission site, similar to the situation in pure $\text{KAu(CN)}_2$.

Extended Hückel calculations have been carried out for different oligomers of $[\text{Au(CN)}_2^-]$ units. These calculations have been performed for both ground as well as the first excited states. For a given oligomer, the first excited state has a shorter Au-Au bond distance, deeper potential well and higher binding energy compared to the ground state indicating excimer/exciplex formation. Based on these calculations, the observed luminescence band at 335 nm is assigned to excited bent trimers while 390 and 425 nm emission bands are assigned to excited linear trimers and tetramers, respectively.

Lifetime data at 77 K indicate that the observed emission bands at 390 and 425 nm are due to phosphorescence. In other words, these emissions originate from triplet excited states.
Raman spectroscopic measurements have been performed for the three batches of [Au(CN)\textsubscript{2}]/KCl as well as pure KAu(CN)\textsubscript{2} at room temperature. Raman spectra show \textit{CN} bands corresponding to various sites of [Au(CN)\textsubscript{2}]\textsubscript{n} clusters in the doped crystals, which are correlated with the luminescence spectra. The Raman spectra of batch 2 of [Au(CN)\textsubscript{2}]/KCl and pure KAu(CN)\textsubscript{2} show only one peak at 2176 cm\textsuperscript{-1} in the cyanide stretching frequency region. Also, the Raman spectrum of batch 1 of [Au(CN)\textsubscript{2}]/KCl shows two peaks at 2169 and 2176 cm\textsuperscript{-1} while batch 3 shows an additional peak at 2189 cm\textsuperscript{-1}. The doped crystal with the highest Au content shows three major bands in the luminescence as well as in the Raman spectra, indicating three different sites of [Au(CN)\textsubscript{2}]\textsubscript{n} in the crystal. Single crystals with lower Au content and pure KAu(CN)\textsubscript{2} crystals show only one band in the luminescence and Raman spectra, which indicates one site for the [Au(CN)\textsubscript{2}]\textsuperscript{-1} units in these two systems.

In order to further validate the correspondence between the Raman and the luminescence spectroscopy results, single crystals of different concentrations of [Ag(CN)\textsubscript{2}]/KCl host lattice were synthesized and compared with pure KAg(CN)\textsubscript{2}. Atomic absorption measurements show that batches 1 and 2 of [Ag(CN)\textsubscript{2}]/KCl have 1.21 and 2.23 % Ag by weight. At 77 K, upon excitation at 245 nm, single crystals of both batches 1 and 2 of [Ag(CN)\textsubscript{2}]/KCl show two emission bands at 296 and 415 nm while pure KAg(CN)\textsubscript{2} shows only one band at 415 nm. On the other hand, upon excitation at 275 nm, single crystals of both batches 1 and 2 of [Ag(CN)\textsubscript{2}]/KCl show two emission bands at 338 and 415 nm while pure KAg(CN)\textsubscript{2} shows only one emission band at 415 nm. Using extended Hückel calculations, the emission band at 296 nm is assigned
as excited dimers while emission bands at 338 and 415 nm are assigned as excited bent trimers and linear trimers respectively.

The Raman spectrum of pure KAg(CN)\textsubscript{2} shows only one peak at 2159 cm\textsuperscript{-1} in the cyanide stretching frequency region. Also, the Raman spectrum of a single crystal of [Ag(CN)\textsubscript{2}]/KCl batch 1 shows two major peaks at 2128, and 2124 cm\textsuperscript{-1} while batch 2 shows an additional peak at 2159 cm\textsuperscript{-1}. The doped crystals with the highest Ag content shows three major bands in the luminescence as well as in the Raman spectra, indicating three different sites of [Ag(CN)\textsubscript{2}]\textsuperscript{−} in the crystal.

Since observed luminescence bands are due to metal-metal bonded exciplexes, these results represent an example of the "exciplex tuning" phenomenon. Exciplex tuning in a doped crystal of [Au(CN)\textsubscript{2}]/KCl can be achieved by varying the excitation wavelength (site-selective excitation) and by varying the dopant concentration. By varying the dopant concentration, an unusual trend has been observed: as the dopant concentration increases, the size of the oligomers increases and it accompanied by a shorter Au-Au bond distance. At the highest dopant concentration, the Au-Au bond distance is shorter than found in the pure KAu(CN)\textsubscript{2} crystal. In contrast, at the highest doping level of the [Ag(CN)\textsubscript{2}]/KCl system, the Ag-Ag bond distance is equal to the same bond length as the corresponding pure crystal.

7.3. Optical Memory Studies of Dicyanoargentate(I) and Dicyanoaurate(I) Ions Doped in Potassium Chloride Crystals

At 77 K, the emission spectrum of a single crystal of [Ag(CN)\textsubscript{2}]/KCl batch 1 (1.21 % Ag by wt) shows two emission bands at 338 (HE) and 415 (LE) nm when excited
at 275 nm. With exposure to 266 nm laser, the intensity of the HE band increases concurrently as the intensity of the LE band decreases. The same trend has been observed for batch 2 (2.23 % Ag by wt) and pure KAg(CN)₂. It is worth mentioning here that at 77 K, the emission spectrum of pure KAg(CN)₂ shows only one emission band at 415 nm but with laser exposure, the emission band at 338 nm started growing.

According to extended Hückel calculations, the emission band at 338 nm is assigned to excited bent trimers while the emission band at 415 nm is assigned as linear trimers. With the laser exposure, linear trimers change to bent trimers. In other words, only a conformational change takes place with laser exposure. The rate of change in LE to HE decreases in the direction of batch 1 > batch 2 > pure KAg(CN)₂.

After 266 nm laser exposure, and then warming the crystals back to room temperature, the intensity of HE and LE peaks go back to their original value. The recovery of [Ag(CN)₂]/KCl batch 1 is 98 %, the corresponding value for batch 2 is 76, and for pure KAg(CN)₂ 90 % respectively. By exposing to 266 nm laser, the memory has been stored in the crystal, and after warming the crystal back to room temperature, the memory has been erased.

For [Ag(CN)₂]/KCl crystals, the temperature dependent studies have been carried out without 266 nm laser. Upon increasing temperature, the intensity of the LE band increases concurrently as the intensity of the HE band decreases. In other words, as the temperature increases, the energy transfer from bent trimers to linear trimers has occurred. After plotting \( \ln(I_2/I_1) \) versus \( 1/T \), the activation energy (Ea) values have been calculated. At 77 K, the Ea value for [Ag(CN)₂]/KCl batch 1 is 260.79 \( \pm \) 0.04 J mol⁻¹. The corresponding Ea value for batch 2 is 1437.55 \( \pm \) 0.01 J mol⁻¹. These results indicate
that the energy transfer from 338 nm emission band to 415 nm emission band should be faster in batch 1 compared to batch 2. Experimentally, in a particular temperature, the change in 338 nm emission band to 415 nm emission band is greater in batch 1 compared to batch 2 of [Ag(CN)₂⁻]/KCl.

In the presence of a 266 nm laser, upon increasing the temperature, the intensity of the HE band increases concurrently as the intensity of the LE band decreases. After recording emission spectra at different temperatures, the forward (k₁) and reverse (k₂) rate constants have been calculated. The ΔG* values have been calculated after plotting k_{rate}/T versus 1/T. At 77 K, the ΔG* values for the [Ag(CN)₂⁻]/KCl batch 1 (1.21 %Ag), batch 2 (2.23 %Ag), and pure KAg(CN)₂ are +132.70 ± 1.14, +380.50 ± 0.98, and +1466.52 ± 1.23 J mol⁻¹ respectively. In other words, the forward reaction is non-spontaneous at 77 K. However, the forward reaction can occur if the 266 nm laser light is provided. Similar to the [Ag(CN)₂⁻]/KCl system, the optical memory of three different batches of [Au(CN)₂⁻]/KCl have been studied and compared with pure KAu(CN)₂. At 77 K, the emission spectra of [Au(CN)₂⁻]/KCl batches 1 (0.45 % Au by wt) and 3 (2.20 % Au by wt) show three emission bands at 335, 390, and 425 nm when excited at 275 nm. According to extended Hückel calculations, the emission band at 335 nm is assigned as excited bent trimers whereas the emission bands at 390 and 425 nm are assigned as excited linear trimers and tetramers.

In the emission spectra of [Au(CN)₂⁻]/KCl batches 1 and 3, the intensities of all three emission bands go down but the change in the 390 nm emission band is very dramatic. On the other hand, the [Au(CN)₂⁻]/KCl batch 2 and pure KAu(CN)₂ show only one emission band at 390 nm and it goes down with increasing laser exposure. The
change in 390 nm emission peak area with laser exposure follows the order of batch 1 < batch 3 < batch 2 < pure KAu(CN)₂. With laser exposure, the disproportionation of [Au(CN)₂⁻] takes place. The possible reaction can be \(3[\text{Au(CN)}_2^-] \rightarrow 2\text{Au(0)} + \text{Au(CN)}_4^- + 2\text{CN}^-\).

Warming crystals back to room temperature and recooling down to 77 K, intensities of emission bands went back to their original value indicating that single crystals of [Au(CN)₂⁻]/KCl and pure KAu(CN)₂ represent optical memory phenomenon. Optical memory experiments for all three batches of KAu(CN)₂⁻]/KCl and pure KAu(CN)₂ were carried out at different temperatures to calculate kinetic parameters. At different temperatures, using emission intensity change with exposure time, the forward \((k_1)\) and reverse \((k_2)\) reaction rate constants have been calculated. After plotting \(k_{rate}/T\) versus \(1/T\), the \(\Delta G^*\) values have been calculated. The positive \(\Delta G^*\) values for each system indicate that the disproportionation reaction is spontaneous only in the presence of 266 nm laser.

### 7.4. d⁰⁻d¹⁰ and d⁰⁻d⁸ Mixed Metal Compounds

Two types of mixed metal systems, d⁰⁻d¹⁰ (KAu(CN)₂-KAg(CN)₂) and d⁰⁻d⁸ (KAu(CN)₂:K₂Pt(CN)₄, KAg(CN)₂:K₂Pt(CN)₄) have been synthesized and characterized.

Four different d⁰⁻d¹⁰ mixed metal single crystals have been synthesized using different ratios of KAu(CN)₂ and KAg(CN)₂. Atomic absorption measurements have been carried out for each sample and it was found that the ratio of Au:Ag incorporated in the crystal is different from the starting Au:Ag ratio.
The d^{10}-d^{10} mixed metal sample with a Au:Ag ratio of 1:1.45 shows significant gold-silver delocalization in the excited state. For example, at 4 K, the emission spectrum of a single crystal of a d^{10}-d^{10} mixed metal sample with a Au:Ag ratio of 1:1.45 shows five emission bands at 312, 343, 372, 386 and 415 nm. On the other hand, at 4 K, the emission spectrum of a single crystal of pure KAu(CN)_2 shows only one emission band at 390 nm while pure KAg(CN)_2 shows two emission bands at 312 and 415 nm. After comparison of the emission spectra of pure Au and Ag samples versus the d^{10}-d^{10} mixed metal sample with Au:Ag ratio of 1:1.45, it is obvious that the emission bands at 343, and 372 nm are due to mixed metal delocalization.

For a single crystal of a d^{10}-d^{10} mixed metal sample with a Au:Ag ratio of 1:1.45, the emission and excitation spectra have been recorded at different temperatures ranging from 4 K to room temperature. As the temperature increases from 4 K to 77 K, energy transfer from the higher energy emissive states to the lower energy emissive states has been observed.

At 4 K or 77 K, the observed emission bands in the emission spectra of a single crystal of a d^{10}-d^{10} mixed metal sample with a Au:Ag ratio of 1:1.45 can be tuned by varying the excitation wavelength. Also, each emission band observed in these emission spectra has a characteristic excitation maximum. This gives the opportunity to resolve emission bands by selecting the excitation wavelength (site-selective excitation).

Lifetime measurements have been carried for emission bands observed in the emission spectra of a single crystal of d^{10}-d^{10} mixed metal sample with Au:Ag ratio of 1:1.45 at 4 K as well as 77 K. At 4 K, the 343 nm emission bands shows a nanosecond lifetime indicating that this emission originated from a singlet excited state.
(fluorescence). All other emission bands (372, 386, and 415 nm) have microsecond scale lifetimes giving an indication of a triplet to singlet energy transition (phosphorescence) at 4K. On the other hand, at 77 K, all observed emission bands show microsecond scale lifetimes (phosphorescence).

Upon increasing the temperature from 4 K to 77 K, the lifetime value for a given emission band increases with the temperature. Also, the lifetime value for a given emission band in the d^{10}-d^{10} mixed system gets smaller compared to the pure Au and Ag systems.

Extended Hückel calculations give excellent agreement with observed experimental data. These calculations have been carried out for the ground and the first excited states of the eclipsed [Ag(CN)₂]₂ dimer, eclipsed [Au(CN)₂]₂ dimer, eclipsed [Ag(CN)₂Au(CN)₂]²⁻ dimer, linear [Au(CN)₂]₃ trimer, linear [Ag(CN)₂]₃ trimer, linear [AgAu₂(CN)₆]³⁻ trimer and linear [AuAg₂(CN)₆]³⁻ trimer units. The ground state and the first excited state calculations show that the equilibrium distance as well as the HOMO-LUMO gap of [Ag(CN)₂Au(CN)₂]²⁻ dimer lies in between the values of [Au(CN)₂]₂ and [Ag(CN)₂]₂ dimers. This agrees with the experimental data: at 4 K, the emission energy of d^{10}-d^{10} mixed metal bands (343, and 372 nm) lies in between emission energies of pure KAg(CN)₂ (312 nm) and pure KAu(CN)₂ (390 nm). Therefore, the emission energies of the d^{10}-d^{10} mixed metal system arise from the delocalization of Ag and Au emissive states.

Also, after comparison of linear [Au₂Ag(CN)₆]³⁻ trimer versus linear [Ag₂Au(CN)₆]³⁻ trimer, the [Ag₂Au(CN)₆]³⁻ trimer has a higher Au-Ag overlap population than the corresponding value for the [Au₂Ag(CN)₆]³⁻ trimer. This gives a
possible explanation for the experimental result of more $d^{10}$-$d^{10}$ mixed metal delocalization for a sample having a Au:Ag ratio of 1:1.45 ($[\text{Ag}_2\text{Au}(\text{CN})_3]^{3-}$ trimer) than Au:Ag the ratio of 1:0.51 ($[\text{Au}_2\text{Ag}(\text{CN})_6]^{3-}$ trimer).

Each calculation carried out for the mixed metals shows considerable Au-Au or Ag-Ag overlap populations other than Au-Ag overlap populations in both ground and first excited states. This gives an explanation for seeing emission bands corresponding to pure $\text{KAu(CN)}_2$ and pure $\text{KAg(CN)}_2$ along with the bands due to delocalized excited states in the emission spectra of $d^{10}$-$d^{10}$ mixed metal samples.

As examples for $d^{10}$-$d^8$ systems, two types of systems have been studied. Two types involved 1 mole of $\text{KAu(CN)}_2$: 1 mole of $\text{K}_2\text{Pt(CN)}_4$ (Au-Pt sample) and 1 mole of $\text{KAg(CN)}_2$: 1 mole of $\text{K}_2\text{Pt(CN)}_4$ (Ag-Pt sample). In these systems, energy transfer between $\text{KAu(CN)}_2$ or $\text{KAg(CN)}_2$ ($d^{10}$) and $\text{K}_2\text{Pt(CN)}_4$ ($d^8$) has been observed. In the emission spectra, two emission bands due to Au and Pt lowest emissive states (also Ag and Pt) have been observed. Also, observed emission bands are tunable: that is, different emission bands can be observed by varying the excitation wavelength.

### 7.5. Suggested Future Work

Quantum yield calculations allow us to determine the efficiency of emitting light for a particular crystal. Therefore, research needs to be conducted to calculate quantum yield values for single crystals of pure $\text{KAg(CN)}_2$, pure $\text{KAu(CN)}_2$, different concentrations of single crystals of $[\text{Ag(CN)}_2^\cdot]/\text{KCl}$ as well as $[\text{Au(CN)}_2^\cdot]/\text{KCl}$ at low temperatures. Also, these quantum yield measurements need to be extended to the $d^{10}$-$d^{10}$ mixed metal system.
We have discovered that observed luminescence bands are due to different orientations and different aggregations of [Ag(CN)₂⁻] and [Au(CN)₂⁻] units and Raman spectroscopy can be correlated with the measured photoluminescence spectra. In order to understand the process during 266 nm laser exposure in optical memory studies, optical memory experiments for each system, [Ag(CN)₂⁻]/KCl as well as [Au(CN)₂⁻]/KCl needs to be conducted at 77 K along with Raman spectroscopic measurements. In other words, Raman spectrum (including both cyanide stretching and bending frequency regions) can be obtained for a single crystal of a particular system at 77 K. After that the same crystal at 77 K can be exposed to 266 nm laser for a short period and the Raman spectrum can be obtained again. After comparison of the two Raman spectra (before and after laser exposure), the process during 266 nm laser exposure can be understand easily. This experiment will be very useful to confirm photodecomposition products of [Au(CN)₂⁻]/KCl system. After laser exposure, the same crystal can be warmed up to room temperature and recooled down to 77 K, and the Raman spectra can be obtained again as a recovery step to observe optical memory phenomenon.

Extended Hückel calculations need to be carried out for different [Ag(CN)₂⁻]ₙ and [Au(CN)₂⁻]ₙ oligomers in a KCl lattice in order to explain optical memory data more accurately.

The presence of Ag-Ag or Au-Au stretching frequency modes in the low frequency region of the Raman spectra provide a better indication of Ag-Ag or Au-Au interactions. Therefore, Raman experiments need to be conducted for single crystals of pure KAg(CN)₂, pure KAu(CN)₂ as well as for the d¹⁰-d¹⁰ mixed metal samples to see whether Ag-Ag, Au-Au or Ag-Au stretching frequency modes are present in these
samples. The presence of Ag-Au stretching frequency modes will provide an excellent verification of having Ag-Au delocalization in d^{10}-d^{10} mixed metal samples.

For d^{10}-d^{8} systems (KAg(CN)_2: K_2Pt(CN)_4 or KAu(CN)_2: K_2Pt(CN)_4), single crystals need to synthesize with different molar ratios to observe d^{10}-d^{8} delocalization.
BIBLIOGRAPHY


Appendix A

OPTICAL MEMORY STUDIES ON DICYANOARGENTATE(I) AND DICYANOAUROATE(I) IONS DOPED IN POTASSIUM CHLORIDE CRYSTALS

A.1. Crystal Growing

1 mole Ag(CN)₂⁻: 1 mole Au(CN)₂⁻ doped in KCl were synthesized as follows: In a clean beaker, 0.375 g of KCl and 0.25 g of pure KAg(CN)₂ were dissolved in ~15 ml of distilled and deionized water. In a separate beaker, 5 g of KCl and 0.2 g of KAu(CN)₂ were dissolved in ~15 ml of distilled and deionized water. The two solutions were poured together and allowed to evaporate slowly at room temperature. The first set of crystals was harvested after one day. The remaining mother solution was evaporated longer and a second set of crystals was harvested after 4 days. Again, the remaining mother solution was evaporated slowly and then the third and fourth sets of crystals were harvested after 9 and 15 days, respectively.

A.2. Atomic Absorption Measurements

Table A.1. Atomic absorption spectroscopic (AA’S) results of each batch.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Measured Au:Ag Ratio by AA’S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag-Au batch 1</td>
<td>0.33</td>
</tr>
<tr>
<td>Ag-Au batch 2</td>
<td>0.37</td>
</tr>
<tr>
<td>Ag-Au batch 3</td>
<td>0.42</td>
</tr>
<tr>
<td>Ag-Au batch 4</td>
<td>0.79</td>
</tr>
</tbody>
</table>
Figure A1. Emission spectra of single crystals of four batches of KAg(CN)$_2$•KAu(CN)$_2$, (1.1 molar)/KCl at 77 K upon excitation at 275 nm.
Figure A2. Emission spectra of single crystals of four batches of KAg(CN)$_2$:KAu(CN)$_2$ (1:1 molar)/KCl at 77 K upon excitation at 245 nm.
Figure A3. Emission spectra of a single crystal of KAg(CN)$_2$·KAu(CN)$_2$ (1:1 molar) /KCl batch 4 at 77 K as a function of excitation wavelength.
Figure A4. Excitation spectra of a single crystal of KAg(CN)₂:KAu(CN)₂ (1:1 molar)/KCl batch 4 at 77 K as a function of emission wavelength.
Figure A5. Raman spectra of single crystals of four batches of KAg(CN)$_2$:KAu(CN)$_2$ (1:1 molar)/KCl in the region of the cyanide stretching frequency.
Figure A6. Raman spectra of single crystals of four batches of KAg(CN)$_2$·KAu(CN)$_2$ (1:1 molar)/KCl in the region of the cyanide bending frequency.
Figure A7. \( \text{KAg(CN)}_2 \cdot \text{KAu(CN)}_2 \) (1:1 molar) /KCl batch 1 386 and 430 nm emission peak area variation (ex 275 nm) with 266 nm laser exposure time at 77 K.
Figure A8. K\text{Ag}\text{(CN)}_2\cdot(1.1\text{ molar})/K\text{Cl}\text{ batch 2 386 and 430 nm emission peak area variation (ex 275 nm)} with 266 nm laser exposure time at 77 K.
Figure A9. KAg(CN)$_2$ KAu(CN)$_2$ (1:1 molar) /KCl batch 3 386 and 430 nm emission peak area variation (ex 275 nm) with 266 nm laser exposure time at 77 K.
Figure A10. KAg(CN)$_2$·KAu(CN)$_2$ (1:1 molar)/KCl batch 4 386 and 430 nm emission peak area variation (ex 275 nm) with 266 nm laser exposure time at 77 K.
Figure A11. KAg(CN)$_2$:KAu(CN)$_2$ (1:1 molar) /KCl batch 2 emission spectra variation (ex 275 nm) before and after laser exposure as well as the recovery step at 77 K.
Figure A12. KAg(CN)_2:KAu(CN)_2 (1:1 molar) /KCl batch 4 emission spectra variation (ex 275 nm) before and after laser exposure as well as the recovery step at 77 K.
Appendix B

SPECTROSCOPIC STUDIES ON K[Au(SCN)$_2$] AND [Bu$_4$N]$_2$[Au(SCN)$_2$]

Figure B1. Emission and excitation spectra of K[Au(SCN)$_2$] at 4 K.
Figure B2. K[Au(SCN)$_2$] emission spectra (ex 320 nm) variation with the temperature.
Table B.1. Lifetime data for the observed luminescence bands in K[Au(SCN)₂] at 77K.

<table>
<thead>
<tr>
<th>Emission band, nm</th>
<th>( \tau, \mu s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>442</td>
<td>2.15</td>
</tr>
<tr>
<td>515</td>
<td>24.11</td>
</tr>
</tbody>
</table>
Figure B3. Emission and excitation spectra of $[\text{Bu}_4\text{N}]_2\{\text{Au(SCN)}_2\}_2$ at 4 K.
Figure B4. $[\text{Bu}_4\text{N}]_2\{\text{Au(SCN)}_2\}_2$ emission spectra (ex 365 nm) variation with the temperature.
BIOGRAPHY OF THE AUTHOR

Samanthika Ruvinie Hettiarachchi was born in Elpitiya, Sri Lanka on October 14, 1967. She finished her high school at Ananda Central College, Elpitiya, Sri Lanka in 1987. She entered the University of Ruhuna, Matara, Sri Lanka and obtained her Bachelor's degree (Special degree in Chemistry) in 1996. After that, Ruvinie served as an assistant lecturer in the department of Chemistry, University of Ruhuna, Matara, Sri Lanka. Ruvinie was married to Jinasena on December 4, 1996 and came to Maine with him in August 1997. She entered the University of Maine Chemistry Department graduate program in August 1998 to pursue a Doctor of Philosophy degree in Chemistry. Ruvinie is a mother of two daughters, Nethmi and Sithmi.

After receiving her Ph.D. degree, she will be going back to Sri Lanka. Ruvinie is a candidate for the Doctor of Philosophy degree in Chemistry from The University of Maine in December, 2002.