

Synthesis and Characterization of Lanthanide(III) (La, Gd, Yb, Y) Disalicylidene-1,2-phenylenediamine (H₂dsp) Schiff-Base Complexes

Huiyong Chen and Ronald D. Archer*

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

Received June 3, 1994[®]

A new type of lanthanide(III) (La, Gd, Yb, or Y) disalicylidene-1,2-phenylenediamine (H₂dsp) Schiff-base complex with the formula M[Ln(dsp)₂] (where M⁺ is an alkali metal ion: Li⁺, Na⁺, K⁺, or Cs⁺) has been synthesized. Investigation of the known Ln₂dsp₃ complexes in dimethyl sulfoxide (DMSO) solution by ultraviolet–visible absorption and proton nuclear magnetic resonance spectroscopies shows that an equilibrium Ln₂dsp₃ ⇌ [Ln(dsp)]⁺ + [Ln(dsp)₂][−] exists in solution. The equilibrium is affected by the different size:charge ratios of the different lanthanide ions. Possible structures are suggested for M[Ln(dsp)₂] and Ln₂dsp₃ based on the results; e.g., Ln₂dsp₃ apparently has one dsp^{2−} acting as a bridging ligand with each of its oxygen atoms coordinated to two Ln³⁺ simultaneously. The new M[Ln(dsp)₂] complexes exhibit high thermal stability. The choices of both the alkali metal and the lanthanide ions strongly affect the thermal stability and the DMSO solubility of the M[Ln(dsp)₂] species. The [Ln(dsp)₂][−] ions have excellent stability in DMSO solution. Syntheses of new yttrium complexes with the formula M[Y(sal)₄] (where M = Li⁺ and Na⁺ and sal[−] = the anion of salicylaldehyde) are also reported.

Introduction

Numerous kinds of lanthanide (Ln) Schiff-base complexes have been prepared previously.^{1–5} Complexes formed by Ln³⁺ ions and tetradentate Schiff-base ligands with a −2 charge usually have the Ln₂L₃ formula.^{3,6} Most work has concentrated on lanthanide(III) complexes with the Schiff base H₂salen.^{3,7–11} Depending on the preparative conditions, several complexes with different compositions have been reported for Ln(III) H₂salen complexes. For example, Ln(H₂salen)₃·nH₂O, Ln(H₂salen)₃·X₃·nH₂O, Ln(H₂salen)₂·X₃·nH₂O, and Ln₂(H₂salen)₃·X₆·nH₂O (X[−] = a halogen ion) have been reported.⁷ Eu(Hsalen)(salen),⁹ Eu(salen)₂Hpip·0.5H₂O, and Eu(sal-1,3-pn)₂Hpip·2H₂O (where pip = piperidine)¹⁰ are the only previous examples of complexes in which a Ln³⁺ ion coordinates with two tetradentate ligands. Structurally characterized Eu(Hsalen)(salen) has a dodecahedral coordination geometry.⁹ Although complexes formed by Ln(III) with the Schiff base H₂dsp (*N,N'*-disalicylidene-1,2-phenylenediamine) with the composition Ln₂dsp₃ were reported as early as 1968,⁶ no structural characterization was provided, and no other type of Ln(III) complexes with the H₂dsp Schiff base has been reported.

Our interest in lanthanide(III) dsp^{2−} complexes was sparked by an idea to prepare coordination polymers formed by lanthanide(III) ions with Schiff-base ligands similar to the coordination polymer [Ce(tsdb)]_n¹² synthesized in our lab previously. Conditions for high yield synthesis of the M[Ln-

(dsp)₂] species, a monomer and precursor for coordination polymers, were considered essential prior to attempting the synthesis of the polymers. La, Gd, and Yb were chosen in our research to represent the whole series of lanthanide elements. Yttrium was also included because its similarities in size and hardness with the lanthanides and the easy characterization of its diamagnetic complexes (along with those of lanthanum) by proton nuclear magnetic resonance and is included as a lanthanide (Ln) in general discussions of the complexes.

Although some Ln(sal)₃ and [Ln(sal)₃L] adducts (L = neutral organic ligands such as pyridine) have been prepared before,^{13,14} and similar complexes with β-diketones, e.g., Na[Ln(acac)₄] (acac = acetylacetonate), have been known for decades,^{15,16} M[Ln(sal)₄] species have not been reported previously. Charles¹³ pointed out that it is difficult to prepare pure Ln(sal)₃ for the heavy lanthanide elements (from Gd to Lu) and that the products obtained were mixtures, probably of M(sal)₃ and Na(sal) with indefinite composition. Syntheses of new alkali tetrakis-(salicylaldehydato)yttrate(III) {M[Y(sal)₄] } complexes are now reported in this paper.

The new M[Ln(dsp)₂] complexes (where M represents an alkali metal ion) have been successfully prepared by several methods. Usually, the lanthanide(III) dsp^{2−} complexes have low solubility in organic solvents with low dielectric constants. However, they are soluble in polar organic solvents such as dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), and *N*-methylpyrrolidone (NMP). Newly prepared complexes also show this polar organic solvent solubility. Both the counter ion and the lanthanide ion itself play important roles in the solubility and thermal stability of the complex salts. The complexes have been characterized by Fourier-transform infrared (IR), ultraviolet–visible (UV–vis), and Fourier-transform nuclear magnetic resonance (NMR) spectroscopies, by conduc-

* Author to whom correspondence should be addressed.

[®] Abstract published in *Advance ACS Abstracts*, October 1, 1994.

- (1) Fenton, D. E.; Vigato, P. A. *Chem. Soc. Rev.* **1988**, *17*, 69.
- (2) Vigato, P. A.; Fenton, D. E. *Inorg. Chim. Acta* **1987**, *139*, 39.
- (3) Afshar, S.; Bullock, J. *Inorg. Chim. Acta* **1980**, *38*, 145.
- (4) Dutta, R. L.; Das, B. R. *J. Sci. & Ind. Res.* **1988**, *47*, 547.
- (5) Liu, G.; Na, C.; Li, B.; Mao, K. *Polyhedron* **1990**, *9*, 2019.
- (6) Dutt, N. K.; Nag, K. *J. Inorg. Nucl. Chem.* **1968**, *30*, 2493.
- (7) Bullock, J. I.; Tajmir-Riahi, H. A. *J. Chem. Soc., Dalton Trans.* **1978**, 36.
- (8) Dutt, N. K.; Nag, K. *J. Inorg. Nucl. Chem.* **1968**, *30*, 2779.
- (9) Huang, L.; C., H.; Xu, G. *Jiegou Huaxue (J. Struct. Chem.)* **1990**, *9*, 100.
- (10) Nowicki, W.; Zachara, S. *Spectroscopy Letters* **1992**, *25*, 593.
- (11) Huang, L.; Huang, C.; Xu, G. *Jiegou Huaxue (J. Struct. Chem.)* **1989**, *8*, 1.

- (12) Chen, H.; Cronin, J. A.; Archer, R. D. *Macromolecules* **1994**, *27*, 2174.
- (13) Charles, R. G. *J. Inorg. Nucl. Chem.* **1964**, *26*, 2298.
- (14) Rohatgi, K. K.; Sen Gupta, S. K. *J. Inorg. Nucl. Chem.* **1972**, *34*, 3061.
- (15) Melby, L. R.; Rose, N. J.; Abramson, E.; Caris, J. C. *J. Am. Chem. Soc.* **1964**, *86*, 5117.
- (16) Dutt, N. K.; Sur, S. *J. Inorg. Nucl. Chem.* **1971**, *33*, 115.

Table 1. Infrared and Proton Nuclear Magnetic Resonance Spectral Data for Compounds

assignt	infrared (cm ⁻¹) ^a				proton NMR (ppm) ^b			
	O—H	C=N or C=O	C=C	Ph—O ^c	O—H	aldimine	aromatic	
H ₂ dsp	3450	1613	1562	1277	12.4 (s) (2)	8.6 (s) (2)	7.5–7.1 (m) (8)	7.1–6.8 (m) (4)
Na ₂ dsp		1606	1531	1340		8.2 (s) (2)	7.1–6.7 (m) (8)	6.3–5.9 (m) (4)
Ce(dsp) ₂		1604	1538	1301		8.69 (s) (4)	7.3–7.0 (m) (16)	6.6 (t) (4) 5.9 (d) (4)
La ₂ dsp ₃ ·3H ₂ O	3450	1608	1545	1286		8.46 (s)	7.5–6.7 (m)	6.6–6.0 (m) ^d
			1534	1322		8.01 (s)		
				1345				
Y ₂ dsp ₃ ·2H ₂ O	3450	1611	1551	1287		8.63 (s)	7.8–6.9 (m)	6.8–5.4 (m) ^e
			1535	1329		8.33 (sh)		
				1348		8.23 (s)		
Na[La(dsp) ₂]		1608	1537	1310		8.01 (s) (4)	7.1–6.7 (m) (16)	6.4–6.1 (t) (8)
				1331				
Na[Y(dsp) ₂]		1612	1537	1324		8.3, 8.15 (s) (4)	7.3–6.7 (m) (16)	6.4–5.5 (m) (8)
				1344				
Na[Y(sal) ₄]		1629	1536	1333		9.8 (s) (4)	7.3–7.1 (m) (8)	6.5–6.2 (m) (8)

^a KBr pellets. ^b DMSO-*d*₆ solvent; s = singlet; d = doublet; t = triplet; m = multiplet; relative intensities in parentheses. ^c Ph—O = phenoxy C—O. ^d Figure 8. ^e Figure 9.

Table 2. Ultraviolet–Visible Spectral Data for Compounds (nm)^a

hexane	H ₂ dsp in different solvents			Na ₂ dsp	Na[Y(sal) ₄]	assignt
	CH ₃ Cl	DMSO				
		449 (2.05, sh)		444 (4.03)	384 (3.97)	n-π*
339 (4.24)	336 (4.27)	334 (4.25)		392 (4.00)		
				333 (4.06)	330 (3.93)	
270 (4.40)	274 (4.37)	276 (4.32)		289 (4.25)		π-π*
				273 (4.19, sh)	271 (4.04)	
	La	Gd	Y	Yb		assignt
Li[Ln(dsp) ₂]	383 (4.52)	390 (4.52)	385 (4.52)	379 (4.43)		n-π*
	333 (4.34)	333 (4.34)	333 (4.33)	333 (4.38)		
	291 (4.58)	291 (4.57)	291 (4.55)	291 (4.57)		π-π*
	273 (4.53, sh)	273 (4.52, sh)	273 (4.50, sh)	273 (4.43, sh)		
Ln ₂ dsp ₃	382 (4.64)	287 (4.71)	382 (4.67)	384 (4.59)		n-π*
	333 (4.49)	325 (4.52)	328 (4.53)	328 (4.50)		
	291 (4.68)	291 (4.74)	291 (4.74)	291 (4.72)		π-π*
	273 (4.63, sh)	273 (4.66, sh)	273 (4.67, sh)	273 (4.56, sh)		

^a log ε (molar extinction coefficient in M⁻¹ cm⁻¹) in parentheses; sh = shoulder; DMSO solvent for all lanthanide complexes and Na₂dsp.

tivity, and by thermal and elemental analyses. The UV–vis, NMR, and conductivity results show that an ionic equilibrium exists for the Ln₂dsp₃ complexes in DMSO solution. Results from infrared spectra strongly indicate that each oxygen atom of the bridging dsp²⁻ ligand in Ln₂dsp₃ coordinates to two Ln³⁺ ions at the same time. On the basis of these experimental results, possible structures are suggested for both the Ln₂dsp₃ and M[Ln(dsp)₂] complexes.

Experimental Section

Reagents. Reagent grade and HPLC grade solvents and chemicals were used throughout. Prior to use, dimethyl sulfoxide (DMSO) and *N,N*-dimethylformamide (DMF) were stirred for 2 days with barium oxide and fractionally distilled over calcium hydride under reduced pressure. Salicylaldehyde (Hsal) was distilled under reduced pressure. *o*-Phenylenediamine (pd) was recrystallized from methanol before use.

H₂dsp. This Schiff base was prepared by the condensation reaction between *o*-phenylenediamine and salicylaldehyde in methanol at room temperature as noted previously.^{17–19} Spectral characterization is shown in Tables 1 and 2.

Dimethyl Sulfoxide Complexes of Lanthanide and Yttrium Nitrates, Ln(NO₃)₃·*n*DMSO (Ln = La, *n* = 4; Ln = Gd, Yb, Y, *n* = 3). A modified literature method²⁰ was used to prepare these compounds. First 5 mmol of Ln(NO₃)₃·*n*H₂O for Ln = La or Y [or

2.5 mmol of Ln₂O₃ (99.9%) plus 15 mmol of HNO₃ for Ln = Gd or Yb] was dissolved in 30 mL of methanol, and then 15.5 mmol of DMSO (for Y or Yb) or 20.5 mmol of DMSO (for La or Gd) was added. The resulting solution was distilled by rotary evaporation under reduced pressure to dryness. The white product that was obtained was washed with ether, dried *in vacuo* at 100 °C for 1 day and put in a desiccator over P₂O₅ under reduced pressure for several days. Anal. Calcd for La(NO₃)₃·4DMSO: La, 21.8. Calcd for Ln(NO₃)₃·DMSO: Gd, 27.2; Y, 17.5; Yb, 29.2. Found: La, 21.7; Gd, 26.9; Y, 17.5; Yb, 29.4.

Lithium Tetrakis(salicylaldehydato)yttrate(III), Li[Y(sal)₄]. LiOH (1.28 g, 53.3 mmol) was added to a solution of Hsal (6.50 g, 53.3 mmol) in 40 mL of methanol and heated to reflux conditions. A solution of Y(NO₃)₃·5H₂O (4.86 g, 13.3 mmol) in 20 mL of methanol was added dropwise with concurrent magnetic stirring. A precipitate soon appeared. After 2 h under reflux, the solution was cooled and filtered. The pale yellow precipitate was washed with distilled water and methanol and dried *in vacuo* at 100 °C. Yield: 6.3 g, 82%. Anal. Calcd for Li[Y(C₇H₅O₂)₄]: Y, 15.3; C, 57.9; H, 3.45. Found: Y, 15.4; C, 57.2; H, 3.42.

Sodium Tetrakis(salicylaldehydato)yttrate(III), Na[Y(sal)₄]. Salicylaldehyde (1.20 g, 9.83 mmol) and 0.393 g (9.83 mmol) of NaOH were added to a solution of 1.00 g (2.74 mmol) of Y(NO₃)₃·5H₂O in 30 mL of methanol. The resulting solution was allowed to reflux for 2 h. The yellow precipitate which formed was filtered, washed with methanol, and dried *in vacuo* at 66 °C. The product was redissolved in 10 mL of Hsal at 90 °C. Fresh NaOCH₃ (0.192 g, 3.56 mmol) in 10 mL of methanol was added to the solution. A precipitate soon appeared. The solution was allowed to react at 70 °C for 1 h before another 10 mL of methanol was added, and the reaction was continued for another 30 min. The pale yellow product was filtered, washed thoroughly with methanol, and dried *in vacuo* at 100 °C. Yield: 1.3

(17) Archer, R. D.; Day, R. O.; Illingsworth, M. L. *Inorg. Chem.* **1979**, *18*, 2908.

(18) Pfeiffer, P.; Hesse, T.; Pfitzner, H. *J. Prakt. Chem.* **1937**, *149*, 217.

(19) Senior, A.; Shephard, F. G.; Clarke, R. *J. Chem. Soc.* **1912**, *101*, 1955.

(20) Ranalingam, S. K.; Soundararajan, S. *J. Inorg. Nucl. Chem.* **1967**, *29*, 1763.

Table 3. Results of Composition Analysis of Lanthanide Schiff-Base Complexes^a

complex	% C	% H	% N	% Ln	% DMSO or % H ₂ O
La ₂ dsp ₃ ·3H ₂ O	56.9 (56.7)	3.70 (3.77)	6.57 (6.59)	22.0 (21.8)	4.03 (4.24)
Gd ₂ dsp ₃ ·2H ₂ O	56.0 (55.7)	3.64 (3.56)	6.44 (6.60)	24.4 (24.3)	2.89 (2.78)
Y ₂ dsp ₃ ·2H ₂ O	62.0 (62.3)	3.87 (3.98)	7.37 (7.27)	15.6 (15.4)	3.03 (3.11)
Yb ₂ dsp ₃ ·2H ₂ O	54.2 (54.4)	3.47 (3.47)	6.22 (6.34)	26.1 (26.1)	2.54 (2.72)
Li[Y(dsp) ₂]	65.8 (66.3)	3.87 (3.87)	7.64 (7.73)	12.3 (12.3)	
Li[Gd(dsp) ₂]	60.0 (60.2)	3.59 (3.54)	7.00 (7.07)	19.6 (19.8)	
Li[Yb(dsp) ₂]	59.5 (59.4)	3.48 (3.47)	6.94 (6.93)	21.5 (21.4)	
Li[La(dsp) ₂] ₂ ·2.2DMSO	56.0 (56.3)	4.37 (4.36)	5.92 (5.92)	14.6 (14.7)	17.9 (18.1)
Na[La(dsp) ₂]	60.1 (60.7)	3.61 (3.54)	7.03 (7.09)	17.7 (17.6)	
Na[Y(dsp) ₂] ₂ ·DMSO	61.8 (61.6)	4.12 (4.15)	6.93 (6.85)	11.2 (10.9)	9.67 (9.53)
K[Y(dsp) ₂] ₂ ·0.4DMSO	62.2 (62.2)	3.84 (3.86)	7.20 (7.11)	11.1 (11.3)	4.12 (3.96)
Cs[Y(dsp) ₂] ₂ ·0.4DMSO	56.0 (55.6)	3.69 (3.86)	6.31 (6.35)	10.1 (10.1)	3.56 (3.66)
Na[Yb(dsp) ₂]				21.1 (21.0)	
Na[Gd(dsp) ₂] ₂ ·DMSO				17.7 (17.8)	8.98 (8.80)
K[La(dsp) ₂] ₂ ·0.3DMSO				16.7 (16.8)	2.79 (2.82)
K[Gd(dsp) ₂] ₂ ·0.5DMSO				18.4 (18.2)	4.63 (4.52)
K[Yb(dsp) ₂] ₂ ·0.4DMSO				20.1 (20.0)	4.72 (4.63)
Cs[La(dsp) ₂] ₂ ·0.4DMSO				15.1 (14.9)	3.50 (3.40)
Cs[Gd(dsp) ₂] ₂ ·0.3DMSO				16.9 (16.7)	2.79 (2.48)
Cs[Yb(dsp) ₂] ₂ ·0.4DMSO				17.7 (17.9)	3.15 (3.23)

^a Theoretical value in parentheses.

g, 80%. Anal. Calcd for NaY(C₇H₅O₂)₄: Y, 14.9; C, 56.4; H, 3.36. Found, Y, 14.8; C, 55.9; H, 3.37.

Na₂dsp. Fresh NaOCH₃ (0.376 g, 6.96 mmol) was added to 70 mL of dry benzene solution which contained 1.40 g (4.43 mmol) of H₂-dsp. The reaction proceeded under reflux and N₂ for about 12 h. The yellow precipitate was filtered, washed with benzene and ether, and dried *in vacuo* at 100 °C. Anal. Calcd for Na₂C₂₀H₁₄N₂O₂·0.25-NaOCH₃: C, 65.0; H, 3.95; N, 7.50; Found: C, 64.8; H, 3.95; N, 7.54.

Y(acac)₃·3H₂O. A literature method²¹ was used to prepare the 2,4-pentanedionate or acetylacetonate (acac⁻) of yttrium. Anal. Calcd for Y(C₇H₅O₂)₃·3H₂O: Y, 20.2. Found: Y, 20.3.

Ln₂dsp₃·nH₂O. H₂dsp (2.00 g, 6.33 mmol) was dissolved in 30 mL of DMF at 70 °C. A lanthanide nitrate, Ln(NO₃)₃·nH₂O (4.22 mmol) (Ln = La, Gd, Yb, Y), in 30 mL of methanol was added followed by 1.92 g (19.0 mmol) of triethylamine. The resulting solution was allowed to react at 70 °C for 2 h before 100 mL of methanol was added, and a yellow precipitate was obtained after heating the solution at 70 °C for an additional 30 min. The solution was cooled, and the product was filtered, washed with methanol, and dried *in vacuo* at 100 °C. Yield: 60–80%.

The compounds were purified through reprecipitation from DMF solutions by the addition of methanol. See Table 3 for analyses of these and the rest of the Schiff-base complexes which follow.

Y₂dsp₃·2H₂O was also synthesized by adding H₂dsp (1.07 g, 3.39 mmol) in 10 mL of benzene to 40 mL of a methanol solution containing 1.00 g (2.26 mmol) of Y(acac)₃·3H₂O. The resulting solution was heated under reflux conditions for 2 h. After the solution had cooled, the resulting yellow precipitate was filtered and washed with methanol. Purification was the same as above. Both methods provide the same product, which was confirmed by IR and NMR spectral characterization.

Li[Ln(dsp)₂]. Ln(NO₃)₃·3DMSO (1.58 mmol; Ln = Gd, Y, Yb) was added to a solution of H₂dsp (1.00 g, 3.16 mmol) in 30 mL of DMSO. The resulting solution was neutralized by adding 0.152 g (6.32 mmol) of LiOH and was stirred at 70 °C under N₂ for 3 h. A yellow precipitate appeared after about 1 h. After cooling, the product was filtered, washed with methanol and dried *in vacuo* at 100 °C. Yield: 85–95%.

Li[Y(dsp)₂]. *o*-Phenylenediamine (0.372 g, 3.44 mmol) was added to a solution of Li[Y(sal)₄] (1.00 g, 1.72 mmol) in 30 mL of DMSO. The resulting solution was allowed to react under N₂ at 70 °C for 4 h. A yellow precipitate, which appeared after about 1 h, was treated as above. Yield: 90%.

Li[La(dsp)₂]. La(NO₃)₃·4DMSO (1.01 g, 1.58 mmol) was added to a solution of 1.00 g of H₂dsp (3.16 mmol) in 30 mL of DMSO. The resulting solution was neutralized with 0.152 g (6.32 mmol) of LiOH, heated to 70 °C, and allowed to react at that temperature for 3 h. The red solution was filtered, and 30 mL of benzene was added to the

filtrate. The solution was allowed to stand at room temperature for 5 days during which time brown crystals were obtained. The crystals were washed with methanol, dried *in vacuo* at 65 °C, and recrystallized from DMSO by the addition of benzene.

Na[Ln(dsp)₂]. Ln(NO₃)₃·3DMSO (1.58 mmol; Ln = Y, Gd) was added to a solution of 1.00 g of H₂dsp (3.16 mmol) in 30 mL of DMSO. The resulting solution was neutralized with 0.303 g (7.58 mmol) of NaOH in 8 mL of methanol and stirred at 70 °C under N₂ for 3 h. Yellow crystals were obtained by adding 30 mL of methanol and allowing the solution to stand for 2 days at room temperature. Yield: 50–60%.

Na[Y(dsp)₂]. *o*-Phenylenediamine (0.362 g, 3.36 mmol) was added to a solution of 1.00 g (1.68 mmol) of Na[Y(sal)₄] in 30 mL of DMSO. The resulting solution was allowed to react at 70 °C under N₂ overnight. A yellow precipitate was obtained by adding 100 mL of methanol and keeping the solution at 70 °C for 30 min. Yield: 80%. Purification involved redissolving 0.500 g of the product in 15 mL of DMSO with 0.0270 g of NaOH and 4 mL of methanol. The resulting solution was filtered, and 45 mL of methanol was added to reprecipitate the product.

Na[Ln(dsp)₂]. Ln(NO₃)₃·nDMSO (1.34 mmol, for La or Yb) in 10 mL of methanol was added dropwise to a solution of Na₂dsp·0.25NaOCH₃ (1.00 g, 2.68 mmol) in 20 mL of methanol and heated under reflux conditions. A yellow precipitate soon appeared; however, the reaction was allowed to proceed under reflux for 2 h. The product was treated as above. Yield: >80%.

K[Ln(dsp)₂] and Cs[Ln(dsp)₂]. Ln(NO₃)₃·nDMSO (1.58 mmol; Ln = La, Gd, Yb, Y) was added to a solution of H₂dsp (1.00 g, 3.16 mmol) in 30 mL of DMSO. The resulting solution was neutralized with 7.58 mmol of KOH or CsOH in 8 mL of methanol and stirred at 70 °C under N₂ for 3 h. In the case of Cs salts, a yellow precipitate soon appeared. At the end of the reaction, 100 mL of methanol was added to the solution and the solution was kept at 70 °C for 30 min. The yellow product was filtered, washed with methanol, and dried *in vacuo* at 100 °C. Yield: 80–90%.

Ce(dsp)₂. The preparation of this complex was described previously.¹²

Analysis. C, H, and N were analyzed by standard microanalysis methods in the University of Massachusetts Microanalysis Laboratory. The Ln³⁺ ions were analyzed by EDTA titration by using Eriochrome Black T as an indicator and DMSO as the solvent. The percentage of H₂O or DMSO in the compounds was determined from the weight loss obtained by heating 0.2000 g of Ln₂dsp₃·nH₂O at 150 °C or of M[Ln(dsp)₂]₂·nDMSO at 230 °C to a constant weight.

Physical Measurements. Proton Fourier-transform nuclear magnetic resonance (NMR) measurements were taken with Varian models XL 80 and XL 200 using DMSO-*d*₆ as the solvent. To study the solution behavior of the lanthanide ions with the Schiff-base ligands, La(NO₃)₃·4DMSO [or Y(NO₃)₃·3DMSO] was gradually added to a solution of Na₂dsp (0.301 mmol) in 5 mL of DMSO-*d*₆ to provide Ln³⁺:

(21) Stites, J. G.; McCarty, C. N.; Quill, L. L. *J. Am. Chem. Soc.* **1948**, *70*, 3142.

dsp^{2-} mole ratios in solution of 1:4, 1:2, 2:3, and 1:1. NMR spectra were taken 10 min after the Ln^{3+} aliquot was added to the dsp^{2-} solution.

Infrared spectra were obtained as KBr pellets with a Mattson 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. In order to investigate the solution behavior of the Schiff-base complexes in DMSO with UV–vis absorption, a series of DMSO solutions were prepared with a constant Na_2dsp concentration of 7.15×10^{-4} M. The concentration of $\text{La}(\text{NO}_3)_3 \cdot 4\text{DMSO}$ [or $\text{Y}(\text{NO}_3)_3 \cdot 3\text{DMSO}$] was gradually increased in this series of solutions to provide a variable mole ratio of $\text{Ln}^{3+}/\text{dsp}^{2-}$. Absorption measurements at room temperature were made 5 min after the solutions were prepared. The wavelengths used for the measurements were 459 nm for the $\text{La}^{3+}/\text{dsp}^{2-}$ solutions and 471 nm for the $\text{Y}^{3+}/\text{dsp}^{2-}$ solutions.

Molar conductances were measured with a YSI Model 34 conductance/resistance meter in DMF at 30.0 ± 0.1 °C.

Thermal analyses were conducted with a Perkin-Elmer TGS-2 with a heating rate of 40 °C/min under N_2 or held at constant temperature as appropriate. The system includes Perkin-Elmer thermal analysis data stations and system 4 microprocessors.

CAChe (Tektronics) molecular modeling hardware and CAChe molecular modeling software (v. 3.5) were used to provide energy-minimized structures consistent with the spectral results and earlier single-crystal structures of related complexes.

Results and Discussion

$\text{Ln}(\text{NO}_3)_3 \cdot n\text{DMSO}$. $\text{Ln}(\text{NO}_3)_3 \cdot n\text{DMSO}$ is a good starting material for the preparation of $\text{M}[\text{Ln}(\text{dsp})_2]$ complexes. A method in the literature²⁰ was modified to include rotary evaporation to dryness (to avoid occasional failures to get the product by simply cooling the solution). For La, Y, and Yb, the same compositions were obtained as those reported previously.²⁰ The Gd complex analyzes as $\text{Gd}(\text{NO}_3)_3 \cdot 3\text{DMSO}$ after it is dried at 100 °C *in vacuo* overnight rather than the four molecules of DMSO obtained by room temperature drying over P_4O_{10} .²⁰

$\text{M}[\text{Y}(\text{sal})_4]$. $\text{LiY}(\text{sal})_4$ can be directly prepared by using stoichiometric amounts of the starting materials in methanol. $\text{Li}[\text{Y}(\text{sal})_4]$ can be easily prepared in methanol because of its extremely low solubility in this solvent. The special properties of the Li^+ ion resulting from its small radius distinguish it from the other alkali metal ions, as is discussed further below.

The direct method does not work for $[\text{NaY}(\text{sal})_4]$. Therefore, two steps were used in this synthesis; first, an impure $\text{Y}(\text{sal})_3$ product {containing some $\text{Na}[\text{Y}(\text{sal})_4]$ } was prepared using the method suggested above for the lithium salt; second, it was converted to pure $\text{Na}[\text{Y}(\text{sal})_4]$ using salicylaldehyde as the solvent by taking advantage of the low solubility of $\text{Na}[\text{Y}(\text{sal})_4]$ in salicylaldehyde and the large excess of salicylaldehyde available. Fresh NaOCH_3 must be used in this second step. The IR spectra of the mixture and of pure $\text{Na}[\text{Y}(\text{sal})_4]$ show a difference in the phenolic C–O stretching vibration peaks. Two peaks at 1333 and 1316 cm^{-1} are found for the mixture, whereas only one peak at 1333 cm^{-1} is found for the pure $\text{Na}[\text{Y}(\text{sal})_4]$ salt. Only one phenolic C–O peak is observed for normal $\text{Ln}(\text{sal})_3$ species, too. This strongly suggests that in the solid state all four sal^- ligands in $\text{Na}[\text{Y}(\text{sal})_4]$ coordinate to Y^{3+} in a bidentate manner so that the coordination number of Y^{3+} is eight, as in the case of $[\text{Ln}(\text{acac})_4]^-$.²²

The molar conductance of both $\text{M}[\text{Y}(\text{sal})_4]$ complexes in DMF solution (Table 4) also show that they are 1:1 electrolytes in solution, too. However, the proton NMR spectra of the mixture and of $\text{M}[\text{Y}(\text{sal})_4]$ show no differences in DMSO- d_6 solution and neither do the UV–vis spectra of the mixture and

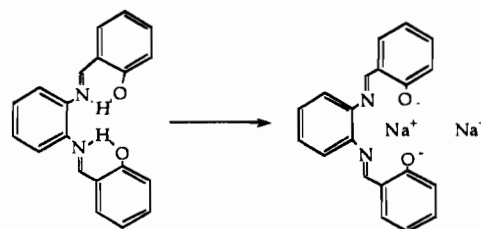


Figure 1. Intramolecular hydrogen-bond loss when Na^+ replaces H^+ in H_2dsp .

$\text{M}[\text{Y}(\text{sal})_4]$. These results indicate that the $[\text{Y}(\text{sal})_4]^-$ complex is labile in DMSO solution and that exchange of sal^- between $[\text{Y}(\text{sal})_4]^-$ and $\text{Y}(\text{sal})_3$ or replacement of sal^- by solvent molecules can take place quickly. This is consistent with the water-exchange rate for yttrium(III).²³ The preparation of $\text{Na}[\text{Y}(\text{sal})_4]$ with Hsal as the solvent (plus added base) avoids this problem because the deprotonated solvent and the ligand are identical.

Efforts to prepare $\text{Na}[\text{La}(\text{sal})_4]$ by this method failed to give good results. Our failure to prepare $\text{M}[\text{La}(\text{sal})_4]$ can be attributed to the appreciably larger radius of La^{3+} (103 pm) relative to Y (90 pm)²⁴ and the weak coordinating ability of the salicylaldehydato ligand.

Na_2dsp has not been reported before. The successful preparation of Na_2dsp allows us to explore the composition of lanthanide Schiff-base complexes in solution and provides another effective way to synthesize complexes of the formulation $\text{Na}[\text{Ln}(\text{dsp})_2]$. One vital point in preparing this compound is the choice of solvent. If a polar or protic solvent such as methanol or acetone is used, the color of the solution changes from orange to a very dark green during the reaction and isolation of the product from the solution is impossible. Aliphatic hydrocarbons are unable to provide sufficient solubilities for the reaction components; therefore, benzene was used as the solvent and provided satisfactory results. Also, a strong base is required to remove both protons from H_2dsp . Our experiments show that Na metal or fresh NaOCH_3 give satisfactory results. One drawback of using NaOCH_3 is its low solubility in benzene. A long reaction time is required, and any remaining NaOCH_3 is difficult to separate from the Na_2dsp product. When Na metal is used in the preparation, the excess metal can be easily removed by picking out the excess sodium, but the product obtained in this way contains a little NaOH , which comes from the oxidation of the Na metal. The IR and proton NMR spectra show that the same product is obtained in both ways. Na_2dsp is quite stable if sealed in a bottle or put in a desiccator, but air oxidation causes its color to change gradually from yellow to greenish gray. The IR spectra show that the peak due to phenolic C–O stretching vibration shifts from 1277 cm^{-1} in H_2dsp to 1340 cm^{-1} in Na_2dsp , and the peak due to C=N stretching vibration shifts from 1613 cm^{-1} in H_2dsp to 1606 cm^{-1} in Na_2dsp . The loss of the intramolecular hydrogen bonds (Figure 1) should be responsible for the latter shift, and metal substitution for protons always shifts the phenolic C–O peak above 1300 cm^{-1} because of the weaker oxygen–metal interaction, which in turn strengthens the C–O bond. The NMR spectrum clearly shows that the O–H proton signal, which is at 12.4 ppm in H_2dsp (Table 1), completely disappears when Na^+ replaces H^+ . The UV–vis spectrum of Na_2dsp (Figure 2) shows two extra peaks at 449 and 392 nm with high extinction coefficients (Table 2) relative to H_2dsp . These two peaks should come from the $n-\pi^*$

(23) Cotton, F. A.; Wilkinson, G. *Comprehensive Inorganic Chemistry*, 5th ed.; Wiley-Interscience: New York, 1988; pp 1288–1289.

(24) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: New York, 1984; pp 1105, 1430.

(22) Bauer, H.; Blanc, J.; Ross, D. L. *J. Am. Chem. Soc.* **1964**, *86*, 5125.

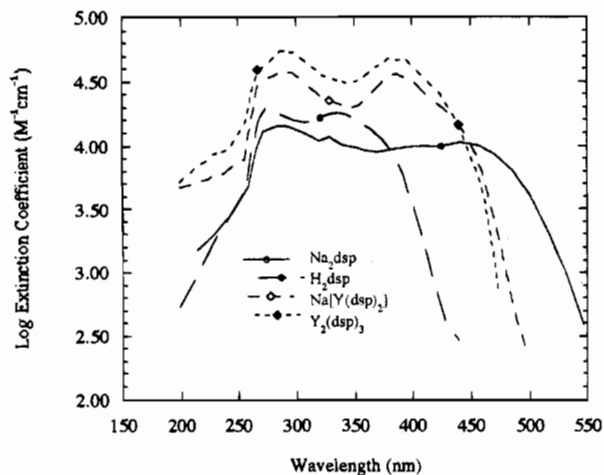


Figure 2. UV-vis spectra of some of the lanthanide Schiff-base compounds.

transitions of the nonbonding electrons of the phenoxy anion. The large charge accumulation on the phenoxy oxygen atom when Na^+ replaces H^+ greatly reduces the energy gaps between the n and π^* levels and increases the dipole and intensity of the $n-\pi^*$ transitions. The molar conductance of Na_2dsp (Table 4) in DMF is similar to 1:1 electrolytes in DMF. The negative charges on the two oxygens plus chelate ring formation with one metal ion yields a predominance of the $[(\text{Na})^+(\text{dsp})_2]^-$ ion pair (plus the other Na^+ ion) in DMF.

Ln_2dsp_3 Syntheses. Ln_2dsp_3 can be prepared in DMF, as in this study, or in acetone⁶ or in methanol.¹⁰ Very fine needle-like crystals can be obtained by carefully controlling the amount of methanol added to the DMF solution and allowing the resulting solution to stand at room temperature for several days. Efforts to prepare single crystals suitable for x-ray structural analysis were not successful although many different solvents and preparation conditions were attempted.

$\text{M}[\text{Ln}(\text{dsp})_2]$ Syntheses. Our experiments have shown that $\text{M}[\text{Ln}(\text{dsp})_2]$ complexes can be prepared by carefully controlling the synthetic conditions and choosing suitable counter ions. Ln^{3+} ions tend to form complexes with coordination numbers greater than 6 because of their large sizes, as noted above; thus, it is quite reasonable to assume that two tetradentate dsp^{2-} ligands can coordinate with one Ln^{3+} ion and form an 8-coordinate complex.

The preparations of $\text{M}[\text{Ln}(\text{dsp})_2]$ can be classified into two groups according to the solubility of the $\text{M}[\text{Ln}(\text{dsp})_2]$ complexes in DMSO solution. DMSO was chosen as the solvent because of its ability as an efficient H_2O scavenger.^{12,25} Complexes with low solubility in DMSO, such as the Li^+ or Cs^+ salts, $\text{M}[\text{Ln}(\text{dsp})_2]$ $\{\text{M} = \text{Li}$ and Cs , except for $\text{Li}[\text{La}(\text{dsp})_2]\}$, spontaneously precipitate from DMSO solution during the synthesis. The low solubility was expected for the Cs^+ salts because the large $[\text{Ln}(\text{dsp})_2]^-$ anions tend to form less soluble salts with the large Cs^+ cation. However, the low solubility of the Li^+ salts was unexpected. The low solubility of all the Li^+ salts, except for the La^{3+} complex, suggests a three-dimensional structure resulting from the small Li^+ cations linking with more than one lanthanide Schiff-base anion similar to hydrogen bonding. The fact that no DMSO coordinates to the Li^+ ions in these complexes of low solubility agrees with this suggestion, because if Li^+ combines with more than one $[\text{Ln}(\text{dsp})_2]^-$ unit, it can not accommodate any solvent molecules. The reason that the soluble $\text{Li}[\text{La}(\text{dsp})_2]\cdot 2\text{DMSO}$ does not follow the other Ln^{3+} complexes is uncertain, but may be due to fact that the larger

La^{3+} ion distorts and possibly adds DMSO to its coordination sphere and sterically weakens the three dimensional network between the lithium ions and the lanthanum Schiff-base anions. If one (or both) DMSO molecules are coordinated to the lithium ion in $\text{Li}[\text{La}(\text{dsp})_2]\cdot 2\text{DMSO}$, its good solubility in DMSO is also logical.

The $\text{M}[\text{Ln}(\text{dsp})_2]$ complexes having good solubility in DMSO are more difficult to synthesize. Successful synthesis in DMSO depends mostly on the type and the amount of base used to remove the protons from the H_2dsp . It is important to form dsp^{2-} ligands by removing both protons from H_2dsp . Only then can $\text{M}[\text{Ln}(\text{dsp})_2]$ complexes be isolated from solvents in which they are quite soluble. Otherwise, the neutral Ln_2dsp_3 complexes are the sole products. Attempts to prepare $\text{Ln}(\text{Hdsp})(\text{dsp})$ by partially neutralizing one of the two H_2dsp ligands fails to give positive results and only $\text{Ln}_2(\text{dsp})_3$ complexes can be obtained. This is quite different from the Ln^{3+} complexes with the more flexible H_2salen ; in fact, $\text{Eu}(\text{salen})(\text{Hsalen})$ species have been isolated.⁹ With H_2dsp , a single proton effectively ties up the ligand and prevents it from being a strong ligand. A sizable number of bases, such as the alkali metal hydroxides, ammonia, and alkylamines were used in initial experiments to deprotonate H_2dsp and provide counterions. Only the alkali metal bases gave the desired $\text{M}[\text{Ln}(\text{dsp})_2]$ products. The other bases yield Ln_2dsp_3 products instead. Ammonia and alkylamines can only provide monodeprotonated Hdsp^- (a very weak acid). Stronger bases are required for total deprotonation. A slight excess of base is also important in the preparation of these complexes.

The best way to synthesize the sodium complexes in this group is to use premade Na_2dsp with Ln^{3+} in methanol solution which takes advantage of the low solubility of the complexes in methanol. $\text{Na}[\text{Y}(\text{sal})_4]$ in DMSO can also be used to prepare $\text{Na}[\text{Y}(\text{dsp})_2]$ by in situ Schiff-base formation. In this case it is necessary to allow enough time for the reaction to go to completion. A small amount of base during the purification helps prevent hydrolysis.

The results of composition analysis (Table 3) show that when a $\text{M}[\text{Ln}(\text{dsp})_2]$ product is obtained as an amorphous precipitate, it contains no DMSO or an indefinite number of DMSO molecules, but when the product is crystalline, it contains a definite number of DMSO molecules, such as $\text{Li}[\text{La}(\text{dsp})_2]\cdot 2\text{DMSO}$, $\text{Na}[\text{Y}(\text{dsp})_2]\cdot \text{DMSO}$, and $\text{Na}[\text{Gd}(\text{dsp})_2]\cdot \text{DMSO}$. Efflorescence took place with a partial loss of DMSO molecules when the crystals were stored for several months. Only the percentages of the lanthanide ion and DMSO were analyzed for some of the products once the stoichiometry of the series had been shown. Although several $\text{Li}[\text{La}(\text{dsp})_2]$ and $\text{Na}[\text{Y}(\text{dsp})_2]$ crystals have been isolated, none of them meet the requirements for X-ray structural analysis.

Structures of Ln_2dsp_3 and $\text{M}[\text{Ln}(\text{dsp})_2]$. Although several Ln_2dsp_3 complexes (where $\text{Ln} = \text{La}$, Pr , Eu , and Nd) were reported previously,^{6,10} no characterization of their properties or structural analysis has been given. However, one possible structure was suggested,⁶ and is still in use,⁴ for $\text{Ln}_2\text{salen}_3$, in which one of salen^{2-} acts as a bridging ligand and total coordination number for Ln^{3+} is 6 (Figure 3). From the results we have obtained, the structure of the Ln_2dsp_3 species is **not** the same as the suggested structure in Figure 3. The strongest evidence comes from the IR spectra of the complexes (Figure 4 and Table 1). Three phenolic C—O stretching vibrations from 1286–1348 cm^{-1} (Table 1) are found for all the Ln_2dsp_3 complexes. Only two peaks around 1323–1348 cm^{-1} are found in the IR spectra of the $\text{M}[\text{Ln}(\text{dsp})_2]$ complexes—the peak at 1286 cm^{-1} is not there. This low frequency peak in the Ln_2dsp_3 species indicates that some of the phenolic C—O bonds

(25) Archer, R. D.; Illingsworth, M. L.; Rau, D. N.; Hardiman, C. J. *Macromolecules* **1985**, *18*, 1371.

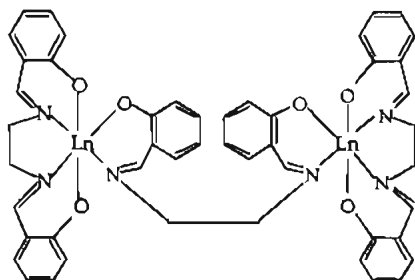


Figure 3. Structure suggested for $\text{Ln}_2\text{salen}_3$ in the literature.⁶

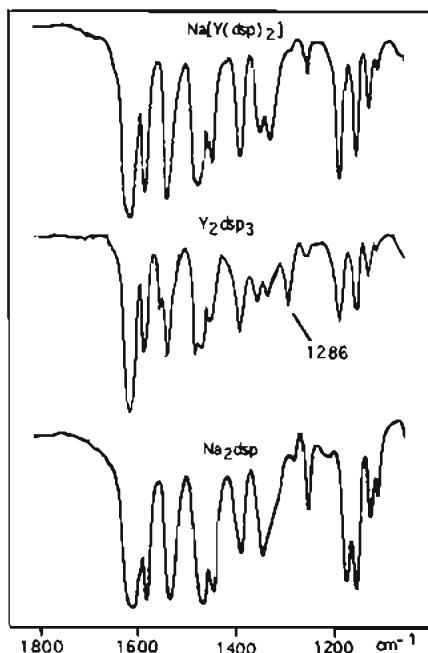


Figure 4. Infrared spectra of Na_2dsp , Y_2dsp_3 , and $\text{Na}[\text{Y}(\text{dsp})_2]$.

are much weaker than the others in Ln_2dsp_3 (as well as all the phenolic C—O bonds in the $\text{M}[\text{Ln}(\text{dsp})_2]$ complexes) apparently because some of the oxygen atoms in Ln_2dsp_3 are affected much more strongly by the Ln^{3+} ions. If the structure of the Ln_2dsp_3 complexes is similar to that shown in Figure 3, all phenolic C—O bonds should be in similar environments and have similar stretching vibration frequencies.

Based on these experimental results, the antiprismatic structure of $\text{Ce}(\text{dsp})_2$,²⁶ which has a lanthanide ion of similar size, and the common coordination number of 8 (or more) for the lanthanide ions,^{27,28} a possible structure for Ln_2dsp_3 is shown in Figure 5a, in which one of the three dsp^{2-} ligands acts as a bridging ligand connecting the two Ln^{3+} ions. In this structure, the oxygen atoms of this bridging dsp^{2-} ligand coordinate to two Ln^{3+} ions at the same time. The increased charge density near these oxygen atoms greatly reduces the strength of the adjacent phenolic C—O bonds and results in the low frequency vibrations observed at 1286 cm^{-1} in the IR spectra. Where no bridge structures exist, as in the $\text{M}[\text{Ln}(\text{dsp})_2]$ species, this peak is not seen. The hypothesized structure has a tetradentate terminal ligand and two bridging oxygens on each metal ion with the two nitrogens of the bridging ligand on one metal ion and two H_2O molecules on the other one, thus providing a coordination number of 8 for both Ln^{3+} ions in the Ln_2dsp_3 complexes. The structure as shown is a CACHE molecular

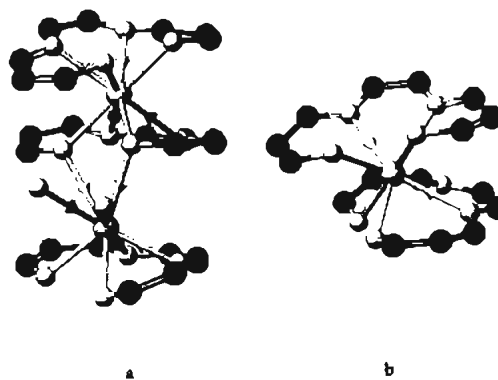


Figure 5. Possible structures of (a) $\text{Ln}_2\text{dsp}_3 \cdot 2\text{H}_2\text{O}$ and (b) $[\text{Ln}(\text{dsp})_2]^-$ based on CACHE molecular modeling software, where the O and N donors and metal ions are light colored. For ease in viewing, the C atoms not in the chelate rings and the H atoms are not shown.

mechanics minimized energy structure and has no detectable steric hindrance.

The La^{3+} species has a third water molecule, so one of its ions is apparently 9-coordinate consistent with its larger ionic radius (103 pm for La^{3+} ; 94, 90, 87, and 88 pm for Gd^{3+} , Y^{3+} , Yb^{3+} , and Ce^{4+} , respectively²⁴). The same C=N stretching vibration in the respective Ln_2dsp_3 and $\text{M}[\text{Ln}(\text{dsp})_2]$ species means that nitrogen coordination is similar in the two structures, which is more consistent with Figure 5a where all three ligands form tetradentate chelate rings antiprismatic with regard to the metal ions. In the earlier structural suggestion (Figure 3), one ligand spans two metals, which should make the N—M (and hence the C=N) bonds different from the others; however, the small shifts generally observed for C=N peaks²⁹ makes a definitive statement difficult. The coordination number of 8 for the Ln^{3+} ions in the new structure (Figure 5a) is more reasonable because of the large radii of the lanthanide ions as noted above. In fact, one paper³ has pointed out that $\text{Ln}_2\text{-busalen}_3$ complexes [$\text{Ln} = \text{Nd, Pr, and Sm}$; busalen = *N,N'*-ethylenebis(5-*tert*-butylsalicylideneamine)] contain 8-coordinate metal ions both in the solid state and in solution. The paper claims strong (but undefined) spectroscopic evidence. An alternate eight-coordinate Ln_2dsp_3 structure with one nitrogen of the bridging ligand and one water molecule on each lanthanide metal ion cannot be absolutely ruled out, but is less consistent with the IR results.

Although no similar $\text{M}[\text{Ln}(\text{dsp})_2]$ complexes have been reported previously, $\text{Ce}(\text{dsp})_2$ can be used as a structural reference for the $\text{M}[\text{Ln}(\text{dsp})_2]$ species, too, as the Ce^{4+} ion is similar in size to Y^{3+} , Yb^{3+} , and Gd^{3+} . The similarity of their IR and NMR spectra (Table 1) suggests that they have similar structures. Therefore, we have assigned an 8-coordinate square antiprismatic structure (Figure 5b) similar to that of $\text{Ce}(\text{dsp})_2$ ²⁶ to the Ln^{3+} ions in the $\text{M}[\text{Ln}(\text{dsp})_2]$ complexes. The other common 8-coordinate dodecahedral structure found for similar complexes with slightly smaller ions, like Zr(IV) (72 pm³⁰),¹⁷ or with more flexible ligands like salen^{2-,9} is less favorable for the larger Ln^{3+} ions with the less flexible dsp^{2-} ligands. Attempts to minimize dodecahedral structures with the CACHE molecular mechanics program gave structures with appreciably higher energies (ca. 80 kJ/mol). The DMSO found in the crystals of $\text{Li}[\text{La}(\text{dsp})_2] \cdot 2\text{DMSO}$ has been discussed above. The DMSO in $\text{Na}[\text{Y}(\text{dsp})_2] \cdot \text{DMSO}$ and $\text{Na}[\text{Gd}(\text{dsp})_2] \cdot \text{DMSO}$ is probably coordinated to the sodium ions because no DMSO is found in analogous products when these complexes are prepared in methanol by the reaction between Na_2dsp and $\text{Ln}(\text{NO}_3)_3$.

(26) Terzis, A.; Menzafos, D.; Tajmir-riahi, H. A. *Inorg. Chim. Acta* **1984**, *84*, 187.

(27) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: New York, pp 1434–1435.

(28) Cotton, F. A.; Wilkinson, G. *Comprehensive Inorganic Chemistry*, 5th ed.; Wiley-Interscience: New York, 1988; p 959.

(29) Patel, M. N.; Patil, S. H. *J. Macromol. Sci.-Chem.* **1981**, *A16*, 1429.

(30) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: New York, 1984; p 1114.

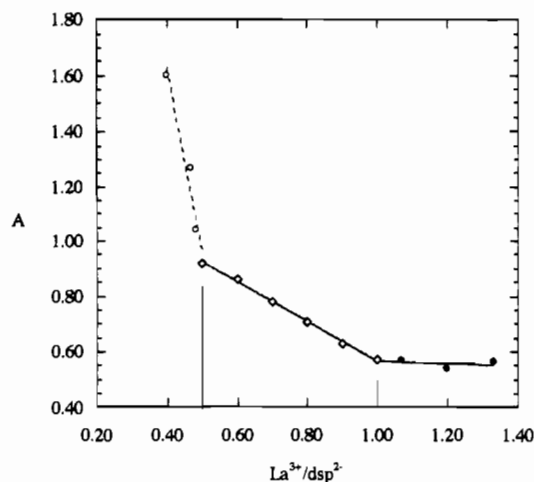


Figure 6. Absorbance (*A*) changes at 459 nm for DMSO solutions as the $\text{La}^{3+}/\text{dsp}^{2-}$ ratio varies with the dsp^{2-} concentration held constant at 7.15 mM.

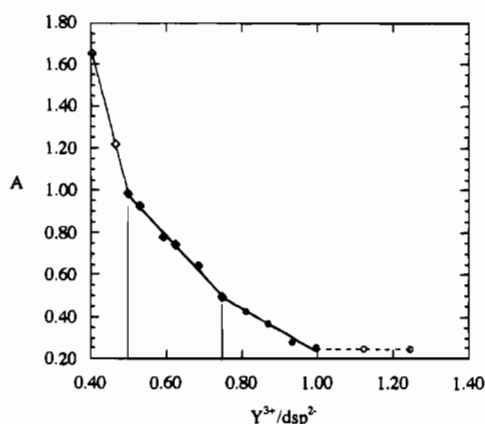


Figure 7. Absorbance (*A*) changes at 459 nm for DMSO solutions as the $\text{Y}^{3+}/\text{dsp}^{2-}$ ratio varies with the dsp^{2-} concentration held constant at 7.15 mM.

*n*DMSO. If DMSO coordinates to the Ln^{3+} ions, it should be present in these products, too, as sometimes occurs.¹¹

Complexes in Solution. UV-vis absorption spectra (Figures 2, 6, and 7) and proton NMR spectra (Figures 8 and 9) were used to investigate the complexes in DMSO (and $\text{DMSO}-d_6$) solution. The results from the UV-vis absorption (Figure 6) show that with La^{3+} only two species with $\text{La}^{3+}:\text{dsp}^{2-}$ ratios of 1:1 and 1:2 are observable in the DMSO solutions. No apparent inflection is found at the $\text{La}^{3+}:\text{dsp}^{2-}$ ratio of 2:3 at this or at any other wavelength. This is different from the results obtained for the Y^{3+} complexes as shown in Figure 7, where a third inflection exists at the $\text{Y}^{3+}:\text{dsp}^{2-}$ ratio of 2:3.

Further investigation by proton NMR (Figure 8) also shows that La^{3+} only has two Schiff-base species— $[\text{La}(\text{dsp})]^+$ and $[\text{La}(\text{dsp})_2]^-$, each with their own NMR spectrum—and that Y^{3+} has a third with peaks that are at maximum intensity at the composition Y_2dsp_3 . Gradual changes in the Ln^{3+} to dsp^{2-} ratio by adding Ln^{3+} to a dsp^{2-} solution has been followed by comparing the changes in intensity of the aldimine proton NMR signals (*ca.* 8–9 ppm) in the different species (Figures 8 and 9). The intensity of the Na_2dsp aldimine protons at about 8.2 ppm decreases as that from $[\text{Ln}(\text{dsp})_2]^-$ at about 8.0 ppm increases for both La^{3+} and Y^{3+} . For La^{3+} the intensity of the aldimine protons of $[\text{La}(\text{dsp})_2]^-$ decreases as that from $[\text{La}(\text{dsp})]^+$ increases (Figure 8), and the NMR spectrum of the solution with a $\text{La}^{3+}:\text{dsp}^{2-}$ ratio of 2:3 shows a mixture with the spectral features of both $[\text{La}(\text{dsp})]^+$ and $[\text{La}(\text{dsp})_2]^-$. However, in the case of Y^{3+} (Figure 9), the spectrum of the solution with a $\text{Y}^{3+}:\text{dsp}^{2-}$ ratio of 2:3 is not simply a composite

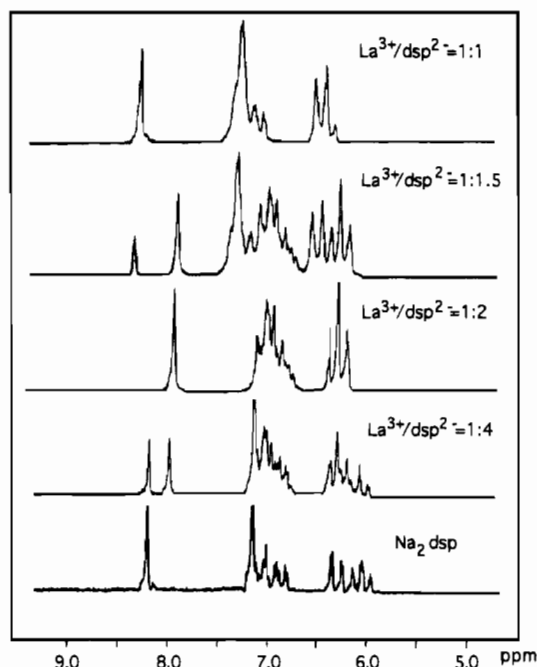


Figure 8. Proton NMR spectra of a series of $\text{DMSO}-d_6$ solutions containing different $\text{La}^{3+}/\text{dsp}^{2-}$ ratios.

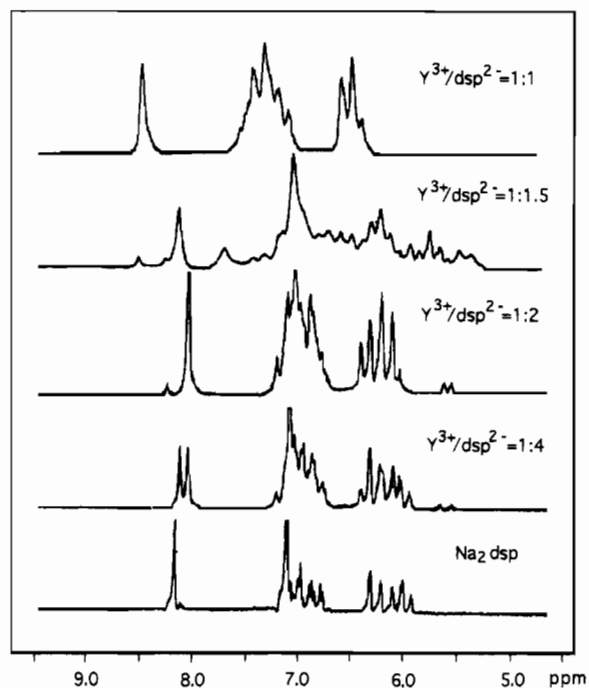


Figure 9. Proton NMR spectra of a series of $\text{DMSO}-d_6$ solutions containing different $\text{Y}^{3+}/\text{dsp}^{2-}$ ratios.

of the spectra of $[\text{Y}(\text{dsp})]^+$ and $[\text{Y}(\text{dsp})_2]^-$, although the peaks of these two ions are also apparent. New aldimine proton peaks that are different from those of both $[\text{Y}(\text{dsp})]^+$ and $[\text{Y}(\text{dsp})_2]^-$, as well as extra peaks in the aromatic region below 8 ppm, indicate the existence of a new Y_2dsp_3 species.

These results show that the Y_2dsp_3 species does exist in DMSO solution, but that it is partially ionized. Schematically:

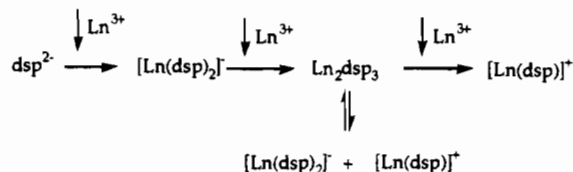


Table 4. Molar Conductivity in DMF Solution ($\text{cm}^2 \text{mol}^{-1} \Omega^{-1}$)^a

Na ₂ dsp	75	La ₂ dsp ₃	50	Na[La(dsp) ₂]	66	Li[Y(dsp) ₂]	70
Na[Y(sal) ₄]	69	Gd ₂ dsp ₃	39	Na[Gd(dsp) ₂]	62	K[Y(dsp) ₂]	62
Li[Y(sal) ₄]	70	Y ₂ dsp ₃	22	Na[Y(dsp) ₂]	66	Cs[Y(dsp) ₂]	66
Ce(dsp) ₂	3	Yb ₂ dsp ₃	7	Na[Yb(dsp) ₂]	62	Na(acac)	67

^a Results based on 1.00 mM DMF solutions at 30.0 ± 0.1 °C.

There is an equilibrium in DMSO solution for the Ln₂dsp₃ complexes as shown above, with the nonionized Ln₂dsp₃ becoming more stable from La³⁺ to Yb³⁺ as the ion size decreases and thus the charge:radius ratio of the ions increases. From the NMR it appears that almost all the La₂dsp₃ separates to [La(dsp)]⁺ and [La(dsp)₂]⁻ in DMSO solution. But only a small percentage of the Y₂dsp₃ species ionizes. The molar conductance results (Table 4) of Ln₂dsp₃ strongly support this conclusion. Molar conductance for La₂dsp₃ is $50 \text{ cm}^2 \text{mol}^{-1} \Omega^{-1}$, which is close to the value of the 1:1 electrolyte Na(acac), but Yb₂dsp₃ is $7 \text{ cm}^2 \text{mol}^{-1} \Omega^{-1}$, which is close to the value for the nonelectrolyte Ce(dsp)₂, with the Gd³⁺ and Y³⁺ complexes in between.

Assignments for the UV-vis absorption peaks are given in Table 2. For H₂dsp, the peak at 339 nm has a blue shift as the polarity of the solvents increases. This shift is characteristic of n-π* transitions.³¹ For the M[Ln(dsp)₂] complexes, the spectra are the same for different alkali salts and the peak at about 385 nm should be assigned as a n-π* transition because it shifts to higher energy as the radius of the Ln³⁺ ion decreases (except for La³⁺). A charge-transfer band would shift in the opposite direction. The Ln₂dsp₃ complexes have UV-vis spectra that are similar to those of M[Ln(dsp)₂]. No charge-transfer bands were observed in any of these compounds.

Stability of Compounds in Solution. Unlike the Ln₂dsp₃ complexes, the [Ln(dsp)₂]⁻ complexes, even [La(dsp)₂]⁻, are quite stable in polar solvents such as DMSO, NMP, or DMF. The stability can be seen clearly from the molar conductance which gives a value consistent with a 1:1 electrolyte and NMR spectra that show only one kind of ligand in solution. These tetradentate ligands are not expected to exchange on an NMR time scale, as shown by the spectra (Figures 8 and 9), so the single peaks are not environmentally averaged peaks. The stability of the [Ln(dsp)₂]⁻ complexes in DMSO solution provides the possibility to prepare similar Schiff-base coordination polyelectrolytes with the lanthanide ions, and some work has begun in this area.

The stability of Na[La(dsp)₂] to hydrolysis by small amounts of water have been investigated in DMSO-*d*₆. The results show that the spectra of Na[La(dsp)₂] and Na[Y(dsp)₂] remain unchanged for 1 day after one drop of water has been added to 1 mL of a DMSO-*d*₆ solution of either Na[La(dsp)₂] or Na[Y(dsp)₂] (*C* = 5 mM). The spectra also remain unchanged after the solutions have been kept at 75 °C for 8 h. These results show excellent hydrolytic stability for [Ln(dsp)₂]⁻ in DMSO solution. This stability comes from two factors. One is from the stability of the [Ln(dsp)₂]⁻ anion (a chelate effect). The other is from the DMSO solvent, which has demonstrated its strong water scavenging ability in our earlier work.^{12,25}

(31) Williams, D. H.; Fleming, I. *Spectroscopic Methods in Organic Chemistry*, 3rd ed.; McGraw-Hill Book Company (UK) Limited: New York, 1980; p 7.

Table 5. Decomposition Temperatures of Compounds (°C)^a

H ₂ dsp	Na ₂ dsp	LiY(sal) ₄	NaY(sal) ₄	La ₂ dsp ₃	Gd ₂ dsp ₃	Y ₂ dsp ₃	Yb ₂ dsp ₃
228	301	287	290	320 ^b	335 ^b	360 ^b	390 ^b
M[Ln(dsp) ₂]							
M	Ln = La	Ln = Gd	Ln = Y	Ln = Yb			
Li	489 ^b	519	578	576			
Na	463	513 ^b	527 ^b	528			
K	441 ^b	447 ^b	457 ^b	460 ^b			
Cs	418 ^b	420 ^b	448 ^b	450 ^b			

^a Heating rate of 40 °C/min under N₂. ^b Solvated species loses solvent at a lower temperature.

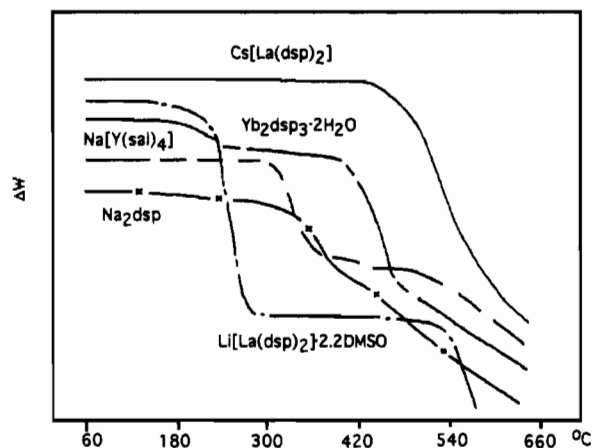


Figure 10. Thermal-gravimetric weight-loss plots for several compounds prepared.

Thermal Stability of Compounds. Results from thermal gravimetric analysis (Table 5 and Figure 10) reveal several tendencies. First, all complexes have a much higher thermal stability than the Schiff base H₂dsp, and the M[Ln(dsp)₂] complexes are much more thermally stable (to as high as 570 °C) than the corresponding Ln₂dsp₃ (≤ 390 °C). Second, for different lanthanide ions the thermal stability increases from La³⁺ to Yb³⁺ for both Ln₂dsp₃ and the M[Ln(dsp)₂] series. A smaller Ln³⁺ ion provides a stronger attraction between the Ln³⁺ ions and the dsp²⁻ ligands and results in more thermally stable complexes. Third, the M[Ln(dsp)₂] complexes become less thermally stable from Li⁺ to Cs⁺. Smaller alkali ions form stronger ionic forces with the anionic complexes in the solid state. The stronger forces result in increased thermal stability.

In conclusion, a series of complexes of Ln³⁺ represented by La³⁺, Gd³⁺, Yb³⁺, and Y³⁺ with the Schiff-base H₂dsp ligand have been synthesized and characterized. This work also paves the way for the synthesis of analogous coordination polyelectrolytes, which will be reported later.

Acknowledgment. The authors acknowledge with thanks the financial support of the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the University of Massachusetts for this research. The Camille and Henry Dreyfus Foundation Special Grant Program in the Chemical Sciences and the University of Massachusetts financed the Tektronics CAChe system used in this study. The detailed critique provided by one of the reviewers is also gratefully acknowledged.