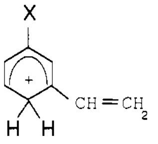
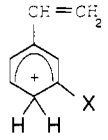
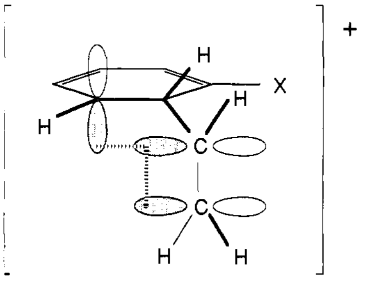
to rapid vinyl group migration within the arenium ions from eq i, irrespective of their excitation energy, leading to the thermodynamically most stable arenium ion structure, which, according to the substituted styrene distribution of Table I, appears to be either III and/or IV.


(III)


(IV)

Such a pronounced migrating ability is typical of unsaturated groups,[27] where the transition state for a concerted 1,2-shift may be stabilized by bonding interactions of the migrating substituent with the adjacent reaction center, as shown in V. The same stereoelectronic configuration of structure V helps in explaining the predominance of 1,2 vinyl group shift over the competing hydrogen transfer from the ring ipso position of V to the unsaturated side chain to give eventually the thermodynamically most stable $\alpha$-methyl benzylic structure,[9b] a process that would immediately suppress vinyl group transfer within V.


(V)

**Conclusions.** The present investigation of the reactivity and selectivity properties of unsubstituted vinyl cation, $C_2H_3^+$, is allowed by the unique features of the nuclear-decay technique, which permits generation of free cationic electrophiles of defined structure and energy content from multitritiated hydrocarbon precursors, namely ethylene in the present study. The unparalleled constancy of the nature of the nuclear-decay formed vinyl cation over an extended range of physical conditions affords the unusual possibility of evaluating the reactivity pattern of an otherwise elusive electrophile in largely different media, as a function of the reaction environment. A rationale for the observed differences in reactivity of $C_2H_3^+$ toward the selected aromatic substrates in liquid and gaseous systems can be found in the greatly enhanced efficiency of collisional stabilization in the liquid media, which allows a much larger fraction of the excited arenium ions from reaction i to survive fragmentation and isomerization. An additional reason for the different reactivity can arise from a change in the actual nature of the vinylating reactant in the gaseous systems, when additives, such as Ar or CO, are present.

To our knowledge, in the search to substantiate the long-postulated[4,5] occurrence of the unsubstituted vinyl cation $C_2H_3^+$ in non-nucleophilic solvents, the present study provides the first data concerning the reactivity of an unsolvated $C_2H_3^+$ cation, free of any counterions[21] even in the liquid phase. Consequently, a comparison of the $C_2H_3^+$ reactivity with that of a few typical representatives of more tractable trisubstituted vinyl cations in solution appears of interest.

Significantly, the substrate and positional selectivity of the free $C_2H_3^+$ cation, while extremely close to that of other very reactive, unsolvated cations, such as $CH_3^+$,[23] is largely different from those of more stable but heavily encumbered trisubstituted vinyl cations, such as those arising from the solvolysis of 1-anisyl-2,2-diphenylvinyl bromide[28] and of 1-phenyl-2,2-dimethylvinyl triflate.[29] In fact, the vinylating reactants formed from these precursors display a substrate selectivity spanning over at least 3 orders of magnitude from chlorobenzene to anisole, whereas their positional selectivity, although characterized by the expected ortho–para distribution, shows a very pronounced preference for the less encumbered para position ($4.6 < \text{para}:{}^1/_2\text{ortho} < 78$).

**Acknowledgment.** This work was supported by grants from the Ministero della Pubblica Istruzione and from the Strategic Project "Dinamica Molecolare e Catalisi" of the Consiglio Nazionale delle Ricerche of Italy.

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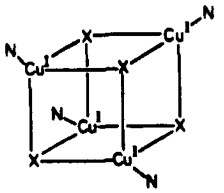
# Photoluminescence of Cubic Mixed-Metal Tetrameric Clusters

**Maher Henary and Jeffrey I. Zink***

*Contribution from the Department of Chemistry and Biochemistry, University of California—Los Angeles, Los Angeles, California 90024-1569.* *Received March 16, 1989*

**Abstract:** The low-temperature luminescence spectra of tetrameric mixed-metal clusters of the type $(DENC)_3Cu_3M(NS)Cl_4$ and $(DENC)_3Cu^I_2Cu^{II}Co(NS)_2Cl_4$ (DENC = *N,N*-diethylnicotinamide; NS$^-$ = *S*-methylhydrazinecarbodithioate Schiff base; and M = Co(II), Ni(II), Cu(II), or Zn(II)) in anhydrous methylene chloride are reported. The parent cluster containing four Cu(I) atoms emits at 15 100 cm$^{-1}$. The clusters containing three Cu(I) atoms and a fourth first-row transition metal emit at $\lambda_{max}$ = 13 500 cm$^{-1}$ for M = Co(II), $\lambda_{max}$ = 14 000 cm$^{-1}$ for M = Ni(II), $\lambda_{max}$ = 13 150 cm$^{-1}$ for M = Cu(II), and $\lambda_{max}$ = 15 000 cm$^{-1}$ for M = Zn(II). The cluster containing two Cu$^I$, one Cu$^{II}$, and one Co$^{II}$ emits at 13 300 cm$^{-1}$. The emission from all of the clusters is centered on the coppers (not on the ligands or the other metals) and is related to the $3d^94s^1$ excited state strongly modified by copper–copper interactions. The presence of the other metals only slightly perturbs the energy of the emission centered on the coppers. In the case of the mixed-metal clusters containing Co(II) and Cu(II) metals in the core, the emission is not from the lowest excited state of the cluster. In these cases ligand field states centered on the M(II) are lower in energy than the Cu(I) centered emitting state. The emission lifetimes are shortest for the clusters with low-lying d–d excited states.

The luminescence of tetrameric copper cluster compounds is attracting increasing interest.[1-7] These clusters contain the cubic core consisting of four copper(I) ions and four halide ions shown below. Generally, nitrogen-donor ligands such as pyridine and



substituted pyridines are bonded to the copper ions.[3,8,9] The luminescence of these clusters displays a variety of interesting properties. Of particular interest have been the properties of luminescence thermochromism, luminescence in fluid solution, and dual emissions.[2] The luminescence spectrum usually consists of an intense band in the red region of the visible spectrum and frequently a less intense band at higher energy. The intense band has been assigned to a transition related to the Cu(I) $3d^9 4s^1$ excited state strongly modified by the copper–copper interactions.[1-7]

Mixed-metal tetrameric clusters containing both copper(I) ions and first-row transition metal ions in the +2 oxidation state have recently been synthesized.[10,11] The largest series of compounds contains three copper(I) ions and one Co(II), Ni(II), Cu(II), or Zn(II) ion. The compound containing the $\mathrm{Cu^I{}_3Cu^{II}}$ core is formally a mixed valence compound. In all of the known examples, the M(II) ions are coordinated by the methyl hydrazinecarbodithioate Schiff base ligand, called NS in the literature and in this paper. In addition to the $\mathrm{Cu_3M^{II}}$ compounds, a mixed-metal compound containing two copper(I) ions, one copper(II) ion, and one Cobalt(II) ion is known.[10,12-14]

The replacement of a Cu(I) ion by a more highly oxidized transition metal in the core of the cluster would be expected to have a profound effect on the luminescence of the cluster if the emission originated from an orbital delocalized on the cubic core. Large differences in the luminescence properties would also be expected if the M(II) had excited electronic states lower in energy than the copper(I)-centered state responsible for the emission in the all-copper cluster. In order to characterize these aspects of the spectroscopy, the spectra of the mixed-metal clusters were studied.

In this paper we report the luminescence spectra and the lifetimes of the mixed-metal compounds containing the $\mathrm{Cu^I{}_3M^{II}}$ core and the $\mathrm{Cu^I{}_2Cu^{II}Co^{II}}$ core. The presence of the M(II) ions in the core causes only small changes in the energies and the lifetimes of the luminescence, even when the M(II) center has low-lying d–d excited states.

## Experimental Section

**Materials.** *N,N*-Diethylnicotinamide, DENC (Aldrich), was distilled under reduced pressure before use. Methylene chloride was distilled from phosphorus(V) oxide and stored over 4-Å molecular sieves. Copper(I) chloride and methyl isopropylidenehydrazinecarbodithioate, NS, were prepared by the literature methods.[15-18]

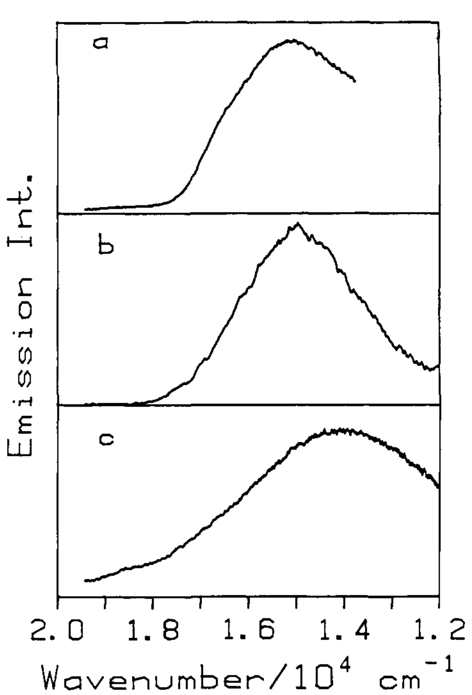


**Figure 1.** Emission spectra of (a) $(\mathrm{DENC})_4\mathrm{Cu_4Cl_4}$, (b) $(\mathrm{DENC})_3\mathrm{Cu_3Zn(NS)Cl_4}$, and (c) $(\mathrm{DENC})_3\mathrm{Cu_3Ni(NS)Cl_4}$ at 13 K excited at 488 nm.

The synthesis of the mixed-metal clusters and the intermediates in their preparations followed literature procedures.[10-14] The general reaction schemes to prepare the mixed-metal clusters are given in eq 1 and 2. One mole of $(\mathrm{DENC})_4\mathrm{Cu_4Cl_4}$ reacts with 1 mol of $\mathrm{M(NS)_2}$ (M =

$$(\mathrm{DENC})_4\mathrm{Cu^I{}_4Cl_4} + \mathrm{M(NS)_2} \xrightarrow[\mathrm{N_2}]{\mathrm{MC}} (\mathrm{DENC})_3\mathrm{Cu_3{}^IM(NS)Cl_4} + \mathrm{DENC} + \mathrm{Cu(NS)} \quad (1)$$

$$(\mathrm{DENC})_4\mathrm{Cu_4{}^ICl_4} + \mathrm{Co(NS)_3} \xrightarrow[\mathrm{N_2}]{\mathrm{MC}} (\mathrm{DENC})_3\mathrm{Cu_2{}^ICu^{II}Co(NS)_2Cl_4} + \mathrm{DENC} + \mathrm{Cu(NS)} \quad (2)$$

Co(II), Ni(II), Cu(II), or Zn(II)) in anhydrous $\mathrm{CH_2Cl_2}$ under nitrogen at room temperature to produce the mixed-metal cluster of the type $\mathrm{Cu_3M^{II}}$ (eq 1)[11,12] or with 1 mol of $\mathrm{Co(NS)_3}$ to produce the mixed-metal cluster $\mathrm{Cu_2Cu^{II}M^{II}}$ (eq 2). All of the clusters are air sensitive and are handled under nitrogen.

**Spectra.** Luminescence spectra were obtained from frozen solutions of the mixed-metal clusters in methylene chloride. Approximately $2.5 \times 10^{-3}$ M solutions of the cluster were placed in glass capillary tubes and sealed under nitrogen. The tubes were mounted in an Air Products Displex closed cycle helium refrigerator. Spectra were taken at temperatures between about 10 K and room temperature. The spectra were obtained by using a Spex 0.75-m monochromator, a cooled C31034 photomultiplier, photon counting, and computer data collection.[19] Excitation sources were an argon ion laser at wavelengths of 458, 476.5, and 488 nm and an excimer pumped dye laser at 406 nm.

The emission lifetimes of frozen solutions of the mixed-metal clusters in methylene chloride were determined at 13 K by using 406.0-nm pulsed excitation (10-ns width) from a XeCl excimer pumped dye laser (DPS in *p*-dioxane). The emitted light was passed through a Spex 1701 single monochromator and detected by a terminated RCA C31034 photomultiplier tube. The signal was collected and stored with a Tektronix RTD 710 transient digitizer interfaced to an IBM XT computer. The instrument response time was about 15 ns. The data were later transferred to a VAX 780 computer for further processing.

Electronic absorption spectra were taken of the mixed-metal clusters under nitrogen in methylene chloride or nitrobenzene at room tempera-

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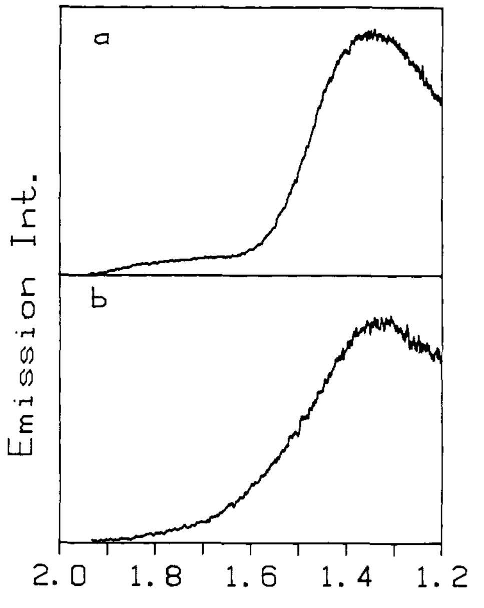

**Figure 2.** Emission spectra of (a) $(DENC)_3Cu_3Co(NS)Cl_4$ and (b) $(DENC)_3Cu_3Cu(NS)Cl_4$ at 13 K excited at 488 nm.

ture. The spectra were obtained by using a Beckman DK-1A or a Cary 14 spectrophotometer.

## Results

**Luminescence Spectra.** All of the tetrameric cluster compounds which have been studied luminesce in the red region of the spectrum. The emission spectra were obtained from frozen methylene chloride solutions in sealed capillary tubes under nitrogen because the mixed-metal compounds are all air sensitive. The spectra are categorized according to the degree of substitution of the tetrameric metal core. The parent reference compound contains the $Cu_4$ core. The first category of compounds are those with a tetrameric core containing three copper(I) metals and one metal(II) atom. The second category contains two copper(I) atoms, one copper(II) atom, and one metal(II) atom. The first category is further divided according to whether or not the emitting state is the lowest energy excited state of the molecule (vide infra.).

The emission spectra of the $Cu_3Zn^{II}$, $Cu_3Ni^{II}$, and the parent compound $Cu_4$ are shown in Figure 1. The spectra consist of an intense band centered near 15 000 cm$^{-1}$ and a weaker broad shoulder to higher energy. The well-defined peak maxima are at 15 000 cm$^{-1}$ for the parent $Cu_4$ compound, 15 000 cm$^{-1}$ for the $Cu_3Zn^{II}$ compound, and 14 000 cm$^{-1}$ for the $Cu_3Ni^{II}$ compound.

The emission spectra of $Cu_3Co^{II}$ and $Cu_3Cu^{II}$ are shown in Figure 2. The spectra of these compounds consist of an intense peak centered at about 13 000 cm$^{-1}$ and a weaker broad shoulder to higher energy. The well-defined peak maxima are at 13 500 cm$^{-1}$ for the $Cu_3Co^{II}$ compound and at 13 150 cm$^{-1}$ for the $Cu_3Cu^{II}$ compound. The shoulders to high energy are significantly less intense in these two compounds than are those in the zinc and nickel mixed-metal clusters.

The emission spectrum of $Cu_2Co^{II}Cu^{II}$ is shown in Figure 3. The spectrum of this compound again consists of an intense peak in the red region of the spectrum and a weaker broad band to higher energy. The maximum of the intense peak is at 13 300 cm$^{-1}$. The band to high energy at about 17 200 cm$^{-1}$ is better resolved than are those in the zinc and nickel mixed-metal clusters.

The emission intensity of the parent $Cu_4$ compound is qualitatively larger than that of any of the mixed-metal cluster compounds. Because of the air sensitivity of the mixed-metal compounds, quantitative measurements of their intensities were not attempted.

The temperature dependence of the emission was studied for the parent compound and the $Cu_3Zn^{II}$, $Cu_3Co^{II}$, and $Cu_2Co^{II}Cu^{II}$ mixed-metal compounds. The red emission band from the $Cu_4$ and $Cu_3Zn^{II}$ compounds is discernible at room temperature. However, the luminescence spectra of the other mixed-metal compounds at room temperature is dominated by the broad band to the blue. The emission intensity of the $Cu_2Co^{II}Cu^{II}$ compound decreases with increasing temperature up to 240 K, at which point it becomes too weak to record relative to the broad band at higher energy. The band maximum blue shifts about 700 cm$^{-1}$ with increasing temperature between 13 and 240 K. The $Cu_3Co^{II}$ compound was studied between 13 and 150 K. Its peak maximum blue shifts about 500 cm$^{-1}$ with increasing temperature.

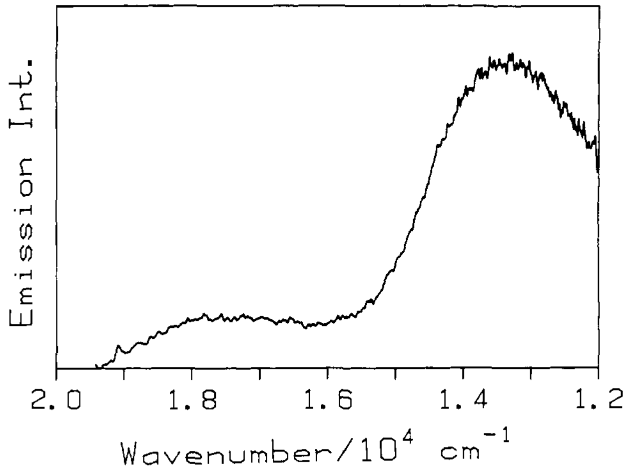

**Figure 3.** Emission spectrum of $(DENC)_3Cu_2CuCo(NS)_2Cl_4$ in frozen methylene chloride at 13 K excited at 488 nm.

**Table I.** Emission Maxima and Lifetimes of Mixed-Metal Clusters at 13 K Excited at 406.0 nm

| compound | emission max (cm$^{-1}$) | lifetime ($\mu$s) |
|---|---|---|
| $(DENC)_4Cu^I_4Cl_4$ | 15 100 | 7.3 ± 0.4 |
| $(DENC)_3Cu^I_3Co(NS)Cl_4$ | 13 500 | 5.9 ± 0.4 |
| $(DENC)_3Cu^I_3Ni(NS)Cl_4$ | 14 000 | 7.0 ± 0.4 |
| $(DENC)_3Cu^I_3Cu^{II}(NS)Cl_4$ | 13 150 | 5.4 ± 0.4 |
| $(DENC)_3Cu^I_3Zn(NS)Cl_4$ | 15 000 | 8.3 ± 0.4 |
| $(DENC)_3Cu^I_2Cu^{II}Co^{II}(NS)_2Cl_4$ | 13 300 | 5.5 ± 0.4 |

The emission spectra of three other substances which will figure in the subsequent discussion, (the $N_2S_2$ dimer of the NS ligand, the DENC ligand, and the glass capillary tube) were obtained under conditions identical with those used to obtain the spectra of the mixed-metal compounds. The emission spectrum of the $N_2S_2$ dimer consists of a single peak at 17 200 cm$^{-1}$. The emission spectrum of the uncoordinated DENC ligand consists of a peak at 18 500 cm$^{-1}$ with a weaker tail extending out to about 16 000 cm$^{-1}$. The glass capillary tube luminesces only when excited in the UV. The peak maximum is about 19 400 cm$^{-1}$.

**Emission Lifetimes.** The lifetimes of the emission from frozen solutions of the mixed-metal clusters in methylene chloride were measured at 13 K. Plots of ln (intensity) versus time were linear for at least two decay lifetimes. The measured lifetimes are collected in Table I. The shortest lifetimes are found for those clusters with low-lying d–d states and the longest for those with no low-lying d–d states.

**Visible/Near-IR Absorption Spectra.** The absorption spectra of the mixed-metal compounds containing Co(II) and Cu(II) under nitrogen in nitrobenzene or methylene chloride contain bands with maxima at energies lower than 20 000 cm$^{-1}$. The Ni(II), Zn(II), and all Cu(I) compounds do not have any absorption band maxima in this region, but have long tails extending past 20 000 cm$^{-1}$. The spectrum of the $Cu_3Co^{II}$ compound (Figure 4) contains a series of overlapping bands between 18 180 and 14 815 cm$^{-1}$ which are characteristic of five-coordinate cobalt(II).[10–13] In addition, weak ($\epsilon$ = 80 and 67 M$^{-1}$ cm$^{-1}$) bands in the near-IR at 7143 and 6250 cm$^{-1}$ are observed. The spectrum of the $Cu_2Cu^{II}Co^{II}$ compound contains a series of overlapping bands between 18 180 and 14 815 cm$^{-1}$, which are characteristic of

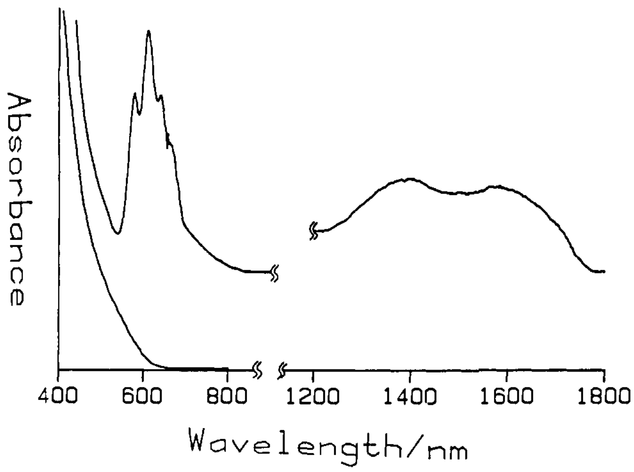

Figure 4. Absorption spectra of $(DENC)_3Cu_3Co(NS)Cl_4$ (upper traces) and $(DENC)_4Cu_4Cl_4$ (bottom trace) in $CH_2Cl_2$ at room temperature. The molar absorptivity is 850 $M^{-1}$ $cm^{-1}$ for the band at 630 nm, 80 $M^{-1}$ $cm^{-1}$ for the band at 1400 nm, and 67 $M^{-1}$ $cm^{-1}$ for the band at 1600 nm. The molar absorptivity of the tail in the spectrum of $(DENC)_4Cu_4Cl_4$ at 500 nm is 20 $M^{-1}$ $cm^{-1}$.

five-coordinate cobalt(II), and a very broad band centered at about 11 765 $cm^{-1}$, which is characteristic of five-coordinate Cu(II) in the compound.[10,12,13]

## Discussion

**1. General Features of the Luminescence Spectra.** The luminescence spectra of all of the clusters reported here contain an intense band in the red region of the spectrum and a weaker shoulder or poorly resolved band to the blue. The luminescence spectra of the all-Cu(I) clusters have been extensively studied by Hardt[2,3] and Vogler.[1] The latter author assigned the red emission of $[Cu(pyridine)I]_4$ and $[Cu(morpholine)I]_4$ to the metal-centered $3d^94s^1$ excited state strongly modified by copper–copper interactions. The energy of the transition is slightly sensitive to the nitrogen donor ligand and to the halide ion comprising the cubic core. The luminescence spectrum of the parent compound in this study (which contains the DENC ligand bound to the copper and the chloride ion in the cubic core) is very similar to that of the $[Cu(pyridine)I]_4$ complexes previously reported.[1,2]

In order to eliminate the possibility that decomposition products contribute to the red luminescence, two experiments were carried out. First, the luminescence spectra of the known decomposition products were measured. The oxidation of $(DENC)_3Cu_3M(NS)_nCl_4$ occurs by the reaction

$$(DENC)_3Cu_3M(NS)_nCl_4 + O_2 \rightarrow (DENC)_3Cu_3MCl_4O_2 + nN_2S_2 \quad (3)$$

where $N_2S_2$ is the disulfide resulting from the oxidation of the coordinated NS on M. The $N_2S_2$ molecule luminesces with its band maximum at 17 200 $cm^{-1}$. It thus may be a contributor to the blue shoulder on the main red luminescence band, but it is not the source of the red luminescence. Second, the $(DENC)_3Cu_3M(NS)_nCl_4$ compounds were deliberately exposed to air. The resulting solution was frozen and excited under the same conditions as those used to obtain the spectra of the mixed-metal clusters. A broad luminescence band centered in the blue at 17 200 $cm^{-1}$ was observed. No red luminescence was found. Thus the decomposition products of the air-sensitive mixed-metal compounds may contribute to the blue shoulder but are not responsible for the red luminescence band.

The blue shoulder on the intense red emission band which is observed in Figures 1–3 is the superposition of luminescence from one or more of the following three origins. First, the DENC ligand luminesces with an emission maximum of 18 500 $cm^{-1}$. Traces of the uncoordinated ligand may contribute to the emission in the region of the blue shoulder. Second, the uncoordinated NS ligand luminesces in the blue at 17 200 $cm^{-1}$. Unreacted traces of this ligand may contribute to the blue shoulder. Finally, the cluster itself may luminesce weakly in this region. Blue shoulders have been reported in the low-temperature spectra of the $Cu_4$ complexes.[2] Recent studies have shown that this emission arises from a copper to nitrogen donor ligand charge-transfer excited state.[7]

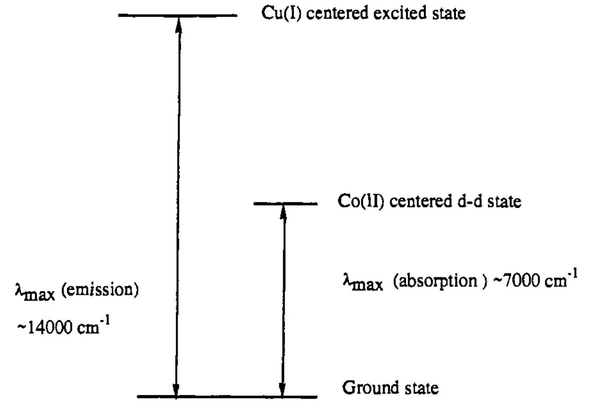

Figure 5. Schematic energy level diagram of the lowest excited states of the $Cu_3Co^{II}$ cluster.

**2. Effects of Metal Substitution on the Luminescence Spectra.** The luminescence spectra of the metal clusters containing three copper(I) ions and one metal(II) ion and that of the cluster containing two copper(I) ions, one copper(II) ion, and one metal(II) ion are all very similar to that of the cluster containing four copper(I) ions. Changing the metals in the core causes small changes in the emission energy (Table I). The $Cu_3Zn^{II}$ cluster is the most similar to the $Cu_4$ cluster. Its luminescence maximum is red shifted by about 100 $cm^{-1}$ from that of the parent all-copper cluster. The emission maximum of the $Cu_3Ni^{II}$ cluster is red shifted from that of the parent by 1000 $cm^{-1}$, that of the $Cu_3Co^{II}$ cluster by 1600 $cm^{-1}$, that of the $Cu_3Cu^{II}$ cluster by 1950 $cm^{-1}$, and that of the $Cu_2Cu^{II}Co^{II}$ cluster by 1800 $cm^{-1}$. The magnitudes of these shifts are similar to those caused by changing the ligands directly bonded to the copper ions or by changing the halide ions in the core of the all copper cluster compounds.

The emission lifetimes of the mixed-metal clusters studied here are surprisingly insensitive to variations of the metals in the cubic ions. The differences between the longest lifetimes ($Cu_3Zn^{II}$, 8.3 $\mu$s) and the shortest ($Cu_3Cu^{II}$, 5.4 $\mu$s) are small, especially in view of the significant changes in the lowest electronic excited state (vide infra.). However, the difference is significantly larger than the experimental uncertainties and can be meaningfully interpreted (vide infra.).

The small changes in the emission energies and lifetimes which are observed when a copper(I) in the $Cu_4$ cluster is replaced by a metal(II) suggest that the emission is not from a delocalized molecular orbital involving the entire core but rather from orbitals on the Cu(I) atoms which are not strongly coupled to the other noncopper metal orbitals. These observations are consistent with the assignment of the emission to a transition related to the $3d^94s^1$ excited state strongly modified by copper–copper interactions. The small changes in emission energy as the metal is changed are probably the result of small changes in the structure of the cubic core which perturb the copper–copper interactions.

**3. Cu(I) Emission from Clusters with Low-Lying M(II) d–d States.** The most interesting and unusual feature of the excited-state properties of these clusters is the luminescence from excited states which are not the lowest energy excited state of the molecule. The most dramatic example is that of the $Cu_3Co^{II}$ cluster. The relevant excited states are shown schematically in Figure 5. The cobalt(II) center in this compound has d–d excited states in the near-IR region of the spectrum and yet the cluster emits in the visible. The d–d bands are clearly seen in the absorption spectrum of the cluster at 7143 and 6250 $cm^{-1}$. They are related to the $^4A_2$ to $^4T_1(F)$ ligand field transition which is well known in tetrahedral cobalt(II) complexes.[20] In the $Co(NS)_2$

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[20] Cotton, F. A.; Goodgane, M. *J. Am. Chem. Soc.* **1981**, *83*, 1777. Cotton, F. A.; Sacco, A. *J. Am. Chem. Soc.* **1962**, *84*, 2043.

complex a similar absorption band is found at 7200 cm$^{-1}$.[21]

The other examples of emission from an excited state which is not the lowest are found in the emission spectra of the clusters containing a copper(II) ion. In these clusters the copper(II) center has a broad absorption band with a peak maximum at 11 765 cm$^{-1}$ and a tail which extends well past 13 973 cm$^{-1}$. This band probably originates from d–d transitions on the copper(II). The emission maximum is at least 1000 cm$^{-1}$ higher in energy than the absorption band maximum.

The emission lifetimes are shortest for those clusters with low-lying M(II)-centered d–d states and longest for those whose Cu(I) excited states lie lower. The Cu$_3$Co$^{II}$, Cu$_3$Cu$^{II}$, and Cu$_2$Cu$^{II}$Co$^{II}$ clusters have lifetimes ranging from 5.4 to 5.9 $\mu$s, while those with metals not possessing low-lying d–d states have lifetimes greater than 7.0 $\mu$s. The low-lying d–d states provide a deactivation pathway which shortens the lifetime. These low-lying states are obviously not strongly coupled to the states involving the copper, and the magnitude of the effect is small.

## Summary

Tetrameric mixed-metal clusters of the type Cu$^{I}_{3}$M$^{II}$ and Cu$^{I}_{2}$Cu$^{II}$M$^{II}$ are luminescent. The emission from all of the clusters is copper(I) centered and is related to the 3d$^9$4s$^1$ excited state strongly modified by copper–copper interactions. In the case of the mixed-metal clusters containing Co(II) or Cu(II) in the core, the emission is not from the lowest excited state of the cluster. In these cases, ligand field states centered on M(II) are lower in energy than the emitting state centered on the Cu(I)'s. Changing of the metal M in the Cu$^{I}_{3}$M$^{II}$ core slightly shifts the emission maximum with respect to the Cu$_4$ cluster. The emission lifetimes of these clusters are shortest for those clusters containing low-lying d–d states.

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# Electronic and Stereochemical Factors Contributing to the Lability of *trans*-Aquomethyl(tetraazamacrocycle)cobalt(III) Complexes. Kinetic and Molecular Mechanics Studies[1]

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**Abstract:** The origin and variability of the trans-labilizing influence of the Co–alkyl bond have been investigated by using the anation reactions of a series of *trans*-Co(N$_4$)(OH$_2$)CH$_3^{2+}$ (N$_4$ is a tetraazamacrocyclic ligand) complexes as probes. Anation reactions of some related *trans*-Co(N$_4$)(OH$_2$)Cl$^{2+}$ complexes have also been examined to provide a basis for comparison with closely related, classical coordination complexes. The coordinated water in the methyl–aquo complexes is 10$^4$–10$^7$ times more labile than found in "normal" coordination complexes. Stereochemically uncluttered coordination sites, such as the axial positions when N$_4$ = 1,4,8,11-tetraazacyclotetradecane, are labilized the most. The labilizing influence of the cobalt–methyl bond is the least at stereochemically conjested coordination sites for which molecular mechanics calculations show that there is considerable relaxation of strain and interligand repulsion in the dissociative transition state; i.e., for those complexes with N$_4$ = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene (Me$_6$[14]dieneN$_4$) and in which substitution occurs at a site near equatorial ligand geminal methyl groups. Substitution at the stereochemically uncongested site of an isomer of this complex, obtained by interchanging the axial methyl and water ligands, is at least 10$^4$ times faster. In such stereochemically complicated ligands, the axial geminal-methyl and other equatorial ligand groups tend to protect the adjacent coordination site from an incoming ligand until the leaving group has moved more than 1 Å away from its coordination site at the metal center. Such an effect could not retard rates in a purely dissociative substitutional mechanism. Rather axial substitution in these complexes is inferred to occur by an interchange mechanism in which the entering and leaving groups become equivalent at a distance ($r_{TS}$) before the bond to the leaving group is completely broken. A simple electrostatic model for substitution in Co(N$_4$)(OH$_2$)$_2^{2+}$, Co(N$_4$)(OH$_2$)CH$_3^{2+}$, and Co(N$_4$)(OH$_2$)Cl$^{2+}$ complexes suggests that $r_{TS}$ may be only about 0.1 Å longer for substitution at the stereochemically cluttered site of Co(Me$_6$[14]dieneN$_4$)(OH$_2$)CH$_3^{2+}$ than the uncluttered site. The methyl–aquo complexes are in the middle of this correlation, implying that the effective electron density at the cobalt center of these complexes is intermediate between that of the classical Co(III) and Co(II) coordination complexes.

The catalytic roles of the alkylcobalamin compounds have stimulated many studies of the nature and properties of cobalt-alkyl compounds.[3] Much of the recent interest has focused on the properties of the cobalt–alkyl bond and how these properties can be modified through steric and electronic interactions with other coordinated ligands.[3-13] The Co–R bond has been found

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