J. Am. Chem. Soc. **1992**, *114*, 6081-6087

Synthesis and Characterization of Lanthanide $[Ln(L)]_2$ Complexes of N_4O_3 Amine Phenol Ligands with Phenolate Oxygen Bridges: Evidence for Very Weak Magnetic Exchange between Lanthanide Ions

Shuang Liu,[1] Lucio Gelmini, Steven J. Rettig, Robert C. Thompson, and Chris Orvig*

Contribution from the Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, British Columbia V6T 1Z1, Canada. *Received December 20, 1991*

Abstract: The synthesis and characterization of three potentially heptadentate (N_4O_3) amine phenols and of a series of their mononuclear and dinuclear lanthanide complexes are reported. The heptadentate ligands are KBH_4 reduction products of the Schiff bases derived from the condensation reactions of tris(2-aminoethyl)amine with 3 equiv of one of salicylaldehyde (tris(((2-hydroxybenzyl)amino)ethyl)amine (H_3L1)), 5-chlorosalicylaldehyde (tris(((2-hydroxy-5-chlorobenzyl)amino)ethyl)amine (H_3L2)), and 5-bromosalicylaldehyde (tris(((2-hydroxy-5-bromobenzyl)amino)ethyl)amine (H_3L3)). The reaction of an amine phenol with 1 equiv of a lanthanide (Ln) nitrate produces the mononuclear complex $[Ln(H_3L)(NO_3)_3]$; homodinuclear complexes $[Ln(L)]_2$ were obtained from the reaction of lanthanide salts with the respective ligand in the presence of a base (hydroxide or acetate). The X-ray structure of $[Gd(L1)]_2{\cdot}2CHCl_3$ (H_3L1 = tris(((2-hydroxybenzyl)amino)ethyl)amine) has been determined; it is the first structurally characterized example of an $[Ln(L)]_2$ complex, a homodinuclear eight-coordinate lanthanide complex $[Ln(L)]_2$ with heptadentate ligands only. The complex crystallizes as a chloroform solvate in the triclinic space group $P\bar{1}$ with $a = 12.002$ (2) Å, $b = 12.248$ (2) Å, $c = 11.889$ (2) Å, $\alpha = 109.22$ (1)°, $\beta = 108.29$ (1)°, $\gamma = 71.64$ (1)°, $Z = 1$, and $V = 1522.5$ (4) Å^3. The structure was solved by conventional heavy-atom methods and was refined by full-matrix least-squares procedures to $R = 0.034$ and $R_w = 0.040$ for 8771 reflections with $I \geq 3\sigma(I)$. The dinuclear complex $[Gd(L1)]_2{\cdot}2CHCl_3$ has a distorted bicapped octahedral (or cubic) coordination geometry around each gadolinium atom which is coordinated by an N_4O_4 donor set. The two gadolinium atoms are bridged by two phenolate O atoms, one from each heptadentate ligand. Angles at the oxygen bridgeheads are 113.12 (8)°, and the Gd–Gd separation is 3.9841 (2) Å. The Gd–N distances range from 2.615 (3) to 2.813 (3) Å. The bridging O–Gd bond lengths are 2.384 (2) and 2.391 (2) Å, while the terminal Gd–O distances are 2.269 (2) and 2.237 (2) Å. Room-temperature magnetic susceptibilities of some of the mononuclear and homodinuclear complexes give no indication of magnetic interaction between the two Ln^{3+} ions and are discussed in relation to their structures. A variable-temperature (4.2–82 K) magnetic susceptibility study of the $[Gd(L1)]_2{\cdot}2CHCl_3$ complex revealed a good fit of the data to two very weakly antiferromagnetically coupled $S = {}^7/_2$ ions ($g = 2.00$, $-J = 0.045$ (1) cm^{-1}).

Introduction

We are interested in lanthanide coordination chemistry generally and in the potential application of lanthanide complexes as magnetic resonance contrasting agents specifically.[2,3] Recently, we reported[4,5] several potentially heptadentate Schiff base ligands and their lanthanide complexes. The ligands were prepared from the condensation reactions of tris(aminoethyl)amine (commonly abbreviated tren) with various ketones: 2,4-pentanedione (to give H_3trac), 2-hydroxyacetophenone (H_3hatren), and 2-hydroxy-4,5-dimethylacetophenone (H_3datren). These ligands were either tridentate[4] or heptadentate[5] depending on the conditions of preparation. The seven-coordinate complexes, which contained these triply deprotonated ligands as the only ligands, were very unstable to moisture and to strong σ-donor solvents such as DMSO and pyridine. The instability of these complexes likely results from metal-enhanced hydrolysis of the ligand in water or from solvent competition.[4,5] To solve this problem, we decided to reduce the imine CH=N bonds to the very much more stable amine CH_2—NH functionality. We were determined to retain the tribasic character (with reasonable pK_a's) in the ligand in order to conserve the overall neutral complex charge, an important factor for the in vivo mobility of metal complex imaging agents.[6,7]

In this report we present the synthesis and characterization of three potentially heptadentate amine phenol ligands and of a series of their mononuclear and homodinuclear lanthanide complexes. The potentially heptadentate Schiff base ligands, derived from condensation reactions of tren with various ring-substituted salicylaldehydes, have been prepared, and their coordination chemistry with a number of transition metals has been extensively investigated;[8-12] however, the amine phenol ligands (H_3L1, H_3L2, and H_3L3), which we have prepared from the reduction of the corresponding Schiff base ligands, have not been previously reported.

Homo- and heteropolynuclear complexes containing rare earth metals are of great interest because of their unique physicochemical properties.[13-15] Dinuclear complexes of rare earth metals are considered to be good simple models for more complex new materials, particularly oxides.[16] In addition, homo- or heterodinuclear complexes should provide valuable information regarding Ln^{3+}–Ln^{3+} interactions, depending on bridging ligands.

Recently, several homodinuclear lanthanide complexes with macrocyclic Schiff base ligands have been reported.[16-20] To date,

---

* To whom correspondence should be addressed.

(1) Natural Sciences and Engineering Research Council Postdoctoral Fellow 1991–1993.

(2) (a) Lauffer, R. B. *Chem. Rev.* **1987**, *87*, 901. (b) The January 1988 issue (*15* (1)) of *Nucl. Med. Biol.* is devoted to this topic.

(3) Hart, F. A. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, England, 1987; Vol. 3, p 1059.

(4) Smith, A.; Rettig, S. J.; Orvig, C. *Inorg. Chem.* **1988**, *27*, 3929.

(5) Berg, D. J.; Rettig, S. J.; Orvig, C. *J. Am. Chem. Soc.* **1991**, *113*, 2528.

(6) Clevette, D. J.; Lyster, D. M.; Nelson, W. M.; Rihela, T. J.; Webb, G. A.; Orvig, C. *Inorg. Chem.* **1990**, *29*, 667.

(7) Zhang, Z.; Rettig, S. J.; Orvig, C. *Inorg. Chem.* **1991**, *30*, 509.

(8) Broomhead, J. A.; Robinson, D. J. *Aust. J. Chem.* **1968**, *21*, 1365.

(9) Cook, D. F.; Cummins, D.; McKenzie, E. D. *J. Chem. Soc., Dalton Trans.* **1976**, 1369.

(10) Alcock, N. N.; Cook, D. F.; McKenzie, E. D.; Worthington, J. M. *Inorg. Chim. Acta* **1980**, *38*, 107.

(11) Malek, A.; Dey, G. C.; Nasreen, A.; Chowdbury, T. A.; Alyea, E. C. *Synth. React. Inorg. Met.-Org. Chem.* **1979**, *9*, 145.

(12) Alyea, E. C.; Malek, A.; Vougioukas, A. E. *Can. J. Chem.* **1982**, *60*, 667.

(13) Guerriero, P.; Vigato, P. A.; Bünzli, J.-C. G.; Moret, E. *J. Chem. Soc., Dalton Trans.* **1990**, 647.

(14) Casellato, U.; Guerriero, P.; Tamburini, S.; Vigato, P. A.; Graziani, R. *J. Chem. Soc., Dalton Trans.* **1990**, 1533.

(15) Guerriero, P.; Sitran, S.; Vigato, P. A.; Marega, C.; Marigo, A.; Zametti, R. *Inorg. Chim. Acta* **1990**, *171*, 103.

(16) Daolio, S.; Facchin, B.; Pagura, C.; Guerriero, P.; Sitran, S.; Vigato, P. A. *Inorg. Chim. Acta* **1990**, *178*, 131.

(17) Kahwa, I. A.; Selbin, J.; Hsieh, T. C.-Y.; Laine, R. A. *Inorg. Chim. Acta* **1986**, *118*, 179.

0002-7863/92/1514-6081$03.00/0

no structural data are available on these dinuclear species; obtaining suitable crystals for X-ray diffraction studies has proven to be extremely difficult. Dinuclear lanthanide complexes with a tricyclic cryptand,[21] a tridentate ligand pyridine-2-carboxaldehyde 2-pyridylhydrazone,[22] a pyridino alkoxide Schiff base,[23] and a 2:2 Schiff base derived from 2,6-diacetylpyridine and carbohydrazide[24] have also been reported. The X-ray structures of the dinuclear praseodymium (2.2.1) cryptate[21] and the ytterbium complex with pyridine-2-carboxaldehyde 2-pyridylhydrazone[22] show in both cases that the two lanthanide atoms are bridged by two hydroxo groups. The present homodinuclear complex, $[Gd(L1)]_2 \cdot 2CHCl_3$, represents the first structurally characterized example in which two Gd atoms are coordinated by heptadentate ligands only and are bridged by two phenolate O atoms from separate heptadentate ligands.

Experimental Section

(1) Materials. Hydrated lanthanide salts, tris(aminoethyl)amine (tren), potassium borohydride, salicylaldehyde, 5-chlorosalicylaldehyde, and 5-bromosalicylaldehyde were obtained from Aldrich or Alfa and were used without further purification.

(2) Instrumentation. NMR spectra (200 and 500 MHz) were recorded on Bruker AC-200E (^1H–^1H COSY and APT ^{13}C NMR) and Varian XL 500 (^1H, ^{13}C, and ^1H–^{13}C heteronuclear correlation) spectrometers, respectively. Mass spectra were obtained with either a Kratos MS 50 (electron-impact ionization, EI) or an AEI MS-9 (fast-atom-bombardment ionization, FAB) instrument. Infrared spectra were recorded as KBr disks in the range 4000–200 cm^{-1} on a Perkin-Elmer PE 783 spectrophotometer and were referenced to polystyrene. Melting points were measured on a Mel-Temp apparatus and are uncorrected. Analyses for C, H, N were performed by Mr. Peter Borda in this department. Room-temperature (293.5 K) magnetic susceptibilities of some lanthanide complexes were measured on a Johnson Matthey magnetic susceptibility balance, using $Hg[Co(NCS)_4]$ as the susceptibility standard. Diamagnetic corrections were estimated by using Pascal's constants.[25] Magnetic susceptibilities of $[Gd(L1)]_2 \cdot 2CHCl_3$ were measured from 4.2 to 82 K using a PAR Model 155 vibrating-sample magnetometer as described previously.[26] Measurements were made at a field of 7501 Oe. The sample was corrected for diamagnetism using a value of -376×10^{-6} cm^3 mol^{-1} per Gd unit.

(3) Synthesis of Ligands. (a) **Tris((salicylideneamino)ethyl)amine** (H_3**saltren**). This ligand was prepared according to ref 11 with some modifications. To a solution of salicylaldehyde (7.3 g, 60 mmol) in diethyl ether (50 mL) was added tren (2.92 g, 20 mmol) in absolute ethanol (50 mL); almost immediately a yellow precipitate formed. After the mixture was cooled in an ice bath for 2 h, the resulting solid was filtered off, washed with diethyl ether, and dried in air: yield 8.5 g (93%); mp 82–83 °C (lit.[11] 82–83 °C). Mass spectrum (EI): $m/e = 458$ (M^+, $[C_{27}H_{30}N_4O_3]^+$). IR (cm^{-1}, KBr disk): 3600–2200 (b, ν_{O-H}), 3000–2800 (w or m, ν_{C-H}), 1635, 1610, 1585, and 1550 (vs, $\nu_{C=N}$ and $\nu_{C=C}$).

(b) **Tris(((5-chlorosalicylidene)amino)ethyl)amine** (H_3-5-Cl-saltren). The ligand was prepared according to ref 11 with some modifications. To a hot solution of 5-chlorosalicylaldehyde (9.36 g, 60 mmol) in absolute ethanol (150 mL) was added tren (2.92 g, 20 mmol). The resulting yellow solution was refluxed for 30 min and then concentrated to 40 mL; yellow microcrystals formed. The mixture was cooled in an ice bath for 30 min, and the yellow microcrystals were collected by filtration, washed with absolute ethanol and diethyl ether, and dried in air: yield 8.5 g (76%); mp 127–128 °C (lit.[11] 127–129 °C). Mass spectrum (EI): $m/e = 560$ (M^+, $[C_{27}H_{27}Cl_3N_4O_3]^+$). IR ($cm^{-1}$, Nujol mull/KBr): 3500–3300 (w, ν_{O-H}), 1635, 1610, 1575, and 1465 (vs, $\nu_{C=N}$ and $\nu_{C=C}$).

Table I. Analytical Data for Amine Phenol Compounds and Their Lanthanide Complexes

compound	anal. calcd (found), % C	H	N
$H_3L1 \cdot H_2O$	67.17 (67.09)	7.94 (7.82)	11.62 (11.44)
$H_3L2 \cdot 1.5H_2O$	54.48 (54.78)	6.10 (5.80)	9.42 (9.30)
$H_3L3 \cdot 1.5H_2O$	44.53 (44.55)	4.98 (4.57)	7.69 (7.33)
$[La(H_3L1)(NO_3)_3] \cdot 2CH_3OH$	40.81 (40.97)	5.20 (4.89)	11.49 (11.37)
$[Pr(H_3L1)(NO_3)_3] \cdot H_2O$	40.06 (39.89)	4.73 (4.73)	12.11 (12.17)
$[Nd(H_3L1)(NO_3)_3] \cdot 2.5H_2O$	38.61 (38.71)	4.92 (4.95)	11.67 (11.10)
$[Gd(H_3L1)(NO_3)_3] \cdot 1.5C_2H_5OH$	41.09 (41.21)	5.15 (5.17)	11.18 (11.20)
$[Y(L1)]_2 \cdot 1.5CHCl_3$	52.08 (52.05)	5.32 (5.35)	8.75 (8.75)
$[La(L1)]_2 \cdot 2H_2O$	52.41 (52.33)	5.70 (5.64)	9.06 (8.89)
$[Pr(L1)]_2 \cdot 2CHCl_3$	46.56 (45.93)	4.75 (4.73)	7.77 (7.61)
$[Nd(L1)]_2 \cdot 2CHCl_3$	46.35 (46.16)	4.73 (4.76)	7.73 (7.67)
$[Gd(L1)]_2 \cdot 1.5CHCl_3$	47.05 (46.60)	4.80 (4.75)	7.91 (7.86)
$[Dy(L1)]_2 \cdot 1.5CHCl_3$	46.71 (47.22)	4.77 (4.97)	7.85 (7.82)
$[La(L2)]_2 \cdot 3H_2O$	44.37 (44.61)	4.55 (4.25)	7.67 (7.47)
$[Pr(L2)]_2 \cdot H_2O$	45.37 (45.17)	4.37 (4.37)	7.84 (7.50)
$[Nd(L2)]_2 \cdot C_2H_5OH$	45.93 (46.01)	4.54 (4.66)	7.65 (7.72)
$[Gd(L2)]_2 \cdot 2H_2O$	43.78 (43.77)	4.36 (4.13)	7.57 (7.67)
$[La(H_3L2)(NO_3)_3] \cdot CH_2Cl_2 \cdot H_2O$	33.77 (33.59)	3.75 (3.80)	9.85 (9.81)
$[Pr(H_3L2)(NO_3)_3] \cdot CH_2Cl_2 \cdot H_2O$	33.70 (33.78)	3.74 (3.78)	9.83 (9.90)
$[Nd(H_3L2)(NO_3)_3] \cdot CH_2Cl_2$	34.21 (34.32)	3.59 (3.80)	9.97 (9.80)
$[Gd(H_3L2)(NO_3)_3] \cdot CH_2Cl_2 \cdot H_2O$	33.16 (33.20)	3.68 (3.69)	9.67 (9.28)
$[La(L3)]_2 \cdot 4H_2O$	37.12 (37.03)	3.92 (3.49)	6.42 (6.24)
$[Nd(L3)]_2 \cdot 8CHCl_3$	28.21 (28.41)	2.60 (2.97)	4.24 (4.41)
$[Gd(L3)]_2 \cdot 3H_2O$	36.75 (36.98)	3.77 (3.71)	6.35 (6.17)
$[Pr(H_3L3)(NO_3)_3] \cdot CH_3OH$	31.72 (31.84)	3.52 (3.76)	9.25 (9.18)
$[Nd(H_3L3)(NO_3)_3] \cdot H_2O$	30.90 (31.08)	3.36 (3.65)	9.34 (9.03)
$[Gd(H_3L_3)(NO_3)_3] \cdot 3H_2O$	29.52 (29.46)	3.58 (3.36)	8.92 (8.66)

(c) **Tris(((5-bromosalicylidene)amino)ethyl)amine** (H_3-**5-Br-saltren**). To a solution of 5-bromosalicylaldehyde (6.03 g, 30 mmol) in absolute ethanol (150 mL) was added tren (1.46 g, 10 mmol). The resulting yellow solution was stirred for 20 min at room temperature. The bright yellow microcrystals were filtered off, washed with diethyl ether, and dried in air: yield 5.6 g (81%); mp 144–145 °C. Mass spectrum (EI): $m/e = 695$ (M^+, $[C_{27}H_{27}Br_3N_4O_3]^+$). IR ($cm^{-1}$, KBr disk): 3600–2200 (broad weak band, ν_{O-H}), 3070–2800 (w or m, ν_{C-H}), 1635, 1610, 1575, and 1475 (vs, $\nu_{C=N}$ and $\nu_{C=C}$).

(d) **Tris(((2-hydroxybenzyl)amino)ethyl)amine** (H_3**L1**). To a solution of H_3salten (4.58 g, 10 mmol) in methanol (150 mL) at room temperature was added $Na_2B_4O_7$ (2.0 g) and then KBH_4 (2.12 g, 40 mmol) in small portions over 30 min. After the addition was complete, the reaction mixture was stirred at room temperature for an additional 2 h. The solvent was removed under reduced pressure. To the residue was added NH_4Cl (10 g) in water (100 mL), and the mixture was extracted with chloroform (3 × 150 mL). The organic fractions were combined, washed with water, and dried over anhydrous $MgSO_4$. The solution was filtered, and chloroform was removed on a rotary evaporator to afford a pale-yellow solid. The solid was dried overnight under vacuum: yield 3.7 g (80%); mp 45–47 °C. Mass spectrum (FAB): $m/e = 465$ (M + 1, $[C_{27}H_{37}N_4O_3]^+$). IR (cm^{-1}, KBr disk): 3320 (m, ν_{N-H}), 1615 and 1590 (s, δ_{N-H}), 1490–1420 (vs, $\nu_{C=C}$).

(e) **Tris(((2-hydroxy-5-chlorobenzyl)amino)ethyl)amine** (H_3**L2**). To a suspension of H_3-5-Cl-saltren (2.83 g, 5.0 mmol) in hot methanol (150 mL) were added $Na_2B_4O_7$ (1.0 g) and then KBH_4 (1.06 g, 20 mmol) in portions over 1 h. After addition, the reaction mixture was refluxed for 1 h. The solvent was removed on a rotary evaporator, and to the residue was added NH_4Cl (5 g) in water (50 mL). The mixture was extracted with chloroform (3 × 100 mL). The organic fractions were combined, washed with water, and dried over anhydrous $MgSO_4$. The solution was filtered, and chloroform was removed under reduced pressure to afford an off-white solid. The solid was dried under vacuum overnight: yield 2.5 g (88%); mp 56–58 °C. Mass spectrum (FAB): $m/e = 567, 569$ (M + 1, $[C_{27}H_{34}Cl_3N_4O_3]^+$). IR ($cm^{-1}$, KBr disk): 3340–3280 (m, ν_{N-H}),

---

[18] Kahwa, I. A.; Fronczek, F. R.; Selbin, J. *Inorg. Chim. Acta* **1987**, *126*, 227.

[19] Kahwa, I. A.; Fronczek, F. R.; Selbin, J. *Inorg. Chim. Acta* **1988**, *148*, 273.

[20] Guerriero, P.; Tamburini, S.; Vigato, P. A.; Benelli, C. *Inorg. Chim. Acta* **1991**, *189*, 19.

[21] Rebizant, J.; Spirlet, M. R.; Barthelemy, P. P.; Desreux, J. F. *J. Inclusion Phenom.* **1987**, *5*, 505.

[22] Baraniak, E.; Bruce, R. St. L.; Freeman, H. C.; Hair, N. J.; James, J. *Inorg. Chem.* **1976**, *15*, 2226.

[23] Sakamoto, M. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1546.

[24] Nelson, S. M. *Pure Appl. Chem.* **1980**, *52*, 2461.

[25] Mabbs, F. E.; Machin, D. J. *Magnetism and Transition Metal Complexes*; Chapman and Hall: London, 1973.

[26] Haynes, J. S.; Oliver, K. W.; Rettig, S. J.; Thompson, R. C.; Trotter, J. *Can. J. Chem.* **1984**, *62*, 891.

Table II. Infrared Spectral Data (cm^{-1}, KBr Disk) for Lanthanide Complexes of Amine Phenol Ligands

compound	ν_{N-H} or ν_{OH}	δ_{N-H}	$\nu_{NO_3^-}$
$[La(H_3L1)(NO_3)_3]\cdot 2CH_3OH$	3600–3000 b	1598 s, 1565 m	1475 s, 1280 s
$[Pr(H_3L1)(NO_3)_3]\cdot H_2O$	3650–2700 b	1598 s, 1563 m	1470 s, 1280 s
$[Nd(H_3L1)(NO_3)_3]\cdot 2.5H_2O$	3650–2700 b	1598 s, 1565 m	1475 s, 1280 s
$[Gd(H_3L1)(NO_3)_3]\cdot 1.5C_2H_5OH$	3650–2700 b	1598 s, 1565 m	1470 s, 1285 s
$[Y(L1)]_2\cdot 1.5CHCl_3$	3262 m, 3250 m	1590 vs, 1575 m	
$[La(L1)]_2\cdot 2H_2O$	3570 w, 3265 m	1594 vs	
$[Pr(L1)]_2\cdot 2CHCl_3$	3280 m, 3260 m	1595 vs, 1560 m	
$[Nd(L1)]_2\cdot 2CHCl_3$	3280 m, 3260 m	1595 vs, 1560 m	
$[Gd(L1)]_2\cdot 1.5CHCl_3$	3275 m, 3256 m	1595 vs, 1560 m	
$[Dy(L1)]_2\cdot 1.5CHCl_3$	3270 m, 3250 m	1598 vs, 1578 s	
$[La(L2)]_2\cdot 3H_2O$	3440 b, m, 3265 m	1588 s, 1552 w	
$[Nd(L2)]_2\cdot C_2H_5OH$	3440 b, m, 3265 m	1588 s, 1554 w	
$[Pr(L2)]_2\cdot H_2O$	3440 b, w, 3265 m	1588 s, 1554 w	
$[Gd(L2)]_2\cdot 2H_2O$	3450 b, w, 3260 m	1590 s, 1558 w	
$[La(H_3L2)(NO_3)_3]\cdot CH_2Cl_2\cdot H_2O$	3680–2800 b	1593 m, 1550 w	1485 s, 1287 s
$[Pr(H_3L2)(NO_3)_3]\cdot CH_2Cl_2\cdot H_2O$	3640–2700 b	1590 m, 1554 w	1480 s, 1285 s
$[Nd(H_3L2)(NO_3)_3]\cdot CH_2Cl_2$	3600–2700 b	1590 w, 1552 w	1475 s, 1280 s
$[Gd(H_3L2)(NO_3)_3]\cdot CH_2Cl_2\cdot H_2O$	3680–2700 b	1590 w, 1554 w	1470 s, 1280 s
$[La(L3)]_2\cdot 4H_2O$	3440 b, 3260 m	1585 s, 1550 w	
$[Nd(L3)]_2\cdot 8CHCl_3$	3270 m, 3258 m	1590 vs, 1555 m	
$[Gd(L3)]_2\cdot 3H_2O$	3440 b, 3260 m	1580 s, 1550 w	
$[Pr(H_3L3)(NO_3)_3]\cdot CH_3OH$	3680–2700 b	1587 w, 1550 w	1480 s, 1280 s
$[Nd(H_3L3)(NO_3)_3]\cdot H_2O$	3680–2600 b	1585 m, 1550 w	1480 s, 1280 s
$[Gd(H_3L3)(NO_3)_3]\cdot 3H_2O$	3650–2800 b	1585 m, 1550 w	1470 s, 1290 s

Table III. FAB Mass Spectral and Room-Temperature Magnetic Moment (per Metal for Dimers) Data for Lanthanide Complexes of Amine Phenol Ligands

compound	m/e (M$^+$)			μ_{eff}, μ_B
	$[Ln(L)]_2^+$	$[Ln(HL)]^+$	$[Ln(H_2L)(NO_3)]^+$	
$[La(H_3L1)(NO_3)_3]$		601	664	diamag
$[Pr(H_3L1)(NO_3)_3]$		603		3.35
$[Nd(H_3L1)(NO_3)_3]$		606		3.50
$[Gd(H_3L1)(NO_3)_3]$		620		7.87
$[Y(L1)]_2$	1102	551		diamag
$[La(L1)]_2$	1201	601		diamag
$[Pr(L1)]_2$	1206	603		3.32
$[Nd(L1)]_2$	1213	606		3.59
$[Gd(L1)]_2$	1235	618		7.89
$[Dy(L1)]_2$	1249	624		
$[La(L2)]_2$	1407	703		diamag
$[Gd(L2)]_2$	1445	722		7.83
$[La(H_3L2)(NO_3)_3]$		707	771	diamag
$[Pr(H_3L2)(NO_3)_3]$	1411	707	768	3.26
$[Nd(H_3L2)(NO_3)_3]$		704	768	3.52
$[Gd(H_3L2)(NO_3)_3]$				7.88
$[La(L3)]_2$		837		diamag
$[Nd(L3)]_2$	1685	842		
$[Gd(L3)]_2$		856		7.86
$[Pr(H_3L3)(NO_3)_3]$		839	902	3.33
$[Nd(H_3L3)(NO_3)_3]$		842	905	3.49
$[Gd(H_3L3)(NO_3)_3]$		856	918	7.84

Table IV. Selected Crystallographic Data for $[Gd(L1)]_2\cdot 2CHCl_3$

formula	$C_{56}H_{68}Cl_6Gd_2N_8O_6$	V, Å^3	1522.5 (4)
fw	1476.42	Z	1
crystal system	triclinic	T, °C	21
space group	$P\bar{1}$	ρ_c, g/cm^3	1.610
a, Å	12.002 (2)	λ, Å	0.71069
b, Å	12.248 (2)	μ(Mo Kα), cm^{-1}	24.87
c, Å	11.889 (2)	crystal decay	7.7%
α, deg	109.22 (1)	$R(F_o)$	0.034
β, deg	108.29 (1)	$R_w(F_o)$	0.040
γ, deg	71.64 (1)		

1615 and 1590 (s, δ_{N-H}), 1490–1420 (vs, $\nu_{C=C}$).

(f) Tris(((2-hydroxy-5-bromobenzyl)amino)ethyl)amine (H_3L3). A procedure similar to that above was followed using 3.48 g (5.0 mmol) of H_3-5-Br-saltren, 1.0 g of $Na_2B_4O_7$, 1.06 g (20.0 mmol) of KBH_4, and 3 g of NH_4Cl. The white solid obtained was dried under vacuum overnight: yield 2.5 g (71%); mp 95–97 °C. Mass spectrum (FAB): m/e = 703 (M + 1, $[C_{27}H_{34}Br_3N_4O_3]^+$). IR (cm^{-1}, KBr disk): 3600–2000 (m, ν_{N-H}), 1605 and 1590 (s, δ_{N-H}), 1490–1420 (vs, $\nu_{C=C}$).

(4) Synthesis of Lanthanide Complexes. Since many of the syntheses were similar, detailed procedures are given only for representative examples. All complexes, their analytical data, and their physical properties are listed in Table I. IR spectral, room-temperature magnetic moment, and mass (FAB) spectral data are reported in Tables II and III.

(a) General Methods for Type III Complexes. (i) $[La(L1)]_2\cdot 2H_2O$. Method 1. To a solution of $LaCl_3\cdot 7H_2O$ (371 mg, 1.0 mmol) in methanol (20 mL) was added $H_3L1\cdot H_2O$ (500 mg, 1.04 mmol) in the same solvent (10 mL). Upon addition of 2 M NaOH solution (2.0 mL) dropwise, white solid formed gradually. The mixture was stirred for 30 min at room temperature. The white solid was filtered off, washed with methanol and diethyl ether, and dried in air: yield 440 mg (71%).

Method 2. To a solution of $La(NO_3)_3\cdot 6H_2O$ (217 mg, 0.50 mmol) in methanol (40 mL) was added $H_3L1\cdot H_2O$ (280 mg, 0.58 mmol) in chloroform (20 mL); the solution became cloudy. Upon addition of 2 N NaOH (2.0 mL) dropwise, the cloudy solution became clear. The solution was filtered immediately, and the filtrate was left standing at room temperature; slow evaporation yielded colorless microcrystals. These were collected by filtration, washed with ethanol and diethyl ether, and dried in air. The product was shown by IR and elemental analysis to be identical to that obtained by method 1.

(ii) **$[Gd(L1)]_2\cdot 2CHCl_3$.** The complex was prepared similarly to the lanthanum complex (method 2) using $Gd(NO_3)_3\cdot 5H_2O$ (226 mg, 0.50 mmol) and $H_3L1\cdot H_2O$ (270 mg, 0.56 mmol). Suitable crystals for X-ray diffraction studies were isolated from the original reaction mixture. Upon exposure to air for several days at room temperature, most of them cracked and disintegrated due to the loss of $CHCl_3$. Only 25% of the chloroform in the disolvate could be removed (even after the crystals were carefully pulverized) by prolonged drying in vacuo at 70 °C.

(iii) **$[Gd(L2)]_2\cdot 2H_2O$.** To a solution of $Gd(NO_3)_3\cdot 6H_2O$ (226 mg, 0.50 mmol) in 30 mL of methanol were added $H_3L2\cdot 1.5H_2O$ (300 mg, 0.51 mmol) in 10 mL of chloroform and sodium acetate trihydrate (300 g, 4.0 mmol) in 10 mL of methanol. The reaction mixture was filtered immediately, and the filtrate was left standing at room temperature; colorless crystals formed. These were collected by filtration, washed with cold methanol and diethyl ether, and dried in air.

(b) General Method for Type I Complexes. Solutions of a lanthanide nitrate (1.0 mmol) in methanol (50 mL) and of the respective ligand $H_3L\cdot xH_2O$ (1.0 mmol) in dichloromethane (30 mL) were mixed; a precipitate formed immediately. The resulting mixture was left standing at room temperature for 3–5 h. The precipitate was collected by filtration, washed with ethanol and diethyl ether, and dried in air. Yields ranged from 50% to 90%.

(5) X-ray Crystallographic Analysis of $[Gd(L1)]_2\cdot 2CHCl_3$. A summary of crystal data is given in Table IV. The final unit-cell parameters were obtained by least-squares fitting of the setting angles for 25 reflections with 2θ = 37.2–41.7°. The intensities of three standard reflections, measured every 200 reflections throughout the data collection, decayed uniformly by 7.7%. The data were processed[27] and corrected for Lorentz and polarization effects, decay, and absorption (empirical, based on azimuthal scans for four reflections). A total of 13 862 reflections with $2\theta \leq 70°$ were collected on a Rigaku AFC6S diffractometer: of these 13 343 were unique (R_{int} = 0.022), and those 8771 having $I \geq 3\sigma(I)$ were employed in the solution and refinement of the structure.

The structure was solved by conventional heavy-atom methods, the coordinates of the Gd atom being determined from the Patterson function and those of the remaining non-hydrogen atoms from a subsequent difference Fourier synthesis. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were fixed in calculated positions (N–H/C–H = 0.98 Å, B(H) = 1.2B(bonded atom)). Neutral atom scattering factors and anomalous dispersion corrections for the non-hydrogen atoms were taken from ref 28. Bond lengths and bond angles appear in Tables V and VI, respectively. A more detailed table of crystallographic data (Table SI) and tables of hydrogen atom parameters (Table SII), anisotropic thermal parameters (Table SIII), torsion angles (Table SIV), intermolecular contacts (Table SV), least-squares planes (Table SVI), measured and calculated structure factor amplitudes

---

(27) TEXSAN/TEXRAY structure analysis package which includes versions of the following: DIRDIF, direct methods for difference structures, by P. T. Beurskens; ORFLS, full-matrix least-squares, and ORFFE, function and errors, by W. R. Busing, K. O. Martin, and H. A. Levy; ORTEP II, illustrations, by C. K. Johnson.

(28) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England (present distributor D. Reidel: Dordrecht, The Netherlands), 1974; Vol. IV, pp 99–102, 149.

Table V. Bond Lengths (Å) with Estimated Standard Deviations[a]

Gd(1)–O(1)	2.384 (2)	C(3)–C(4)	1.501 (5)
Gd(1)–O(1)′	2.391 (2)	C(4)–C(5)	1.410 (4)
Gd(1)–O(2)	2.269 (2)	C(4)–C(9)	1.387 (5)
Gd(1)–O(3)	2.237 (2)	C(5)–C(6)	1.389 (5)
Gd(1)–N(1)	2.813 (3)	C(6)–C(7)	1.403 (5)
Gd(1)–N(2)	2.657 (3)	C(7)–C(8)	1.378 (7)
Gd(1)–N(3)	2.694 (3)	C(8)–C(9)	1.377 (7)
Gd(1)–N(4)	2.615 (3)	C(10)–C(11)	1.510 (5)
Cl(1)–C(28)	1.743 (7)	C(12)–C(13)	1.497 (5)
Cl(2)–C(28)	1.671 (6)	C(13)–C(14)	1.426 (4)
Cl(3)–C(28)	1.698 (6)	C(13)–C(18)	1.393 (5)
O(1)–C(5)	1.358 (3)	C(14)–C(15)	1.411 (4)
O(2)–C(14)	1.325 (4)	C(15)–C(16)	1.399 (5)
O(3)–C(23)	1.322 (4)	C(16)–C(17)	1.364 (6)
N(1)–C(1)	1.479 (4)	C(17)–C(18)	1.394 (6)
N(1)–C(10)	1.484 (4)	C(19)–C(20)	1.505 (5)
N(1)–C(19)	1.489 (4)	C(21)–C(22)	1.519 (5)
N(2)–C(2)	1.466 (4)	C(22)–C(23)	1.413 (5)
N(2)–C(3)	1.493 (4)	C(22)–C(27)	1.397 (5)
N(3)–C(11)	1.461 (4)	C(23)–C(24)	1.393 (5)
N(3)–C(12)	1.483 (4)	C(24)–C(25)	1.396 (6)
N(4)–C(20)	1.469 (4)	C(25)–C(26)	1.385 (7)
N(4)–C(21)	1.483 (4)	C(26)–C(27)	1.387 (6)
C(1)–C(2)	1.521 (5)		

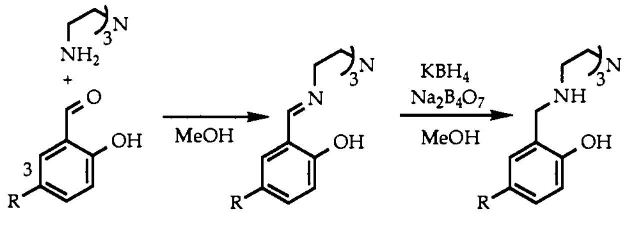
[a] Here and elsewhere, primes refer to the symmetry operation $1 - x$, $1 - y$, $-z$.

Table VI. Bond Angles (deg) with Estimated Standard Deviations

O(1)–Gd(1)–O(1)′	66.88 (8)	Gd(1)–N(4)–C(20)	112.9 (2)
O(1)–Gd(1)–O(2)	101.31 (7)	Gd(1)–N(4)–C(21)	110.4 (2)
O(1)–Gd(1)–O(3)	123.31 (8)	C(20)–N(4)–C(21)	112.7 (3)
O(1)–Gd(1)–N(1)	115.42 (7)	N(1)–C(1)–C(2)	112.5 (3)
O(1)–Gd(1)–N(2)	74.14 (8)	N(2)–C(2)–C(1)	109.3 (3)
O(1)–Gd(1)–N(3)	170.76 (7)	N(2)–C(3)–C(4)	110.3 (3)
O(1)–Gd(1)–N(4)	73.53 (8)	C(3)–C(4)–C(5)	118.7 (3)
O(1)′–Gd(1)–O(2)	84.56 (8)	C(3)–C(4)–C(9)	121.8 (3)
O(1)′–Gd(1)–O(3)	80.96 (8)	C(5)–C(4)–C(9)	119.4 (3)
O(1)′–Gd(1)–N(1)	166.22 (7)	O(1)–C(5)–C(4)	120.6 (3)
O(1)′–Gd(1)–N(2)	127.86 (8)	O(1)–C(5)–C(6)	120.9 (3)
O(1)′–Gd(1)–N(3)	116.62 (8)	C(4)–C(5)–C(6)	118.5 (3)
O(1)′–Gd(1)–N(4)	103.74 (8)	C(5)–C(6)–C(7)	121.3 (4)
O(2)–Gd(1)–O(3)	121.34 (8)	C(6)–C(7)–C(8)	119.4 (4)
O(2)–Gd(1)–N(1)	107.62 (8)	C(7)–C(8)–C(9)	119.9 (4)
O(2)–Gd(1)–N(2)	70.34 (8)	C(4)–C(9)–C(8)	121.6 (4)
O(2)–Gd(1)–N(3)	71.20 (8)	N(1)–C(10)–C(11)	112.8 (3)
O(2)–Gd(1)–N(4)	166.99 (8)	N(3)–C(11)–C(10)	109.7 (3)
O(3)–Gd(1)–N(1)	87.03 (9)	N(3)–C(12)–C(13)	112.2 (3)
O(3)–Gd(1)–N(2)	151.07 (9)	C(12)–C(13)–C(14)	118.8 (3)
O(3)–Gd(1)–N(3)	65.90 (8)	C(12)–C(13)–C(18)	122.2 (3)
O(3)–Gd(1)–N(4)	70.46 (9)	C(14)–C(13)–C(18)	119.0 (3)
N(1)–Gd(1)–N(2)	64.06 (8)	O(2)–C(14)–C(13)	120.7 (3)
N(1)–Gd(1)–N(3)	63.44 (8)	O(2)–C(14)–C(15)	121.0 (3)
N(1)–Gd(1)–N(4)	65.54 (8)	C(13)–C(14)–C(15)	118.3 (3)
N(2)–Gd(1)–N(3)	97.85 (8)	C(14)–C(15)–C(16)	120.1 (3)
N(2)–Gd(1)–N(4)	96.67 (9)	C(15)–C(16)–C(17)	121.8 (4)
N(3)–Gd(1)–N(4)	112.57 (8)	C(16)–C(17)–C(18)	118.7 (3)
Gd(1)–O(1)–Gd(1′)	113.12 (8)	C(13)–C(18)–C(17)	122.0 (4)
Gd(1)–O(1)–C(5)	124.4 (2)	N(1)–C(19)–C(20)	112.1 (3)
Gd(1)′–O(1)–C(5)	122.2 (2)	N(4)–C(20)–C(19)	110.2 (3)
Gd(1)–O(2)–C(14)	138.6 (2)	N(4)–C(21)–C(22)	116.1 (3)
Gd(1)–O(3)–C(23)	138.7 (2)	C(21)–C(22)–C(23)	123.9 (3)
Gd(1)–N(1)–C(1)	110.4 (2)	C(21)–C(22)–C(27)	117.1 (3)
Gd(1)–N(1)–C(10)	109.4 (2)	C(23)–C(22)–C(27)	118.7 (4)
Gd(1)–N(1)–C(19)	109.4 (2)	O(3)–C(23)–C(22)	121.7 (3)
C(1)–N(1)–C(10)	109.3 (3)	O(3)–C(23)–C(24)	119.5 (3)
C(1)–N(1)–C(19)	109.1 (3)	C(22)–C(23)–C(24)	118.8 (3)
C(10)–N(1)–C(19)	109.1 (3)	C(23)–C(24)–C(25)	121.6 (4)
Gd(1)–N(2)–C(2)	118.0 (2)	C(24)–C(25)–C(26)	119.6 (4)
Gd(1)–N(2)–C(3)	113.5 (2)	C(25)–C(26)–C(27)	119.5 (4)
C(2)–N(2)–C(3)	112.1 (3)	C(22)–C(27)–C(26)	121.8 (4)
Gd(1)–N(3)–C(11)	119.3 (2)	Cl(1)–C(28)–Cl(2)	114.5 (4)
Gd(1)–N(3)–C(12)	115.6 (2)	Cl(1)–C(28)–Cl(3)	107.4 (3)
C(11)–N(3)–C(12)	113.0 (3)	Cl(2)–C(28)–Cl(3)	112.6 (4)

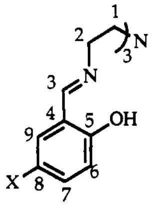
(Table SVII), and final atomic coordinates and equivalent isotropic thermal parameters (Table SVIII) are included as supplementary material (see paragraph at end of paper).

Scheme I



R = H, Cl and Br

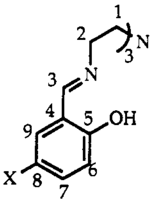
Table VII. ^1H NMR Data for Schiff Bases (in $CDCl_3$)



δ, ppm			
H_3saltren	H_3-5-Cl-saltren	H_3-5-Br-saltren	assgnt
2.82 (m, 6 H)	2.80 (m, 6 H)	2.80 (m, 6 H)	H1
3.56 (m, 6 H)	3.50 (m, 6 H)	3.50 (m, 6 H)	H2
7.80 (s, 3 H)	7.80 (s, 3 H)	7.80 (s, 3 H)	H3
6.92 (d, 3 H)[a]	6.90 (d, 3 H)[a]	6.70 (s, 3 H)	H6
7.15 (t, 3 H)[a]	7.20 (d, 3 H)[a]	7.30 (d, 3 H)[a]	H7
6.60 (t, 3 H)[a]			H8
6.05 (d, 3 H)[a]	6.20 (s, 3 H)	6.40 (s, 3 H)	H9
13.50 (b s, 3 H)	13.70 (b s, 3 H)	13.75 (b s, 3 H)	OH

[a] $^3J_{HH}$ = 6.8–7.0 Hz.

Table VIII. ^{13}C NMR Data for Schiff Bases (in $CDCl_3$)



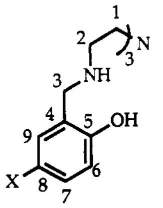
δ, ppm			
H_3saltren	H_3-5-Cl-saltren	H_3-5-Br-saltren	assgnt
55.9	55.3	55.3	C1
58.0	57.5	57.5	C2
166.1	165.1	165.1	C3
118.6	119.0	119.6	C4
161.1	159.5	158.0	C5
116.8	118.2	118.6	C6
131.7	132.4	135.3	C7
118.5	123.6	110.5	C8
131.9	130.3	133.3	C9

Results and Discussion

Three potentially heptadentate amine phenol ligands have been easily prepared (as shown in Scheme I) by KBH_4 reduction of the Schiff base ligands which were formed from the reaction of tren with 3 equiv of salicylaldehyde or its 5-substituted derivatives. They are all soluble in polar solvents such as chloroform, acetone, and methanol. Unlike their Schiff base analogs, they are hydrolytically stable under both basic and acidic conditions.

The ^1H and ^{13}C NMR data for the three Schiff bases and the three amine phenols are given in Tables VII–X. The NMR spectral assignments were based on ^1H–^1H COSY and ^1H–^{13}C heteronuclear correlation with the attached proton test (APT). The analytical (Table I) and spectral data are consistent with the proposed formulations. Infrared spectra of the new ligands show the disappearance of the bands at 1630–1500 cm^{-1}, which are characteristic of imine C═N bonds of the Schiff bases, and the

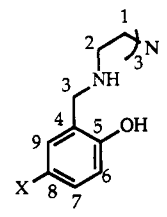
Table IX. ^{1}H NMR Data for Heptadentate Amine Phenols (in $CDCl_3$)



δ, ppm			
H_3L1 (X = H)	H_3L2 (X = Cl)	H_3L3 (X = Br)	assgnt
2.58 (m, 6 H)	2.56 (m, 6 H)	2.50 (m, 6 H)	H1
2.70 (m, 6 H)	2.68 (m, 6 H)	2.60 (m, 6 H)	H2
3.96 (s, 6 H)	3.86 (s, 6 H)	3.85 (s, 6 H)	H3
6.78 (d, 3 H)[a]	6.54 (d, 3 H)[a]	6.50 (d, 3 H)[a]	H6
7.16 (t, 3 H)[a]	6.98 (d, 3 H)[a]	7.10 (d, 3 H)[a]	H7
6.77 (t, 3 H)[a]			H8
6.95 (d, 3 H)[a]	6.84 (s, 3 H)	7.00 (s, 3 H)	H9
6.05 (b s, 6 H)	6.05 (b s, 6 H)	5.90 (b s, 6 H)	OH, NH

[a] $^3J_{HH}$ = 6.8–7.0 Hz.

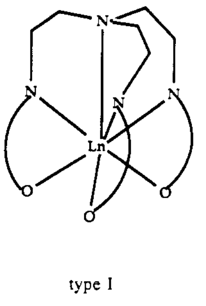
Table X. ^{13}C NMR Data for Heptadentate Amino Phenols (in $CDCl_3$)



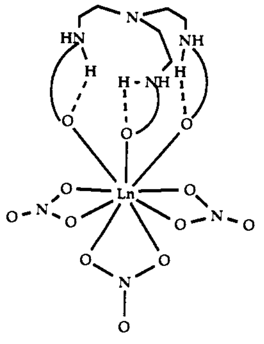
δ, ppm			
H_3L1 (X = H)	H_3L2 (X = Cl)	H_3L3 (X = Br)	assgnt
54.5	54.3	54.4	C1
46.1	46.1	46.1	C2
52.5	52.2	52.1	C3
122.4	123.5	124.3	C4
158.1	156.7	157.2	C5
116.3	117.6	118.1	C6
128.7	128.4	130.8	C7
119.1	123.7	110.8	C8
128.4	128.0	131.4	C9

presence of two new bands at 1610–1580 cm^{-1}, probably due to N—H bending vibrations. This confirms that the C═N bonds have been reduced to the CH_2—NH amine linkages. This conclusion is also supported by the ^{1}H NMR data, which show the absence of CH═N hydrogen resonances at about 8 ppm and the presence of new benzylic CH_2 resonances at about 4 ppm.

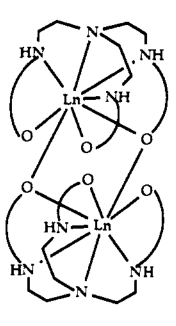
Like their Schiff base analogs,[4,5] which form seven-coordinate complexes (type I), these three ligands form two types of complexes, one of which (type III) is new, however. Homodinuclear lanthanide complexes (type III) with the formulation [Ln(L)]$_2$ were prepared from reactions of Ln^{3+} with potentially heptadentate amine phenol ligands in the presence of excess base (hydroxide or acetate). These type III complexes could also be prepared from the reaction of lanthanide nitrate with a large excess of the amine phenol, since the latter can act as a base. The type III complexes have been characterized by IR spectroscopy, mass spectrometry, elemental analysis, and, in the case of [Gd(L1)]$_2$·2CHCl$_3$, X-ray crystallography. These homodinuclear complexes contain two lanthanide ions, each of which is coordinated by a triply deprotonated N_4O_3 heptadentate ligand. One phenolate O atom on each ligand acts as a bridge between the two metal centers. Unlike the corresponding heptadentate Schiff base lanthanide complexes,[4,5] heptadentate amine phenol lanthanide complexes are very stable under basic or weakly acidic conditions both in the solid state and in solution.



type I



type II



type III

Reactions of the free ligand with 1 equiv of a lanthanide nitrate salt in the absence of base produce mononuclear complexes (type II) with the formulation [Ln(H$_3$L)(NO$_3$)$_3$]. They may have a nine-coordinate structure very similar to that found in their corresponding Schiff base complexes.[4] The type II complexes are quite air-stable and can be easily converted to type III complexes by reacting with 3–4 equiv of sodium hydroxide. Mass spectral and infrared data for all complexes were completely consistent with the indicated formulations.

Type II complexes show IR (N–H) stretches characteristic of the hydrogen-bonded protons bridging the N–O portion of the ligand. These are absent in the type III complexes. The nitrate IR bands (1480 and 1285 cm^{-1}) suggest the presence of bidentate nitrates in all of the type II complexes.[4] All type III complexes show IR bands at 3270–3250 cm^{-1} due to N–H stretches of the coordinated secondary amine groups and at 1595–1560 cm^{-1} due to N–H bending vibrations. Upon coordination to the metal ion, the N–H bending frequencies undergo a general bathochromic shift (about 15 cm^{-1}). New bands appear below 600 cm^{-1} in the spectrum of each coordinated ligand, and they are likely to be ν_{Ln-O} or ν_{Ln-N}; however, assignments of these bands are very difficult in this region because of the low energies associated with these vibrations.[12]

The ^{1}H NMR spectra of type II lanthanum(III) complexes in DMSO showed chemical shifts of the free ligand or broad peaks. This suggests that, in the strong σ-donor solvent DMSO, the complexes may decompose to form the multisolvated Ln^{3+} species in solution. The ^{1}H NMR spectra of type III complexes were not obtained due to their very low solubility in common organic solvents.

The FAB mass spectra of both type II and type III complexes were obtained in a 3-nitrobenzyl alcohol matrix in the positive-ion detection mode. Results are presented in Table III. In general, for type III complexes, both monomeric ([Ln(L)]$^+$) and dimeric ([Ln(L)]$_2$$^+$) molecular ion peaks were detected with the intensity of the latter being higher than that of the former. This clearly established the dinuclear nature of the type III complexes and is consistent with the structural findings for [Gd(L1)]$_2$·2CHCl$_3$. In the spectra of all type III complexes, there were also fragmentation patterns indicative of the respective ligand. In the FAB spectra of most type II complexes, only peaks corresponding to the [Ln(HL)]$^+$ and [Ln(H$_2$L)(NO$_3$)]$^+$ ions were observed with no molecular ion peaks ([Ln(H$_3$L)(NO$_3$)$_3$]$^+$) being detected.

The ORTEP stereo drawing of [Gd(L1)]$_2$ is illustrated in Figure 1, and the Gd coordination environment is presented in Figure 2. The unit cell contains one dinuclear [Gd(L1)]$_2$ molecule with two CHCl$_3$ molecules in the crystal lattice for each dimer. There are no abnormally short intermolecular contacts. The dinuclear complex [Gd(L1)]$_2$ has two identical eight-coordinate Gd atoms, each of which is surrounded by a N_4O_4 donor set (Figure 2). The two Gd centers are bridged by one phenolate O atom from each of the two separate heptadentate ligands. The two gadolinium and two bridging oxygen atoms form a planar four-membered ring with a metal–metal separation of 3.9841 (2) Å and angles at the oxygen bridgeheads of 113.12°. The molecule is centrosymmetric; thus the two heptadentate ligand project on the opposite sides of the Gd$_2$O$_2$ plane. The geometry around each gadolinium atom can be viewed as a distorted bicapped octahedron, in which the

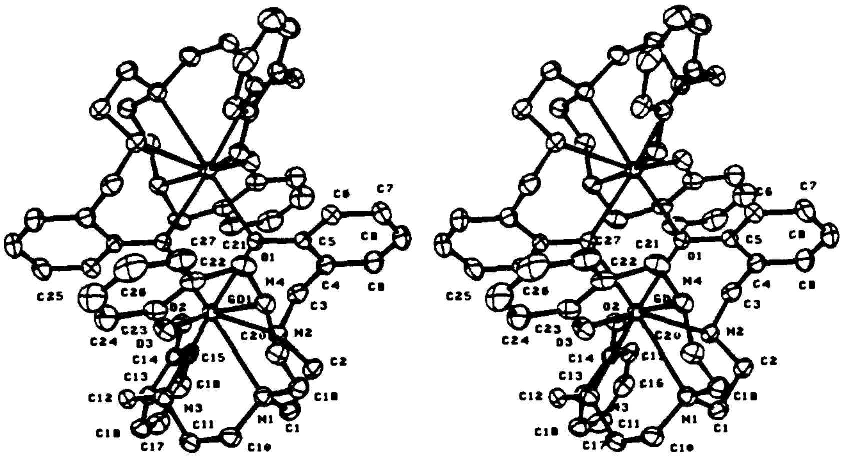


Figure 1. ORTEP stereoview of $[Gd(L1)]_2 \cdot 2CHCl_3$.

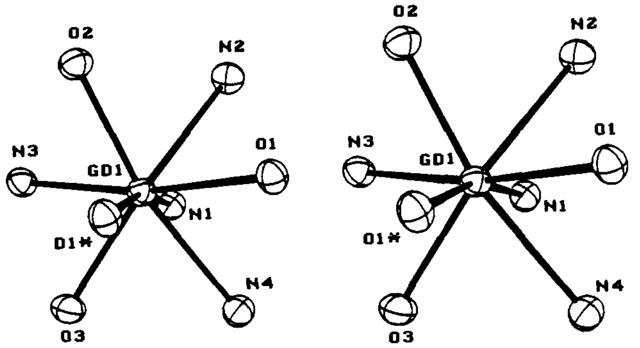


Figure 2. Coordination environment of Gd in $[Gd(L1)]_2 \cdot 2CHCl_3$.

octahedron composed of two sets of donor atoms, O(1), O(2), O(3) and N(2), N(3), N(4), is flattened by the coordination of two capping atoms O(1)′ and N(1) to the metal center. As a result, the geometry around each gadolinium atom is distorted toward cubic with the two metal coordination spheres sharing the same edge O(1)–O(1)′. The angles O(1)–Gd(1)–N(3), O(1)′–Gd(1)–N(1), O(2)–Gd(1)–N(4), and O(3)–Gd(1)–N(2) are 170.8, 166.2, 167.0, and 151.1°, respectively, illustrating the distortion toward cubic geometry. The largest deviation occurs at O(3)–Gd(1)–N(2), which is probably caused by crowding from the other half of the dimeric molecule and by the small angle N(1)–Gd(1)–N(2) enforced by the $N(1)CH_2CH_2N(2)$ arm of the heptadentate ligand (as is often found in five-membered chelate rings of lanthanide complexes[29,30]).

Inspection of the structure of $[Gd(L1)]_2$ reveals that the heptadentate capability of the ligand has been realized by removing the three "acidic" phenolic protons, but formation of the dinuclear complex $[Gd(L1)]_2$ is unexpected. This is probably caused by the higher coordination requirements of lanthanide metal ions and the small cavity in the heptadentate ligand. Homodinuclear lanthanide complexes with single-atom bridges are rare.[21] Only five complexes of this kind have been structurally characterized so far: a dimeric praseodymium (2.2.1) cryptate,[21] in which the two metal atoms are bridged by two μ-hydroxo groups, a dinuclear bis(μ-hydroxo)diytterbium complex with pyridine-2-carboxaldehyde 2-pyridylhydrazone,[22] a La_2Cl_2 complex of a tridentate Schiff base,[31] an acetate-bridged Y_2 species,[32] and a (μ-O)Pr_2 complex with trifluoroacetate and crown ether ligands.[33] In three of the five cases, the complexes are partially hydrolyzed products formed in the presence of an excess of a ligand which is a strong base.[21,22,33] The lack of structural data on dinuclear lanthanide complexes is probably due, in part, to difficulties in isolating crystals suitable for structural analysis and, in part, to the fact that complex hydrolysis most often leads to the precipitation of lanthanide hydroxides instead of well-defined soluble complexes.[21] In $[Gd(L1)]_2$, the hydrolysis has been prevented by the tribasic heptadentate ligand. The dinuclear lanthanide complexes described herein are likely formed by the dimerization of the two seven-coordinated monomeric species [Ln(L)], which are still coordinatively unsaturated.

The bond lengths and selected bond angles are listed in Tables V and VI, respectively. The Gd–N bond lengths are 2.813, 2.657, 2.694, and 2.615 Å for Gd(1)–N(1), Gd(1)–N(2), Gd(1)–N(3), and Gd(1)–N(4), respectively, with an average of 2.69 Å. These are consistent with those found in a nine-coordinated Gd(III) complex [Gd(L)] (L = [18]-N_3O_3-triacetate, Gd–N = 2.641, 2.642, and 2.686 Å).[34] The Gd–O bond lengths fall into two categories. The bridging Gd(1)–O(1) and Gd(1)–O(1)′ distances in the four-membered ring are 2.384 and 2.391 Å, respectively, while the terminal Gd–O bond lengths are 2.269 (Gd(1)–O(2)) and 2.237 Å (Gd(1)–O(3)), with an average of 2.25 Å. These values are consistent with those found in an eight-coordinated complex $[Er(salen)_2]^-$ (Er–O = 2.22–2.35 Å)[35] after correcting for the ionic radii differences of the two metal ions. Since the bridging oxygen atoms O(1) and O(1)′ form two strong Gd–O bonds, their basicity should be lowered relative to singly bonded oxygen atoms; the bridging Gd–O distances are 0.13 Å longer than those of terminal Gd–O bonds.

The magnetic properties of some of the mononuclear and dinuclear lanthanide complexes reported here were investigated in order to determine if there are magnetic interactions between two metal centers of the type III complexes. The room-temperature magnetic moments of the lanthanide complexes are given in Table III. In general, the magnetic moments of type III complexes are very close to those of their type II analogs, suggesting that there are very weak or no magnetic interactions between the two phenolate-bridged metal centers in the dinuclear complexes. This is probably due to the long distance between two metal centers (e.g. Gd–Gd = 3.9841 (2) Å) and also to the fact that the 4f orbitals do not contribute significantly to metal–ligand bonding.[36] Similar results have also been reported by Raymond's[37] and Freeman's[22] groups. The experimental magnetic moment values of both type II and type III complexes show very little deviation from the theoretical ($\mu_{eff} = g[J(J+1)]^{1/2}$) values ($Pr^{3+}$, 3.58 μ_B;

---

(29) Spirlet, M.-R.; Rebizant, J.; Loncin, M.-F.; Desreux, J. F. *Inorg. Chem.* **1984**, *23*, 4278.

(30) Spirlet, M.-R.; Rebizant, J.; Desreux, J. F.; Loncin, M.-R. *Inorg. Chem.* **1984**, *23*, 359.

(31) Blech, P.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1990**, 3557.

(32) Ribot, F.; Toledano, P.; Sanchez, C. *Inorg. Chim. Acta* **1991**, *185*, 239.

(33) Harrison, D.; Giorgetti, A.; Bünzli, J.-C. G. *J. Chem. Soc., Dalton Trans.* **1985**, 885.

(34) Chen, D.; Squattrito, P. J.; Martell, A. E.; Clearfield, A. *Inorg. Chem.* **1990**, *29*, 4366.

(35) Mangani, S.; Takeuchi, A.; Yamada, S.; Orioli, P. *Inorg. Chim. Acta* **1989**, *155*, 149.

(36) Karraker, D. G. *J. Chem. Educ.* **1970**, *47*, 424. Johnson, O. *Ibid.* **1970**, *47*, 431.

(37) Baker, E. C.; Brown, L. D.; Raymond, K. N. *Inorg. Chem.* **1975**, *14*, 1376.

Nd^{3+}, 3.62 μ_B; Gd^{3+}, 7.94 μ_B)[38] and from those for their octahydrated sulfates,[38] suggesting that the 4f electrons in these complexed lanthanide ions are well-shielded by the outermost s and p electrons.

For the Gd complexes, whether monomeric or dimeric, Gd^{3+} has a $4f^7$ configuration; since there is no orbital degeneracy associated with this configuration, the ^8S ground term leads to a magnetic moment which is very close to the spin-only value ($\mu_{eff} = g[S(S+1)]^{1/2} = 7.94$ μ_B per Gd^{3+}), independent of ligand field effects. Magnetic susceptibility measurements were made on a powdered sample of $[Gd(L1)]_2{\cdot}2CHCl_3$ over the temperature range 4.2–82 K. The effective magnetic moment at 81.7 K is, within error, identical to the spin-only value of 7.94 μ_B per Gd^{3+}. Below this temperature, the moment decreases slightly with decreasing temperature, becoming significantly less than the spin-only value by 30 K (7.81 μ_B) and reaching a value of 7.30 μ_B at 4.2 K. Since such behavior may arise from magnetic coupling between the metal centers in the dimer, the magnetic susceptibility data over the whole temperature range studied were compared to theory for two antiferromagnetically coupled $S = {}^7/_2$ ions.[25] Good agreement between experiment and theory was obtained for $g = 2.00$ and $-J = 0.045$ (1) cm^{-1}. There is evidence, then, for weak antiferromagnetic coupling in this compound although the strength of the coupling is clearly much less than that in any related homodinuclear lanthanide Schiff base compound.[20]

In conclusion, tripodal heptadentate amine phenol ligands have been prepared from KBH_4 reduction of the corresponding Schiff bases. Reaction of these ligands with lanthanide nitrates yields type III dinuclear complexes in the presence of a base (hydroxide or acetate), while type II complexes are obtained from the reactions of lanthanide nitrate with 1 equiv of the free ligand. Unlike mononuclear lanthanide complexes of heptadentate Schiff base ligands,[4,5] both types of complexes reported in this study are quite air-stable. From the structure of $[Gd(L1)]_2{\cdot}2CHCl_3$, it seems that the formation of the dinuclear complex is caused by the higher coordination requirements of lanthanide ions and/or by the small cavity of the heptadentate ligand. There are two ways to prevent this dimerization: one is to introduce bulky groups onto aromatic benzene rings at the 3-position and the other is to increase the length of three chelating "arms". Further studies on heptadentate tripod ligands with longer "arms" (to increase the cavity of the N_4O_3 donor set) and with a variety of substituents on the aromatic rings (to modify the steric hindrance and lipophilicity) are in progress.

Acknowledgment is made to the Natural Sciences and Engineering Research Council of Canada for an NSERC Postdoctoral Fellowship (S.L.) and operating grants (R.C.T., C.O.) and to the U.S. Public Health Service for an operating grant (CA 48964). We also thank Professor J. Trotter for the use of his crystallographic facilities and Dr. P. Wassell for the use of his magnetometer for the room-temperature studies.

Supplementary Material Available: A more detailed table of crystallographic data (Table SI) and tables of hydrogen atom parameters (Table SII), anisotropic thermal parameters (Table SIII), torsion angles (Table SIV), intermolecular contacts (Table SV), least-squares planes (Table SVI), and final atomic coordinates and equivalent isotropic thermal parameters (Table SVIII) (17 pages); a listing of measured and calculated structure factor amplitudes (Table SVII) (45 pages). Ordering information is given on any current masthead page.

---

[38] Figgis, B. N. *Introduction to Ligand Fields*; Wiley Interscience: New York, 1961; p 326.

Mechanism of Benzene Loss from Tp′Rh(H)(Ph)(CN-neopentyl) in the Presence of Neopentyl Isocyanide. Evidence for an Associatively Induced Reductive Elimination

William D. Jones* and Edward T. Hessell

Contribution from the Department of Chemistry, University of Rochester, Rochester, New York 14627. Received January 6, 1992

Abstract: Thermolysis of Tp′Rh(H)(Ph)(CN-neopentyl) (**1**) (Tp′ = hydrotris(3,5-dimethylpyrazolyl)borate) in benzene in the presence of added isocyanide gives $Tp'Rh(CN\text{-}neopentyl)_2$ (**2**). The rate of reaction increases with increasing isocyanide concentration, but the dependence is nonlinear and approaches zero order at high isocyanide concentrations. When the reaction is conducted with Tp′Rh(D)(d_5-Ph)(CN-neopentyl) in benzene-d_6, an inverse kinetic isotope effect of 0.85 ± 0.02 is observed. Measurement of the temperature dependence of the rate of the reaction at a single isocyanide concentration gives $\Delta H^* = 15.2 \pm 1.2$ kcal/mol and $\Delta S^* = -36 \pm 3$ eu. Thermolysis of **1** in the presence of added 2,6-xylyl isocyanide shows no evidence for the formation of Tp′Rh(H)(Ph)(2,6-xylyl isocyanide) (**3**). Thermolysis of isotopically labeled Tp′Rh(H)(d_5-Ph)(CN-neopentyl) at 60 °C in either THF-d_8 or toluene-d_8 results in intramolecular migration of the metal hydride into all of the phenyl proton positions at the same time and rate. A mechanism is proposed to account for all of the above observations which involves initial reductive elimination of benzene from **1** to give an η^2-benzene intermediate in which the rhodium atom can migrate around the benzene ring. Subsequent associative exchange of isocyanide for benzene occurs in a second step.

Introduction

The formation of a C–H bond by reductive elimination from a transition metal center is a fundamental process in organometallic chemistry[1] (eq 1) and is a crucial step in many reactions catalyzed by homogeneous transition metal complexes.[2] Studies of the mechanism of this process for various systems have provided important insight into the requirements for the opposite reaction (i.e., oxidative addition of C–H bonds to a transition metal).[3]

(1)

---

[1] Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 332. (b) Norton, J. R. *Acc. Chem. Res.* **1979**, *12*, 139.

[2] Chan, A. S. C.; Halpern, J. *J. Am. Chem. Soc.* **1980**, *102*, 838.

0002-7863/92/1514-6087$03.00/0