Inorg. Chem. **1998,** *37,* 2089−2095

Synthesis, Characterization, and Luminescence of Europium(III) Schiff Base Complexes[1a]

Ronald D. Archer* and Huiyong Chen[1b]

Department of Chemistry, University of Massachusetts,
Amherst, Massachusetts 01003-4510

Larry C. Thompson

Department of Chemistry, University of Minnesota,
Duluth, Minnesota 55812-2496

Received March 6, 1996

New europium(III) Schiff base compounds and polyelectrolytes luminesce with quantum yields consistent with the intramolecular energy transfer mechanism (ligand triplet state to ^5D_o europium(III) state) established for europium(III) β-diketone complexes. The emission spectra also clearly show that the two Eu(III) ions in Eu_2L_3 complexes, where L is a tetradentate Schiff base ligand, are in different environments, that the Na[Eu(L)$_2$] complexes exhibit higher quantum yields than the corresponding Eu_2L_3 species, and that luminescence is negligible when the ligand triplet state lies below the ^5D_o state of europium(III).

The luminescence of rare-earth or lanthanide β-diketone coordination compounds,[2−10] supramolecules,[11−13] and polymers[14−17] has been widely investigated because of the strong line emission important for luminescent and laser materials.[18] However, less research has been reported on the luminescence of lanthanide Schiff base complexes[19−24] relative to the corresponding β-diketone analogues, even though many lanthanide Schiff base complexes have been prepared.[25−31]

Because of their special structures, lanthanide Schiff base complexes have some advantages for luminescence research. First, the Schiff base ligands can be tetradentate, which greatly stabilizes the complexes in solution relative to the bidentate β-diketone complexes. Second, the high extinction coefficients of many Schiff base ligands in the near-ultraviolet−visible range provides more effective energy transfer from the ligands to the coordinated lanthanide ion centers—the mechanism well documented for lanthanide β-diketone complexes.[9,32−34] Furthermore, by choosing the proper bis(tetradentate) Schiff base ligands, lanthanide Schiff base polymers[35,36] or polyelectrolytes[37] with 8-coordinate lanthanide ions in the polymer backbones *without* solvent coordination can be synthesized. Totally chelated species should have high luminescent intensities[38,39] and overcome the solvent-quenching problem that exists in polymers containing solvated lanthanide ions.[40,41]

We have prepared both monomeric M[Eu(L$_2$)] and dimeric Eu_2L_3 europium(III) Schiff base complexes including *N,N′*-disalicylidene-1,2-phenylenediamine (H_2dsp) and *N,N′*-disalicylideneethylenediamine (H_2salen) derivatives.

Luminescence in solution has been carefully investigated both at room temperature and at 77 K. The triplet-state energies of the complexes were determined by measurements with the corresponding Y(III) complexes, which have no accessible f-electron levels for energy transfer. The combined results show that energy transfer between the Schiff base ligands and the europium(III) ions is quite efficient and appears to follow the well-known intramolecular energy transfer mechanism exhibited by lanthanide β-diketone complexes.[9,32−34] The highest quantum yields were obtained for Eu_2(salen)$_3$ (60%) at room temperature and for Na[Eu(dsp)$_2$] (55%) at 77 K. Comparisons with previously reported europium polyelectrolytes[42] are also in agreement.

Experimental Section

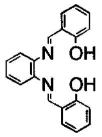
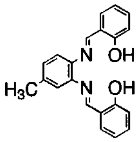
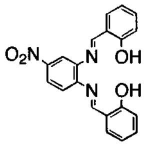
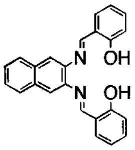
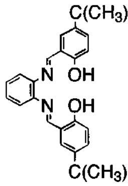
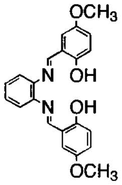
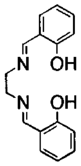
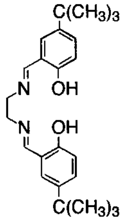
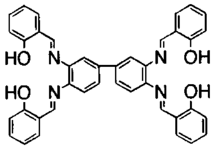
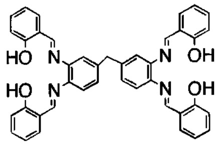
Reagents. Reagent grade and HPLC grade solvents and chemicals were used throughout. Prior to use, dimethyl sulfoxide (DMSO) was stirred for 2 days with barium oxide and fractionally distilled over calcium hydride under reduced pressure. *N*-Methylpyrrolidone (NMP) and dimethylformamide (DMF) were further purified following litera-

---

(1) (a) Taken in part from the Ph.D. Dissertation of H. Chen, University of Massachusetts, Amherst, MA, 1995. (b) Current affiliation: SRI, Menlo Park, CA.
(2) Remuiñán, M. J.; Román, H.; Alonso, M. T.; Rodríguez-Ubis, J. C. *J. Chem. Soc., Perkin Trans. 2* **1993**, *2*, 1099.
(3) Wang, S.; Luo, Q.; Zhou, X.; Zeng, Z. *Polyhedron* **1993**, *12*, 1939.
(4) Prodi, L.; Maestri, M.; Ziessel, R.; Balzani, V. *Inorg. Chem.* **1991**, *30*, 3798.
(5) Buono-Core, G. E.; Li, H. *Coord. Chem. Rev.* **1990**, *99*, 55.
(6) Horrocks, W. D., Jr. Albin, M. *Progr. Inorg. Chem.* **1984**, *31*, 1.
(7) Forsberg, J. H. In *Gmelin Handbook of Inorganic Chemistry*, 8th ed.; Moeller, T., Schleitzer-Rust, E., Eds.; Gmelin: New York, 1981; Vol. 39, Sc, Y, La−Lu, Part D3, pp 65−76.
(8) Sato, S.; Wada, M.; Seki, T. *Jpn. J. Appl. Phys.* **1968**, *7*, 7.
(9) Crosby, G. A. *Mol. Cryst.* **1966**, *1*, 37.
(10) Sinha, S. P. *J. Inorg. Nucl. Chem.* **1966**, *28*, 193.
(11) Sabbatini, N.; Guardigli, M. *Coord. Chem. Rev.* **1993**, *123*, 201.
(12) Balzani, V. *Tetrahedron* **1992**, *48*, 10443.
(13) Pietraszkiewicz, M.; Karpiuk, J.; Rout, A. K. *Pure Appl. Chem.* **1993**, *65*, 563.
(14) Taniguchi, H.; Tomisawa, H.; Kido, J. *Appl. Phys. Lttr.* **1995**, *66*, 1578.
(15) Carlos, L. D.; Assuncao, M.; Alcacer, L. *J. Mater. Res.* **1995,** *19*, 202.
(16) Nishide, H.; Cho, M. D.; Kaku, T.; Okamoto, Y. *Macromolecules* **1993**, *26*, 3798.
(17) Okamoto, Y. *J. Macromol. Sci.-Chem.* **1987**, *A24*, 455.
(18) Weber, M. J. *Rare Earth Lasers*; North-Holland Publishing Co.: Amsterdam, 1979; Vol. 4, pp 275−315.
(19) Nowicki, W.; Zachara, S. *Spectrosc. Lett.* **1992**, *25*, 593.
(20) Carugo, O. *Polyhedron* **1992**, *11*, 21.
(21) Guerriero, P. G.; Vigato, P. A.; Bunzli, J. G.; Moret, E. *J. Chem. Soc., Dalton Trans.* **1990**, 647−55.
(22) Kahwa, I. A.; Selbin, J.; O'Connor, C.; Foise, J. W.; McPherson, G. L. *Inorg. Chim. Acta* **1988**, *148*, 265.
(23) Calienni, J. J.; Brittain, H. G. *Inorg. Chim. Acta* **1986**, *116*, 163.
(24) Yang, X.; Brittain, H. G. *Inorg. Chim. Acta* **1982**, *59*, 261.
(25) Chen, H.; Archer, R. D. *Inorg. Chem.* **1994**, *33*, 5195.
(26) Dutta, R. L.; Das, B. R. *J. Sci. Ind. Res.* **1988**, *47*, 547.
(27) Kahwa, I. A.; Fronczek, F. R.; Selbin, J. *Inorg. Chim. Acta* **1987**, *126*, 227.
(28) Forsberg, J. H. In *Gmelin Handbook of Inorganic Chemistry,* 8th ed.; Moeller, T., Schleitzer-Rust, E., Eds.; Gmelin: New York, 1982; Vol. 39, Sc, Y, La−Lu, Part D2, p 25.
(29) Tajmir-Riahi, H. A. *Can. J. Spectrosc.* **1982**, *28*, 128.
(30) Afshar, S.; Bullock, J. *Inorg. Chim. Acta* **1980**, *38*, 145.
(31) Agarwal, S. K.; Tandon, J. P. *J. Inorg. Nucl. Chem.* **1975**, *37*, 949.
(32) Whan, R. E.; Crosby, G. A. *J. Mol. Spectroscopy* **1962**, *8*, 315.
(33) Crosby, G. A.; Whan, R. E.; Alire, R. M. *J. Chem. Phys.* **1961**, *34*, 743.
(34) Weissman, S. I. *J. Chem. Phys.* **1942**, *10*, 214.
(35) Chen, H.; Cronin, J. A.; Archer, R. D. *Macromolecules* **1994**, *27*, 2174.
(36) Chen, H.; Cronin, J. A.; Archer, R. D. *Inorg. Chem.* **1995**, *34*, 2306.
(37) Chen, H.; Archer, R. D. *Macromolecules* **1995**, *28*, 1609.
(38) Charles, R. C.; Riedel, E. P. *J. Inorg. Nucl. Chem.* **1966**, *28*, 3005.
(39) Brecher, C.; Samelson, H.; Lempicki, A. *J. Chem. Phys.* **1965**, *42*, 1081.
(40) Ueba, Y.; Zhu, K. J.; Banks, E.; Okamoto, Y. *J. Polym. Sci.: Polym. Chem. Ed.* **1982**, *20*, 1271.
(41) Ueba, Y.; Banks, E.; Okamoto, Y. *J. Appl. Polym. Sci.* **1980**, *25*, 2007.
(42) Chen, H.; Archer, R. D. *Macromolecules* **1996**, *29*, 1957.

S0020-1669(96)00244-3 CCC: $15.00

Table 1. Preparation of Schiff Bases

Schiff base[a]	structure	reference
N,N'-disalicylidene-1,2-phenylenediamine **(H_2dsp)**		35
N,N'-disalicylidene-3,4-diaminotoluene **(H_2dst)**		46
4-nitro-N,N'-disalicylidene-1,2-phenylenediamine **(H_2ndsp)**		47[b]
N,N'-disalicylidene-2,3-naphthalenediamine **(H_2dsn)**		50
N,N'-bis(5-*t*-butylsalicylidene-1,2-phenylenediamine **(H_2bsp)**		35
N,N'-bis(5-methoxysalicylidene)-1,2-phenylenediamine **(H_2mdsp)**		48
N,N'-disalicylideneethylenediamine **(H_2salen)**		49
N,N'-bis(5-*t*-butylsalicylidene)ethylenediamine **(H_2bsalen)**		30
N,N',N'',N'''-tetrasalicylidene-3,3'-diamino-benzidine **(H_4tsdb)**		35
N,N',N'',N'''-tetrasalicylidene-3,3'4,4'-tetraamino-diphenylmethane **(H_4tstm)**		36

[a] Synthesized by condensation of appropriate amine and hydroxyaldehyde. See reference for synthetic details. [b] Procedure modified. See Experimental Section

Table 2. Composition of Ln(III) Schiff Base Complexes[a]

compound	%C	%H	%N	%Ln	%DMSO
$Eu_2dsp_3 \cdot 0.7DMSO$	56.7 (56.7)	3.72 (3.56)	6.47 (6.48)	23.1 (23.4)	4.30 (4.20)
$Eu_2dst_3 \cdot 0.5DMSO$	57.2 (57.9)	3.61 (3.84)	6.38 (6.33)	22.7 (22.9)	2.85 (2.93)
$Eu_2dsn_3 \cdot 1.5DMSO$	59.2 (59.5)	3.50 (3.77)	5.59 (5.55)	20.3 (20.1)	7.62 (7.73)
$Eu_2mdsp_3 \cdot 1.6DMSO$	53.4 (53.5)	5.40 (5.42)	4.10 (4.10)	19.6 (19.6)	7.90 (8.05)
$Eu_2ndsp_3 \cdot 1.4DMSO$	49.9 (50.6)	2.79 (3.18)	8.50 (8.46)	20.2 (20.4)	7.44 (7.32)
$Eu_2bsp_3 \cdot 0.4DMSO$	62.8 (63.1)	5.85 (5.73)	5.23 (5.21)	18.7 (18.9)	2.09 (1.93)
$Eu_2salen_3 \cdot 0.3DMSO$	51.3 (51.8)	3.80 (3.89)	7.42 (7.46)	26.8 (27.0)	2.10 (2.08)
$Na[Eu(dsp)_2] \cdot 0.7DMSO$	57.5 (57.9)	3.61 (3.75)	6.58 (6.53)	17.5 (17.7)	6.27 (6.37)
$Na[Eu(dst)_2] \cdot 0.6DMSO$	59.3 (59.1)	3.78 (3.92)	6.40 (6.38)	17.3 (17.3)	5.60 (5.33)
$Y_2bsp_3 \cdot 0.7DMSO$	68.2 (67.8)	6.21 (6.24)	5.51 (5.55)	12.1 (11.8)	3.65 (3.61)

	$Y_2dsp_3 \cdot 0.6DMSO$	$Y_2dst_3 \cdot 0.5DMSO$	$Y_2dsn_3 \cdot 0.6DMSO$	$Y_2salen_3 \cdot 0.4DMSO$	$Y_2bsalen_3 \cdot 0.5DMSO$
%Y	15.0 (15.2)	14.8 (14.8)	13.8 (13.5)	15.4 (15.5)	13.3 (13.1)
%DMSO	4.20 (4.01)	3.25 (3.50)	4.16 (4.06)	3.25 (3.10)	2.35 (2.87)

	$Eu_2bsalen_3 \cdot 0.4DMSO$	$Y_2mdsp_3 \cdot 0.8DMSO$	$Y_2ndsp_3 \cdot 0.4DMSO$	$Na[Y(dsp)_2] \cdot 0.6DMSO$	$Na[Y(dst)_2] \cdot 0.6DMSO$
%Ln	20.5 (20.6)	13.4 (13.1)	14.0 (13.9)	11.3 (11.3)	10.7 (10.9)
%DMSO	2.30 (2.11)	4.60 (4.58)	2.59 (2.43)	5.80 (5.94)	5.60 (5.74)

[a] Theoretical value in parentheses.

ture procedures.[43] Salicylaldehyde (Hsal) was distilled under reduced pressure. *o*-Phenylenediamine (pd) was recrystallized from methanol. 3,3′-Diaminobenzidine (db) was purified just prior to use by using the method of Vogel and Marvel.[44,45] The aromatic amine compounds were kept under an inert atmosphere of N_2 or Ar to avoid oxidation of the amine groups.

Schiff Bases. All the tetradentate Schiff base ligands, except H_2ndsp, were prepared according to previously published procedures (Table 1) involving Schiff base condensations between diamines and hydroxyaldehydes in absolute ethanol or methanol and were purified by recrystallization from a dichloromethane/hexane mixed solvent through the partial evaporation of the more volatile dichloromethane.

H_2ndsp was prepared by dissolving 2.80 g (18.3 mmol) of 4-nitro-*o*-phenylenediamine in 20 mL of salicylaldehyde (serving as both solvent and reactant) at 80 °C under N_2. The resulting solution was kept under these conditions for 5 h. Some yellow precipitate resulted, and more was obtained by the addition of 100 mL of methanol after stirring for 30 min. The product was filtered, washed with methanol, and dried at 100 °C in vacuo. Yield: 5.60 g, 85%. Purification was accomplished by recrystallization from dichloromethane/hexane mixed solvent as above. Melting point: 218−219 °C (uncalibrated). Proton NMR in $CDCl_3$: phenolic O−H [12.47 (s, 0.74); 12.40 (s, 0.74)]; aldimine protons [8.72 (s, 1); 8.64 (s, 1)]; aromatic protons [8.3−8.1 (m, 2); 7.6−7.2 (m, 5); 7.1−6.6 (m, 4)].

DMSO Solvates of Europium(III) and Yttrium(III) Nitrates $Ln(NO_3)_3 \cdot 3DMSO$. The synthesis of the DMSO solvate from aquated yttrium(III) nitrate by recrystallization in DMSO was reported previously.[25] The europium(III) analogue was prepared similarly. Weight loss at about 250 °C confirmed the trisolvate formulation.

Europium(III) and Yttrium(III) [Ln] Dimeric Tetradentate Schiff Base [L] Complexes Ln_2L_3. The appropriate Schiff base (3.20 mmol) was dissolved in 15 mL of DMF by heating to 75 °C, and then 20 mL of methanol and 2 mL of triethylamine were added. With stirring, the resulting solution was slowly added to 2.13 mmol of $Eu(NO_3)_3 \cdot 3DMSO$ or $Y(NO_3)_3 \cdot 3DMSO$ in 30 mL of methanol. The reaction was continued for 1 h under reflux conditions. The yellow precipitate that occurred in each case was filtered, washed with methanol, and dried in vacuo at 100 °C. Yield: 80−95%.

Purification involved dissolution of the complexes in a minimal amount of hot DMF and reprecipitation with methanol and cooling. DMSO replaced DMF in the purification step for $Eu_2(bsalen)_3$, which does not dissolve in DMF.

Europium(III) and Yttrium(III) Monomeric Schiff Base Complexes $Na[Ln(dsp)_2]$ (Ln = Eu, Y) and $Na[Eu(dst)_2]$. The appropriate Eu_2L_3 or Y_2dsp_3 complex (0.642 mmol) was dissolved in 30 mL of DMSO at 75 °C containing 0.642 mmol of the appropriate H_2L (Schiff base). A solution of NaOH (1.54 mmol) in 10 mL of methanol was added. The resulting solution was allowed to react at 75 °C under N_2 for 2 h. Precipitates were obtained after 100 mL of methanol was added to each solution. Products were filtered, washed with methanol, and dried in vacuo at 100 °C. Yields: 80−90%.

Microanalyses were obtained for the europium complexes that had not been reported previously to confirm their composition (See Table 2). All yttrium complexes and the known europium complexes were confirmed by analysis of lanthanide element and DMSO content and by spectral characterization of the compounds. All of the compounds were characterized by FT-IR, UV−visible, and luminescence spectroscopy.

Lanthanide(III) Schiff Base Polyelectrolytes. $[NaEu(tsdb)]_n$, $[NaY(tsdb)]_n$, $[NaEu(tsdb)]_n$, $[NaY(tstm)]_n$, and $([NaY_xEu_{1-x}(tstm)]_n$, where H_4tsdb is *N*,*N*′,*N*″,*N*‴-tetrasalicylidene-3,3′-diaminobenzidine and H_4tstm is *N*,*N*′,*N*″,*N*‴-tetrasalicylidene-3,3′,4,4′-tetraaminobiphenylmethane, were prepared as previously reported.[37,42]

$Eu(hfa)_3 \cdot 2H_2O$. A literature method for preparing $Ln(acac)_3$ compounds was used.[51] Yield, 95%; melting point, 130−131 °C (125 °C, lit.[52]) Anal. Calcd for $EuC_{15}H_3F_{18}O_6 \cdot 2H_2O$: Eu, 18.8. Found: Eu, 18.7. When the product was further heated in vacuo at 100 °C, anhydrous $Eu(hfa)_3$ was obtained with a melting point of 202−204 °C (196 °C, lit.[52]). Anal. Calcd for $EuC_{15}H_3F_{18}O_6$: Eu, 19.7. Found: Eu, 19.7.

Analysis. C, H, and N were analyzed by standard microanalysis methods in the University of Massachusetts Microanalysis Laboratory. Ln^{3+} percentages were analyzed by EDTA titration by using Eriochrome Black T as the indicator and DMSO as the solvent. The percent of DMSO in the compounds was estimated from the weight loss obtained by heating 0.2000 g of the samples at 230 °C to a constant weight.

Characterization. Infrared spectra were obtained as KBr pellets with a Mattsen Cygnus 100 Fourier transform infrared (FT-IR) spectrometer.

Ultraviolet−visible spectra were obtained with a Perkin-Elmer model 3840 Lambda-array spectrophotometer coupled with an IBM personal computer using software supplied by Perkin-Elmer.

---

(43) Vogel, A. *Textbook of Practical Organic Chemistry,* 4th ed.; Longman Group Limited: New York, 1978; p 277.
(44) Vogel, H.; Marvel, C. S. *J. Polym. Sci.* **1963**, *A1*, 1531.
(45) Vogel, H.; Marvel, C. S. *J. Polym. Sci.* **1961**, *50*, 511.
(46) Wang, B. Ph.D. Dissertation, University of Massachusetts, Amherst, MA, 1989.
(47) Illingsworth, M. L.; Rheingold, A. L. *Inorg. Chem.* **1987**, *26*, 4312.
(48) Illingsworth, M. L. Ph.D. Thesis, University of Massachusetts, Amherst, MA, 1979.
(49) Dutt, N. K.; Nag, K. *J. Inorg. Nucl. Chem,* **1968**, *30*, 2493.
(50) Senier, A.; Shepheard, F. G.; Clarke, R. *J. Chem. Soc.* **1912**, *101*, 1955.
(51) Stites, J. G.; McCarty, C. N.; Quill, L. L. *J. Am. Chem. Soc.* **1948**, *70*, 3142.
(52) Halverson, F.; Brinen, J. S.; Leto, J. R. *J. Chem. Phys.* **1964**, *40*, 2790.

Thermal analyses were conducted with Perkin-Elmer TGS-2 and DSC-7 thermal analyzers under nitrogen gas with a heating rate of 20 °C/min. Both systems include Perkin-Elmer thermal analysis data stations and system 4 and 7 microprocessors, respectively.

Low-resolution luminescence and phosphorescence spectra were obtained with a Perkin-Elmer model MPF-44 spectrometer with an R100A recorder. All emission spectra were obtained as soon as possible after the solutions were prepared. Liquid N_2 cooling was used to obtain the luminescence and phosphorescence spectra at low temperature (77 K). A mixed solvent (4:3:3 DMF/methanol/ether by volumes) was used to obtain clear rigid glasses at 77 K as follows: First, the compounds were dissolved in hot DMF and cooled to room temperature. Next, methanol and ether were added and the solution was carefully cooled in a quartz NMR tube in liquid nitrogen to make a glass suitable for emission spectral evaluation. [***Caution:*** Rapid cooling in liquid nitrogen ***or*** rapid heating while part of the sample is still a glass can cause cracking of the quartz tube in which the rigid mixed-solvent sample is housed.] For solid-state luminescence measurements, a powdered compound was put in the tube and measured at 77 K. To minimize inner-filter effects, absorbance wavelengths were used that provided maximum emission, not the maximum absorbance wavelength.

Measurement slit values on the MPF-44 were as follows: emission/excitation slits = 2/2 nm for room-temperature investigations, and emission/excitation = 6/10 nm for 77 K studies.

High-resolution emission spectra (shown in Å) were obtained at 77 K on solid samples in 3 mm i.d. quartz tubes. The instrument consisted of a McPherson RS-10 spectrophotometer equipped with the model 606 fluorescence attachment, and excitation was obtained from a 100-W mercury lamp filtered through a GU-330 filter. The monochromator slits were set for a resolution of 1 Å.

The triplet-state energies of the europium complexes were estimated by obtaining their values with the corresponding yttrium(III) Schiff base complexes at 77 K. The instrument slits for these measurements were set at emission/excitation = 20/20 nm.

The quantum yields of the Eu(III) compounds were measured with $Eu(hfa)_3 \cdot 2H_2O$ as the standard. Its quantum yield is 43.6% in DMF at room temperature[53] and 39% in EPA (2:5:5 ethanol/isopentane/ether) solution at 77 K.[54] Eu(III) Schiff base complex concentrations of 1 mM were used in these experiments.

The quantum yields of the Eu(III) complexes were calculated by the equation:[55]

$$\frac{\Phi_x}{\Phi_{sta}} = \frac{I_x}{I_{sta}} \frac{A_{sta}}{A_x} \left[\frac{n_x}{n_{sta}}\right]^2 \qquad (1)$$

where Φ is the quantum yield, I is the intensity of the luminescence, A is the absorbance, and n is the refractive index of the sta (standard) and x (unknown) solutions. When eq 1 was used to calculate the quantum yields, the absorption values, A_{sta} and A_x, were based on room-temperature measurements. The quantum yield results are provided in Table 3.

Results and Discussion

Synthesis of H_2ndsp. The condensation reaction between 4-nitro-*o*-phenylenediamine and *two* salicylaldehydes in alcohol is very slow and gives a low yield[47] because of the nitro group deactivation and the very low solubility of the single salicylidene condensation intermediate in alcohol. Using salicylaldehyde as a solvent eliminates this problem and accelerates the reaction because the intermediate is soluble in salicylaldehyde.

Synthesis of Eu(III) Schiff Base Dimers and Monomers. Two kinds of lanthanide(III) Schiff base complexes with metal:ligand ratios of 2:3 and 1:2 can be obtained by controlling the relative amounts of the starting materials and the amount of alkaline base used, as has been noted for other $NaLn(dsp)_2$ and $Ln_2(dsp)_3$ species previously.[25] Only the $Na[Eu(dsp)_2]$ and $Na[Eu(dst)_2]$ monomers, which are representative of series that exhibit good luminescent properties, are detailed herein. Microanalysis gives satisfactory results as indicated in Table 2. The number of DMSO solvent molecules in the products (as determined by thermal gravimetric analysis) depends on the synthetic conditions. No completely desolvated products can be prepared for the $Ln_2(dsp)_3$ species because of their structural characteristics, as noted previously.[25]

Table 3. Triplet-State Energy *vs* Quantum Yields of Eu(III) Schiff base Complexes

compound	triplet-state energy (cm^{-1})[a]	quantum yield
$Eu_2(salen)_3$	20 410	0.26, 0.60[b]
$Eu_2(bsalen)_3$	19 610	0.17, 0.21[b]
Eu(III)	19 020 ($^5D_1$)[c]	
$Na[Eu(dsp)_2]$	17 510	0.55
$Eu_2(dsp)_3$	17 450	0.34
$Eu_2(bsp)_3$	17 300	0.23
$[NaEu(tstm)]_n$	172 70	0.44
$Na[Eu(dst)_2]$	17 270	0.39
$Eu_2(dst)_3$	17 270	0.23
Eu(III)	17 250 ($^5D_0$)[c]	
$Eu_2(ndsp)_3$	17 120	0.13
$Eu_2(dsn)_3$	17 010	0.03
$[NaEu(tsdb)]_n$	16 890	0.02
$Eu_2(mdsp)_3$	16 160	0.00

[a] The tripletstate energy obtained from the corresponding Y(III) Schiff base compounds at 77 K in DMF/methanol/ether solvent. [b] Quantum yield at room temperature in DMF. [c] Resonance levels of the Eu(III) ion.[33]

UV−visible and infrared spectra data for some typical compounds are provided as Supporting Information. Only the important peaks in the IR spectra that shift upon complexation are reported along with their assignments. The UV peaks of the Schiff base complexes exhibit high extinction coefficients ($\epsilon > 10\,000$ M^{-1} cm^{-1}), and their assignments are based on the results obtained for the $Ln_2(dsp)_3$ and $M[Ln(dsp)_2]$ complexes.[25]

Phosphorescence and Triplet-State Energy. The triplet-state energies of the Schiff base ligands of europium(III) have been estimated from the analogous yttrium(III) complexes by measuring the phosphorescence spectra of the yttrium species. The phosphorescence emission of yttrium complexes is strong with two or three clearly defined bands with the shortest-wavelength 0−0 transition phosphorescence band[56] being reported in Table 3. Because the yttrium ions have no accessible f-electron levels, ligand triplet-state phosphorescence is observed. Because the europium(III) and yttrium(III) ions are very similar in size and equal in charge, the effect of the metal ions on the ligands should also be similar. For similar reasons, complexes of La(III), Gd(III), Y(III), or Lu(III) have all been used in various papers to obtain the triplet-state energies,[33,57−59] but the La(III) and Lu(III) ions are somewhat larger and smaller, respectively. On the other hand, no phosphorescence ligand peak can be observed in the europium complexes with accessible energy-transfer possibilities because energy transfer occurs to the f-electron states of europium.

Luminescence. All of the europium Schiff base compounds except $Eu_2(mdsp)_3$ exhibit the characteristic luminescence spectrum of the Eu(III) ion at 77 K, and $Eu_2(salen)_3$ and Eu$_2$-

---

(53) Bhaumik, M. L.; Telk, C. L. *J. Opt. Soc. Am.* **1964**, *54*, 1211.
(54) Bhaumik, M. L. *J. Chem. Phys.* **1964**, *40*, 3711.
(55) Morisige, K. *J. Inorg. Nucl. Chem.* **1978**, *40*, 843.
(56) Sager, W. F.; Filipesen, N.; Serafin, F. A. *J. Phys. Chem.* **1965**, *69*, 1092.
(57) Brown, T. D.; Shepherd, T. M. *J. Chem. Soc., Dalton Trans.* **1973**, 336.
(58) Sato, S.; Wada, M. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1955.
(59) Brinen, J. S.; Halverson, F.; Leto, J. R. *J. Chem. Phys.* **1965**, *42*, 4213.

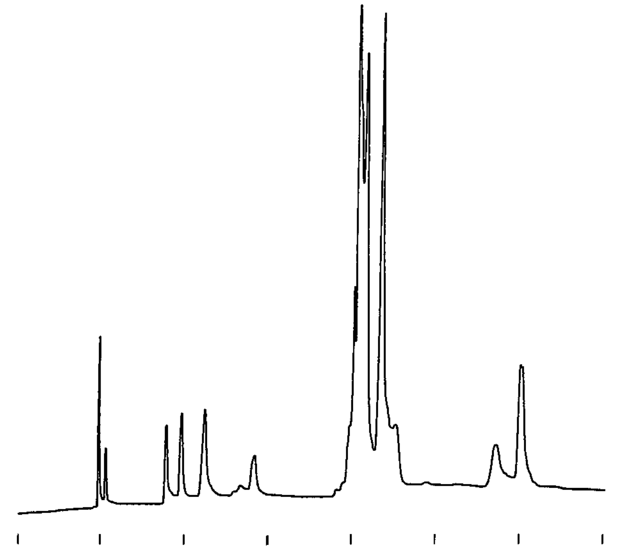


Figure 1. High-resolution emission spectrum of $Eu_2(dsp)_3$.

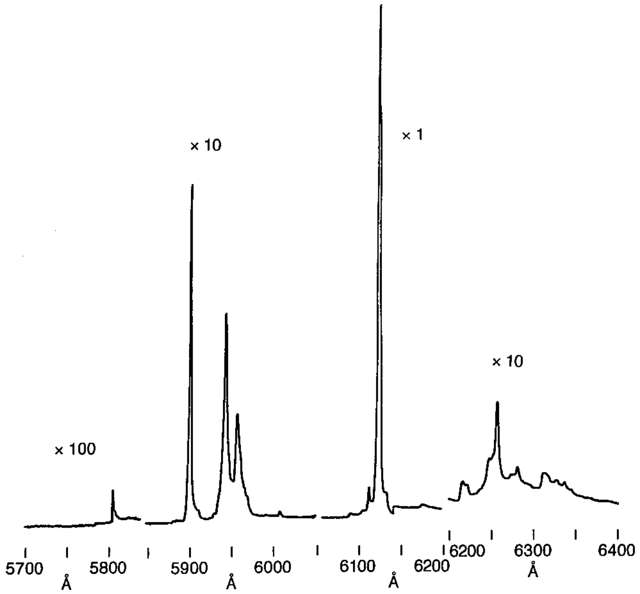
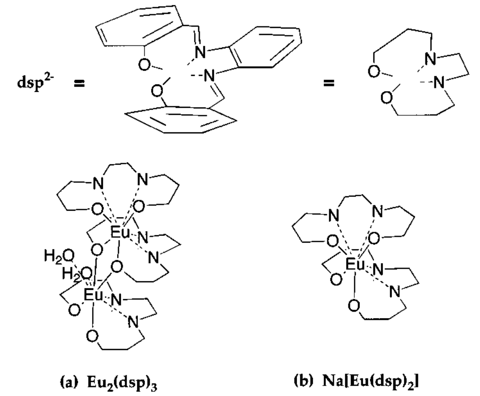


Figure 2. High-resolution emission spectrum of $Na[Eu(dsp)_2]$, with enhancedsensitivities as labeled, except for the 6050−6200 Å region.

$(bsalen)_3$ luminesce at room temperature as well. The solid-state compounds give the same luminescence spectra as those of the compounds in the DMF−methanol−ether glasses. Two different types of luminescence spectra were obtained for the europium Schiff base compounds. One is for the Eu_2L_3 complexes (Figure 1); the other is for the $Na[Eu(L)_2]$ complexes and the polyelectrolytes (Figure 2). The Eu_2L_3 emission spectrum has two peaks at 580 nm for the forbidden $^5D_0-^7F_0$ transition (Figure 1) {that can barely be observed for the $Na[Eu(L)_2]$ species when the sensititivity is increased 100-fold (Figure 2)}, peaks around 593 nm for $^5D_0-^7F_1$, peaks around 613 and 627 nm for $^5D_0-^7F_2$, peaks around 655 nm for $^5D_0-^7F_3$, and peaks around 680 and 703 for $^5D_0-^7F_4$.[60] No $^5D_1-^7F_J$ transition peaks around 530−550 nm were observed in any of the species. Note that all of the peaks of the Eu_2L_3 complexes are split into doublets (Figure 1) or even higher multiplets. The emission spectra of the $Na[Eu(L)_2]$ species consist of $^5D_0$ to



(a) $Eu_2(dsp)_3$ (b) $Na[Eu(dsp)_2]$

Figure 3. Postulated structures for the (a) dimeric and (b) monomeric europium Schiff base complexes.[25]

$^7F_1$, $^7F_2$, $^7F_3$, and $^7F_4$ transitions at similar energies with multiplet transitions consistent with low-symmetry complexes;[19,60] however, the number of peaks is consistently lower than for the Eu_2L_3 species.

The $^5D_0-^7F_0$ forbidden transition observed in the Eu_2L_3 complexes, but 2 orders of magnitude weaker in the $Na[Eu(L)_2]$ complexes, means a total lack of centrosymmetry in the Eu_2L_3 species and higher symmetry in the $Na[Eu(L)_2]$ ones, although the maximum true symmetry of the latter species is not higher than C_2, which explains why a weak peak is observed at high sensistivities. As noted previously,[25] the probable structure of the Eu_2L_3 complexes includes a bridging dsp^{2-} ligand whose oxygen atoms coordinate to both Eu(III) ions simultaneously, which provides a coordination number for Eu(III) of eight (including contributions from two solvent molecules) with a square (or Archimedian) antiprismatic arrangement around each Eu(III) ion. The structures of the $M[(Eu(L)_2]$ species are also anticipated to be square antiprismatic but more symmetrical (Figure 3). Furthermore, the doublets found for the Eu_2L_3 $^5D_0-^7F_0$ emissions at about 5800 Å (Figure 1) indicate that the two Eu(III) ions in Eu_2L_3 are in different environments, because in any single symmetry the $^5D_0-^7F_0$ transition must be a singlet. This gives strong support for a structure, such as that suggested for Ln_2L_3 in which the two Eu ions are unequal because of solvent coordination.[25] Furthermore, the intensity difference for the two $^5D_0-^7F_0$ transition peaks is consistent with two europium ions with unequal coordination. The luminescence spectra found in the solid state and glass state are virtually identical to the solution luminescence spectra for these compounds, which indicates that the solid compounds maintain virtually the same structures as in solution.

Quantum Yields and the Intramolecular Energy-Transfer Mechanism. Quantum yields were determined for the europium Schiff base complexes and polyelectrolytes both in DMF or DMSO solution at room temperature and in the mixed solvent glass at 77 K. The calculated quantum yields remain constant for concentrations between 0.15 and 1.0 mM. Although different paths have been suggested for the energy transfer from ligand excited states to the resonance states of Ln(III) in lanthanide β-diketone complexes,[9] the favorite mechanism (somewhat simplified) involves ligand excitation by the absorption of ultraviolet energy to an excited singlet (S_1) state, followed by energy migration via nonradiative intersystem crossing to a ligand triplet (T) state and energy transfer from the triplet state to a resonance state of a Ln(III) ion, from which the emission occurs. To luminesce, the lowest triplet-state energy level of the complex must be nearly equal to, or lie above, the resonance

---

(60) Carlos, L. D.; Videira, A. L. L. *Phys. Rev. B* **1994**, *49*, 11721.

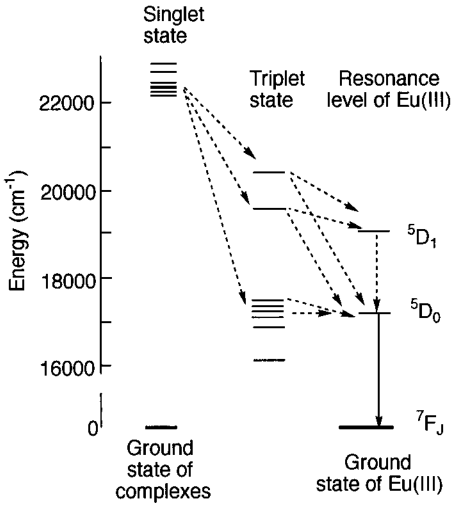


Figure 4. The probable mechanism of intramolecular energy transfer for the europium(III) Schiff base complexes. The triplet states for the various complexes are shown in the middle of the figure.

energy level of the lanthanide ion.[7,11,33] The results of our luminescence experiments with europium Schiff base complexes are consistent with this mechanism for intramolecular energy transfer. Strong evidence comes from the triplet-state energy of the complexes shown in Table 3. For those compounds whose triplet-state energy is lower than the resonance-state energy of Eu(III), very low quantum yields are obtained, which indicates that very little or no energy transfer takes place in these complexes. For those complexes with a triplet-state energy higher than the resonance state of Eu(III) ions, high quantum yields are obtained under suitable conditions. The reason that a low temperature is required for luminescence in the complexes containing dsp^{2-} and its derivatives comes from the fact that the triplet-state energies of these complexes are so close to the resonance state of the Eu(III) ions that the quenching of the emitting level via thermal excitation back to the lowest triplet state of the ligand takes place at room temperature.[58] The higher rates of collision between the complexes and the solvent molecules at room temperature provides further quenching.[62−64] When the triplet-state energy is as high as that in Eu$_2$salen$_3$ or Eu$_2$bsalen$_3$, strong room-temperature luminescence is observed because significant energy transfer back to the ligand is insignificant. Another possible temperature-dependent quenching mechanism involving ligand-to-metal charge-transfer (LMCT) excited states[11,65] seems unlikely for these complexes because no apparent LMCT band has been observed nor are they expected at the low energies operative in these systems. The fact that no peaks for the $^5D_1-^7F_J$ transitions were detected for the complexes where this is possible (Eu$_2$salen$_3$ and Eu$_2$bsalen$_3$) means that almost all of the energy is transferred to $^5D_0$. This energy transfer can go through the $^5D_1$ state[58] in Eu$_2$salen$_3$ or Eu$_2$bsalen$_3$, or go directly from the ligand triplet states. The preferred intramolecular energy transfer mechanism for the europium Schiff base complexes is shown schematically in Figure 4.

The 77 K results (Table 3) show that Na[EuL$_2$] species have higher quantum yields than the Eu$_2$L$_3$ ones. A comparison of the quantum yields at 613 nm for Eu$_2$(Schiff base)$_3$ and Na[Eu(Schiff base)$_2$] type species with ligand triplet-state energies of between 16 800 and 17 600 cm^{-1} is shown in Figure 5. The differences in their structures are apparently responsible. Eight-coordinated Na[Eu(L)$_2$] with two tetradentate ligands per metal ion transfers the energy more efficiently than Eu$_2$L$_3$, in which half of Eu^{III} ions attain 8-coordination through the use of solvent molecules. As observed by other workers previously,[38,41,66] higher coordination numbers from chelating ligands surrounding the Eu^{III} ions shields the ions from solvent nonradiative deactivation (which mainly takes place via coupling with the high-energy O−H vibrations) and play an important role in more efficient energy transfer. The possibility of Eu−Eu self-quenching in the dimers is also a potential contributor to the lower quantum yields for the dimers. The 8-coordinate square antiprismatic structure of Na[Eu(dsp)$_2$] is similar to the complexes formed by the cage-type supramolecules[12] and provides particularly good shielding of the lanthanide ion from solvent interactions that can lead to the nonradiative deactivation.

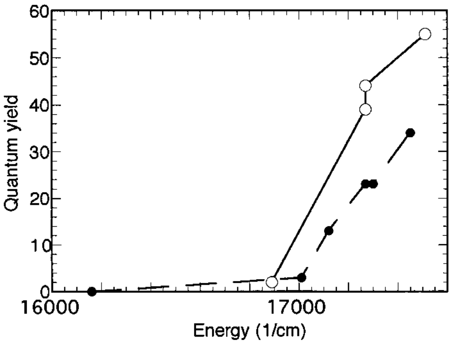


Figure 5. Quantum yields at 613 nm for Na[Eu(Schiff base)$_2$] (○) and Eu$_2$(Schiff base)$_3$ (●) species with ligand triplet-state energies of between 16 100 and 17 600 cm^{-1}.

The high quantum yield of Eu$_2$salen$_3$ at room temperature (0.60) relative to 77 K (0.26) could be caused by the solvent effects. Luminescence intensity usually increases with the polarity of the solvent,[64] except for alcoholic solutions.[67] In many cases the quantum yields of the Eu(III) complexes more than double with changes in solvent polarity.[53,58] The room-temperature emission spectra were obtained in DMF solutions, whereas the 77 K spectra were obtained in DMF/methanol/ether glasses. The much smaller quantum yield change for the analogous *tert*-butyl derivative (0.21/0.17) is logical on the basis of the greater shielding of the π-system provided by the butyl groups.

The europium(III) polyelectrolytes are 8-coordinate with two tetradentate ligands. This provides completely filled coordination spheres for the chelated Eu^{III} ions. The fully chelated coordination spheres shield the europium ions from solvent deactivation and should show improved luminescence over lanthanide polymers in which the lanthanide ion is on the side chain. Furthermore, the ligands have strong absorption in near-UV−visible spectral region and polyelectrolytes with suitable triplet-state energy can be synthesized. Whereas [NaEu(tsdb)]$_n$ has a low triplet-state energy, as noted above, placing the methylene spacer between the conjugated Schiff base entities raises the triplet state to 17 270 cm^{-1} and the quantum yield to 0.44. The high quantum yields found for some of the Eu^{III} complexes, either at room temperature or at 77 K, indicates that

---

(61) Li, W.; Mishima, T.; Adachi, G.; Shiokawa, J. *Inorg. Chim. Acta* **1986**, *121*, 97.

(62) Dawson, W. R.; Kropp, J. L.; Windsor, M. W. *J. Chem. Phys.* **1966**, *45*, 2410.

(63) Mikula, J. J.; Salomon, R. E. *J. Chem. Phys.* **1968**, *48*, 1077.

(64) Filipescu, N.; McAvoy, N. *J. Inorg. Nucl. Chem.* **1966**, *28*, 253.

(65) Blasse, G.; Buys, M.; Sabbatini, N. *Phys. Lett.* **1986**, *124*, 538.

(66) Okamoto, Y.; Ueba, Y.; Nagata, I.; Banks, E. *Macromolecules* **1981**, *14*, 807.

(67) Filipescu, N.; Mushrush, G. W.; Hurt, C. R. M., N. *Nature* **1966**, *211*, 960.

these 8-coordinate europium(III) Schiff base complexes have excellent intramolecular energy transfer ability, which provides the possibility of exploring new types of luminescent and laser materials.

Summary

(a) Schiff base complexes have excellent luminescence properties with high quantum yields because of strong absorption in the near-UV−visible region by the Schiff base ligands, the effective intramolecular energy transfer from the ligands to europium(III) ions, and the supramolecule-like structures of the complexes. These factors plus the stability of the $Eu(L)_2^-$ aromatic amine tetradentate Schiff base complexes in solution make such Schiff base complexes good candidates as luminescence and laser materials.

(b) Intramolecular energy transfer from ligands to ions appears to follow the well-established mechanism developed for lanthanide β-diketone complexes.

(c) The nonequivalence of the two lanthanide ions in the Ln_2L_3 species[25] is further confirmed by the doublet nature of the $^5D_o-^7F$ luminescence spectra of the europium complexes. These results coupled with the infrared, nuclear magnetic resonance, and molecular modeling evidence of the earlier paper[25] are quite compelling.

(d) The $Na[Ln(L)_2]$ complexes exhibit a stronger luminescence intensity than the Ln_2L_3 species because of the structural differences required for eight-coordination. That is, no solvent coordination occurs in the $Na[Ln(L)_2]$ complexes eliminating any direct solvent luminescent quenching.

Acknowledgment is made to an anonymous donor for europium chemicals before other support was available for this study, and acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for major financial support of this research. The constructive criticism provided by referees of this paper has also been quite helpful.

Supporting Information Available: Spectroscopic (UV−visible and infrared) data for some of the Schiff bases and their europium(III) complexes (1 page). Ordering information is given on any current masthead page.

IC960244D