Photoluminescence Studies of Lanthanide Ion Complexes of Gold and Silver Dicyanides. 2. A New Low Dimensional Solid State Class for Nonradiative Excited State Energy Transfer[†]

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The excited state properties of the layered compounds Dy[Au(CN)$_2$]$_3$, [DyAu], Gd[Au(CN)$_2$]$_3$, [GdAu], and Dy[Ag(CN)$_2$]$_3$, [DyAg], have been examined. The donor Au(CN)$_2^-$ ion both in [DyAu] and [GdAu] systems show a strong and structured emission at low temperatures. Due to the lack of donor–acceptor spectral overlap, energy transfer in the [DyAu] system in inefficient, and thus, emission arising from the acceptor Dy^{3+} ion is weak at all temperatures. Similarly, no emission has been observed from the Gd^{3+} ion as the lowest excited state in the acceptor ion is situated at a much higher energy position than the donor level. From the resonance Raman studies, the structure in the luminescence spectrum of the [DyAu] compound has been assigned to the Au–C symmetric stretching mode and other Raman active modes. Emission from the donor Ag(CN)$_2^-$ ion in the [DyAg] system is totally quenched at all temperatures whereas the acceptor Dy^{3+} ion emits strongly. The rare earth emission intensity in the [DyAg] system increases with a temperature increase, indicating an efficient energy transfer from the donor Ag(CN)$_2^-$ to the Dy^{3+} ion. The $^4G_{11/2}$ excited state of the Dy^{3+} ion is suggested as the principal acceptor state. An exchange mechanism originating from the overlap of the N atoms of the CN$^-$ ligands and the lanthanide, Dy^{3+} ion, is suggested as the dominant mechanism for the energy transfer process.

Introduction

Lanthanide luminescent probes have been convenient tools in studying metal ion sites in macro cyclic compounds and in biological systems. Due to their long excited state lifetime the Eu^{3+} and Tb^{3+} ions, in particular, are suitable probes in the determination of metal ion distances in biological systems.[1] In addition several rare earth complexes have been developed recently for magnetic resonance imaging[2] and radio therapeutic applications.[3] As a result of those interesting spectroscopic applications compounds of lanthanide ions are currently under intensive investigation.

On the other hand, emission arising due to excited state energy transfer has been reported in layered low dimensional rare earth complexes such as uranyl phosphates,[4] cryptates[5] and platinum tetracyanides.[6] The photoluminescence (PL) properties of the low dimensional rare earth compounds of the type Eu[M(CN)$_2$]$_3$ (M = Au, Ag) are also interesting in this regard. We recently reported[7] that efficient excited state energy transfer from the Au(CN)$_2^-$ and Ag(CN)$_2^-$ ions to the Eu^{3+} ion enhances the PL observed from the rare earth ion.

Continuing with this research, we have now extended our investigation to other rare earth–gold dicyanide and –silver dicyanide systems. In this paper we report the temperature dependent PL properties of the Dy[Au(CN)$_2$]$_3$ [DyAu], Gd[Au(CN)$_2$]$_3$, [GdAu], and Dy[Ag(CN)$_2$]$_3$, [DyAg], compounds. We wish to compare the efficiency of excited state energy transfer in these compounds with the Eu[Au(CN)$_2$]$_3$, [EuAu], and Eu[Ag(CN)$_2$]$_3$, [EuAg], systems that have been reported recently.[7]

Experimental Section

The compounds Dy[Au(CN)$_2$]$_3$, [DyAu], and Gd[Au(CN)$_2$]$_3$, [GdAu], were prepared by addition of stoichiometric amounts of Dy(NO$_3$)$_3$·6H$_2$O and Gd(NO$_3$)$_3$·6H$_2$O (Alfa) to an aqueous solution of KAu(CN)$_2$ (Pfaltz & Bauer). Colorless crystals were grown by slow evaporation of the aqueous solution. Crystals of Dy[Ag(CN)$_2$]$_3$, [DyAg], were prepared by mixing stoichiometric amounts of aqueous solutions of KAg(CN)$_2$ (Alfa) and Dy(NO$_3$)$_3$·6H$_2$O. The crystals were checked under a microscope and those which were clear and hexagonally shaped were chosen for optical studies.

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.[8] The output from the lock-in amplifier and the boxcar averager was collected

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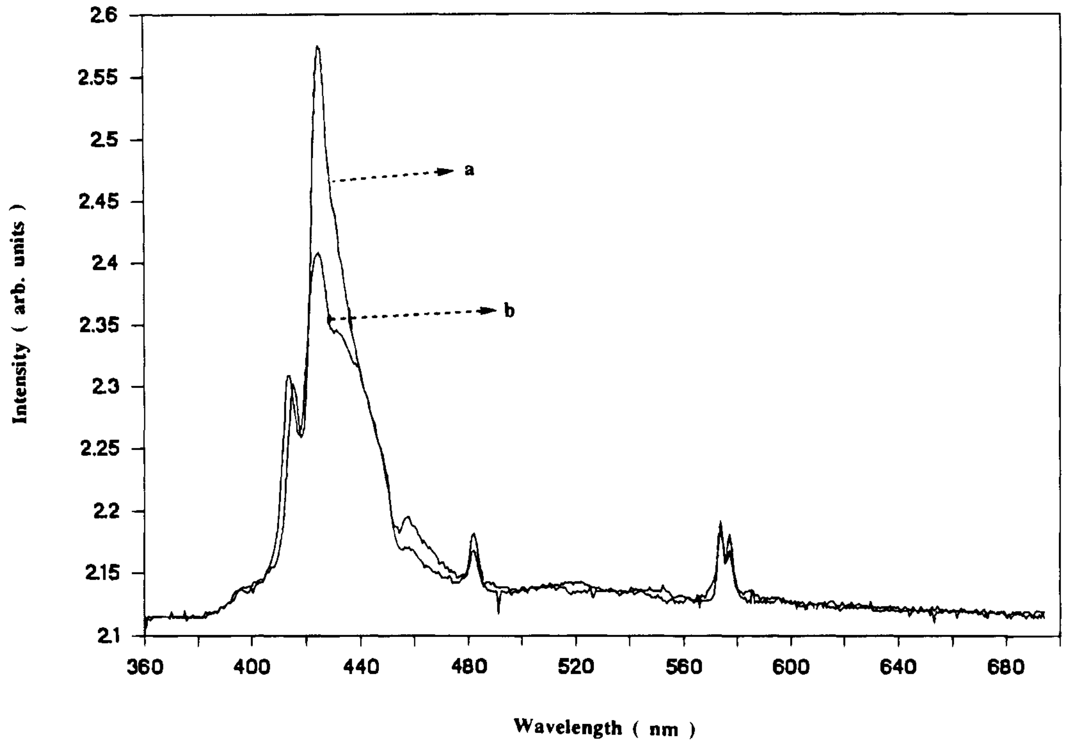

Figure 1. Temperature dependent luminescence spectra of $Dy[Au(CN)_2]_3$ recorded using a nitrogen pulsed laser as the excitation source: (a) 10 K; (b) 60 K.

Table 1. Vibronic Components of the Donor $Au(CN)_2^-$ Emission Band for the [DyAu] Compound Shown in Figure 1[a]

$Au(CN)_2^-$ emission band			
nm	cm^{-1}	ΔE (cm^{-1})	assignment
413.2	24201		
424.9	23534	667	470 + 190 = 660
433	23094	1107	470 × 2 + 156 = 1096
448	22321	1880	470 × 4 = 1880
456.5	21905	2296	470 × 3 + 190 × 3 + 156 × 2 = 2292

[a] The nitrogen pulsed laser was used as an excitation source. The band assignments correspond to the spectra obtained at 10 K.

on a Personal Apple IIE computer with an APM-08 A/D converter 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 dysprosium ion were collected with a Spectra Physics 2020 double monochromator using an Ar ion laser as the excitation source. The blue line at 456 nm and the green line at 514 nm were used to excite the sample. Low temperature measurements were conducted using a Model Lt-3-110 Heli-Tran refrigeration system. Crycon grease was used to attach the sample on the sample holder. Crycon grease alone was scanned for baseline subtraction purposes.

Results

1. Photoluminescence Studies. The single crystal photoluminescence spectra of the [DyAu] system obtained at 10 K is shown in Figure 1. The high energy region (400−460 nm) of the spectrum shows an intense structured band in the temperature range of 5−60 K. Three well resolved bands are observed at 413.2, 424.9 and 456.5 nm (Table 1). Two bands also appear as shoulders at ca. 433 and 448 nm. The structured behavior of this band appears to have a vibronic origin. Even though the spacings between the bands are not uniform, the average separation of the five bands is ca. 574 cm^{-1}. The intensity of the broad emission band decreases and slightly blue shifts with a temperature increase.

The lower energy region of the emission spectrum contains sharp but weak bands which are characteristic of f−f transitions. A high resolution emission spectrum of the [DyAu] compound covering the Dy^{3+} ion f−f transition region is shown in Figure 2. The spectrum was recorded with a Spectra Physics 2020 argon ion laser using the 456 nm blue line as the excitation source. Two bands corresponding to the Dy^{3+} ion f−f transitions are observed ca. 481 and 572 nm.

In Table 2 are given the lifetime data for the [DyAu] and [GdAu] systems. When the broad emission band in [DyAu] was monitored at 430 nm, a single exponential decay provided a lifetime of 0.21 μs at 78 K. Both the 481 and 572 nm Dy^{3+} ion f−f emission lines also show a monoexponential decay curve and the lifetime obtained is 7.8 μs (at 78 K). For crystals grown from D_2O solution no change in the donor $Au(CN)_2^-$ emission lifetime has been observed. However, the Dy^{3+} ion emission lifetime increased significantly to 26 μs. The presence of H_2O and D_2O in the respective crystals has been confirmed by FTIR measurements.

The PL spectra of the [GdAu] system recorded at 10 and 78 K are compared in Figure 3. At 10 K a strong broad emission band centering at ca. 440 nm is evident. The lifetime of this emission band is 0.17 μs at 78 K. In addition the high-energy side of the emission spectrum shows a structured behavior with bands appearing at ca. 406 and 415 nm. With a temperature increase the luminescence intensity decreases drastically and the band blue shifts slightly. At 78 K the broad emission band is observed at ca. 433 nm which corresponds to a blue shifting of ca. 400 cm^{-1} when compared to the 10 K spectrum.

In Figure 4 is shown the photoluminescence spectra of the $Dy[Ag(CN)_2]_3$, [DyAg], system recorded at 10 and 60 K. Unlike the case of the [DyAu] and [GdAu] systems, no emission band has been observed in the high energy region (400−460 nm) of the spectrum. In the low energy region, two strong and sharp emission lines corresponding to the Dy^{3+} f−f transitions

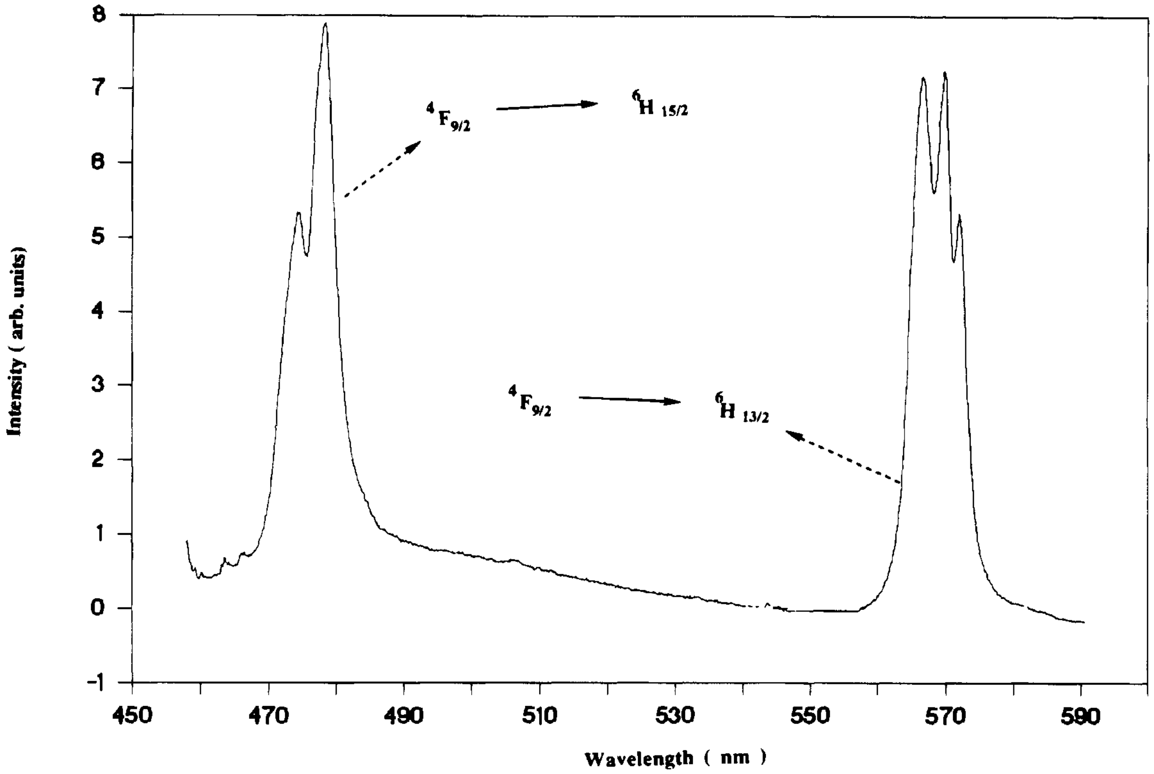

Figure 2. High resolution emission spectrum of Dy[Au(CN)$_2$]$_3$ recorded at 78 K using a Spectra Physics 2020 argon laser source. The 456 nm laser line was used for excitation.

Table 2. Temperature Dependent Emission Lifetime Data for the [DyAu] System[a]

	[DyAu]			[GdAu]
temp (K)	Au(CN)$_2^-$ (425 nm) (μs)	Dy^{3+} band (571 nm) (μs)		Au(CN)$_2^-$ (430 nm) (μs)
		H$_2$O	D$_2$O (μs)	
78	0.21	7.8	26	0.17
150	0.18	7.6	16	
200	0.17	7.3	12	
250	0.15	7.3	10	
298	0.15			

[a] Single crystals were used in this measurement. The donor Au(CN)$_2^-$ emission decay was monitored at 425 nm, and the Dy^{3+} emission was monitored at 571 nm. Samples prepared from both aqueous and D$_2$O solutions are compared for the Dy^{3+} ion emission. The presence of H$_2$O and D$_2$O in the crystal was confirmed by FTIR measurements, which showed bands at 3400 and 2500 cm^{-1}, respectively. The donor emission lifetime for the [GdAu] system is also given for comparison.

are observed at 481 and 573.7 nm. The emission intensities of these bands increase with a temperature increase. The lifetime of the Dy^{3+} ion emission line measured at 573.7 nm is ca. 3.2 μs (at 60 K). In Figure 5 the acceptor Dy^{3+} ion emission intensities in the [DyAu] and [DyAg] systems are compared with an identical instrumental setup. The spectra were measured at 10 K and clearly indicate that emission arising from the [DyAg] system is much stonger than that from the [DyAu] system.

2. Resonance Raman Studies. The low temperature Raman spectrum of the [DyAu] system is shown in Figure 6a. In order to facilitate the band assignments, the spectra of the [EuAu] and [GdAu] systems are also included in Figure 6b,c. The vibrational bands and their assignments are given in Table 3. Several peaks appear in the 100–2200 cm^{-1} region of the Raman spectrum of the [DyAu] system (Figure 6a). The totally symmetric (ν_1) stretching mode for the CN$^-$ appears at 2178 cm^{-1}. The peak at 470 cm^{-1} corresponds to the Au–C symmetric stretching vibration (ν_2) and the Au–CN bending mode appears at 352 cm^{-1}. Two more weak Raman bands appear at the lower frequency region, at 156 and 190 cm^{-1}. In the [EuAu] system these low energy Raman bands are highly pronounced and show a resonance enhancement when the excitation frequency is changed from 456 to 488 nm. The intensities of the Raman peaks at 154 and 194 cm^{-1} in [EuAu]

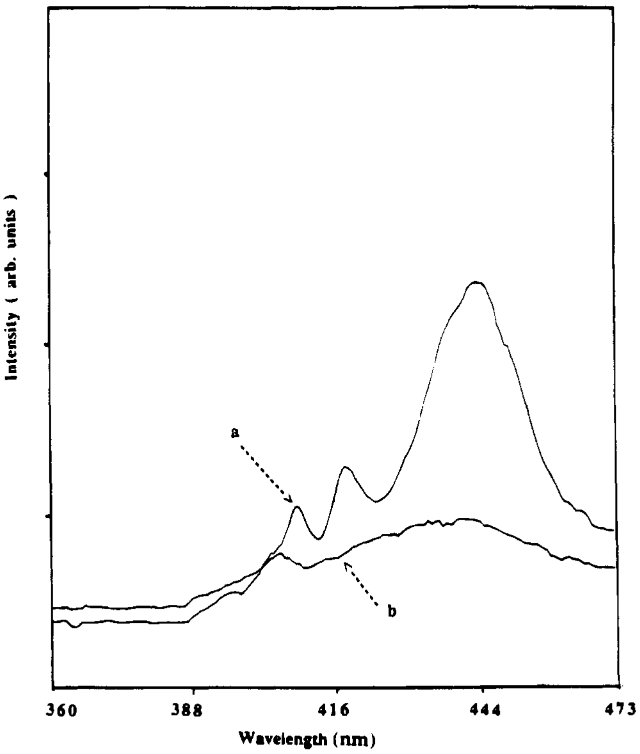

Figure 3. Temperature dependent luminescence spectra of Gd[Au(CN)$_2$]$_3$ recorded using a nitrogen pulsed laser as the excitation source: (a) 10 K; (b) 78 K.

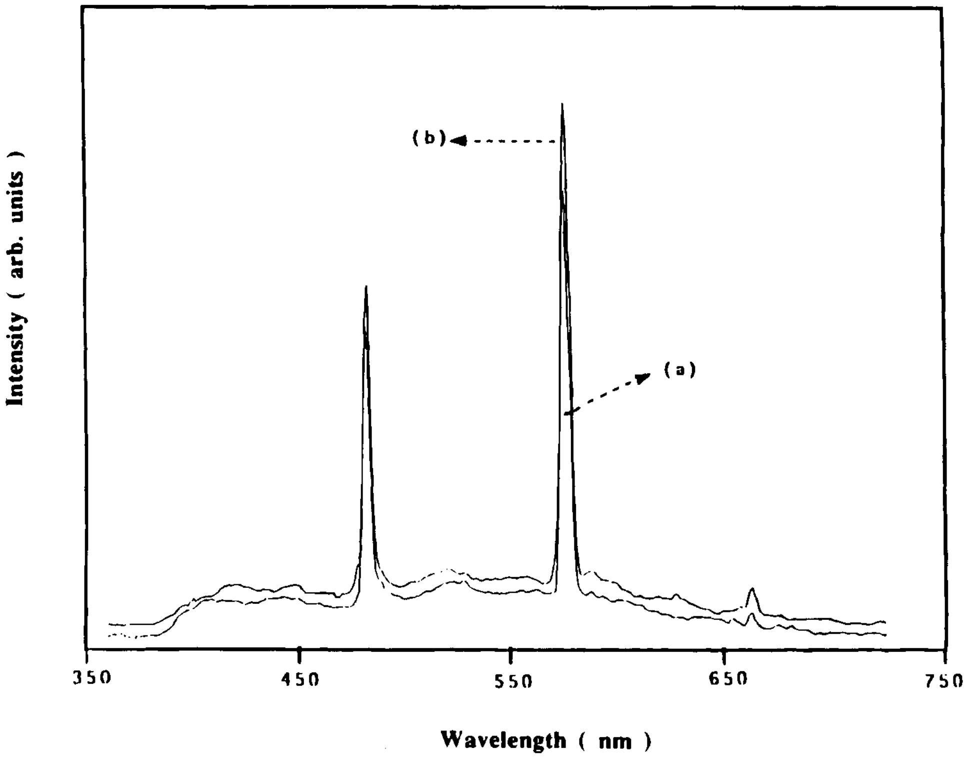

Figure 4. Temperature dependent luminescence spectra of Dy[Ag(CN)$_2$]$_3$ recorded using a nitrogen pulsed laser as the excitation source: (a) 10 K; (b) 60 K.

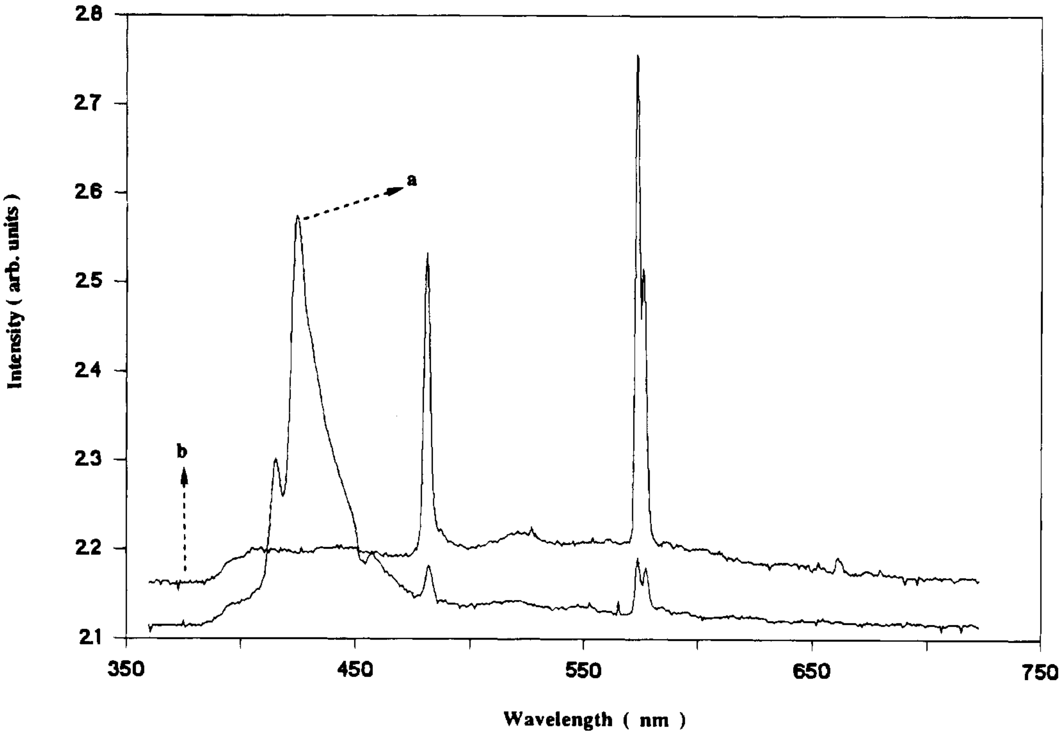

Figure 5. Comparison of the emission intensity of the [DyAu] and [DyAg] systems with an identical instrumental setup. The comparison was conducted at 10 K using a nitrogen pulsed laser as the excitation source: (a) [DyAu]; (b) [DyAg].

are stronger than that of the [DyAu] compound. Additional Raman bands are also observed at 228 and 490 cm^{-1} in the [EuAu] system. These low energy bands all show resonance enhancement in the [EuAu] system when the excitation energy approaches that of the $^7F_0 \rightarrow {}^5D_2$ transition energy of the Eu^{3+} ion. No resonance enhancement has been observed in any of the Raman bands of the [DyAu] system as a result of changing the excitation energy.

Discussion

1. Photoluminescence (PL) Spectra of [DyAu] vs [DyAg]. The PL spectrum of the [DyAu] system is characterized by two regions. An intense high energy band and weak but sharp low energy bands are evident in the spectrum. Assigment of the donor emission band in the [DyAu] system is facilitated by comparison with the [GdAu] system as well as with other gold dicyanide compounds. In [GdAu] where the lowest excited

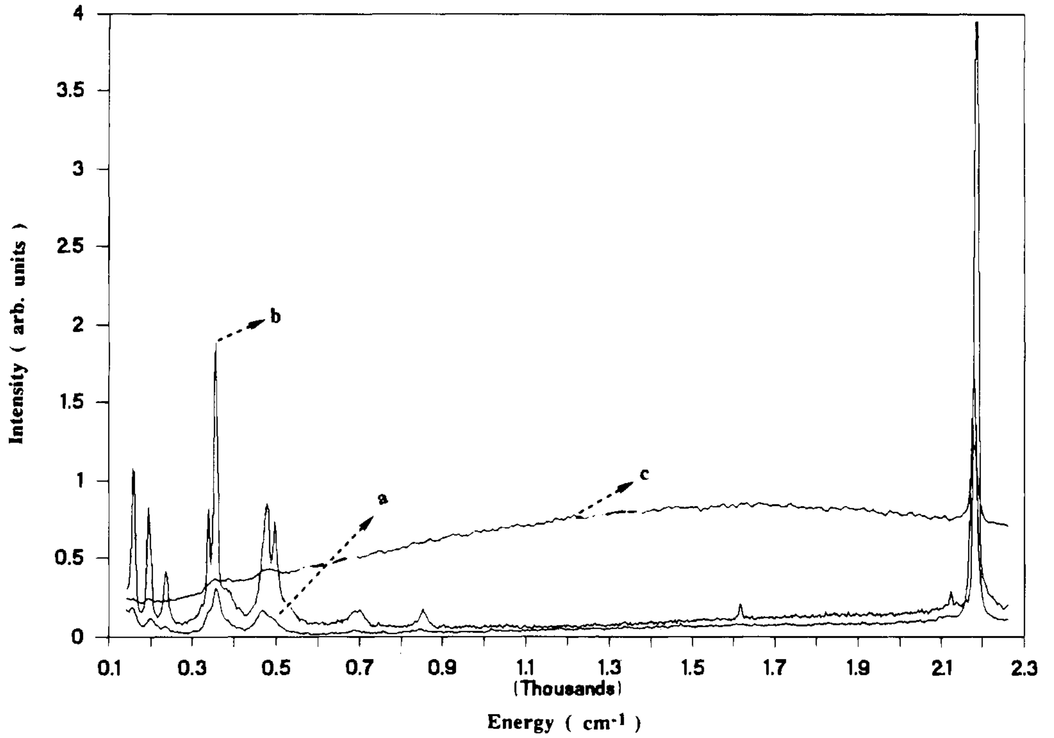

Figure 6. Resonance Raman spectra recorded at 78 K using a Spectra physics 2020 argon laser source. The blue line at 456 nm was used as the excitation source: (a) Dy[Au(CN)$_2$]$_3$; (b) Eu[Au(CN)$_2$]$_3$; (c) Gd[Au(CN)$_2$]$_3$.

Table 3. Assignments of Resonance Raman Bands for the [DyAu] Compound Shown in Figure 6a[a]

Raman band (cm^{-1})	assignment	Raman band (cm^{-1})	assignment
156	lattice mode	470	Au−C str mode
190	C−Au−C bend	2178	CN str mode
352	Au−CN bend		

[a] The 456 nm argon laser line was used as the excitation source. The spectra were collected at 78 K.

state of the acceptor Gd^{3+} ion is situated[6] at a much higher energy, the donor emission has been observed without any emission attributable to an f−f transition. The donor emission in the [GdAu] system closely resembles that of the [DyAu] system both in emission energy and temperature dependent behavior. Moreover, the lifetime values of the donor emission in the two systems are nearly the same (0.21 and 0.17 μs for the [DyAu] and [GdAu] systems, respectively at 78 K). This clearly indicates that the broad high energy band in both systems originates from excitation of the donor $Au(CN)_2^-$ ion.

Interestingly, this feature is quite different from the PL behavior observed in the [EuAu] system.[7] In [EuAu] an exclusive excitation of the donor $Au(CN)_2^-$ ion has resulted in the observance of only the sensitized emission from the Eu^{3+} ion at all temperatures. No emission attributable to the $Au(CN)_2^-$ ion has been observed suggesting an efficient energy transfer between the donor and the acceptor Eu^{3+} ions. Contrary to this observation the donor $Au(CN)_2^-$ ion shows an intense emission both in the [DyAu] and [GdAu] systems. The acceptor ion emission is weak in the former and absent in the latter. This result indicates that the Dy^{3+} ion in [DyAu] is inefficient in quenching the donor emission significantly via energy transfer. In the [GdAu] system the lowest excited state of the Gd^{3+} ion is at a much higher energy position[6] than the donor level and, thus, energy transfer is not expected to take place.

The luminescence bands in several gold dicyanide complexes, assigned by lifetime measurements, show a simple situation where a strong spin−orbit coupling facilitates a rapid intersystem crossing.[9] The emission band of $KAu(CN)_2$ (390 nm), for example, has two lifetimes at low temperatures originating from closely separated singlet and triplet states.[10] As the efficiency of the intersystem crossing is facilitated by higher temperatures, the luminescence shows a single lifetime corresponding to an emission that originates from the triplet state. Theoretical calculations and spectroscopic studies have also indicated that the luminescence band in $Au(CN)_2^-$ compounds originates from an Au ($5d_{z^2}$) $\sigma_g \rightarrow \pi_u$ (CN^- p_{π^*}) transition (assuming $D_{\infty h}$ symmetry).[10,11] This transition is fully allowed by electric dipole selection rules. A strong spin−orbit coupling enhances intersystem crossing from the singlet to the triplet state where the high energy emission originates. Due to the similarities in lifetime and energy positions between the emission bands of [DyAu] and [GdAu] systems and other $Au(CN)_2^-$ salts (such as $KAu(CN)_2$ and $CsAu(CN)_2$), the donor emission is assigned as originating from the triplet state.

With a temperature increase, this high energy emission band blue shifts slightly both in the [DyAu] and [GdAu] systems. Previous studies from this laboratory have confirmed that emission energies in $Au(CN)_2^-$ compounds blue shift with a temperature increase. In fact, blue shifting with a temperature increase is quite a common phenomenon in gold dicyanide compounds and has been associated with a change in Au−Au separation.[6b,10,11] In $KAu(CN)_2$, for example, the emission energy shifts by 1100 cm^{-1} when the sample temperature changes from 78 K to room temperaure.[10] Theoretical calcula-

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tions indicate that an increase in Au−Au separation stabilizes the HOMO and as a result the HOMO−LUMO gap increases.[10] A direct correlation between the luminescence energy and the Au−Au separation has been noted recently in the "torched" dimers of the (TPA)AuX (TPA = 1,3,5-triaza-7-phosphaadamantane, X = halide) compounds that show a close Au−Au interaction in the solid state.[12]

It is, thus, likely that the donor emission in the rare earth gold dicyanides could also be correlated with the aurophilic Au−Au interaction observed in these systems. An increase in the Au−Au separation with a temperature increase has been established in the rare earth−gold dicyanide systems[7] where X-ray crystallographic studies indicate that with a temperature increase the Au−Au separation increases.[7] In the structure of the [EuAg] system that was reported recently[13] a weak M−M interaction has also been observed with a Ag−Ag separation of 3.344 Å. A strong interaction between the CN^- groups and the europium ion is evident in the structure. In addition to six CN^- groups, there are three water molecules in the coordination sphere of the Eu^{3+}. Moreover, a unit cell determination conducted on other rare earth gold and silver dicyanides indicates that all of these compounds are isomorphs and, thus, a similar geometry is anticipated.

On the other hand, the low energy region of the [DyAu] luminescence spectrum consists of sharp but weak emission lines corresponding to the Dy^{3+} ion f−f transitions. It has been shown[5,14] that, compared to direct excitation, emission in rare earth ions is enhanced via energy transfer. However, the emission from the Dy^{3+} ion in the [DyAu] system is too weak (Figure 1) to suggest any appreciable amount of energy transfer. The inefficiency of the excited state energy transfer is postulated due to lack of a proper spectral overlap region between the donor $Au(CN)_2^-$ and the acceptor ion excited states.

Interestingly the PL properties of the [DyAg] compound are very different from the situation observed in the [DyAu] system and closely resemble those of the [EuAg] system that were reported recently.[7] The emission spectra of the [DyAg] system recorded at 10 and 60 K are shown in Figure 4. No bands assignable to the donor $Ag(CN)_2^-$ ion have been observed in the spectrum. Similar to the situation[7] in [EuAg], the sensitized emission of the Dy^{3+} ion is strong in the [DyAg] system. Moreover, the Dy^{3+} ion emission increases in intensity with a temperature increase and, thus, clearly suggests that energy transfer is efficient between the donor $Ag(CN)_2^-$ and the acceptor ions. The emission lines corresponding to f−f transitions of the Dy^{3+} ion are observed at 481, 573.7 and 663 nm.

2. Energy Transfer in [DyAu] vs [DyAg]. In the free Dy^{3+} ion, the lowest excited $^4F_{9/2}$ state is situated at ca. 476 nm (21 000 cm^{-1}) and the next higher acceptor states, $^4G_{11/2}$ and $^4M_{21/2}$, are at ca. 426 and 400 nm, respectively.[15] Comparison of the donor emission, centering at 425 nm (Figure 1) with the acceptor excited states clearly indicates that there is no spectral overlap region between the donor and the lowest excited ($^4F_{9/2}$) state of the Dy^{3+} ion. However, a spectral overlap between the $^4G_{11/2}$ level and the donor emission is likely at low temperature. With a temperature increase, the donor emitting state blue shifts (as discussed earlier) and the spectral overlap with the acceptor $^4G_{11/2}$ state is expected to diminish. Since the next higher acceptor excited state, $^4M_{21/2}$, is >1000 cm^{-1} above the $^4G_{11/2}$ level, no significant overlap between this level and the donor emission is anticipated. Thus, the lack of a spectral overlap region is suggested as the principal cause for the inefficiency of energy transfer between the $Au(CN)_2^-$ and Dy^{3+} ions at higher temperatures.

The lifetime data are also consistent with the inefficiency of the ET process between the donor $Au(CN)_2^-$ and the acceptor Dy^{3+} ions. It is known that efficient energy transfer is accompanied by a concomitant reduction, of several orders, of the donor lifetime. In $Pt(CN)_4^{2-}$ for example, energy transfer has been found to reduce the donor emission lifetime by a large magnitude.[6b,16,17] As shown in Figure 1, the donor $Au(CN)_2^-$ ion emission is relatively strong at low temperatures and, thus, we were able to measure its lifetime. The results are shown in Table 2. The donor emission in the [DyAu] complex has a lifetime of 0.21 μs at 78 K and 0.15 μs at room temperature. Similar values have been observed in other $Au(CN)_2^-$ compounds with cations incapable of accepting the emission energy. In [GdAu] the donor emission has a lifetime of 0.17 μs at 78 K. The emission bands in $TlAu(CN)_2$ and $KAu(CN)_2$ also show a lifetime of ca. 0.2 μs.[8,11] The lack of any significant reduction in the donor lifetime of the [DyAu] system (when compared to the above compounds) clearly indicates that energy transfer has a smaller contribution to the Dy^{3+} ion emission.

Interestingly, the situation in the [DyAg] system is very different. The donor $Ag(CN)_2^-$ emission is totally quenched at all temperatures and the acceptor, Dy^{3+} ion, shows a strong emission. When measured under identical instrumental conditions, at 10 K, the intensity of the acceptor Dy^{3+} ion emission in [DyAg] shows more than a 10-fold increase over the [DyAu] system (Figure 5). Also, the intensity of the Dy^{3+} ion emission in the [DyAg] system increases as the temperature is increased between 10 and 78 K. A similar observation has been reported earlier[7] for the Eu^{3+} ion emission in the [EuAg] system. The increase in the Dy^{3+} ion emission intensity with a temperature increase clearly indicates an increased efficiency in the energy transfer process between the donor $Ag(CN)_2^-$ and the acceptor Dy^{3+} ions.

Energy transfer through either a Förster type or exchange mechanism requires a spectral overlap region between the donor and acceptor excited states.[18] Since the donor $Ag(CN)_2^-$ emission has not been observed in the [DyAg] system, we have undertaken PL studies on other $Ag(CN)_2^-$ complexes with cations incapable of accepting the emission energy. In this regard, the PL studies conducted on the [GdAg] and $TlAg(CN)_2$ systems were informative about the energy position of the donor $Ag(CN)_2^-$ excited states. While the full PL studies on these systems will be reported[19] elsewhere, both of these complexes show emission at 422 nm and the energy position does not show any significant blue shifting as the temperature is increased. The emission band has a relatively long lifetime of ca. 1.2 μs. The extended Hückel molecular orbital calculations performed on $[Ag(CN)_2^-]_2$ dimers also indicate that there is only a minor destabilization of the HOMO orbital when the Ag−Ag separa-

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tion is reduced.[19] In addition, it was recently reported[20] that the HOMO−LUMO gap in silver clusters depends more on the number of silver atoms interacting at a particular site than the individual Ag−Ag distances. Clearly, the PL properties of the donor $Ag(CN)_2^-$ and $Au(CN)_2^-$ systems are different in that the emission energy in the latter is sensitive to the Au−Au separation and blue shifts significantly as the separation increases. The $Ag(CN)_2^-$ system, on the other hand, is insensitive to the metal−metal separation.

It is, thus, reasonable to assume that the donor emitting state in the [DyAg] also centers at 422 nm and shifts insignificantly as the temperature is increased. This makes the donor state in a perfect match with the Dy^{3+}, $^4G_{11/2}$, ion excited state. In addition, due to the expected insignificant blue shifting (as discussed above) of the donor emission energy, there exists a spectral overlap region at all temperatures in this system. The efficiency of energy transfer clearly increases with a temperature increase. The fact that energy transfer occurs only for selected acceptor states shows that the symmetry and overlap requirements for these layered systems obey certain selection rules.

Moreover, the lifetime studies conducted in our laboratories have indicated[7,19] that the $Ag(CN)_2^-$ compounds show a longer lifetime than that of the $Au(CN)_2^-$ compounds. With an exchange mechanism, the efficiency of energy transfer, defined as number of transfers per donor lifetime, is expected to increase when the donor emission lifetime is longer.[18] Since energy transfer in the $Ag(CN)_2^-$ system, which shows a longer lifetime (ca. 1.2 μs), is more efficient than that in the $Au(CN)_2^-$ system longer which shows a shorter lifetime (ca. 0.21 μs), it is likely that the dominant mechanism in these systems is exchange rather than a Förster type dipole mechanism. The exchange mechanism originates from the overlap of the electron clouds of the donor and acceptor ions. As established from X-ray crystallographic work[7,13,19] this interaction takes place through the N atoms of the CN^- ligands on the donor anion and the acceptor Dy^{3+} ion.

3. Raman Studies. The spectrum for the [DyAu] complex covering the region 100−2200 cm^{-1} is compared with the spectra of the [EuAu] and [GdAu] complexes in Figure 6. The bands for [DyAu] are assigned in Table 3 by assuming $D_{\infty h}$ symmetry for the $Au(CN)_2^-$ ion. Raman bands at 156, 190 and 352 cm^{-1} are clearly visible in the low temperature spectra of both the [EuAu] and [DyAu] systems. In the [EuAu] compound, these low energy bands show a resonance enhancement when the excitation is changed from the 456 to 488 nm line. However, the bands in the [DyAu] system show no resonance enhancement upon changing the excitation line. The 156 cm^{-1} band is assigned as a lattice mode according to previous assignments on similar compounds.[21] The $KAu(CN)_2$, $CsAu(CN)_2$ and $LiAu(CN)_2$ compounds all show a band at 152 cm^{-1} which has been assigned to a lattice mode.[21] Similarly, the 190 cm^{-1} band is assigned to a C−Au−C bending mode. The structure observed in the luminescence spectrum of the donor $Au(CN)_2^-$ ion of the [DyAu] system appears to have a vibronic origin and is assigned to the ν_2 (Au−C stretching) vibrational mode coupling with other Raman active modes as shown in Table 1.

Conclusions

In this study we have shown that energy transfer in the [DyAu] system is inefficient due to the lack of a donor−acceptor spectral overlap region. The donor $Au(CN)_2^-$ in the [DyAu] complex shows a strong and structured luminescence at low temperature. In the [GdAu] system, where the lowest excited state of the acceptor ion is situated at a much higher energy position than the donor level, no energy transfer is evident and only emission from the donor ion has been observed. Interestingly, efficient energy transfer has been observed from the donor $Ag(CN)_2^-$ ion to the Dy^{3+} ion in the [DyAg] complex. It is surprising to note that the silver dicyanide compounds characteristically show an efficient energy transfer and an increased emission intensity at higher temperatures. The $^4G_{11/2}$ excited state of the Dy^{3+} ion is suggested as the principal acceptor state. An exchange mechanism originating from the overlap of the electron clouds of the donor and acceptor ions through the N atoms of the CN^- ligands, is suggested as the dominant mechanism for the energy transfer process. From the resonance Raman studies, the structure in the luminescence spectrum of the [DyAu] compound has been assigned to the Au−C symmetric stretching mode and other Raman active modes.

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