Photoluminescence and Molecular Structure of Tetrakis(*N*,*N*-dimethyldithiocarbamato)europate(III)

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Photoexcitation of the sulfur(S)-to-europium(Eu) charge-transfer bands in $Na[Eu(S_2CNMe_2)_4]\cdot3.5H_2O$ at the low temperature (< 100 K) leads to the $^5D_0\rightarrow{}^7F_J$ (J=0-4) luminescence of Eu^{3+} as a result of the energy transfer to the $^5D_0$ state. The luminescence and excitation spectra reveal the dithiocarbamato-ligand phonon-assisted electronic transition involved in the small energy gap (~1800 cm^{-1}) between the $^5D_1$ and $^5D_0$ levels. The luminescence lifetime (0.11 ± 0.01 ms at 4.2 K) decreases with increasing temperature, probably due to the thermal crossover relaxation from $^5D_0$ to the S→Eu charge transfer states.

Although thiolanthanate complexes may be regarded as a discrete model for the luminescent site in lanthanide(Ln)-doped metal sulfide phosphors such as ZnS, CaS, and SrS:Ln, there are only a few reports on the structure of the complexes because of the chemical unstability derived from the mismatched bonding between the hard-charactered Ln and soft-charactered S atoms. A few compounds $[Ln(S_2CX)_4]^-$ (X = NR_2, OR) and $[Ln(S_2PX_2)_4]^-$ (X = R, OR) are stable in air.[1-3] Based on the crystal structures of $Na[La(S_2CNEt_2)_4]$ and $[Ph_4P][Pr(S_2PMe_2)_4]$, it is concluded that eight S atoms at LnS_8 site of these complexes are approximately positioned on two half EuS_4 circles with rectangular crossing.[4,5] The electronic spectra of tetrakis(*N*,*N*-diethyldithiocarbamato)-europate(III) and -ytterbate(III) ($[Eu(S_2CNEt_2)_4]^-$ and $[Yb(S_2CNEt_2)_4]^-$) showed the absorption due to the S→Ln ligand to metal charge transfer (LMCT) transition in the visible wavelength region.[4,6] We found recently that the photoexcitation of the S→Eu LMCT bands of tetrakis(*NN*-dimethyldithiocarbamato)europate(III) led to the luminescence from Eu^{3+} at low temperature. The photoluminescence and crystal structure of $Na[Eu(S_2CNMe_2)_4]\cdot3.5H_2O$ in this paper reveal the phonon-assisted relaxation of the excited energy in the lanthanide sulfide lattice.

$Na[Eu(S_2CNMe_2)_4]\cdot3.5H_2O$ was precipitated as orange crystals[7] immediately by addition of the aqueous solution of $Eu(NO_3)_3\cdot6H_2O$ (0.20 g; 0.45 mmol in 2 ml water) to the solution containing $Na[S_2CNMe_2]\cdot2H_2O$ (5 g; 28 mmol in 8 ml water) with stirring. The crystal structure of $Na[Eu(S_2CNMe_2)_4]\cdot3.5H_2O$ was determined based on X-ray diffraction data.[8] Two crystallographically independent complexes of $[Eu(S_2CNMe_2)_4]^-$ are slightly different: the S-Eu-S bond angle is different within 8° between two complexes. As shown in Figure 1, the EuS_8 site in the $[Eu(S_2CNMe_2)_4]^-$ complex provides approximately a dodecahedral configuration:[9] two least square planes containing Eu and four S atoms make a dihedral angle of 89° as denoted by broken curves. The average Eu-S bond length (2.87(3) Å) is about 0.1 Å shorter than that of La-S bond (2.98(4) Å) for $Na[La(S_2CNEt_2)_4]$, due to the lanthanide contraction.[4] As shown in Figure 1, the S-Eu-S bond angles on the EuS_4 half circle plane can be classified into two types, θ_1 and θ_2 with mean values of 61.6(7)° and 73(2)°, respectively. The former angle is smaller than that (68.0(8)°) for $[Ph_4P][Pr(S_2PMe_2)_4]$ due to short S···S distance (2.94(3) Å) for the S_2C- group compared with that (3.33(2) Å) for the S_2P- group. The latter angle is close to that (72(3)°) for $[Ph_4P][Pr(S_2PMe_2)_4]$.[5]

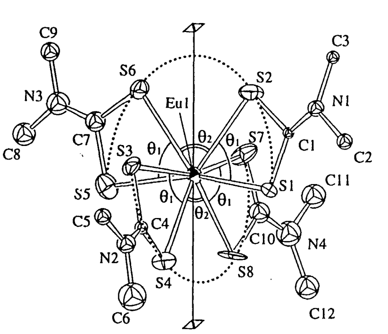

Figure 1. The structure of one of the two crystallographically independent $[Eu(S_2CNMe_2)_4]^-$ anions with approximate D_{2d}-$\bar{4}2m$ symmetry.

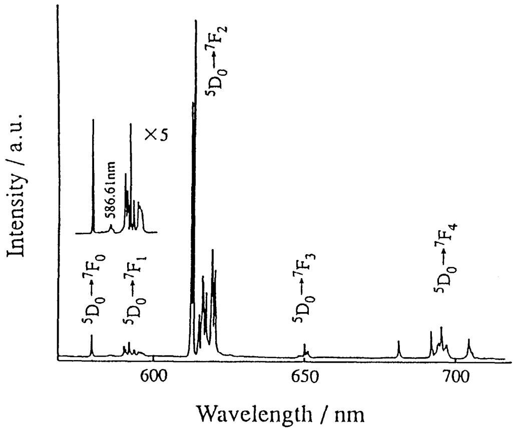

Figure 2. High-resolution photoluminescence spectrum of $Na[Eu(S_2CNMe_2)_4]\cdot3.5H_2O$ under the 490-nm light excitation of S→Eu LMCT bands at 4.2K.

The light source of the photoluminescence measurements is a 500 W xenon lamp (Ushio UI-501C) or a dye laser (LAS OG505 with coumarin 480) pumped by a excimer laser (Questek 2320 XeCl, 308 nm). The high-resolution photoluminescence spectrum (with ±2 cm^{-1} accuracy) was measured by a use of a Spex 750M spectrometer. The excitation spectrum was corrected to a constant photon flux at each wavelength.

Figure 2 shows the photoluminescence spectrum observed under the 490-nm light excitation of the S→Eu LMCT band at 4.2K. The spectrum consists of the $^5D_0\rightarrow{}^7F_J$ (J=0-4) transition lines of Eu^{3+}. The presence of the two distinct Eu^{3+} sites is respect by the feature of the $^5D_0\rightarrow{}^7F_{1,2}$ transitions which indicates large amount of lines. The lifetime of the luminescence is slightly different between the two sites; the $^5D_0\rightarrow{}^7F_2$ lifetimes at 4.2 K measured at 612.83 and 613.36 nm are 0.11 ± 0.01 and 0.09 ± 0.01 ms, respectively. It is noted that a weak line due to the vibronic sideband is observed at 586.61 nm around the $^5D_0 \rightarrow {}^7F_0$ transition line at 580.78 nm. The possibility that the line at 586.61 nm is assigned to the $^5D_1 \rightarrow {}^7F_3$ transition can be excluded, because of no observation of the $^5D_1 \rightarrow {}^7F_J$ (J=0-2) transition line in the region 520-560 nm. Figure 3 shows the absorption spectrum in acetonitrile solution (a), the diffuse reflection spectrum (b), and the normalized excitation spectrum obtained by monitoring the 612.83-nm emission (c) for $Na[Eu(S_2CNMe_2)_4]\cdot 3.5H_2O$. The excitation spectra for the two Eu^{3+} sites are similar. The strong absorption below 400 nm (Figure 3 (a)) due to the pπ→pπ* transitions within the $[S_2CNMe_2]^-$ ligand is absent in the excitation spectrum (Figure 3 (c)). This indicates that the energy transfer from the pπ* states of both $-CS_2-$ and -NCS- groups to the $^5D_0$ state does not occur. On the other hand, the S→Eu LMCT to $^5D_0$ states occurs efficiently, as shown in Figure 3 (c) where the broad S→Eu LMCT bands (at 350-550 nm) consist of at least three peaks at about 490 nm (with a strong intensity), about 420 nm (with a shoulder), and about 380 nm (with a weak intensity). The intensity ratio of these three S→Eu LMCT bands was almost unchanged at 4.2-100 K. The absorption spectrum of $[Eu(S_2CNMe_2)_4]^-$ in acetonitrile shows that the S→Eu LMCT peak at 490 nm is obscured due to the strong absorption at 420 nm.[4] A number of lines (at 530-580 nm) in Figure 3 (c) can be associated with the phonon emission during the relaxation of $^5D_1$ to the $^5D_0$ states within a small energy gap (~1800 cm^{-1}).[10] Table 1 lists their energies (ν_{exc}) and energy differences ($\Delta\nu_{exc}$) from the strongest intensity line of the $^7F_0 \rightarrow {}^5D_0$ transition at 580.8 nm (= 17218 ± 5 cm^{-1}). $\Delta\nu_{exc}$ values (for the lines higher than 17638 ± 5 cm^{-1}) are in good agreement with the vibronic-mode energies (ν_{IR}) for the dimethyldithiocarbamato ligand as indicated by the IR spectrum of the complex. Therefore, the lines at 530-580 nm are attributed to the phonon-assisted electronic transition involving the phonon absorption from the dithiocarbamato ligand, to result in anti-Stokes processes. $\Delta\nu_{exc}$ = 170 cm^{-1} is nearly equal to the energy difference (171 cm^{-1}) between the $^5D_0 \rightarrow {}^7F_0$ (17218 ± 2 cm^{-1}) and the weak line at 586.61 nm (=17047 ± 2 cm^{-1}) in the emission spectrum (Figure 1). Such a symmetric relationship between the two spectra implies that the phonon of 170 cm^{-1} is also involved in the $^5D_1 \rightarrow {}^5D_0$ relaxation process and that $\Delta\nu_{exc}$ = 342 cm^{-1} includes two phonons of the 170 cm^{-1} vibronic mode.

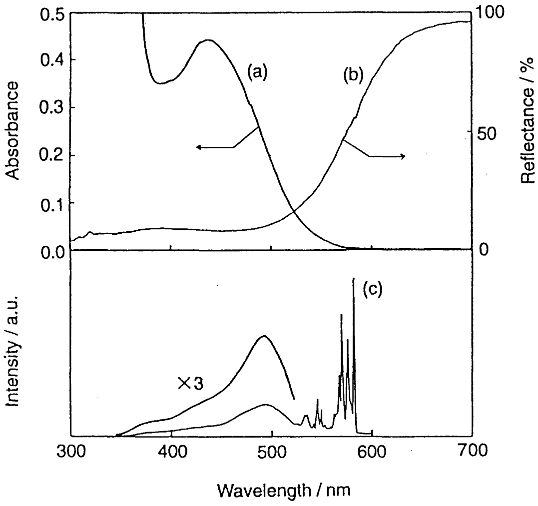

Figure 3. Absorption (a) (in 1mM acetonitrile solution at room temperature), diffuse reflection (b) (at room temperature), and excitation (c) (at 4.2K) spectra for $Na[Eu(S_2CNMe_2)_4]\cdot 3.5H_2O$.

Table 1. The energies of the excitation and IR peaks of $Na[Eu(S_2CNMe_2)_4]\cdot 3.5H_2O$

ν_{exc}/cm^{-1} [a]	$\Delta\nu_{exc}/cm^{-1}$ [b]	ν_{IR}/cm^{-1}
17218	0	
17388	170	
17560	342	
17638	420	429m
17784	566	574m
18196	978	969s
		990s
		1046m
18343	1125	1129s
18468	1250	1249s
18604	1386	1379s
18657	1439	1452sh
18723	1505	1499s

a The accuracy for the ν_{exc} values is within ± 5 cm^{-1} of each value.

b $\Delta\nu_{exc} = \nu_{exc} - \nu_{exc}(^7F_0 \rightarrow {}^5D_0)$. $\nu_{exc}(^7F_0 \rightarrow {}^5D_0)$ is the energy of $^7F_0 \rightarrow {}^5D_0$ transition (= 17218 ± 5 cm^{-1}).

With increasing temperature, the $^5D_0$ lifetime (0.11 ± 0.01 ms at 4.2 K) under the excitation of the S→Eu LMCT band decreases gradually at 4.2-40 K and steeply at more than 50 K. This is in strong contrast with the case of the polyoxometaloeuropates consisting Eu-O bonds, which exhibited little temperature dependence of the $^5D_0$ lifetime.[11,12] In conjunction with the fact that the S→Eu LMCT states of the present complex are positioned at much lower levels (~20500, ~24000, ~26000 cm^{-1}) compared with the O→Eu LMCT band (~32000 cm^{-1}),[13] the observed temperature dependence of the $^5D_0$ lifetime suggests the thermal crossover of the $^5D_0$ state through the S→Eu LMCT levels. In addition, the low-lying absorption edge of the S→Eu LMCT bands is a main reason for the strong vibronic intensities in the dithiocarbamatoeuropate.[14]

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7 Elemental analysis: Found: C, 19.18; H, 4.29; N, 7.28%. Calcd for $C_{12}H_{31}N_4O_{3.5}NaS_8Eu$: C, 20.05; H, 4.35; N, 7.79%.

8 Crystal data: monoclinic, space group $P2_1/a$, a = 32.312(6), b = 10.524(2), c = 17.119(3) Å, β = 101.57(1)°, V = 5703(1) $Å^3$, Z = 8, D_c = 1.67 g/cm^3, R = 0.094, and R_w = 0.078 for 2118 independent data with $I > 3\sigma(I)$.

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