Inorg. Chem. **1993,** *32,* 2773–2778

Bulky Ortho 3-Methoxy Groups on N_4O_3 Amine Phenol Ligands Producing Six-Coordinate Bis(ligand)lanthanide Complex Cations $[Ln(H_3L)_2]^{3+}$ (Ln = Pr, Gd; H_3L = Tris(((2-hydroxy-3-methoxybenzyl)amino)ethyl)amine)

Shuang Liu,[1] Li-Wei Yang, Steven J. Rettig, and Chris Orvig*

Department of Chemistry, University of British Columbia, 2036 Main Mall,
Vancouver, British Columbia V6T 1Z1, Canada

Received January 4, 1993

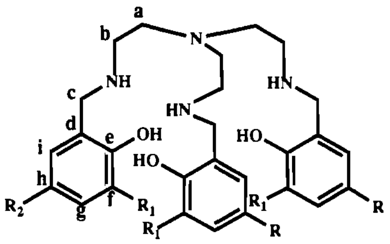
The synthesis and characterization of an N_4O_3 amine phenol (tris(((2-hydroxy-3-methoxybenzyl)amino)ethyl)amine, H_3L4) and its lanthanide complexes $[Ln(H_3L4)(NO_3)_3]$ (Ln = Pr, Nd) and $[Ln(H_3L4)_2](NO_3)_3$ (Ln = Pr, Nd, Gd, Yb) are reported. The N_4O_3 amine phenol ligand is the KBH_4 reduction product of the Schiff base derived from the reaction of tris(2-aminoethyl)amine (tren) and 3 equiv of *o*-vanillin. The reactions of lanthanide nitrates with 1 equiv of H_3L4 produce nine-coordinate type II complexes, $[Ln(H_3L4)(NO_3)_3]$ (Ln = Pr, Nd), in which H_3L4 acts as a tridentate O_3 ligand and six-coordinate bis(ligand) type IV complexes, $[Ln(H_3L4)_2](NO_3)_3$ (Ln = Gd, Yb). The latter were prepared from the reactions of lanthanide nitrates with 2 equiv of H_3L4 in the presence of sodium hydroxide. The X-ray crystal structures of $[Ln(H_3L4)_2](NO_3)_3{\cdot}xH_2O{\cdot}yMeOH$ (Ln = Pr, $x = 5.56$, $y = 0.44$; Ln = Gd, $x = 5.96$, $y = 0.66$) have been determined. Crystals of $[Ln(H_3L4)_2](NO_3)_3{\cdot}xH_2O{\cdot}yMeOH$ (Ln = Pr, $x = 5.56$, $y = 0.44$; Ln = Gd, $x = 5.96$, $y = 0.66$) are isomorphous, crystallizing in the monoclinic space group $C2/c$, with $a = 25.260(2)$ [25.131(2)] Å, $b = 14.927(3)$ [14.990(4)] Å, $c = 21.402(2)$ [21.459(3)] Å, $\beta = 112.912(7)°$ [112.615(7)°], $Z = 4$, and $V = 7433(2)$ [7462(2)] Å^3 (bracketed values refer to the Gd complex). The structures were solved by the Patterson method and were refined by full-matrix least-squares procedures to $R = 0.033$ [0.033] and $R_w = 0.040$ [0.036] for 5032 [5867] reflections with $I \geq 3\sigma(I)$, respectively. In both complexes, the three phenolate O atoms of each of the two tridentate amine phenol ligands coordinate to the metal ions in a slightly distorted octahedral geometry while the secondary amine N atoms are protonated and uncoordinated. The effects of bulky 3-methoxy groups of the phenyl rings on the coordinating behavior toward lanthanide metals are discussed.

Introduction

We are interested in the coordination chemistry of lanthanide ions with polydentate ligands in general, and in the potential application of lanthanide complexes as magnetic resonance contrasting agents in particular.[2,3] Recently, we reported[4] three potentially heptadentate (N_4O_3) amine phenol ligands (H_3L1, H_3L2, and H_3L3 in Chart I). These ligands form mononuclear, $[Ln(H_3L)](NO_3)_3$, and homodinuclear, $[Ln(L)]_2$, lanthanide complexes depending on the conditions of preparation. A structural study revealed the first example, $[Gd(L1)]_2{\cdot}CHCl_3$, of a homodinuclear binary lanthanide complex $[Ln(L)]_2$ with heptadentate ligands.[4] The formation of the dinuclear structure was probably caused by the higher coordination requirements of lanthanide ions.

In order to study the effect of substituents at the ortho position (3-position) of the aromatic rings on the coordination behavior of the N_4O_3 amine phenol ligands toward lanthanide metal ions and to force the halves of the $[Ln(L)]_2$ dimers apart, we have prepared a new amine phenol ligand, tris(((2-hydroxy-3-methoxybenzyl)amino)ethyl)amine (H_3L4), where the 3-substituents of the phenyl rings are methoxy groups. In this paper, we describe the synthesis, structures, and characterization of H_3L4 and its type II, $[Ln(H_3L4)(NO_3)_3]$ (Ln = Pr, Nd), and type IV, $[Ln(H_3L4)_2](NO_3)_3$ (Ln = Pr, Nd, Gd, Yb), complexes.

Chart I. N_4O_3 Amine Phenols



H_3L1: $R_1 = R_2 = H$
H_3L2: $R_1 = H$; $R_2 = Cl$
H_3L3: $R_1 = H$; $R_2 = Br$
H_3L4: $R_1 = OMe$; $R_2 = H$

Experimental Section

Materials. Hydrated lanthanide salts, tris(2-aminoethyl)amine (tren), potassium borohydride, and *o*-vanillin were obtained from Aldrich or Alfa and were used without further purification.

Instrumentation. NMR spectra (200 and 500 MHz) were recorded on Bruker AC-200E (^{1}H–^{1}H COSY and APT ^{13}C NMR) and Varian XL 500 (^{1}H, ^{13}C, ^{1}H–^{13}C heteronuclear correlation) spectrometers, respectively. Chemical shifts in ppm are reported as δ downfield from TMS; assignments were based on ^{1}H–^{1}H COSY and ^{1}H–^{13}C heterocorrelation spectra with the attached proton test (APT). 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. Only the most intense peaks in an isotopic envelope are listed; appropriate isotopic ratios were seen where multiple isotopes were present. Infrared spectra were recorded as KBr disks in the range 4000–400 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, and N were performed by Mr. Peter Borda in this department.

Ligand Synthesis. Tris(((3-methoxysalicylidene)amino)ethyl)amine (H_3vantren). To a solution of *o*-vanillin (9.12 g, 60 mmol) in methanol

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* To whom correspondence should be addressed.

[1] Natural Sciences and Engineering Research Council Postdoctoral Fellow, 1991–1993.

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0020-1669/93/1332-2773$04.00/0

(20 mL) was added tren (2.92 g, 20 mmol) in the same solvent (10 mL). The resulting orange solution was stirred for 10 min while an orange yellow precipitate formed in an exothermic reaction. After the mixture cooled, the precipitate was filtered off, washed with diethyl ether, and dried in air. The yield was 9.85 g (93%); mp 133–134 °C (lit.[5] 119–120 °C). Anal. Calcd (found) for $C_{30}H_{36}N_4O_6 \cdot 0.5CH_3OH$: C, 64.88 (65.12); H, 6.78 (6.79); N, 9.92 (9.81). Mass spectrum (EI): $m/z = 548$ (M^+, $[C_{30}H_{36}N_4O_6]^+$). IR (cm^{-1}, KBr disk): 3600–2200 (br, ν_{O-H}), 3000–2800 (w or m, ν_{C-H}), 1635, 1480 (vs, br, $\nu_{C=N}$, $\nu_{C=C}$). ^1H NMR ($CDCl_3$; the atom labeling is the same as that of the amine phenols in Chart I): 2.78 (t, 6H, H_a), 3.46 (t, 6H, H_b), 3.80 (s, 9H, OCH_3), 5.80 (d, 3H, H_g, $^3J_{HH} = 6.8$ Hz), 6.48 (t, 3H, H_h, $^3J_{HH} = 6.8$ Hz), 6.80 (d, 3H, H_i, $^3J_{HH} = 6.8$ Hz), 7.75 (s, 3H, H_c), 14.20 (b s, 3H, OH). ^{13}C NMR ($CDCl_3$): 55.8 (C_b), 56.0 (OCH_3), 57.1 (C_a), 113.6 (C_i), 117.3 (C_h), 118.1 (C_d), 123.4 (C_g), 148.4 (C_f), 152.6 (C_e), 166.2 (C_c).

Tris(((2-hydroxy-3-methoxybenzyl)amino)ethyl)amine (H_3L4). To a solution of H_3vantren (5.48 g, 10 mmol) in methanol (100 mL) was added KBH_4 (2.12 g, 400 mmol) in small portions over 30 min. After the addition was complete (the orange color disappeared and the solution was colorless or pale yellow), the reaction mixture was stirred for an additional hour. The solvent was removed under reduced pressure, and the residue was taken up with chloroform (250 mL) and washed with 10% NH_4OAc solution (100 mL) and water. The organic fraction was separated from the mixture and dried over anhydrous $MgSO_4$. The solution was filtered, and chloroform was removed on a rotary evaporator to give a pale yellow solid. The solid was dried overnight under vacuum. The yield was 4.35 g (85%); mp 42–45 °C. Anal. Calcd (found) for $C_{30}H_{42}N_4O_6 \cdot 0.5CHCl_3$: C, 59.63 (59.84); H, 6.97 (6.97); N, 9.12 (9.14). Mass spectrum (FAB): $m/z = 555$ ($[M + 1]^+$, $[C_{30}H_{43}N_4O_6]^+$). IR (cm^{-1}, KBr disk): 3600–2200 (br, ν_{O-H} and ν_{N-H}), 3000–2800 (w or m, ν_{C-H}), 1590 (s, δ_{N-H}), 1490–1420 (vs, $\nu_{C=C}$). ^1H NMR ($CDCl_3$): 2.50 (m, 6H, H_a), 2.64 (m, 6H, H_b), 3.80 (s, 9H, OCH_3), 3.92 (s, 6H, H_c), 6.25 (b s, 3H, OH/NH), 6.54 (d, 3H, H_h, $^3J_{HH} = 6.8$ Hz), 6.68 (t, 3H, H_i, $^3J_{HH} = 6.8$ Hz), 6.75 (d, 3H, H_g, $^3J_{HH} = 6.8$ Hz). ^{13}C NMR ($CDCl_3$): 46.0 (C_b), 52.1 (C_c), 54.2 (C_a), 55.9 (OCH_3), 110.8 (C_i), 118.6 (C_h), 120.7 (C_g); 123.1 (C_d), 147.2 (C_f), 147.9 (C_e).

Synthesis of Metal Complexes. $[Pr(H_3L4)(NO_3)_3] \cdot 4H_2O$. To a solution of $Pr(NO_3)_3 \cdot 5H_2O$ (417 mg, 1.0 mmol) in methanol (30 mL) was added H_3L4 (556 mg, 1.0 mmol) in chloroform (10 mL); a precipitate formed immediately. The reaction mixture was stirred for 2 h. The precipitate was filtered off, washed with ethanol and diethyl ether, and dried in air. The yield was 530 mg (56%). Anal. Calcd (found) for $C_{30}H_{50}N_7O_{19}Pr$: C, 37.78 (37.59); H, 5.28 (4.97); N, 10.28 (10.03). Mass spectrum (FAB): $m/z = 819$ ($Pr(H_3L4)(NO_3)_2]^+$), 693 ($[Pr(HL4)]^+$). IR (cm^{-1}, KBr disk): 3700–2500 (br, ν_{O-H}), 1595, 1570 (w, δ_{N-H}), 1380, 1280 (s, ν_{N-O}).

$[Nd(H_3L4)(NO_3)_3] \cdot 3H_2O \cdot 2CH_3OH$. A procedure similar to that for $[Pr(H_3L4)(NO_3)_3] \cdot 4H_2O$ was employed using $Nd(NO_3)_3 \cdot 5H_2O$ (420 mg, 1.0 mmol) and H_3L4 (556 mg, 1.0 mmol). The yield was 730 mg (73%). Anal. Calcd (found) for $C_{32}H_{56}N_7NdO_{20}$: C, 38.32 (38.12); H, 5.63 (5.30); N, 9.77 (9.53). Mass spectrum (FAB): $m/z = 694$ ($[Nd(HL4)]^+$). IR (cm^{-1}, KBr disk): 3700–2500 (br, ν_{O-H}), 1595, 1570 (w, δ_{N-H}), 1380, 1280 (s, ν_{N-O}).

$[Pr(H_3L4)_2](NO_3)_3 \cdot H_2O \cdot 5CH_3OH$. To a solution of $Pr(NO_3)_3 \cdot 5H_2O$ (210 mg, 0.50 mmol) in methanol (30 mL) was added H_3L4 (556 mg, 1.0 mmol) in chloroform (10 mL); a precipitate formed immediately. Upon addition of 2 N NaOH (2.0 mL) dropwise, the precipitate redissolved to give a clear solution. The solution was filtered immediately, and the filtrate was left standing at room temperature; slow evaporation yielded microcrystals. These were collected by filtration, washed with ethanol and diethyl ether, and dried in air. The yield was 435 mg (54%). Suitable crystals were selected for an X-ray diffraction study. Anal. Calcd (found) for $C_{65}H_{106}N_{11}O_{27}Pr$: C, 48.36 (48.37); H, 6.62 (6.51); N, 9.54 (9.17). Mass spectrum (FAB): $m/z = 1247$ ($[Pr(H_2L4)_2]^+$), 693 ($[Pr(HL4)]^+$). IR (cm^{-1}, KBr disk): 3700–2500 (br, ν_{O-H}), 1600, 1575 (w, δ_{N-H}), 1385, 1285 (s, ν_{N-O}).

$[Nd(H_3L4)_2](NO_3)_3 \cdot H_2O \cdot 6CH_3OH$. The complex preparation was similar to that for $[Pr(H_3L4)_2](NO_3)_3 \cdot H_2O \cdot 5CH_3OH$ using $Nd(NO_3)_3 \cdot 5H_2O$ (210 mg, 0.50 mmol) and H_3L4 (556 mg, 1.0 mmol). The yield was 410 mg (50%). Anal. Calcd (found) for $C_{66}H_{110}N_{11}NdO_{28}$: C, 48.05 (48.23); H, 6.72 (6.66); N, 9.34 (9.08). Mass spectrum (FAB): $m/z = 1249$ ($[Nd(H_2L4)_2]^+$), 694 ($[Nd(HL4)]^+$). IR (cm^{-1}, KBr disk): 3700–2500 (br, ν_{O-H}), 1600, 1575 (w, δ_{N-H}), 1380, 1285 (s, ν_{N-O}).

Table I. Selected Crystallographic Data for $[Pr(H_3L4)_2](NO_3)_3 \cdot 5.56H_2O \cdot 0.44CH_3OH$ and $[Gd(H_3L4)_2](NO_3)_3 \cdot 5.96H_2O \cdot 0.66CH_3OH$

	$[Pr(H_3L4)_2](NO_3)_3 \cdot 5.56H_2O \cdot 0.44CH_3OH$	$[Gd(H_3L4)_2](NO_3)_3 \cdot 5.96H_2O \cdot 0.66CH_3OH$
formula	$C_{60.44}H_{96.88}N_{11}O_{26.96}Pr$	$C_{60.66}H_{98.56}GdN_{11}O_{27.62}$
fw	1549.92	1581.15
cryst syst	monoclinic	monoclinic
space group	*C*2/*c*	*C*2/*c*
a, Å	25.260(2)	25.131(2)
b, Å	14.927(3)	14.990(4)
c, Å	21.402(2)	21.459(3)
β, deg	112.912(7)	112.615(7)
V, $Å^3$	7433(2)	7462(2)
Z	4	4
ρ_c, g/cm^3	1.385	1.407
T, °C	21	21
radiation (λ, Å)	Cu (1.541 78)	Mo (0.710 69)
μ(Cu Kα), cm^{-1}	58.64	9.73
transm factor	0.90–1.00	0.91–1.00
R	0.033	0.033
R_w	0.040	0.036

$[Gd(H_3L4)_2](NO_3)_3 \cdot 5H_2O \cdot 2CH_3OH$. Method 1. A procedure similar to that for $[Pr(H_3L4)_2](NO_3)_3 \cdot H_2O \cdot 5CH_3OH$ was employed using $Gd(NO_3)_3 \cdot 6H_2O$ (225 mg, 0.50 mmol) and H_3L4 (556 mg, 1.0 mmol). The yield was 470 mg (59%). Suitable crystals were selected for an X-ray diffraction study. Anal. Calcd (found) for $C_{62}H_{102}GdN_{11}O_{28}$: C, 46.35 (46.33); H, 6.40 (6.24); N, 9.59 (9.26). Mass spectrum (FAB): $m/z = 1262$ ($[Gd(HL4)_2]^+$), 710 ($[Gd(HL4)]^+$). IR (cm^{-1}, KBr disk): 3700–2500 (br, m, ν_{O-H}), 1600, 1575 (w, δ_{N-H}), 1388, 1288 (s, ν_{N-O}).

Method 2. Solutions of $Gd(NO_3)_3 \cdot 6H_2O$ (225 mg, 1.0 mmol) in methanol (30 mL) and of H_3L4 (556 mg, 1.0 mmol) in chloroform (10 mL) were mixed while a precipitate formed immediately. After 2 h of stirring, the precipitate was filtered off, washed with ethanol and diethyl ether, and dried in air. The yield was 700 mg (60%). The product was shown by IR, FAB-MS, and elemental analysis to be identical (with varying solvation) to that obtained by method 1.

$[Yb(H_3L4)_2](NO_3)_3 \cdot 3H_2O \cdot 4CH_3OH$. The complex was prepared similarly to $[Gd(H_3L4)_2](NO_3)_3 \cdot 5H_2O \cdot 2CH_3OH$ using $Yb(NO_3)_3 \cdot 5H_2O$ (225 mg, 0.50 mmol) and H_3L4 (556 mg, 1.0 mmol). The yield was 500 mg (50%). Anal. Calcd (found) for $C_{64}H_{106}N_{11}O_{28}Yb$: C, 46.57 (46.68); H, 6.47 (6.32); N, 9.33 (9.04). Mass spectrum (FAB): $m/z = 1280$ ($[Yb(H_2L4)_2]^+$), 726 ($[Yb(HL4)]^+$). IR (cm^{-1}, KBr disk): 3700–2500 (br, m, ν_{O-H}), 1600, 1576 (w, δ_{N-H}), 1390, 1285 (s, ν_{N-O}).

Conversion of Type II to Type IV Complexes. To a suspension of $[Ln(H_3L4)(NO_3)_3]$ (Ln = Pr or Nd) in a mixture of methanol (30 mL) and chloroform (10 mL) was added 2 N NaOH (2.0 mL) dropwise; the suspension became clear and then cloudy. After being stirred for 10 min, the mixture was filtered (the solid was shown by IR to be lanthanide hydroxide). The filtrate was left standing at room temperature; slow evaporation of solvents afforded a microcrystalline product. This product was collected by filtration, washed with ethanol and diethyl ether, and dried in air; it was shown by IR and elemental analysis to be identical (with varying solvation) to that obtained from the reaction of the appropriate lanthanide nitrate with H_3L4 in the presence of sodium hydroxide.

Attempted Conversion of Type IV to Type I Complexes. Solutions of $Gd(NO_3)_3 \cdot 5H_2O$ (225 mg, 0.50 mmol) in methanol (30 mL) and of H_3L4 in chloroform (10 mL) were mixed. Upon addition of 2 N NaOH (3.0 mL) dropwise, the cloudy solution became clear. The solution was filtered, and the filtrate was left standing at room temperature. After 3–4 h, a small amount of microcrystalline solid formed. The solid was isolated by filtration, washed with methanol, and dried in air. The product was shown by IR, FAB-MS, and elemental analysis to be the type I complex, $[Gd(L4)] \cdot 4H_2O$. Anal. Calcd (found) for $C_{30}H_{47}GdN_4O_{10}$: C, 46.14 (46.22); H, 6.07 (5.63); N, 7.17 (6.93). Mass spectrum (FAB): $m/z = 732$ ($[NaGd(L4)]^+$). IR (cm^{-1}, KBr disk): 3700–2500 (br, m, ν_{O-H}), 3240 (m, ν_{N-H}), 1595, 1570 (w, δ_{N-H}). The filtrate and washings above were combined; further evaporation afforded microcrystals, which were shown by elemental analysis to be a mixture of type I and type IV complexes.

X-ray Crystallographic Analyses. Crystallographic data for the two complexes $[M(H_3L4)_2](NO_3)_3 \cdot xH_2O \cdot yMeOH$ (M = Pr, $x = 5.56$, $y = 0.44$; M = Gd, $x = 5.96$, $y = 0.66$) appear in Table I. The final unit-cell parameters were obtained by least-squares calculations on the setting

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(5) Rothin, A. S.; Banbery, H. J.; Berry, F. J.; Hamor, T. A.; Jones, C. J.; McCleverty, J. A. *Polyhedron* **1989**, *8*, 491.

Table II. Final Atomic Coordinates (Fractional) and B_{eq} (Å^2)[a]

atom	x	y	z	B_{eq}	occ	atom	x	y	z	B_{eq}	occ
$[Pr(H_3L4)_2](NO_3)_3 \cdot 5.56H_2O \cdot 0.44CH_3OH$											
Pr(1)	$^1/_4$	$^1/_4$	$^1/_2$	3.18(1)	0.50	C(3)	0.3140(2)	0.0977(3)	0.6849(2)	5.2(2)	
O(1)	0.3196(1)	0.2496(2)	0.6107(1)	4.6(1)		C(4)	0.3330(2)	0.1862(3)	0.7170(2)	4.9(2)	
O(2)	0.3482(1)	0.4114(2)	0.6651(2)	6.2(2)		C(5)	0.3328(2)	0.2605(3)	0.6765(2)	4.4(2)	
O(3)	0.2775(1)	0.0997(2)	0.5036(1)	4.2(1)		C(6)	0.3487(2)	0.3450(3)	0.7079(2)	5.1(2)	
O(4)	0.2268(1)	−0.0110(2)	0.5608(2)	5.7(1)		C(7)	0.3633(2)	0.3538(4)	0.7770(3)	6.5(2)	
O(5)	0.3279(1)	0.2722(2)	0.4682(1)	4.6(1)		C(8)	0.3639(2)	0.2806(5)	0.8166(3)	7.1(3)	
O(6)	0.3119(1)	0.2458(3)	0.3384(1)	6.3(1)		C(9)	0.3495(2)	0.1972(4)	0.7876(2)	6.1(2)	
O(7)	0.3937(2)	0.0485(4)	0.3169(2)	11.3(3)		C(10)	0.3611(2)	0.4997(4)	0.6931(3)	7.9(3)	
O(8)	0.4480(2)	0.1381(3)	0.3871(2)	9.5(2)		C(11)	0.4539(2)	0.0758(3)	0.5347(2)	5.6(2)	
O(9)	0.4524(2)	0.1252(3)	0.2906(2)	10.6(3)		C(12)	0.4023(2)	0.0291(3)	0.4841(2)	5.3(2)	
O(10)	$^1/_2$	0.3233(5)	$^3/_4$	9.5(4)	0.50	C(13)	0.3039(2)	0.0535(3)	0.3923(2)	5.1(2)	
O(11)	0.4888(2)	0.4453(3)	0.6965(2)	10.1(2)		C(14)	0.2784(2)	−0.0123(3)	0.4253(2)	4.6(2)	
O(12)	0.3552(2)	0.1243(3)	0.1493(3)	9.9(3)		C(15)	0.2647(2)	0.0173(3)	0.4795(2)	4.1(2)	
O(13)	0.449(2)	0.208(3)	0.018(2)	15(1)	0.22	C(16)	0.2377(2)	−0.0442(3)	0.5079(2)	4.8(2)	
O(14)	0.4282(5)	0.188(1)	0.0816(8)	14.8(9)	0.50	C(17)	0.2243(2)	−0.1302(3)	0.4820(3)	6.2(2)	
O(15)	0.516(2)	0.334(2)	0.264(3)	15(1)	0.20	C(18)	0.2379(3)	−0.1571(3)	0.4283(3)	6.9(3)	
O(16)	0.442(1)	0.287(2)	0.037(1)	14.8(8)	0.28	C(19)	0.2656(2)	−0.0997(4)	0.4009(3)	6.2(2)	
O(17)	0.412(1)	0.230(2)	0.015(1)	14.5(7)	0.32	C(20)	0.2019(3)	−0.0705(4)	0.5946(3)	7.8(3)	
O(18)	0.476(2)	0.336(3)	0.197(2)	14(1)	0.17	C(21)	0.4849(2)	0.1855(4)	0.6241(2)	5.8(2)	
O(19)	0.437(3)	0.314(5)	0.093(4)	15(2)	0.09	C(22)	0.4722(2)	0.2749(3)	0.5871(3)	6.1(2)	
O(20)	0.445(2)	0.232(2)	0.155(2)	15(1)	0.20	C(23)	0.4016(2)	0.4028(3)	0.5510(3)	6.1(2)	
N(1)	0.4418(1)	0.1171(3)	0.5902(2)	4.6(1)		C(24)	0.3946(2)	0.3887(3)	0.4787(2)	5.4(2)	
N(2)	0.3489(1)	0.0655(2)	0.6458(2)	4.6(1)		C(25)	0.3564(2)	0.3237(3)	0.4405(2)	4.6(2)	
N(3)	0.3593(1)	0.0940(2)	0.4404(2)	4.6(1)		C(26)	0.3497(2)	0.3113(3)	0.3723(2)	5.3(2)	
N(4)	0.4223(1)	0.3194(3)	0.5934(2)	5.1(2)		C(27)	0.3818(2)	0.3627(4)	0.3457(3)	7.1(3)	
N(5)	0.4310(2)	0.1035(3)	0.3313(2)	6.3(2)		C(28)	0.4195(3)	0.4267(5)	0.3847(4)	8.5(3)	
N(6)	$^1/_2$	0.4016(6)	$^3/_4$	6.9(3)	0.50	C(29)	0.4260(2)	0.4404(4)	0.4514(3)	7.6(3)	
C(1)	0.4443(2)	0.0464(3)	0.6399(2)	5.3(2)		C(30)	0.2984(3)	0.2367(4)	0.2675(2)	8.1(3)	
C(2)	0.4123(2)	0.0732(3)	0.6841(2)	5.2(2)		C(31)	0.370(2)	0.166(3)	0.111(3)	15(1)	0.22
$[Gd(H_3L4)_2](NO_3)_3 \cdot 5.96H_2O \cdot 0.66CH_3OH$											
Gd(1)	$^1/_4$	$^1/_4$	$^1/_2$	2.554(8)	0.50	C(3)	0.3120(2)	0.1009(3)	0.6823(2)	4.5(2)	
O(1)	0.3172(1)	0.2533(2)	0.6076(1)	3.78(9)		C(4)	0.3310(2)	0.1897(3)	0.7138(2)	4.2(2)	
O(2)	0.3466(1)	0.4145(2)	0.6624(2)	5.4(2)		C(5)	0.3307(1)	0.2624(3)	0.6738(2)	3.8(2)	
O(3)	0.2764(1)	0.1034(2)	0.5037(1)	3.6(1)		C(6)	0.3474(2)	0.3479(3)	0.7051(2)	4.6(2)	
O(4)	0.2271(1)	−0.0091(2)	0.5621(2)	5.1(2)		C(7)	0.3620(2)	0.3567(4)	0.7741(3)	5.6(2)	
O(5)	0.3257(1)	0.2731(2)	0.4679(1)	3.7(1)		C(8)	0.3628(2)	0.2827(5)	0.8129(2)	6.3(3)	
O(6)	0.3105(1)	0.2466(2)	0.3385(1)	5.2(1)		C(9)	0.3480(2)	0.2001(4)	0.7841(2)	5.5(2)	
O(7)	0.3937(2)	0.0422(3)	0.3162(2)	10.9(3)		C(10)	0.3600(2)	0.5026(3)	0.6898(3)	7.1(3)	
O(8)	0.4457(2)	0.1379(3)	0.3840(2)	8.7(2)		C(11)	0.4544(2)	0.0790(3)	0.5352(2)	4.8(2)	
O(9)	0.4525(2)	0.1189(3)	0.2897(2)	9.6(2)		C(12)	0.4018(2)	0.0315(3)	0.4839(2)	4.6(2)	
O(10)	$^1/_2$	0.3231(4)	$^3/_4$	8.6(3)	0.50	C(13)	0.3033(2)	0.0575(3)	0.3930(2)	4.3(2)	
O(11)	0.4883(2)	0.4455(3)	0.6964(2)	8.2(2)		C(14)	0.2788(2)	−0.0078(3)	0.4272(2)	3.9(2)	
O(12)	0.3545(2)	0.1196(3)	0.1493(3)	9.3(3)		C(15)	0.2644(2)	0.0210(3)	0.4798(2)	3.6(2)	
O(13)	0.438(1)	0.198(1)	0.008(1)	16(1)	0.41	C(16)	0.2385(2)	−0.0407(3)	0.5095(2)	4.2(2)	
O(14)	0.4255(6)	0.181(1)	0.0722(8)	14.8(4)	0.44	C(17)	0.2257(2)	−0.1270(3)	0.4835(3)	5.7(2)	
O(15)	0.517(1)	0.335(2)	0.259(3)	15(1)	0.26	C(18)	0.2403(2)	−0.1545(3)	0.4308(3)	6.2(2)	
O(16)	0.446(1)	0.281(2)	0.030(1)	14.2(7)	0.34	C(19)	0.2673(2)	−0.0954(3)	0.4033(3)	5.5(2)	
O(17)	0.413(1)	0.235(2)	0.015(2)	13.4(8)	0.29	C(20)	0.2032(2)	−0.0688(4)	0.5969(3)	6.7(3)	
O(18)	0.479(2)	0.337(2)	0.198(2)	13(1)	0.20	C(21)	0.4850(2)	0.1896(3)	0.6236(2)	5.1(2)	
O(19)	0.435(1)	0.337(2)	0.078(2)	15(1)	0.19	C(22)	0.4719(2)	0.2775(3)	0.5867(3)	5.2(2)	
O(20)	0.447(1)	0.232(2)	0.155(2)	14(1)	0.19	C(23)	0.3993(2)	0.4036(3)	0.5497(2)	5.1(2)	
N(1)	0.4421(1)	0.1202(2)	0.5901(2)	4.0(1)		C(24)	0.3927(2)	0.3894(3)	0.4782(2)	4.5(2)	
N(2)	0.3479(2)	0.0691(2)	0.6444(2)	4.1(2)		C(25)	0.3542(2)	0.3241(3)	0.4401(2)	3.8(2)	
N(3)	0.3590(1)	0.0968(2)	0.4408(2)	3.9(1)		C(26)	0.3485(2)	0.3124(3)	0.3728(2)	4.4(2)	
N(4)	0.4211(1)	0.3210(2)	0.5926(2)	4.4(2)		C(27)	0.3805(2)	0.3636(4)	0.3458(2)	5.8(2)	
N(5)	0.4302(2)	0.1000(3)	0.3296(2)	5.8(2)		C(28)	0.4185(2)	0.4268(4)	0.3853(3)	6.8(3)	
N(6)	$^1/_2$	0.4039(5)	$^3/_4$	6.2(3)	0.50	C(29)	0.4243(2)	0.4401(3)	0.4504(3)	6.1(2)	
C(1)	0.4446(2)	0.0505(3)	0.6398(2)	4.7(2)		C(30)	0.2985(2)	0.2355(4)	0.2687(2)	6.8(3)	
C(2)	0.4119(2)	0.0767(3)	0.6833(2)	4.6(2)		C(31)	0.369(1)	0.166(2)	0.116(1)	13(2)	0.33

[a] $B_{eq} = (^8/_3)\pi^2\sum\sum U_{ij}a_i^*a_j^*(\mathbf{a}_i\cdot\mathbf{a}_j)$.

angles for 25 reflections with 2θ = 42.3–52.0 and 19.7–29.5° for the Pr and Gd complexes, respectively. The intensities of three standard reflections, measured every 200 reflections throughout the data collections, decayed uniformly by 6.9% for M = Pr and by 3.1% for M = Gd, presumably a result of slow loss of solvent from the crystal lattices. The data were processed[6] and corrected for Lorentz and polarization effects, linear decay, and absorption (empirical, based on azimuthal scans for three reflections).

The structure of the gadolinium complex 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 subsequent difference Fourier syntheses. The structure analysis of the Gd complex was initiated in the centrosymmetric space group $C2/c$, on the basis of the E statistics and the Patterson function, this choice being confirmed by the subsequent successful solution and refinement of the structure. The analysis of the isomorphous and isostructural Pr complex was initiated using the non-hydrogen atom coordinates of the Gd complex.

The $[M(H_3L4)_2]^{3+}$ cations have crystallographic C_i symmetry, and one of the nitrate anions lies on a crystallographic C_2 axis. The water and methanol solvate molecules (5.56 and 0.44 for the Pr, 5.96 and 0.66 for the Gd derivative) are disordered over nine different sites (only one of which—O(12)—is fully occupied). The site occupancy factors for the

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(6) *TEXSAN/TEXRAY structure analysis package, Version 5.1*; Molecular Structure Corp.: Woodlands, TX, 1985.

Table III. Selected Bond Lengths (Å) for $[Pr(H_3L4)_2](NO_3)_3 \cdot 5.56H_2O \cdot 0.44CH_3OH$ and $[Gd(H_3L4)_2](NO_3)_3 \cdot 5.96H_2O \cdot 0.66CH_3OH$

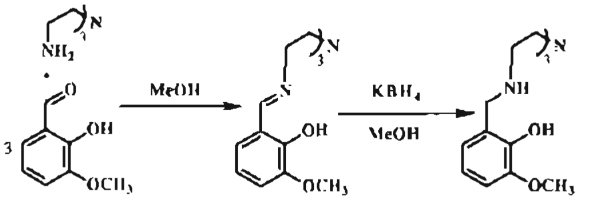
$[Pr(H_3L4)_2](NO_3)_3 \cdot 5.56H_2O \cdot 0.44CH_3OH$		$[Gd(H_3L4)_2](NO_3)_3 \cdot 5.96H_2O \cdot 0.66CH_3OH$	
Pr(1)–O(1)	2.337(2)	Gd(1)–O(1)	2.278(2)
Pr(1)–O(3)	2.342(3)	Gd(1)–O(3)	2.288(3)
Pr(1)–O(5)	2.345(2)	Gd(1)–O(5)	2.284(2)

Table IV. Selected Bond Angles (deg) for $[Pr(H_3L4)_2](NO_3)_3 \cdot 5.56H_2O \cdot 0.44CH_3OH$ and $[Gd(H_3L4)_2](NO_3)_3 \cdot 5.96H_2O \cdot 0.66CH_3OH$[a]

$[Pr(H_3L4)_2](NO_3)_3 \cdot 5.56H_2O \cdot 0.44CH_3OH$			
O(1)–Pr(1)–O(1)′	180.0	O(3)–Pr(1)–O(3)′	180.0
O(1)–Pr(1)–O(3)	82.4(1)	O(3)–Pr(1)–O(5)	82.7(1)
O(1)–Pr(1)–O(3)′	97.6(1)	O(3)–Pr(1)–O(5)′	97.3(1)
O(1)–Pr(1)–O(5)	84.9(1)	O(5)–Pr(1)–O(5)′	180.0
O(1)–Pr(1)–O(5)′	95.1(1)		
$[Gd(H_3L4)_2](NO_3)_3 \cdot 5.96H_2O \cdot 0.66CH_3OH$			
O(1)–Gd(1)–O(1)′	180.00	O(3)–Gd(1)–O(3)′	180.00
O(1)–Gd(1)–O(3)	83.9(1)	O(3)–Gd(1)–O(5)	83.80(9)
O(1)–Gd(1)–O(3)′	96.1(1)	O(3)–Gd(1)–O(5)′	96.20(9)
O(1)–Gd(1)–O(5)	85.63(8)	O(5)–Gd(1)–O(5)′	180.00
O(1)–Gd(1)–O(5)′	94.37(8)		

[a] Primes and double primes refer to symmetry operations ($^1/_2 - x$, $^1/_2 - y$, $1 - z$) and ($1 - x$, y, $^1/_2 - z$), respectively.

Scheme I



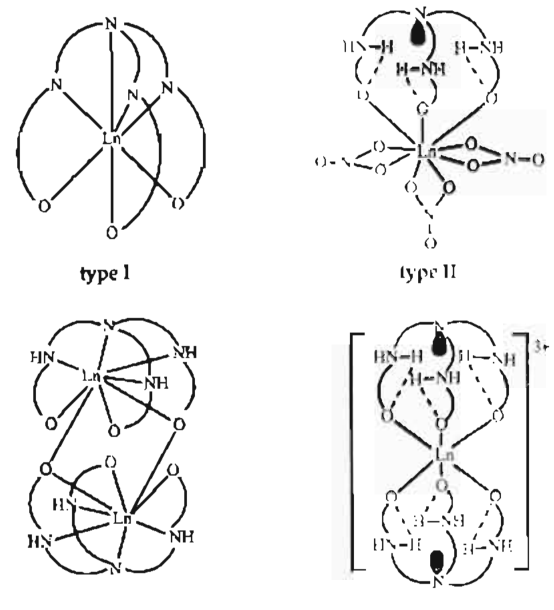
remaining solvent atoms were either refined (for the most prominent sites, which are not quite the same in the two complexes, see Table II) or kept fixed but adjusted as the refinements progressed to give thermal parameters consistent with those of the atoms for which the population parameters were refined. The chemical compositions of the two complexes that are derived from the X-ray analyses are in very good agreement with microanalytical data for the batches of crystals employed in the structure determinations.

All non-hydrogen atoms except for the lower-occupancy solvent sites were refined with anisotropic thermal parameters. The hydrogen atoms associated with the complex cations in both structures were fixed in calculated positions (N–H/C–H = 0.98 Å, $B_H = 1.2B_{\text{bonded atom}}$). A secondary extinction correction was applied for the Pr complex, the final value of the extinction coefficient being 1.50×10^{-7}. Neutral-atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from ref 7.

Final atomic coordinates and equivalent isotropic thermal parameters, selected bond lengths, and selected bond angles appear in Tables II–IV, respectively. Complete tables of crystallographic data, distances, and angles, as well as tables of hydrogen atom parameters, anisotropic thermal parameters, intramolecular distances and angles involving hydrogen atoms, torsion angles, intermolecular contacts, and least-squares planes for the two structures are included as supplementary material (see paragraph at the end of the paper).

Results and Discussion

Chart II



type I

type II

type III

type IV

Ligand Synthesis. The Schiff base H_3vantren was prepared from the reaction of tren with 3 equiv of *o*-vanillin (shown in Scheme I) and was readily characterized. The IR spectrum contained a strong band at 1630 cm^{-1}, characteristic of imine C=N bonds of Schiff bases. Although the preparation of this compound has been reported,[5] there were some discrepancies between the properties of that substance and the material described herein.

The KBH_4 reduction of the Schiff base produced the amine phenol (H_3**L4**). The new compound was soluble in polar solvents such as chloroform and methanol and was hydrolytically stable under both basic and acidic conditions. The analytical and spectral data were completely consistent with the proposed formulation. The IR spectrum of H_3**L4** showed the disappearance of the characteristic imine C=N band at 1630 cm^{-1} and the appearance of a new band at 1590 cm^{-1} from N—H bending vibrations. The ^{1}H NMR spectrum (in $CDCl_3$) showed the presence of benzylic hydrogen signals at ~4 ppm instead of the imine CH=N hydrogen signals at ~8 ppm. These observations confirmed that the C=N bonds were reduced to CH_2—NH amine linkages.

Metal Complexes. Unlike the reactions of the N_4O_3 Schiff bases (H_3trac, H_3hatren, H_3datren)[8,9] and three other N_4O_3 amine phenols (H_3L1–H_3L3),[4] reactions of H_3**L4** with Ln^{3+} in the presence of 3–4 equiv of sodium hydroxide or acetate produced a new type of six-coordinate bis(ligand)lanthanide complex (type IV in Chart II) with a formulation of $[Ln(H_3L4)_2](NO_3)_3$ (Ln = Pr, Nd, Gd, Yb). In the presence of 6–8 equiv of sodium hydroxide, the reaction of H_3**L4** with $Gd(NO_3)_3 \cdot 6H_2O$ produced a small amount of type I complex [Gd(**L4**)] first and then a mixture of both type I and type IV complexes. No analytically pure type I complexes, [Ln(**L4**)], were isolated from the similar reactions for Pr, Nd, or Yb. When more sodium hydroxide (>10 equiv) was employed, lanthanide hydroxide precipitated. All type IV complexes were characterized by elemental analysis, IR, and FAB-MS and, for $[Pr(H_3L4)_2]^{3+}$ and $[Gd(H_3L4)_2]^{3+}$, by X-ray crystallography.

As was found with some Schiff bases[8,9] and the other three amine phenols (H_3L1–H_3L3),[4] reactions of H_3**L4** with 1 equiv of a lanthanide nitrate salt in the absence of base produced type II complexes with a formulation $[Ln(H_3L4)(NO_3)_3]$ (Ln = Pr, Nd). Type IV complexes, $[Ln(H_3L4)_2](NO_3)_3$ for Ln = Gd and Yb, were isolated under similar conditions. This was probably caused by the smaller sizes of Gd^{3+} and Yb^{3+}. The type II complexes are quite air-stable and were easily converted to type IV complexes by reaction with 3–4 equiv of sodium hydroxide. The type II complexes most likely have a nine-coordinate structure

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(7) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974 (present distributor: Kluwer Academic Publishers, Dordrecht, The Netherlands); Vol. IV, pp 99–102, 149.

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

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

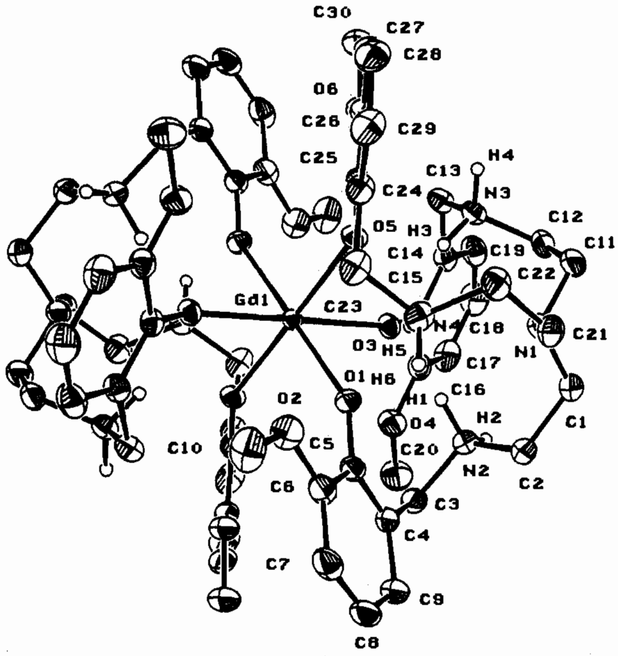

Figure 1. ORTEP view of the $[Gd(H_3L4)_2]^{3+}$ cation ($[Pr(H_3L4)_2]^{3+}$ is isostructural).

very similar to that which was found and structurally characterized in $[Yb(H_3trac)(NO_3)_3]$.[8] The spectral (IR and FAB) and analytical data were completely consistent with the indicated formulations.

The type I complex [Gd(L4)] showed IR bands at 3240 and 1595 cm^{-1} from N–H stretching and bending vibrations, respectively, of the coordinated secondary amine groups. Type IV complexes showed N–H stretches, which are characteristic of the hydrogen-bonded N–H---O portions of the ligand, and IR bands at 1380 and 1280 cm^{-1} from nitrate anions (ν_{N-O}). These were absent in the type III and type I complexes. New bands appeared below 600 cm^{-1} in the spectrum of each coordinated ligand and are difficult to assign because of the low energies associated with these vibrations.

The FAB mass spectra of type I, type II, and type IV complexes were obtained in a 3-nitrobenzyl alcohol matrix in the positive detection mode. The FAB spectrum of [Gd(L4)] showed a molecular ion peak at $m/z = 710$ from $[Gd(HL4)]^+$ without a trace of a dimer peak from $[Gd(L4)]_2$. This clearly established the mono(ligand) nature of this complex. In the FAB spectra of two type II complexes, peaks from $[Ln(HL4)]^+$ and $[Ln(H_3L4)(NO_3)_2]^+$ were detected. The FAB spectra of the type IV complexes showed peaks from mono(ligand) and bis(ligand) cations with no $[Ln(H_3L4)(NO_3)_2]^+$ peaks as were seen in the spectra of the type II complexes. These observations suggest that the nitrate anions in the type IV complexes are uncoordinated and are consistent with the structural findings for $[Ln(H_3L4)_2]^{3+}$ (Ln = Pr, Gd).

Crystal Structures. $[Pr(H_3L4)_2]^{3+}$ and $[Gd(H_3L4)_2]^{3+}$ are isostructural. The ORTEP drawing of $[Gd(H_3L4)_2]^{3+}$ is illustrated in Figure 1. It shows the numbering scheme followed in both structures. Selected bond lengths and bond angles in $[Ln(H_3L4)_2]^{3+}$(Ln = Pr, Gd) are listed in Tables III and IV, respectively. In the unit cell there are four $[Ln(H_3L4)_2](NO_3)_3$ moieties and many partially occupied waters or methanols of solvation. The complex cation $[Ln(H_3L4)_2]^{3+}$ is centrosymmetric with the two amine phenol ligands facially binding to the metal center in a slightly distorted octahedral coordination geometry. The coordinated amine phenol ligands are tridentate with three deprotonated phenolate O atoms coordinating to the metal center and the three secondary amine N atoms protonated. The capping tertiary nitrogen N(1) atom is "tucked in" with its lone pair of electrons pointed at the Ln atom. The three arms of one amine phenol ligand form a left-handed screw down the tertiary N–Ln axis while the three arms of the other amine phenol ligand form a right-handed screw. Both intraarm (average H---O = 2.29 Å for Pr and 2.30 Å for Gd) and interarm (average H---O = 2.13 Å for Pr and 2.12 Å for Gd) hydrogen bonds are observed in each coordinated amine phenol ligand, in which three H atoms (H(1), H(3), H(5)) are oriented endo while the other three hydrogen atoms (H(2), H(4), H(6)) are oriented exo. Each of the three endo-oriented H atoms form both intraarm and interarm hydrogen bonds with the two nearest phenolate O atoms while three exo-oriented H atoms form intermolcular hydrogen bonds with the uncoordinated nitrate anions. Within each structure, the Ln–O bonds are indistinguishable at the 3σ confidence level (average Ln–O = 2.341(4) Å for Pr and 2.283(5) Å for Gd). Three trans O–Ln–O angles are crystallographically dictated to be 180° in each complex cation. The intraligand O–Ln–O angles average 83.3(1.4)° for Pr and 84.4(1.0)° for Gd while the interligand O–Ln–O angles average 96.7(1.4)° for Pr and 95.6(1.0)° for Gd. The shrinking of the intraligand O–Ln–O angles is probably caused by interarm hydrogen bonding and the expansion of the interligand O–Ln–O angles by the crowding between the two coordinated amine phenol ligands.

Concluding Remarks. We recently reported several potentially heptadentate Schiff base ligands (H_3trac, $H_3hatren$, $H_3datren$) and their lanthanide complexes.[8,9] These ligands were either tridentate in type II complexes, $[Ln(H_3L)(NO_3)_3]$ ($H_3L = H_3trac$, $H_3hatren$, $H_3datren$), or heptadentate in type I complexes, [Ln(L)] (L = $trac^{3-}$, $hatren^{3-}$, $datren^{3-}$), depending on the conditions of preparation. The N_4O_3 amine phenols (H_3L1, H_3L2, H_3L3) also form two types[4] of lanthanide complexes: type II (in the absence of a base) and type III $[Ln(L)]_2$ (L = $L1^{3-}$, $L2^{3-}$, $L3^{3-}$) (in presence of sodium hydroxide). The amine phenol ligand (H_3L4) reported in this study forms type II complexes, $[Ln(H_3L4)(NO_3)_3]$ (Ln = Pr, Nd), and six-coordinated bis(ligand) type IV complexes, $[Ln(H_3L4)_2](NO_3)_3$ (Ln = Pr, Nd, Gd, Yb), depending the conditions of preparation. These results clearly show that the 3-methoxy groups of the phenyl rings have a profound influence on the coordination behavior of the N_4O_3 amine phenol ligands toward lanthanide metal ions.

Because of the large size of the Ln^{3+} ions, the binding between lanthanide metals and donor atoms is predominantly ionic in character, and the cations display a strong preference for negatively charged O donor ligands.[10] Therefore it is not unexpected that the two amine phenol ligands in $[Ln(H_3L4)_2](NO_3)_3$ coordinate to the metal ion with only phenolate O donors. Furthermore, coordination numbers of lanthanide complexes are generally high and stereochemistries are largely determined by the steric requirements of the coordinated ligands.[10] In these type IV complexes $[Ln(H_3L4)_2](NO_3)_3$, the coordination geometry around the metal center is a trigonally distorted octahedron. The steric hindrance from the 3-methoxy groups of the two coordinated amine phenol ligands prevents the approach of other O donor ligands such as H_2O, and thus six-coordinated bis(ligand) type IV complexes, $[Ln(H_3L4)_2](NO_3)_3$, were enforced. Furthermore, the interstrand H-bonds highly stabilize type IV complexes, which makes conversion from type IV to either type I or type III complexes very difficult.

In H_3L1–H_3L3, the 3-substituents of the phenyl rings are hydrogens. The type II complexes $[Ln(H_3L)(NO_3)_3]$ (H_3L = H_3L1–H_3L3) can be easily converted to dimeric type III complexes $[Ln(L)]_2$ by adding 3–4 equiv of a base (acetate or hydroxide). The formation of dinuclear complexes does not cause significant crowding between the two coordinated amine phenol ligands. In H_3L4, the hydrogen atoms at 3-positions of the phenyl rings are replaced by three bulky methoxy groups. If $L4^{3-}$ were to

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(10) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon: Toronto, 1987; p 1434.

coordinate to the metal atom as a heptadentate ligand like trac^{3-} in [Yb(trac)][9] or L1^{3-} in [Gd(L1)]$_2$,[4] the steric hindrance between the methoxy groups in the same ligand in [Ln(**L4**)] would weaken the bonding between phenolate O atoms and the metal center while the crowding between the methoxy groups in two amine phenol ligands in [Ln(**L4**)]$_2$ prevents formation of a dinuclear structure. Therefore, the type II complexes [Ln(H$_3$**L4**)$_2$](NO$_3$)$_3$ cannot be easily converted to either type I [Ln(**L4**)] or type III complexes [Ln(**L4**)]$_2$ under similar conditions.

The steric effects of three methoxy groups are also seen in the reaction of a lanthanide nitrate with 1 equiv of H$_3$**L4**. For large metal ions such as Pr^{3+} (ionic radii:[11] 0.99 and 1.13 Å for 6- and 8-coordination, respectively) and Nd^{3+} (ionic radii:[11] 0.98 and 1.11 Å for 6- and 8-coordination, respectively), the coordination of a tridentate H$_3$**L4** ligand to the metal center does not cause significant crowding between the three 3-methoxy groups and the three bidentate nitrate anions; type II complexes [Ln(H$_3$**L4**)(NO$_3$)$_3$] (Ln = Pr, Nd) are formed. For Gd^{3+} (ionic radii:[11] 0.94 and 1.05 Å for 6- and 8-coordination, respectively) and Yb^{3+} (ionic radii: 0.87 and 0.985 Å for 6- and 8-coordination, respectively), the steric hindrance from 3-methoxy groups prevents the approach of all three bidentate nitrate anions. Therefore, the coordination of the second tridentate H$_4$**L4** ligand becomes favorable and six-coordinated bis(ligand) complexes [Ln(H$_3$**L4**)$_2$](NO$_3$)$_3$ (Ln = Gd, Yb) are formed.

In conclusion, a new N$_4$O$_3$ amine phenol ligand with a bulky ortho substituent (H$_3$**L4**) has been prepared. Reactions of H$_3$**L4** with lanthanide nitrate produced the previously known type II and the new type IV lanthanide complexes, depending conditions of preparation. The 3-substituent (or ortho substituent) of the phenyl ring has a profound influence on the coordination of the N$_4$O$_3$ amine phenol ligand to lanthanide ions while those at 5-positions of the phenyl rings have little effect.[9] The steric hindrance from the bulky 3-methoxy group of the phenyl ring makes the formation of either monomeric type I or dimeric type III complexes very difficult.

Acknowledgment is made to the Natural Sciences and Engineering Research Council of Canada for a NSERC Postdoctoral Fellowship (S.L.) and an operating grant (C.O) and to the U.S. Public Health Service for an operating grant (CA 48964). We also thank Professor J. Trotter for the very kind use of his crystallographic facilities.

Supplementary Material Available: Complete tables of crystallographic data, distances, and angles, as well as tables of hydrogen atom parameters, anisotropic thermal parameters, intramolecular distances and angles involving hydrogen atoms, torsion angles, intermolecular contacts, and least-squares planes (42 pages). Ordering information is given on any current masthead page.

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