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Photoluminescence Studies of Lanthanide Ion Complexes of Gold and Silver Dicyanides: A New Low-Dimensional Solid-State Class for Nonradiative Excited-State Energy Transfer[†]

Zerihun Assefa,[‡,§] George Shankle,[∥] Howard H. Patterson,[*,‡] and Ross Reynolds[⊥]

Department of Chemistry, University of Maine, Orono, Maine 04469

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The excited-state properties of the layered compounds $M[Au(CN)_2]_3$ and $M[Ag(CN)_2]_3$ (with M = Eu^{3+}) have been examined. Exclusive excitation of the host ions $Au(CN)_2^-$ and $Ag(CN)_2^-$ leads to photoluminescence (PL) from the Eu^{3+} ion, indicating host to guest excited-state energy transfer. The donor $Au(CN)_2^-$ and $Ag(CN)_2^-$ emissions are totally quenched at all temperatures. The emission intensity from $Eu[Ag(CN)_2]_3$, [EuAg], increases with a temperature increase while the intensity for $Eu[Au(CN)_2]_3$, [EuAu], decreases. High-resolution PL data obtained at 78 K indicate that the Eu^{3+} ion occupies a single site in [EuAg], while multiple-site occupations are indicated in [EuAu]. The covalent Au–Au and Ag–Ag interactions in the two compounds are analyzed by comparing the splittings in the $^5D_0 \rightarrow {}^7F_1$ transitions of Eu^{3+} as well as the intensity ratios of the electric dipole ($^5D_0 \rightarrow {}^7F_2$) and the magnetic dipole ($^5D_0 \rightarrow {}^7F_1$) transitions.

Introduction

The photoluminescence (PL) of the d^{10} Au(I) salts $MAu(CN)_2$ (M = K^+, Cs^+, Tl^+ etc.) has continued to attract our attention. These compounds have a structure consisting of layers of linear $Au(CN)_2^-$ ions alternating with layers of M^{n+} ions. The intralayer Au–Au distances vary with the type of the counterion M^{n+}. The PL properties of the two-dimensional compounds $KAu(CN)_2$ and $CsAu(CN)_2$ have been found to be dictated by the extent of gold–gold covalent interactions.[1–2] We recently reported that the presence of significant Tl–Au and Au–Au covalent interactions in $TlAu(CN)_2$ shifts both the absorption and emission bands to lower energies[3] when compared to those of the otherwise isostructural $CsAu(CN)_2$. Unlike the gold dicyanides, only a few complexes of $Ag(CN)_2^-$ are characterized structurally. However, a layered arrangement of the Ag atoms in the linear CN–Ag–CN groups has been established[4] for the silver dicyanide salts of Na^+, K^+, Ca^{2+}, and Sr^{2+}.

On the other hand, the unique photochemical properties of lanthanide ions have provided the opportunity of studying excited-state energy-transfer processes in layered low-dimensional complexes. In the rare earth complexes of uranyl phosphates,[5] cryptates,[6] and platinum tetracyanides,[7] emissions arising due to energy transfer have been reported. Among the lanthanide ions, the Eu^{3+} ion has the unique photophysical property that both its ground ($^7F_0$) and lowest excited emissive ($^5D_0$) states are nondegenerate and show no ligand field splitting. This property has been extensively used to study metal ion sites and inequivalent moieties in molecular solids and macrocyclic molecules.[8]

Our continued interest in compounds of gold dicyanides has led us to investigate energy-transfer processes in the low-dimensional $Eu[Au(CN)_2]_3$, [EuAu], and $Eu[Ag(CN)_2]_3$, [EuAg], compounds. In this paper we wish to compare the temperature-dependent PL properties of the two systems. The differences in the PL properties of the europium ion observed in the complexes are attributable to the differences in the extent of covalent Au–Au and Ag–Ag interactions. In addition, the intensities of the environmentally "hypersensitive" $^5D_0 \rightarrow {}^7F_2$ bands and the magnetic dipole $^5D_0 \rightarrow {}^7F_1$ transition[9] of the Eu^{3+} ion are compared in both the [EuAu] and [EuAg] compounds. The presence of a low-lying charge-transfer state in the [EuAu] system has been found to alter the PL properties as well as its physical appearance when compared to those of the isostructural [EuAg].

Experimental Section

$Eu[Au(CN)_2]_3$ was prepared by addition of a stoichiometric amount of $Eu(NO_3)_3{\cdot}6H_2O$ (Alfa) to an aqueous solution of $KAu(CN)_2$ (Pfaltz & Bauer). Light yellow hexagonal crystals were grown by slow evaporation of the aqueous solution.

Crystals of $Eu[Ag(CN)_2]_3$ were prepared by mixing stoichiometric amounts of aqueous solutions of $KAg(CN)_2$ (Alfa) and $Eu(NO_3)_3{\cdot}6H_2O$.

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[*] To whom correspondence should be addressed.

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[‡] University of Maine.

[§] Present Address: Department of Chemistry, Texas A&M University, College Station, TX 77843.

[∥] Department of Chemistry, Angelo State University, San Angelo, TX 76909.

[⊥] Department of Physics, Grand Valley State University, Allendale, MI 49401.

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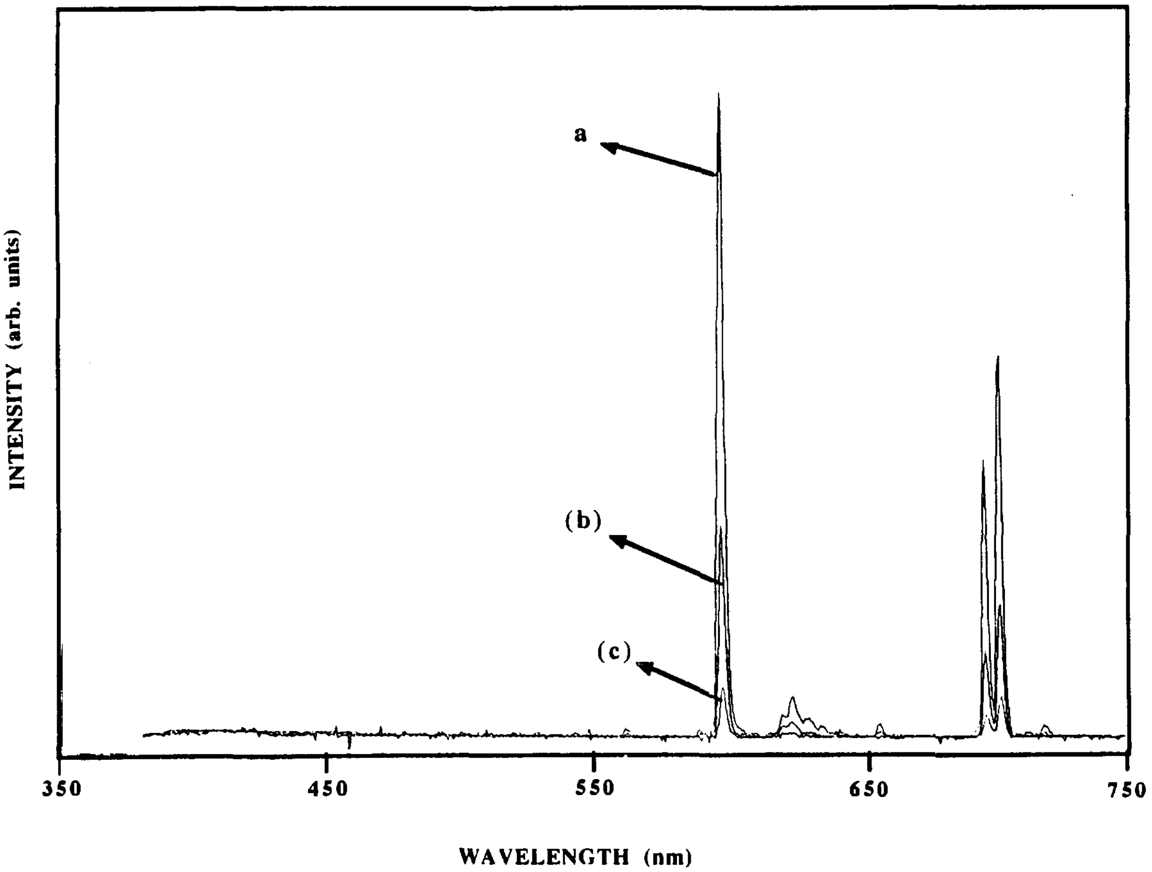

Figure 1. Temperature-dependent luminescence spectra of Eu$[Au(CN)_2]_3$ recorded using a nitrogen-pulsed laser as the excitation source: (a) 10 K; (b) 80 K; (c) 150 K. Emission intensity of the Eu^{3+} ion decreases with increased temperature.

The crystals were checked under a microscope, and those which were clear and hexagonally shaped were chosen for optical studies. Crystals of [EuAg] emit strongly at all temperatures, and thus it was not necessary to grow large crystals.

Excitation and initial luminescence measurements were done on a Perkin-Elmer MPF44A spectrophotometer using a 120-W xenon lamp as the light source. Temperature-dependent luminescence spectra and lifetime measurements were conducted with a Molectron UV series 14 pulsed nitrogen laser using the procedure described elsewhere.[1] The output from the lock-in amplifier and the boxcar averager was collected on an Apple IIE personal computer with an APM-08 A/D convertor board. The APM-08 was programmed with a home-written assembly language program. The data were stored in the Apple IIE computer and later transferred to an IBM personal computer for data manipulation. High-resolution luminescence spectra for the europium ion were collected on a Spectra Physics 2020 double monochromator using an Ar ion laser as the excitation source. The green line at 514 nm and the blue-green 488-nm line were used to excite the sample. Low-temperature measurements were conducted using a Heli-Tran Model Lt-3-110 refrigeration system. Crycon grease was used to attach the sample on the sample holder. Crycon grease alone was scanned for baseline subtraction purposes.

A full data set for X-ray analysis of the [EuAu] complex was collected using monochromated Cu Kα radiation and an Enraf-Nonius CAD4 diffractometer. The change of unit cell parameters, and hence interatomic distances, as a function of temperature was determined using Mo Kα radiation and a PAD 3 diffractometer by monitoring the angular position of maximum intensity for the 800 and 0,0,16 reflections. For each of these reflections the position of the Mo Kα peak was monitored using a vertical slit with ca. 0.05° angular width. Crystals were cooled using the boil-off from a dewar containing liquid nitrogen, and the temperature was monitored by a thermocouple placed within 0.1 mm of the crystal. Cell parameters were determined for temperatures between room temperature and ca. 110 K. Preliminary X-ray data for [EuAg] were collected using Mo Kα radiation and a Nicolet P3F diffractometer.

Results

1. Photoluminescence (PL) Spectra of [EuAu] vs [EuAg]. Temperature-dependent PL spectra of [EuAu] recorded using the N_2-pulsed laser as the excitation source (λ_{exc} = 337 nm) are shown in Figure 1. The spectra consist of sharp emission lines characteristic of Eu^{3+} f–f transitions. The Eu^{3+} emission intensity drastically decreases with a temperature increase. A high-resolution emission spectrum recorded at 78 K with a Spectra Physics 2020 Ar ion laser is shown in Figure 2 for the region covering the Eu^{3+} ion $^5D_0 \rightarrow {}^7F_0, {}^7F_1$ transitions. Six well-resolved bands are observed in this region. In Table 1, the energies of these lines along with their assignments are given. In Figure 3 is shown the emission spectrum of [EuAg] recorded at 10 K. Only four peaks are observable over the Eu^{3+} ion $^5D_0 \rightarrow {}^7F_0, {}^7F_1$ transition regions. Assignments of the peaks corresponding to the Eu^{3+} f–f transitions are given in Table 2. The temperature-dependent PL spectra of the [EuAg] complex recorded using the N_2-pulsed laser excitation are shown in Figure 4. The emission intensity of the [EuAg] complex progressively increases when the temperature is increased (Figure 4) whereas for [EuAu] the emission intensity decreases (Figure 1) with a temperature increase.

2. Photoexcitation (PE) Spectra of [EuAu] vs [EuAg]. The PE spectrum of [EuAu] is shown in Figure 5. When the excitation spectrum is monitored at the Eu^{3+} emission line (594 nm), bands corresponding to f–f transitions are observed at 392 and 465 nm. In addition, broad bands are observed at 348 and 410 nm. In Figure 5, the excitation spectrum of [EuAu] is compared with that of a frozen D_2O solution of $KAu(CN)_2$ in order to facilitate the assignment of the broad excitation bands. Clearly, the 348-nm broad band corresponds to the $Au(CN)_2^-$ ion. The absence of the broad 410-nm band in the spectra of the precursor compounds, $KAu(CN)_2$ and $Eu(NO_3)_3$, indicates that the band is charge transfer in origin. The spectral band assignments are given in Table 3.

Similarly, the excitation spectrum of [EuAg], shown in Figure 6, consists of three sharp lines at 396, 375, and 362 nm and a broad band at 320 nm. The three sharp bands are easily

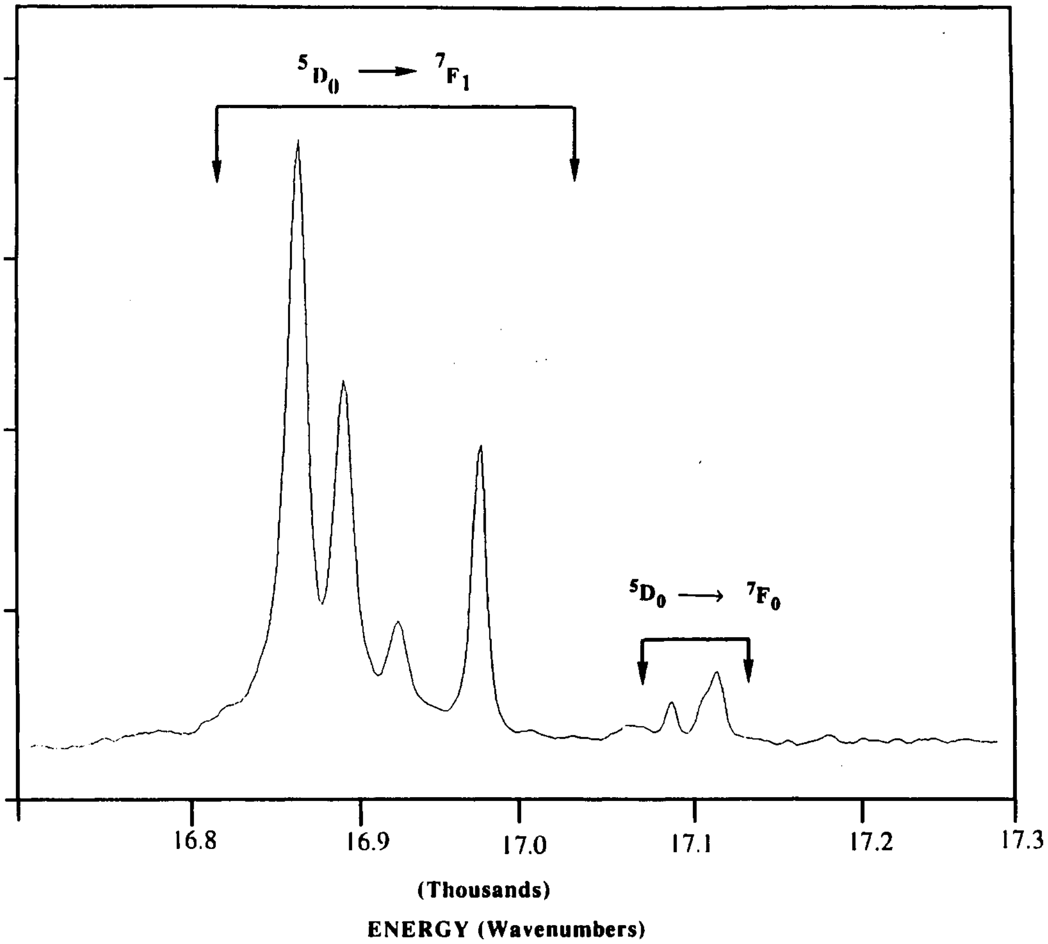

Figure 2. High-resolution emission spectrum of Eu[Au(CN)$_2$]$_3$ recorded at 78 K using a Spectra Physics 2020 argon laser source. The 488-nm laser line was used for excitation. The europium emission region covering only the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_0$ transition region is shown for clarity.

Table 1. Assignments of Bands for the High-Resolution Eu^{3+} Emission Spectrum of the [EuAu] Complex Shown in Figure 2[a]

emission band			
λ, nm	λ^{-1}, cm^{-1}	rel intens	assignment
584.1	17 120	0.18	$^5D_0 \rightarrow {}^7F_0$
585.1	17 090	0.13	$^5D_0 \rightarrow {}^7F_0$
589.2	16 970	0.54	$^5D_0 \rightarrow {}^7F_1$
590.8	16 930	0.24	$^5D_0 \rightarrow {}^7F_1$
592.0	16 890	0.62	$^5D_0 \rightarrow {}^7F_1$
593.1	16 860	1.0	$^5D_0 \rightarrow {}^7F_1$

[a] The 488-nm line of the argon laser was used as the excitation source. The emission band intensities are relative to that of the most intense band observed at 593.1 nm.

recognizable as f–f transitions. In order to facilitate the assignment of the broad 320-nm band, the excitation spectrum of [EuAg] is compared with that of the Gd[Ag(CN)$_2$]$_3$, [GdAg], compound. Since the lowest f–f transition for the Gd^{3+} ion is relatively at a higher energy than the transition within the Ag(CN)$_2^-$ ion, energy transfer between the two species is not expected to take place. As shown in Figure 6, the broad band at 320 nm clearly corresponds to the Ag(CN)$_2^-$ ion. The band assignments are given in Table 4.

3. X-ray Results. Preliminary structural studies of the compounds indicate that both the [EuAu] and [EuAg] are isomorphous. The unit cell parameters for the [EuAu] complex are $a = b = 6.643$ and $c = 9.138$ Å. Doubling of the c-axis was observed for [EuAg]. Our success of refining all the atoms anisotropically was limited by the high absorption correction required for the data. However, the layered nature of the compounds was established from an isotropic model. The intralayer Au–Au and Ag–Ag distances are 3.32 Å in both compounds. The [EuAu] compound contains two water molecules within the coordination sphere of each Eu^{3+} ion (Eu–O separation 2.41 Å). In addition, the N atoms of the cyanide ligands are tilted by ca. 27° toward the Eu^{3+} ion. Four nitrogens are within the coordination sphere of each Eu^{3+} ion at Eu–N distances of 2.46 Å. The Eu–N–C angle is nearly linear (173°). A similar arrangement was observed for [EuAg].

The fractional change in unit cell dimensions was followed as a function of temperature for [EuAu]. Compression in the a axis and expansion in the c axis was observed with a temperature decrease. The compression in the a axis is indicative of a decrease in Au–Au intralayer separation while expansion in the c axis indicates an increase in interlayer separation. Within the temperature range 298–110 K, the intralayer Au–Au separation decreases by ca. 1.5% whereas the interlayer separation increases by ca. 1%. Similar temperature-dependent changes in unit cell parameters were reported for KAu(CN)$_2$.[1] A complete study of the crystal structures of these complexes will appear separately.[3c]

Discussion

1. Photoluminescence (PL) Spectra of [EuAu] vs [EuAg]. The [EuAu] compound is canary yellow while the [EuAg] complex is colorless. Several other rare earth–gold dicyanide systems under investigation in this laboratory are also colorless. It is surprising to note that [EuAu] shows such a marked difference in appearance from the other rare earth complexes, given the similarities in charge and size of the ions.

Exclusive excitation of the gold and silver dicyanide ions in [EuAu] and [EuAg] resulted in the observance of the sensitized emission from the Eu^{3+} ion. One striking difference in the PL properties of the two complexes is the change in luminescence intensity with a change in temperature. The temperature-dependent photoluminescence spectra recorded under identical

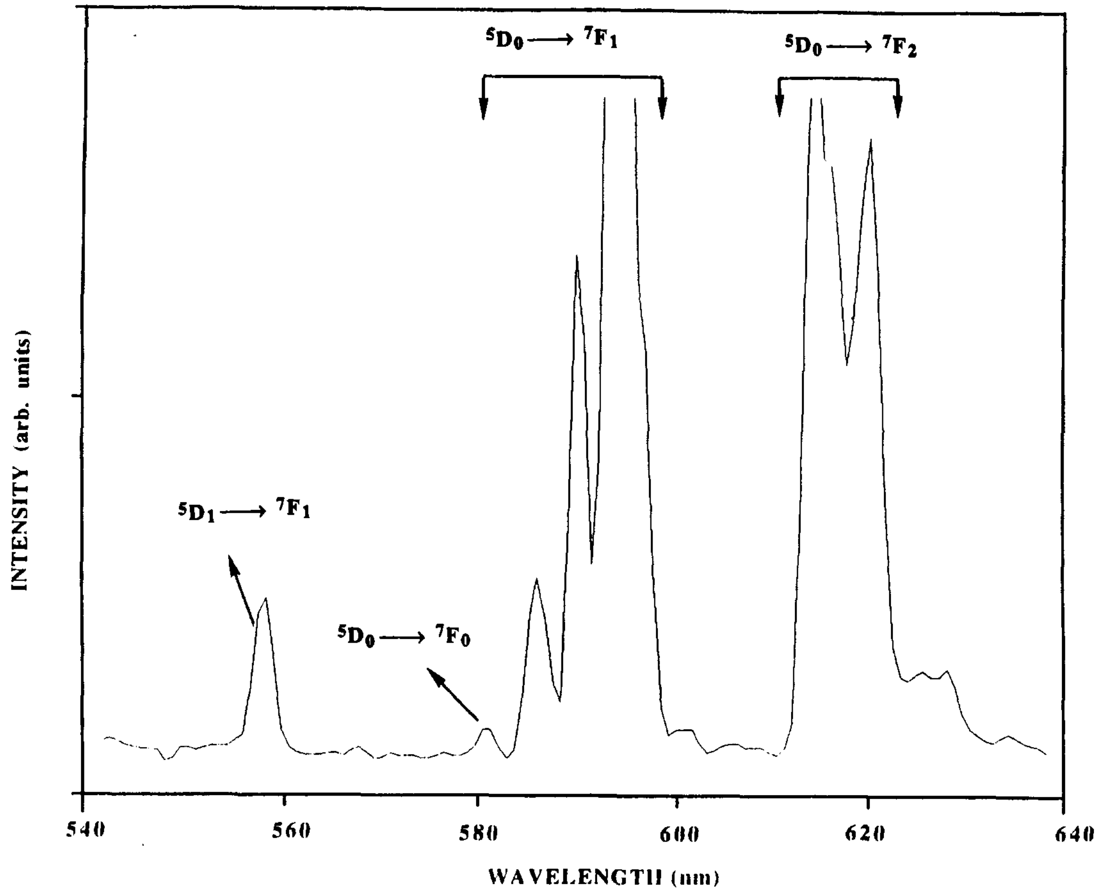

Figure 3. Luminescence spectrum of Eu$[Ag(CN)_2]_3$ recorded at 10 K. The peak at 558.1 nm corresponds to europium emission originating from a higher excited state ($^5D_1$).

Table 2. Assignments of Emission Bands for the Eu^{3+} Spectrum of the [EuAg] Complex Shown in Figure 3[a]

emission band			emission band		
λ, nm	λ^{-1}, cm^{-1}	assignment	λ, nm	λ^{-1}, cm^{-1}	assignment
558.1	17 917	$^5D_1 \rightarrow {}^7F_1$	614.2	16 280	$^5D_0 \rightarrow {}^7F_2$
581.0	17 210	$^5D_0 \rightarrow {}^7F_0$	616.6	16 220	$^5D_0 \rightarrow {}^7F_2$
586.6	17 050	$^5D_0 \rightarrow {}^7F_1$	619.8	16 130	$^5D_0 \rightarrow {}^7F_2$
590.5	16 935	$^5D_0 \rightarrow {}^7F_1$	626.1	15 970	$^5D_0 \rightarrow {}^7F_2$
594.5	16 820	$^5D_0 \rightarrow {}^7F_1$	628.4	15 910	$^5D_0 \rightarrow {}^7F_2$

[a] The spectrum was recorded using a nitrogen-pulsed laser as the excitation source with λ_{exc} = 337.1 nm.

conditions of PMT gain, signal sensitivity, and other instrumental parameters are shown in Figures 1 and 4 for the [EuAu] and [EuAg] complexes, respectively. As shown in Figure 1, the emission intensity of the Eu^{3+} ion in [EuAu] decreases drastically with a temperature increase and is hardly observable at 150 K. The Eu^{3+} emission intensity in the [EuAg] complex, on the other hand, increases with a temperature increase (Figure 4) all the way up to 200 K and starts decreasing slightly thereafter. The intensity is very strong, even at room temperature, showing a higher quantum efficiency of the sensitized emission in [EuAg] than in [EuAu].

The high-resolution luminescence spectrum of [EuAu], shown in Figure 2, consists four well-resolved bands in the 586–600-nm region that correspond to the $^5D_0 \rightarrow {}^7F_1$ transition. Since the maximum number of splittings within the $^5D_0 \rightarrow {}^7F_1$ transition (under low symmetry) is 3, observance of four well-resolved peaks indicates the presence of more than one emitting Eu^{3+} site in the lattice. In addition, the high resolution spectrum (Figure 2) shows two weak bands corresponding to the $^5D_0 \rightarrow {}^7F_0$ transition. Since no splitting in the 0–0 transition, regardless of symmetry, is expected for a single-site occupation, observance of two bands supports the presence of two different emitting sites. In addition, the magnetic dipole $^5D_0 \rightarrow {}^7F_1$ transition is the dominant band in the spectrum, indicating that the symmetry around the Eu^{3+} ion is close to having a center of inversion. The electric dipole $^5D_0 \rightarrow {}^7F_2$ transition, though weak, is also present in the 610–625-nm region (Figure 1). For a totally symmetric environment, this transition is forbidden and no emission band is expected. However, its presence in the [EuAu] complex is indicative of a small electric dipole contribution in the system.

The [EuAg] compound, on the other hand, has only one component for the $^5D_0 \rightarrow {}^7F_0$ transition and three components corresponding to the $^5D_0 \rightarrow {}^7F_1$ transition. The complete removal of the degeneracy of the $^5D_0 \rightarrow {}^7F_0$, $^7F_1$, and $^7F_2$ transitions in the [EuAg] complex indicates that the Eu^{3+} ion has a lower local symmetry than might be predicted from the X-ray studies. Moreover, the PL data are suggestive of a single-site occupation for the Eu^{3+} ion. The emission intensity of the $^5D_0 \rightarrow {}^7F_1$ transition of Eu^{3+} in [EuAg] is nearly 3 times stronger than that of the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition. The dominance of the $^5D_0 \rightarrow {}^7F_1$ transition indicates that magnetic effects contribute more significantly than electric dipole effects to the PL properties of both complexes. On the other hand, the emission intensity of the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition is much stronger in [EuAg] than in [EuAu] and has five components, which points to a less symmetrical Eu^{3+} ion site in the former. A larger distortion from D_{2h} symmetry is thus anticipated for the Eu^{3+} ion in [EuAg] than in [EuAu]. From the PL data it is inferred that the Eu^{3+} ion in [EuAg] has C_{2h} or C_{2v} site symmetry. However, with the present data alone we were unable to differentiate between the two site symmetries.

Another interesting difference in the PL properties of the two compounds lies in the magnitude of the $^5D_0 \rightarrow {}^7F_1$ splitting. Since splitting of the $^7F_1$ ground state arises mainly from the crystal field effect, a large electrostatic contribution from the field is expected to cause a large splitting. Previous studies have

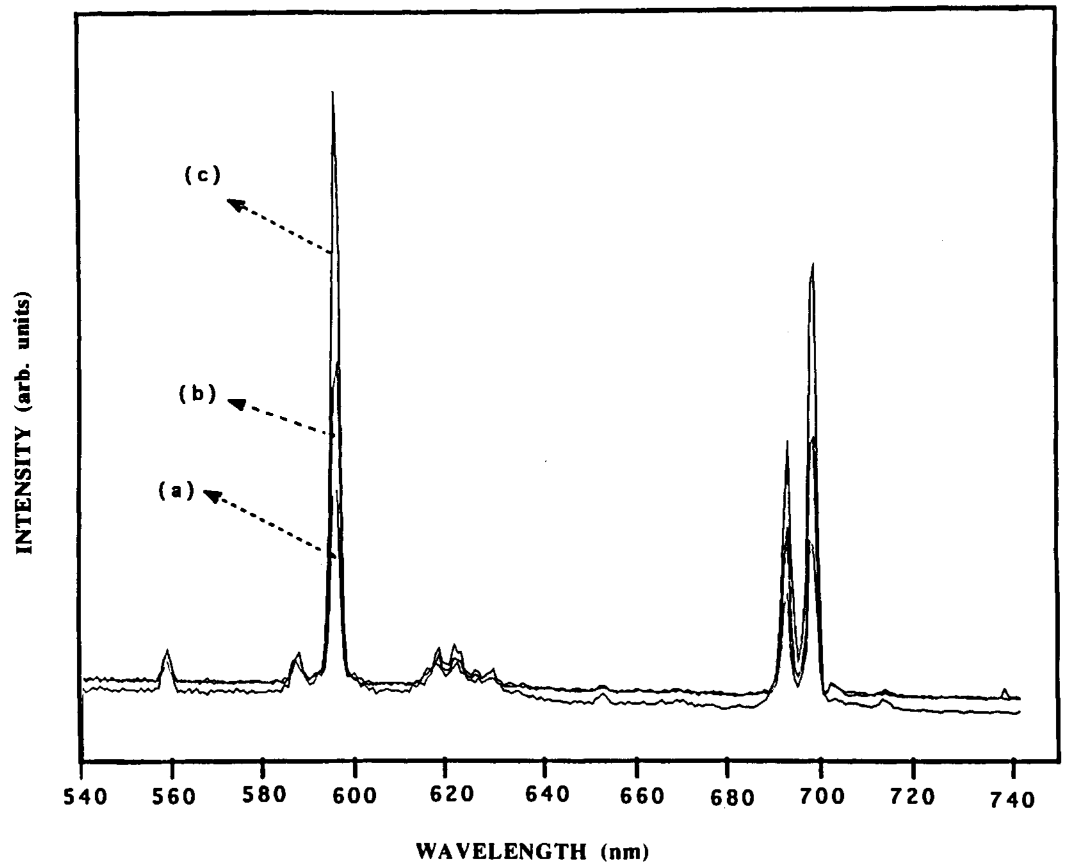

Figure 4. Temperature-dependent emission spectra of Eu[Ag(CN)$_2$]$_3$: (a) 78 K; (b) 150 K; (c) 200 K. Note that the europium emission intensity increases with temperature increase up to 200 K. The complex emits strongly even at room temperature.

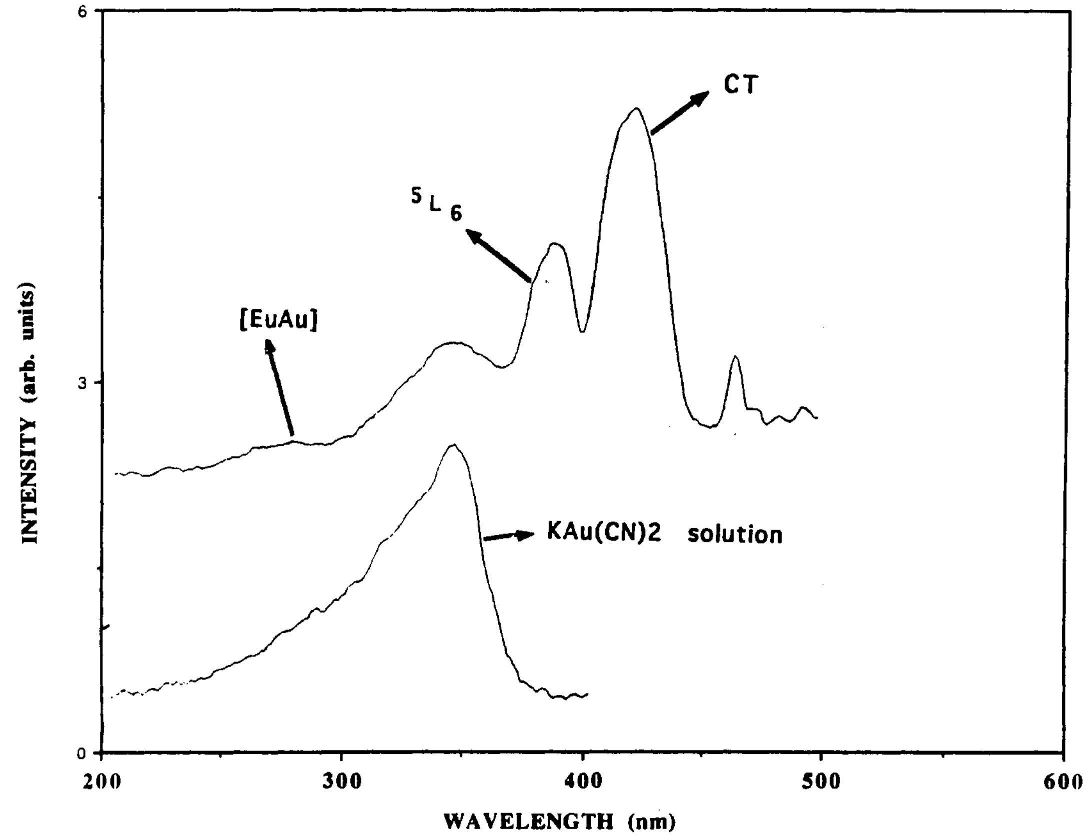

Figure 5. Excitation spectrum of solid Eu[Au(CN)$_2$]$_3$ compared with the excitation spectrum of a D_2O frozen solution of 0.05 M KAu(CN)$_2$. The band at 348 nm corresponds to a Au(CN)$_2^-$ transition while the broad band around 410 nm corresponds to a Au(CN)$_2^-$ → Eu^{3+} charge-transfer transition.

established a direct correlation between the extent of the $^7F_1$ splittings and the electrostatic contribution from the species surrounding the Eu^{3+} ion. For example, an increase in $^7F_1$ splitting has been found when H_2O is replaced by F^- in the europium

Table 3. Assignments of Bands for the Photoexcitation Spectrum of the $Eu[Au(CN)_2]_3$ Complex Shown in Figure 5[a]

excitation band			excitation band		
λ, nm	λ^{-1}, cm^{-1}	assignment	λ, nm	λ^{-1}, cm^{-1}	assignment
348	28 735	$Au(CN)_2^-$	465	21 550	$^5D_2 \leftarrow {}^7F_0$
392	25 510	$^5L_6 \leftarrow {}^7F_0$	528	18 990	$^5D_1 \leftarrow {}^7F_0$
410	24 390	CT ($Eu^{3+} \leftarrow Au(CN)_2^-$)			

[a] The spectrum was recorded at 78 K by monitoring the excitation at the Eu^{3+} emission line.

cryptate[10] systems and was attributed to a decrease in the covalency of the europium–ligand bonding.

In addition to the $^7F_1$ splittings, the position of the $^5D_0 \rightarrow {}^7F_0$ transition has also been used as a sensitive indicator of the strength of the crystal field in the vicinity of the Eu^{3+} ion. Blasse et al.[6b,15] have observed a shift to lower energy in the 0–0 position when H_2O is replaced by the more polarizable Cl^-. Our luminescence data can also be interpreted similarly.

In [EuAu], for example, the total splitting of the $^7F_1$ level is only 120 cm^{-1} while in [EuAg] the splitting is 230 cm^{-1}. The result indicates that the electrostatic contribution of $Au(CN)_2^-$ to the crystal field is much smaller than that of the $Ag(CN)_2^-$ ion. Moreover, when compared to that in [EuAu], the $^5D_0 \rightarrow {}^7F_0$ transition in [EuAg] shifts to lower energy by about 90 cm^{-1} (Tables 1 and 2). As indicated earlier, the interaction between the Eu^{3+} ion and the N atoms of the cyanide ligands has been established for both compounds. Since the cyanides are the common ligands in both cases, the differences in the splittings of the $^7F_1$ levels and the positions of the 0–0 transitions in the two compounds should depend on the covalent nature of the central transition metal atom. The PL results indicate that at 3.32-Å gold–gold separation, relativistic gold–gold interaction withdraws a significant amount of electron density from the cyanide ligands and decreases the electrostatic contribution to the Eu^{3+} ion. Hence the $^5D_0 \rightarrow {}^7F_0$ transition is observed at a lower energy in the [EuAu] complex than in [EuAg]. The result is consistent with the well-established fact that gold is more prone to covalent interaction than silver.[11]

The difference in the intensities of the environmentally sensitive $^5D_0 \rightarrow {}^7F_2$ transitions of the two compounds is also consistent with the above result. A qualitative picture of the extent of covalency in the crystal field can be obtained by comparing the ratio of the intensity of the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition to that of the magnetic dipole $D_0 \rightarrow {}^7F_1$ transition. As the ratio is closely correlated with the polarizability of the coordination sphere, extents of covalency in the two systems can be compared qualitatively. For the [EuAg] and [EuAu] compounds, these ratios are 0.34 and 0.1, respectively. The smaller ratio found for [EuAu] demonstrates the higher covalency expected in this case.

The temperature dependence of the emission lifetime is also another interesting PL feature of the two compounds. The Eu^{3+} emission lifetime of the [EuAg] complex decreases with a temperature increase, and thus, the emission intensity and the lifetime values change in the opposite direction for [EuAg]. On the other hand, the emission lifetime of [EuAu] (0.2 ms) is temperature independent (Table 5) over the range 10–150 K. The lifetime value for the [EuAu] crystal grown from D_2O solution is ca. 1.1 ms and is also temperature independent.

Although Horrocks et al.[12] have shown that a decrease in the Eu^{3+} emission lifetime occurs as a result of quenching by the O–H high vibrational manifolds, the solvent effect in reducing the lifetime has been suggested to be temperature independent.[6b,12c] The fact that the intensity of the Eu^{3+} emission in [EuAu] decreases with a temperature increase without causing a decrease in lifetime indicates the presence of a nonradiative deexcitation mechanism that quenches the excited energy before it reaches the emitting level. The presence of a low-lying charge-transfer state, for example, has been found[6b,13] to quench the Eu^{3+} emission. A schematic configurational coordinate diagram model[8c,14] shows that a CT state can directly feed the ground ^7F manifold, bypassing the luminescent ^5D levels. Excitation experiments conducted on the two compounds provide evidence for the presence of a low-lying CT state in [EuAu] that is responsible for the quenching of the emission intensity at higher temperatures.

2. Photoexcitation Spectra of [EuAu] vs [EuAg]. Assignment of the excitation bands corresponding to the donor $Au(CN)_2^-$ ion has been made by comparing the excitation spectrum of [EuAu] with that of a D_2O frozen solution of $KAu(CN)_2$. This comparison is shown in Figure 5. The excitation spectrum of [EuAu] has also been compared with other gold dicyanide complexes with cations incapable of accepting the excited energy from the $Au(CN)_2^-$ ion. These comparisons clearly indicate that the 348-nm band in the [EuAu] excitation spectrum (Figure 5) corresponds to the $Au(CN)_2^-$ ion. The main argument for energy transfer between the gold dicyanide and the Eu^{3+} ion is based on this excitation spectrum, where bands assignable to the $Au(CN)_2^-$ ion have been observed when the excitation was monitored at the Eu^{3+} emission line.

The excitation spectrum of [EuAu] shown in Figure 5 has another interesting feature in that the most intense band was observed around 410 nm. Weak but sharp excitation bands corresponding to the $^7F_0 \rightarrow {}^5D_3$ transitions were expected in this region. As observed for several other europium complexes, the most intense excitation band is usually observed at ca. 392 nm and corresponds to the next higher $^7F_0 \rightarrow {}^5L_6$ excited-state level. The 392-nm band, being an f–f transition, is also sharp. However, the broadness as well as the intensity of the 410-nm excitation band in [EuAu] suggests that the band does not correspond to an f–f transition.

On the other hand, previous studies[15] have shown the possibility of observing a low-lying charge-transfer state in the excitation spectra of europium complexes. It has been also shown that extinction coefficients of the order of 10^2 L mol^{-1} cm^{-1} are quite normal for absorption into a charge-transfer state of lanthanide ions, because of the small overlap between the donor orbitals and the acceptor 4f orbitals.[6b,16] The broad excitation band observed at 410 nm in the [EuAu] complex is thus assigned to a low-lying charge-transfer (CT) transition from the $Au(CN)_2^-$ to the Eu^{3+} ion.

The excitation spectrum of [EuAg] shown in Figure 6 consists of sharp lines at 372 and 392 nm and very weak bands at longer wavelengths. The bands are characteristic of the Eu^{3+} ion. The broad band maximizing at 320 nm corresponds to the $Ag(CN)_2^-$ excitation. As shown in Figure 5, the assignment is fairly straightforward after comparison with the spectrum of the [GdAg]

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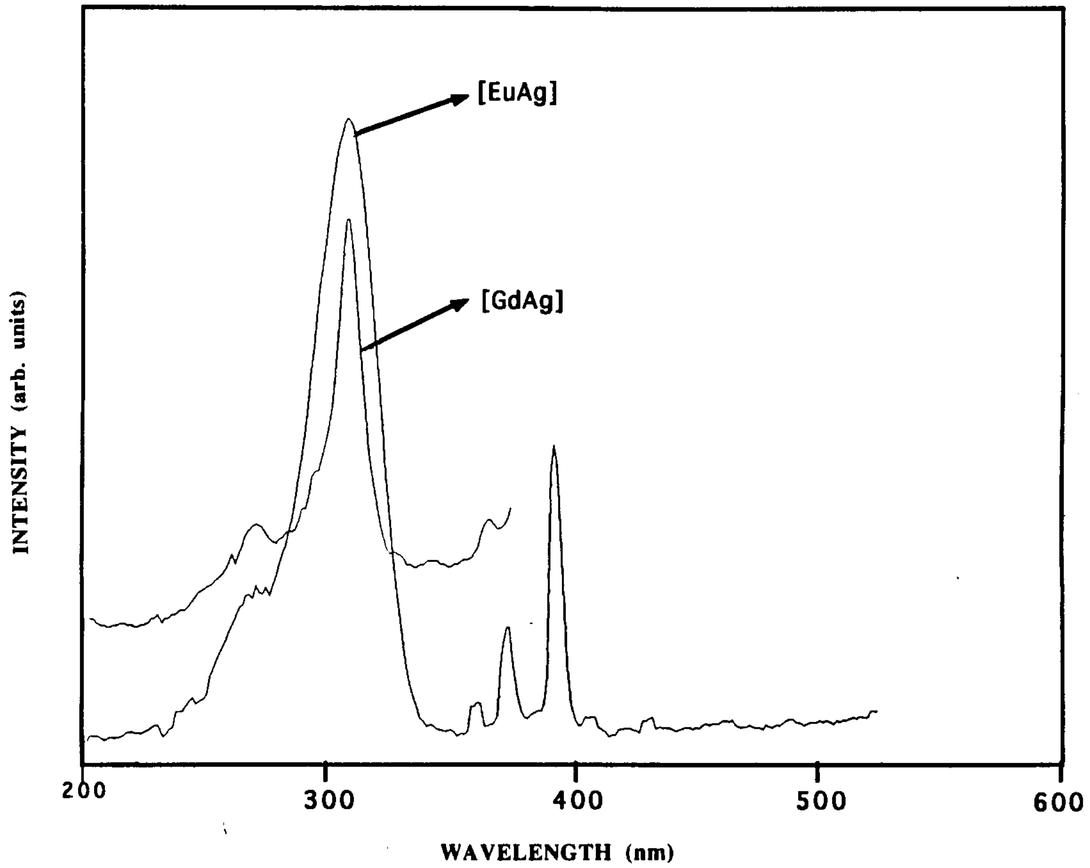

Figure 6. Comparison of the excitation spectrum of $Eu[Ag(CN)_2]_3$ with the excitation spectrum of $Gd[Ag(CN)_2]_3$. The broad band at 320 nm corresponds to a donor $Ag(CN)_2^-$ ion transition.

Table 4. Assignments of Bands for the Photoexcitation Spectrum of the $Eu[Ag(CN)_2]_3$ Complex Shown in Figure 6[a]

excitation band			excitation band		
λ, nm	λ^{-1}, cm^{-1}	assignment	λ, nm	λ^{-1}, cm^{-1}	assignment
271	36 900	$Ag(CN)_2^-$	375	26 660	$^5L_6 \leftarrow {}^7F_0$
320	31 250	$Ag(CN)_2^-$	396	25 250	$^5L_6 \leftarrow {}^7F_0$
362	27 620	$^5L_6 \leftarrow {}^7F_0$			

[a] The spectrum was recorded at 78 K by monitoring the excitation at the Eu^{3+} emission line (593 nm).

Table 5. Temperature-Dependent Emission Lifetime Data for the $Eu[Au(CN)_2]_3$ and $Eu[Ag(CN)_2]_3$ Complexes[a]

	lifetime, μs		
	$Eu[Au(CN)_2]_3$		$Eu[Au(CN)_2]_3$
T, K	H_2O[b]	D_2O[c]	H_2O[b]
10	240	1110	340
20	235	1090	
30	230		300
50	230	1080	280
80	220		230
120	220		210
150	210		180
200			160

[a] Single crystals were used in this measurement. The emission decay was monitored at 593 nm and corresponds to the Eu^{3+} ion $^5D_0 \rightarrow {}^7F_1$ transition. Crystals prepared from H_2O and D_2O solutions are compared for the [EuAu] complex. For [EuAg], the data correspond to crystals prepared from H_2O solution. [b] Crystals were prepared from H_2O solution. [c] Crystals were prepared from D_2O solution.

compound. Observation of the $Ag(CN)_2^-$ band in the excitation spectrum of [EuAg] monitored at the Eu^{3+} emission line is evidence of energy transfer between the donor $Ag(CN)_2^-$ lattice and the acceptor Eu^{3+} ion. No excitation band assignable to a charge-transfer state has been observed in the 350–400-nm region for the [EuAg] system.

3. Energy Transfer in [EuAu] vs [EuAg]. As noted earlier, the $Au(CN)_2^-$ and $Ag(CN)_2^-$ emissions are quenched completely by the Eu^{3+} ion, indicating an efficient energy-transfer process in both complexes. However, the photoluminescence data show that the quantum efficiency in the [EuAu] system is over 2 orders of magnitude less than that found in the [EuAg] complex. The low emission intensity of the [EuAu] complex suggests that at least at higher temperatures a nonradiative deexcitation process via a charge-transfer state competes with the radiative pathway. Quenching of excited-state energy by a charge-transfer state has been observed previously in Eu^{3+}/Ce^{3+} systems[12,17] as well as in europium cryptates.[6,15] These observations indicate that, whether emission is observed or not, a lower quantum efficiency is expected in systems where a charge-transfer state competes with a radiative mechanism.

The model shown in Figure 7 is used to facilitate the discussion of the temperature-dependent photoluminescence and donor–acceptor interaction in the [EuAu] system. At low temperature, the $^5D_3$ excited state of the Eu^{3+} ion shows a spectral overlap region with the donor $Au(CN)_2^-$ emission. The donor level lies below the charge-transfer state, and efficient energy transfer to the $^5D_3$ excited state leads to a strong emission. As confirmed from X-ray studies, the gold–gold separation increases with increased temperature. Hence an increase in the HOMO–LUMO gap is expected.[1,3] With increased temperature, the donor level shifts to higher position and energy transfer to the charge-transfer state competes with the acceptor $^5D_3$ state. Further increase in temperature pushes the donor level to an even higher position, and the overlap with the $^5D_3$ acceptor state diminishes. The charge-transfer state becomes increasingly dominant in accepting the energy. Therefore, the emission intensity of the Eu^{3+} ion is expected to decrease with a temperature increase.

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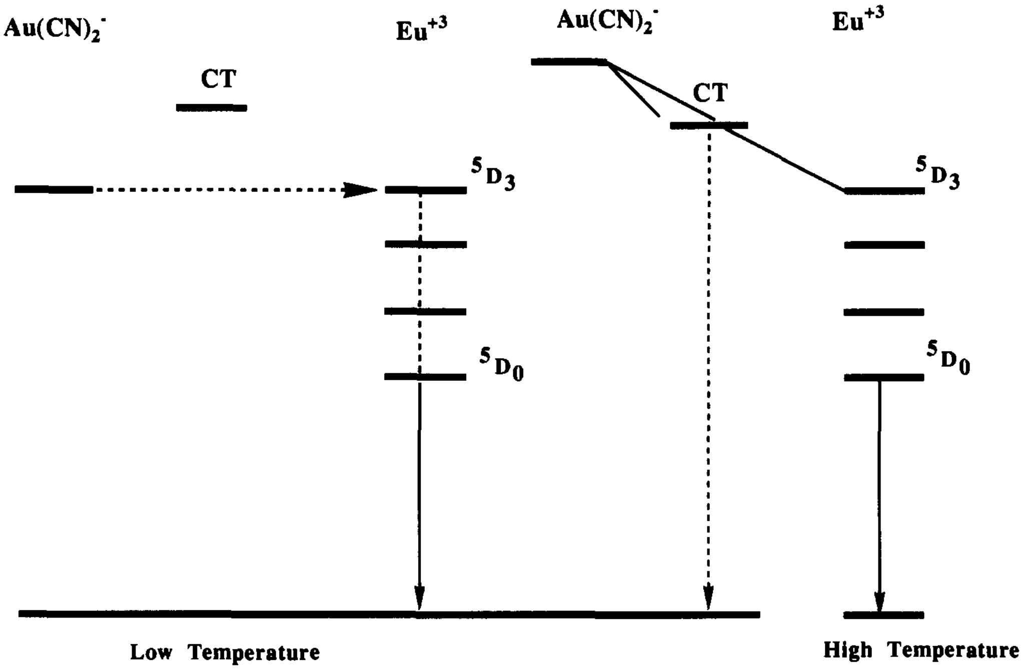

Figure 7. Proposed schematic energy level diagram for the [EuAu] complex. A broken arrow represents a nonradiative deexcitation pathway while a solid arrow indicates a radiative pathway.

The phenomenon is somewhat similar to the "tuning effect" observed in $Eu_2[Pt(CN)_4]_3$, where energy transfer has been tuned on and off by changing the energy position of the donor state via pressure application.[18] The change in the Pt–Pt distance (which changes the HOMO–LUMO separation) has been found to affect the extent of donor–acceptor overlap. In europium cryptates, for example, introducing F^- ions prevented the nonradiative decay by blue-shifting the charge-transfer state.[6,15d] As a result, the quantum yield increased to 1 from a value of 0.03.

We have seen evidence of a temperature tuning effect in [EuAu]. With small temperature increments between 10 and 50 K, the Eu^{3+} emission intensity slightly increases up to ca. 40 K and afterwards decreases drastically. Previous temperature-dependent luminescence experiments on $KAu(CN)_2$, $CsAu(CN)_2$, and $TlAu(CN)_2$ have shown[1-3] that the donor $Au(CN)_2^-$ emission band shifts to higher energy by at least 350 cm^{-1} in the 10–40 K temperature range. Such a shift to higher energy should increase the efficiency of energy transfer because the activation barrier for the energy transfer decreases if the donor is situated at a higher energy level than the acceptor. A further increase in temperature above 40 K allows the charge-transfer state to compete with the $^5D_3$ acceptor state. Above 150 K, acceptance of energy by the CT state almost completely dominates and the Eu^{3+} emission is nearly quenched. Since the donor $Au(CN)_2^-$ emission has been quenched totally at all temperatures, this model supports the complete transfer of energy into a nonemitting charge-transfer state.

The temperature-dependent PL property of [EuAg] shows an interesting phenomenon in that the emission intensity (and by inference the quantum yield) and the lifetime values change in opposite directions. For a single emitting excited state, a decrease in lifetime with a temperature increase should be accompanied by a concomitant decrease in emission intensity. However, in the [EuAg] system, a sharp increase in the emission intensity has been observed with a temperature increase. This result is inconsistent with a single emitting state and suggests the presence of an additional temperature-dependent mechanism that dominates at higher temperatures.

A close observation of the emission spectra of [EuAg] shows that, in addition to the $^5D_0$ state, bands originating from the higher emitting states are also observable. The band at 558.1 nm (Figure 3) for example, corresponds to the $^5D_1 \rightarrow {}^7F_2$ transition. Emission bands corresponding to the $^5D_1 \rightarrow {}^7F_0$, $^7F_1$ levels have also been observed at low temperatures at 525 and 540 nm, respectively. While the intensities of the emission bands originating from the $^5D_1$ state decrease with increased temperature, the intensities of the bands originating from the lowest $^5D_0$ excited state increase. The decrease in the emission intensities of the bands originating from higher excited states and the corresponding increase in the intensity of emission originating from the lowest $^5D_0$ excited state clearly indicate the importance of a temperature-enhanced relaxation process in the system. A possible explanation is that, at higher temperatures, a nonradiative depopulation of the higher excited states increases the excitation residing on the lowest emitting $^5D_0$ level. Therefore, emission originating from the $^5D_0$ level is expected to increase with a temperature increase. In support of this conclusion, the fluorescence spectrum of LaF_3: Eu^{3+} (0.3% doped europium) has been found[19] to show a much stronger intensity at 298 K than at 78 K. The increased intensity at higher temperatures has been attributed to an increase in the rate of nonradiative relaxation from the higher ^5D_J states to the lowest emitting level.

The symmetry of the crystal field might also be an important factor in shortening the lifetime of the europium emission in the [EuAg] system. In an asymmetric crystal field environment, where electric dipole transitions are more probable and have a greater oscillator strength than magnetic dipole transitions, emission with a larger electric dipole contribution would have a shorter lifetime[20] than the one dominated by a magnetic dipole contribution. As discussed earlier, the electric dipole contribution is more important in [EuAg] than in the [EuAu] and thus a shorter lifetime is expected in the former. In addition, an increased rise time with a temperature increase has been noticed during the course of lifetime measurements for [EuAg], showing a buildup from upper excited states. Moreover, the intensity of the electric dipole $^5D_0 \rightarrow {}^7F_2$ transition has been found to increase slightly

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between 10 and 78 K. Thus an increased electric dipole contribution as well as buildup from upper excited states is the main reason for the decrease in the Eu^{3+} emission lifetime that has been observed in the [EuAg] complex.

Conclusions

In this investigation a comparison of excited-state energy transfer has been conducted on two layered dicyanide systems, [EuAu] and [EuAg]. The donors are the ions $Au(CN)_2^-$ and $Ag(CN)_2^-$, and the acceptor is the Eu^{3+} ion. Efficient energy transfer from the donor $Ag(CN)_2^-$ and $Au(CN)_2^-$ ions to the acceptor Eu^{3+} ions has been established. The $^5D_3$ excited state of the Eu^{3+} ion is suggested as the acceptor state in the [EuAg] system, while, in the [EuAu] system, a low-lying charge-transfer state has been established as an increasingly significant acceptor state at higher temperatures. High-resolution luminescence data indicate that the Eu^{3+} ions occupy two lattice sites in the [EuAu] system while a single-site occupation has been inferred for the [EuAg] system. A D_{2h} site symmetry distorted to C_{2h} or C_{2v} is suggested as the possible symmetry for the Eu^{3+} ion in the gold dicyanide complex, while a lower symmetry is indicated fot the silver dicyanide complex. A qualitative measurement of covalent metal–metal interaction in the two compounds has been established by comparing the ratio of the intensity of the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition to that of the magnetic dipole $^5D_0 \rightarrow {}^7F_1$ transition. A smaller ratio has been found for the [EuAu] than for the [EuAg] system. The result is consistent with the prediction that the Au–Au covalent interaction is much stronger in [EuAu] than the Ag–Ag covalent interaction is in [EuAg].

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