on the ring. The pyrazolyl rings of the tris(pyrazolyl)borate ligands also equilibrate with a slightly higher barrier. The two processes do not seem to be correlated. Thus, it is not clear whether the eight-coordinate structure observed in the solid state or a seven-coordinate species formed upon dissociation of the pyrazole is the dynamic species responsible for the equilibration of the $[HB(pz)_3]^-$ pyrazolyl rings.

The mixed acetate–tris(pyrazolyl)borate complexes of yttrium form readily. A chelating ligand such as acetate or acac[4d,5] seems to be necessary to form stable $[HB(pz)_3]_2Y$(ligand) complexes because we have been unable to prepare seven-coordinate $[HB(pz)_3]_2Y(OR)$ complexes even with bulky alkoxide ligands.[17] Molecular weight studies indicate that **3** is a trimer in solution. The closest analogue is $[Cp_2YbO_2CC_6F_5]_2$, which is a dimer in the solid state.[18] A series of similar cyclopentadienyl complexes of the lanthanides have also been shown to be dimers in solution.[19] The trimeric structure of **3** may reflect the increased steric bulk of the tris(pyrazolyl)borate ligand when compared to the cyclopentadienyl ligand.[2] Trimers are favored for complexes having excessively bulky ligands.[20]

Yttrium is stabilized in a seven-coordinate environment in complex **4**. This tetraacetate-bridged dimer does not appear to have an analogue in cyclopentadienyl chemistry of yttrium or the lanthanides. Two examples of similar complexes of early metals, $[CpV(O_2CCF_3)_2]_2$ and $[CpTi(O_2CPh)_2]_2$,[21] have been structurally characterized. Both **3** and **4** show equal-intensity resonances for two types of pyrazolyl rings in low-temperature NMR spectra. For **3**, the acetate methyl groups remain equivalent at low temperature, but for **4**, two methyl resonances are observed. It seems unlikely that limiting low-temperature spectra of these complexes are being observed in either case even at ca. −87 °C. It is difficult to formulate a static structure for either **3** or **4** in which the pyrazolyl rings form a 1/1 equivalent set unless the two $[HB(pz)_3]^-$ ligands are inequivalent but are undergoing a fluxional process to equilibrate the pz rings within each ligand. In fact, in the solid-state structure of **4** the rings form a 1/1/1 set in the centrosymmetric dimer unit. Given that these molecules could demonstrate dynamic behavior by rotation of the tris(pyrazolyl)borate ligands, by rearrangement of the coordination polyhedra, by equilibria involving breaking and re-forming of the acetate bridges or combinations thereof, speculation on the mechanism(s) of these dynamic processes seems unwarranted at this time.

Finally, the preparation of mixed poly(pyrazolyl)borate–cyclopentadienyl complexes of yttrium, like those of zirconium,[1d] have been attempted. Although spectral evidence for complexes such as $[HB(pz)_3]CpYCl$ has been obtained, definitive isolation has not proven possible, to date.[17] Poly(pyrazolyl)borate complexes of several lanthanides analogous to those reported here are also under investigation.[22]

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Supplementary Material Available: Tables of crystallographic data for structural analysis, positional parameters of H atoms, and anisotropic thermal parameters (9 pages); listings of structure factor amplitudes (24 pages). Ordering information is given on any current masthead page.

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Lanthanide Complexes of Potentially Heptadentate Ligands Including the Structure of [Tris(3-aza-4-methylhept-4-ene-6-on-1-yl)amine]tris(nitrato)gadolinium(III)

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Several potentially heptacoordinate N_4O_3 ligands have been prepared and characterized, as has a series of their lanthanide (Ln) complexes. The ligands are the Schiff base condensation products of tris(2-aminoethyl)amine with 3 equiv of either acetylacetone or a hydroxyacetophenone. The ligands are believed to be heptadentate in Ln complexes if the starting lanthanide salt contains a poorly coordinating anion (e.g. Cl^-) and an early (large) Ln; several Ln(L) (Ln = La, Pr; different Ls) complexes have been isolated. When the anion is NO_3^-, the resulting complexes are of the form $Ln(H_3L)(NO_3)_3$ where Ln is from across the series and the ligand is tridentate with the three O atoms coordinating Ln and a hydrogen atom bridging across each of the three N,O arms of the ligand. A Gd complex, $[N(CH_2CH_2NHC(Me)CHC(Me)O)_3]Gd(NO_3)_3$, of the latter type has been studied by single-crystal X-ray diffraction. It is nine-coordinate, and each of the bidentate nitrates is trans to a ligand O rendering the geometry pseudo-*fac*-octahedral if each nitrate is considered to occupy one coordination position. $Gd(C_{21}H_{36}N_4O_3)(NO_3)_3$ crystallizes in the monoclinic space group *Cc* with the crystal parameters a = 16.617 (3) Å, b = 17.083 (1) Å, c = 10.901 (1) Å, β = 101.13 (1)°, and Z = 4. The data were refined by using 5028 reflections with $I \geq 3\sigma(I)$ to R and R_w values of 0.022 and 0.024, respectively.

Introduction

We have been pursuing a continuing project to detail the coordination chemistry of main-group complexes that are water soluble, hydrolytically stable, and lipophilic.[1] Because of their great mobility in vivo, the compounds have presented interesting opportunities for the study of some of these metals in the etiology and diagnosis of disease.[2,3] In an effort to extend these properties

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to higher dentate complexes of the lanthanides (generalized as Ln), we have prepared three potentially heptadentate Schiff base ligands[4] and several Ln complexes of them. We were determined to gain as many coordination sites as possible while retaining a tribasic character to the ligands in order to satisfy the higher coordination requirements of the lanthanides and to conserve the neutral complex charge required for the in vivo mobility found with Al. Current prospects[5] for metal complex (and particularly Gd^{3+}) magnetic resonance imaging contrast agents encouraged this interest.

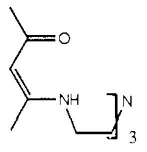
We present the characterization of a series of lanthanide complexes with the ligands H_3trac, H_3hatren, and H_3datren.[4] All the ligands are based on Schiff base condensation of ketones with tris(2-aminoethyl)amine (commonly abbreviated tren), which is itself a well-known tetradentate ligand for the lanthanides.[6-10] The ketones are 2,4-pentanedione (to give H_3trac), 2′-hydroxyacetophenone (H_3hatren), and 2′-hydroxy-4′,5′-dimethylacetophenone (H_3datren). The resulting ligands have the potential to be heptadentate and are somewhat analogous to several known ligands that have been examined in an effort to elucidate aspects of seven coordination.[11]

$(py)_3$tren (prepared from tren and 3 equiv of 2-pyridinecarboxaldehyde) was prepared by Rose and co-workers and forms hexadentate complexes with transition metals.[12] The $(sal)_3tren^{3-}$ ligands[13] (which unlike $(py)_3$tren are tribasic and are prepared from tren and various ring-substituted salicylaldehydes) have been studied with a number of metals,[13-17] and have never been found to be more than hexadentate with the transition metals. The potentially heptadentate ligand $(pyrol)_3tren^{3-}$ formed from pyrrole-2-carboxaldehyde and tren also forms hexadentate complexes with the transition metals.[18] These ligands have been used to observe ligand field effects; however, the hoped-for seven-coordination was never observed—the tertiary N to M distances were nonbonding contacts. Alyea and co-workers have prepared complexes of various $(sal)_3$tren ligands with the lanthanides, but crystalline samples proved elusive and no structures with these larger metals have yet been elucidated.[16,17]

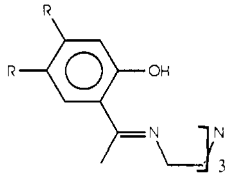
Although not previously reported, the ligand H_3trac, or rather its elusiveness, has been noted in the literature.[16,17,19,20] The preparation of several complexes of it and related ligands will be discussed in this contribution. Also mentioned are the relative labilities of the lanthanide complexes with tridentate versus heptadentate coordination of the tribasic ligands, and the crystal structure of a Gd complex in which H_3trac is tridentate.

Table I. Elemental Analyses of the Complexes

	anal. calcd (found), %		
	C	H	N
La(trac)·$0.5H_2O$	46.92 (47.07)	6.38 (6.53)	10.43 (10.57)
Pr(H_3trac)$(NO_3)_3$	35.06 (34.89)	5.04 (5.00)	13.63 (13.54)
Nd(H_3trac)$(NO_3)_3$	34.90 (34.79)	5.02 (5.00)	13.56 (13.80)
Gd(H_3trac)$(NO_3)_3$	34.28 (34.35)	4.93 (4.94)	13.33 (13.43)
Dy(H_3trac)$(NO_3)_3$	34.04 (33.75)	4.90 (5.00)	13.23 (13.26)
Yb(H_3trac)$(NO_3)_3$	33.56 (33.70)	4.83 (4.84)	13.05 (13.20)
La(hatren)	56.61 (56.76)	5.23 (5.46)	8.80 (8.63)
Pr(hatren)	56.43 (56.09)	5.21 (5.47)	8.77 (9.00)
La(H_3hatren)$(NO_3)_3$	43.65 (43.69)	4.40 (4.40)	11.88 (11.85)
Pr(H_3hatren)$(NO_3)_3$	44.54 (43.31)	4.38 (4.59)	11.85 (12.12)
Nd(H_3hatren)$(NO_3)_3$	43.37 (43.40)	4.37 (4.32)	11.80 (11.82)
Gd(H_3hatren)$(NO_3)_3$	42.70 (42.39)	4.30 (4.43)	11.62 (11.39)
Dy(H_3hatren)$(NO_3)_3$	42.43 (42.80)	4.27 (4.41)	11.55 (11.44)
Yb(H_3hatren)$(NO_3)_3$	41.91 (41.74)	4.22 (4.29)	11.40 (11.32)
La(datren)·CH_3OH	59.04 (59.40)	6.56 (6.70)	7.44 (7.44)
La(H_3datren)$(NO_3)_3$	47.53 (47.00)	5.32 (5.49)	10.78 (10.60)
Pr(H_3datren)$(NO_3)_3$	47.58 (47.70)	4.99 (5.09)	10.79 (10.60)
Nd(H_3datren)$(NO_3)_3$	47.25 (47.30)	5.29 (5.40)	10.71 (10.40)
Gd(H_3datren)$(NO_3)_3$	46.59 (46.33)	5.21 (5.29)	10.56 (10.70)
Dy(H_3datren)$(NO_3)_3$	46.33 (45.99)	5.18 (5.19)	10.51 (10.70)
Yb(H_3datren)$(NO_3)_3$	45.81 (45.64)	5.13 (5.05)	10.39 (10.28)



H_3trac



R = H H_3hatren
CH_3 H_3datren

Experimental Section

Materials and Methods. These were mostly as previously detailed.[1b,21,22] The ligands were prepared as described below. Since many of the complex syntheses were similar, only representative examples are given. Only the major ions observed in the E. I. mass spectra are listed. Proton NMR spectra (300 MHz) of the ligands were recorded with a Varian XL-300 instrument in $CDCl_3$. The lanthanide salts, 2,4-pentanedione, and the hydroxyacetophenones were purchased from Aldrich or Alfa; tren (tris(2-aminoethyl)amine, 98+%) was a gift from the Hampshire Organic Chemicals Division of W. R. Grace and Co. All chemicals were used as received while some solvents were distilled from drying agents under N_2 as required. Elemental analyses were by Peter Borda of this department and are given for the complexes in Table I.

H_3trac. A solution of 8.43 g (0.058 mol) of tren in 60 mL of benzene was added to 17.31 g (0.17 mol) of 2,4-pentanedione and was refluxed for 90 min with a Dean-Stark trap connected. Three milliliters of H_2O were collected. The benzene was removed under reduced pressure. The orange oil was rinsed four times with 20 mL of hexanes in order to remove any unreacted starting material. The oil was then dried in vacuo overnight. (Many attempts to further purify the oil and obtain an acceptable elemental analysis were unsuccessful). Mass spectrum (EI): m/e 392 (molecular ion $M^+ = C_{21}H_{36}N_4O_3$), 280 ($M^+ - C_6H_8O_2$), 222 ($M^+ - C_9H_{14}O_3$). Infrared spectrum (neat oil): 3340 cm^{-1} (br, s, ν(O—H or N—H)); 3080-2830 cm^{-1} (series w–m, ν(C—H)); 1615, 1575, 1520, 1445 cm^{-1} (all vs or s, ν(C=N, C=O, C=C)). ^{1}NMR data: δ 10.8 (3 H, br, O–*H* or N–*H*), 4.93 (3 H, s, CC*H*C), 3.38 (6 H, m, $HNCH_2CH_2N$), 2.78 (6 H, m, $HNCH_2CH_2N$), 2.00 (9 H, s, CCH_3), 1.96 (9 H, s, CCH_3).

H_3hatren. An ethanolic solution (250 mL) of 19.38 g (0.14 mol) of 2′-hydroxyacetophenone and 6.90 g (0.047 mol) of tren was refluxed for 1 h in the presence of 4-Å molecular sieves. The sieves were filtered out

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of the hot solution, which was then stored at −15 °C overnight. The solid mass of bright yellow H_3hatren was filtered out and dried overnight at room temperature for a yield of 20.3 g (86%). The product is a bright yellow flaky solid, mp 118–120 °C. Anal. Calcd (found) for $C_{30}H_{36}N_4O_3$: C, 71.97 (71.70); H, 7.25 (7.35); N, 11.19 (11.05). Mass spectrum (EI): *m/e* 500 ($M^+ = C_{30}H_{36}N_4O_3$), 352 (base, $M^+ - C_9H_{10}NO$). Infrared spectrum (KBr disk): 3420 cm^{-1} (br, s, ν(O—H or N—H)); 3050–2795 cm^{-1} (series w–m, ν(C—H)); 1615, 1580, 1505, 1450 cm^{-1} (all vs or s, ν(C=N, C=C)). ^{1}NMR data: δ 7.25 (3 H, m, Ph*H*), 7.22 (3 H, m, Ph*H*), 6.85 (3 H, m, Ph*H*), 6.60 (3 H, m, Ph*H*), 3.65 (6 H, m, $=NCH_2CH_2N$), 3.03 (6 H, m, $=NCH_2CH_2N$), 2.23 (9 H, s, $CH_3C=N$).

H_3datren. An ethanolic solution (80 mL) of 1.70 g (10.2 mmol) of 2′-hydroxy-4′,5′-dimethylacetophenone and 0.50 g (3.4 mmol) of tren was refluxed for 4 h, and hexanes were added to precipitate the product. The solution was left at −15 °C overnight. The bright yellow precipitate was filtered out and dried overnight at room temperature for a yield of 1.73 g (88%), mp 127–130 °C. Recrystallization was from 2-propanol. Anal. Calcd (found) for $C_{36}H_{48}N_4O_3$: C, 73.94 (73.96); H, 8.27 (8.28); N, 9.58 (9.78). Mass spectrum (EI): *m/e* 584 ($M^+ = C_{36}H_{48}N_4O_3$), 408 (base, $M^+ - C_{11}H_{14}NO$). Infrared spectrum (KBr disk): 3440 cm^{-1} (br, s, ν(O—H or N—H)); 3030–2810 cm^{-1} (series w–m, ν(C—H)); 1620, 1575, 1510, 1450 cm^{-1} (all vs or s, ν(C=N, C=C)). ^{1}NMR data: δ 6.96 (3 H, s, Ph*H*), 6.62 (3 H, s, Ph*H*); 3.60 (6 H, m, $=NCH_2CH_2N$); 2.96 (6 H, m, $=NCH_2CH_2N$); 2.20 (18 H, s, $CH_3C=N$ and/or $PhCH_3$); 2.10 (9 H, s, $CH_3=N$ or $PhCH_3$).

La(trac)·0.5H_2O. To a solution of 0.545 g (1.39 mmol) of H_3trac was added 0.515 g (1.39 mmol) of $LaCl_3 \cdot 7H_2O$. The solution was stirred at room temperature overnight. The white precipitate was filtered out and dried overnight yielding 0.47 g of crude La(trac) (65% based on La). The product was recrystallized from 95% ethanol and dried for 2 days in vacuo at room temperature to yield the hemihydrate La(trac)·0.5H_2O, mp 95–105 °C. Mass spectrum (EI): *m/e* 528 ($M^+ = C_{21}H_{33}LaN_4O_3$). Infrared spectrum (KBr disk): 3210 cm^{-1} (br, s, ν(O—H, H_2O)); 3000–2830 cm^{-1} (series w–m, ν(C—H)); 1610, 1540, 1510, 1440 cm^{-1} (all vs or s, ν(C=N, C=O, C=C)). The compound is soluble in water, methanol, and hot ethanol. Crystals of La(trac) were grown from ethanol in the presence of excess H_3trac; however, these were extremely sensitive to loss of solvent and were never successfully mounted for photographs.

Gd(H_3trac)(NO_3)$_3$. To a solution of 0.807 g (2.05 mmol) of H_3trac in 100 mL of CH_3CN was added 0.916 g (2.03 mmol) of $Gd(NO_3)_3 \cdot 6H_2O$. The solution was stirred for 20 min as a white crystalline precipitate formed slowly. The suspension was left at −15 °C overnight. The resulting solid was filtered out, rinsed with CH_3CN, and dried overnight in vacuo to yield 1.25 g (84%) of Gd(H_3trac)(NO_3)$_3$. Crystals for X-ray analysis were grown from a saturated CH_3CN solution. Mp: >200 °C dec. Mass spectrum (EI): *m/e* 547 (molecular ion for Gd(trac), $M^+ = C_{21}H_{33}GdN_4O_3$, Gd isotope pattern observed). Infrared spectrum (KBr disk): 3225 cm^{-1} (s, ν(N—H)); 3010–2840 cm^{-1} (series w–m, ν(C—H)); 1605, 1550, 1510 cm^{-1} (all vs or s, ν(C=N, C=O, C=C)); 1780, 1740 (both w), 1500–1440 (s, br), 1300 (s, br), 1035, 820 cm^{-1} (NO_3^- bands).

M(H_3trac)(NO_3)$_3$ complexes with the other lanthanides can be prepared in a similar fashion. The lighter lanthanides (Pr, Nd) tend to yield glassy products that are isolated from the reaction mixture by decanting the supernatant CH_3CN solution and rinsing the product out of the flask with diethyl ether. All products yielded good elemental analyses without further purification as shown in Table I. The complexes are soluble in water and methanol and slightly soluble in nitromethane.

La(hatren). To a solution of 0.641 g (1.28 mmol) of H_3hatren in 50 mL of boiling ethanol was added 0.468 g (1.26 mmol) of $LaCl_3 \cdot 7H_2O$. The solution was stirred hot for 10 min and then stored at −15 °C overnight. The yellow precipitate was filtered out, rinsed with ethanol, and dried overnight in vacuo to yield 0.732 g (91%) of product. This product (which contained chloride impurities) was dissolved in methanol. Diethyl ether was added until the solution turned slightly cloudy, and the suspension was left at −15 °C for 2 days. The solvent was decanted and the product rinsed out of the flask with ethanol. The product was dried in vacuo over P_2O_5 at 85 °C for 2 days. Mp: >200 °C dec. Mass spectrum (EI): *m/e* 636 ($M^+ = C_{30}H_{33}LaN_4O_3$). Infrared spectrum (KBr disk): 3060–2840 cm^{-1} (series w–m, ν(C—H)); 1610, 1540, 1510, 1450 cm^{-1} (all vs or s, ν(C=N, C=C)). Pr(hatren) was synthesized in analogous fashion. Both complexes are soluble in methanol, pyridine, and DMSO.

Nd(H_3hatren)(NO_3)$_3$. To a boiling solution of 1.06 g (2.12 mmol) of H_3hatren in 80 mL of CH_3CN were added 0.869 g (2.06 mmol) of $Nd(NO_3)_3 \cdot 6H_2O$. The solution was refluxed for 15 min and filtered hot. The resulting green microcrystalline product was dried overnight to yield 1.58 g (92%) of Nd(H_3hatren)(NO_3)$_3$, mp >200 °C. Crystals were grown in an acetonitrile-saturated solution but were of insufficient quality for X-ray analysis. Mass spectrum (EI): *m/e* 639 (molecular ion for Nd(hatren), $M^+ = C_{30}H_{33}N_4NdO_3$, Nd isotope pattern observed). Infrared spectrum (KBr disk): 3440 (br, ν(N—H)), 2940, 2860 cm^{-1} (w, ν(C—H)); 1610, 1545 cm^{-1} (vs, ν(C=N, C=C)); 1490–1420 (s, br), 1385 (m), 1300 (s, br), 1035, 820 cm^{-1} (NO_3^- bands). This compound was neutral in CH_3NO_2 by conductivity measurement.[23]

M(H_3hatren)(NO_3)$_3$ complexes with other lanthanides can be prepared in a similar fashion. The products are not as crystalline as Nd(H_3hatren)(NO_3)$_3$ or they lose their crystallinity upon aerial exposure over a 2-h period (e.g. Gd(H_3hatren)(NO_3)$_3$). They are all somewhat (0.1–1 mM) soluble in water, methanol, acetonitrile, and nitromethane.

La(datren)·CH_3OH. To a solution of 0.587 g (1.00 mmol) of H_3datren in 20 mL of boiling ethanol was added 0.361 g (0.97 mmol) of $LaCl_3 \cdot 7H_2O$. The suspension was stirred hot for 5 min and quickly filtered. The yellow solid was dried overnight in vacuo to give 0.481 g (70% yield). The product was recrystallized from freshly distilled methanol under inert atmosphere. The recrystallized product (microcrystalline) precipitated immediately from the methanol solution upon cooling and was filtered after being left at −15 °C overnight. The product was dried overnight in vacuo over P_2O_5 at 60 °C for 3 days. Mp: >200 °C dec. Mass spectrum (EI): *m/e* 720 ($M^+ = C_{36}H_{45}LaN_4O_3$). Infrared spectrum (KBr disk): 3400 cm^{-1} (s br ν(OH); 3070–2860 cm^{-1} (series w–m, ν(C—H)); 1615, 1545, 1515, 1450 cm^{-1} (all vs or s, ν(C=N, C=C)). The complex is soluble in methanol, pyridine, and DMSO.

Nd(H_3datren)(NO_3)$_3$. The preparations of the Ln(H_3datren)(NO_3)$_3$ complexes are analogous to the preparations of the Ln(H_3hatren)(NO_3)$_3$ species. The former give crystalline products that turn to powder upon drying overnight or sitting on the lab bench over a couple of days. Mp: >200 °C. Mass spectrum (EI): *m/e* 723 (molecular ion for Nd(datren), $M^+ = C_{36}H_{45}N_4NdO_3$, Nd isotope pattern observed). Infrared spectrum (KBr disk): 2920, 2860 cm^{-1} (w, ν(C—H)); 1620, 1535, 1510 cm^{-1} (vs, ν(C=N, C=C)); 1480–1420 (s, br), 1300 (s, br), 1035, 820 cm^{-1} (NO_3^- bands). The compound is somewhat soluble in water, methanol, and acetonitrile.

X-ray Crystallographic Analysis. Crystallographic data are given in Table II. The final unit cell parameters were obtained by least-squares

Table II. Crystallographic Data[a]

compound	[$N(CH_2CH_2NHC(Me)CHC(Me)O)_3$]Gd($NO_3$)$_3$
formula	$C_{21}H_{36}GdN_7O_{12}$
fw	735.81
cryst syst	monoclinic
space group	*Cc*
a, Å	16.617 (3)
b, Å	17.083 (1)
c, Å	10.901 (1)
β, deg	101.13 (1)
V, Å^3	3036.2 (6)
Z	4
D_c, g/cm^3	1.610
F(000)	1484
μ(Mo Kα), cm^{-1}	22.6
cryst dimens, mm	0.34 × 0.35 × 0.55
transmissn factors	0.461–0.564
scan type	ω–2θ
scan range, deg in ω	0.70 + 0.35 tan θ
scan speed, deg/min	1.6–20.1
data collcd	$\pm h,+k,+l$
$2\theta_{max}$, deg	65
cryst decay	negligible
no. of unique reflcns	5467
no. of reflections with $I \geq 3\sigma(I)$	5028
no. of variables	368
R	0.022
R_w	0.024
S	1.272
mean Δ/σ (final cycle)	0.01
max Δ/σ (final cycle)	0.11
residual density, e/Å^3	−2.0 to +0.7 (near Gd)

[a] Temperature 294 K, Enraf-Nonius CAD4-F diffractometer, Mo Kα radiation ($\lambda_{K\alpha1}$ = 0.709 30, $\lambda_{K\alpha2}$ = 0.713 59 Å), graphite monochromator, takeoff angle 2.7°, aperature (2.0 + tan θ) × 4.0 mm at a distance of 173 mm from the crystal, scan range extended by 25% on both sides for background measurement, $\sigma^2(I) = C + 2B + [0.04(C - B)]^2$ (C = scan count, B = normalized background count), function minimized, $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F)$, $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$, $S = (\sum w(|F_o| - |F_c|)^2/(m-n))^{1/2}$. Values given for *R*, R_w, and *S* are based on those reflections with $I \geq 3\sigma(I)$.

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(23) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81–122.

Table III. Final Positional ($\times 10^4$; Gd $\times 10^6$) and Isotropic Thermal Parameters ($U \times 10^3$ Å^2) with Estimated Standard Deviations in Parentheses

atom	*x*	*y*	*z*	U_{eq}/U_{iso}
Gd	300000	239021 (5)	300000	30
O(1)	2824 (1)	1646 (1)	4735 (2)	43
O(2)	3647 (1)	3204 (1)	4624 (2)	42
O(3)	1860 (1)	3018 (1)	3515 (2)	41
O(4)	2830 (1)	3682 (2)	1871 (2)	48
O(5)	3906 (2)	3029 (2)	1691 (3)	52
O(6)	3703 (2)	4182 (2)	846 (3)	67
O(7)	1926 (1)	1363 (2)	2251 (2)	47
O(8)	2198 (2)	2178 (2)	900 (2)	49
O(9)	1400 (2)	1189 (2)	286 (3)	61
O(10)	3616 (2)	1307 (2)	1994 (3)	63
O(11)	4433 (1)	1831 (2)	3536 (3)	57
O(12)	4881 (2)	924 (3)	2443 (5)	93
N(1)	2212 (2)	3095 (2)	7686 (2)	47
N(2)	1538 (2)	1833 (2)	5945 (2)	42
N(3)	3850 (2)	2735 (2)	7043 (3)	43
N(4)	2020 (2)	4098 (2)	5388 (3)	50
N(5)	3483 (2)	3647 (2)	1442 (2)	44
N(6)	1826 (1)	1559 (2)	1111 (2)	39
N(7)	4329 (2)	1347 (2)	2645 (4)	57
C(1)	1495 (3)	2618 (2)	7807 (4)	49
C(2)	1031 (2)	2357 (2)	6532 (4)	47
C(3)	1651 (2)	1079 (2)	6197 (3)	47
C(4)	2256 (3)	638 (2)	5768 (4)	55
C(5)	2805 (2)	931 (2)	5064 (3)	48
C(6)	3408 (4)	368 (3)	4703 (7)	89
C(7)	1109 (3)	675 (3)	6957 (5)	71
C(8)	2960 (2)	2882 (4)	8572 (3)	59
C(9)	3519 (3)	2333 (3)	8008 (4)	56
C(10)	4430 (2)	3276 (2)	7232 (3)	43
C(11)	4610 (2)	3736 (2)	6265 (3)	44
C(12)	4209 (2)	3700 (2)	5022 (3)	39
C(13)	4446 (3)	4284 (3)	4129 (3)	62
C(14)	4925 (2)	3393 (3)	8529 (3)	62
C(15)	2041 (3)	3932 (3)	7641 (4)	58
C(16)	2417 (2)	4346 (2)	6643 (4)	56
C(17)	1338 (3)	4383 (2)	4734 (4)	58
C(18)	956 (2)	4066 (2)	3576 (4)	56
C(19)	1227 (2)	3411 (2)	3005 (3)	44
C(20)	778 (2)	3161 (3)	1745 (4)	58
C(21)	952 (4)	5077 (4)	5222 (5)	87

methods on $2(\sin\theta)/\lambda$ values for 25 reflections (2θ = 56–61°) measured with Mo Kα_1 radiation. The intensities of three standard reflections, measured every 4000 s of X-ray exposure time throughout the data collection, showed only small random fluctuations. The data were processed and corrected for absorption.[24]

The systematic absences allow space groups *Cc* or *C*2/*c*, the former being chosen on the basis of the number of molecules in the unit cell, mindful that the molecule cannot exhibit $\bar{1}$ (C_i) or 2 (C_2) symmetry. The *y* coordinate of the Gd atom was determined from the Patterson function, the *x* and *z* coordinates both being fixed at 0.30 to determine the origin. The remaining non-hydrogen atoms were positioned from subsequent difference Fourier maps, this process being complicated by the false 2-fold axis generated by the single heavy atom.

In the final stages of full-matrix least-squares refinement, all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were fixed in positions idealized from observed positions with N–H = 0.91 Å, $C(sp^3)$–H = 0.98 Å, $C(sp^2)$–H = 0.97 Å, and $U_H \propto U_{\text{bonded atom}}$ ($U_H = 1.3U_C$ for CH_3 groups, $U_H = U_{\text{bonded atom}} + 0.012$ for others). Neutral-atom scattering factors and anomalous dispersion corrections for Gd were taken from ref 25. A parallel refinement of the structure having the opposite polarity gave substantially higher residuals (R and R_w ratios of 1.072 and 1.060, respectively). Final positional and equivalent isotropic thermal parameters (U_{eq} is one-third of the trace for the diagonalized U) for the non-hydrogen atoms are given in Table III. Bond lengths and bond angles appear in Tables IV and V, respectively. Intraannular torsion angles for the four-membered chelate rings, hydrogen atom parameters, anisotropic thermal parameters, torsion angles, and measured and calculated structure factor amplitudes (Tables VI–X) are included as supplementary material.

Table IV. Bond Lengths (Å) with Estimated Standard Deviations in Parentheses

Gd–O(1)	2.344 (2)	N(1)–C(15)	1.457 (6)
Gd–O(2)	2.342 (2)	N(2)–C(2)	1.459 (5)
Gd–O(3)	2.337 (2)	N(2)–C(3)	1.322 (5)
Gd–O(4)	2.516 (3)	N(3)–C(9)	1.450 (5)
Gd–O(5)	2.515 (2)	N(3)–C(10)	1.323 (4)
Gd–O(7)	2.524 (2)	N(4)–C(16)	1.462 (5)
Gd–O(8)	2.444 (2)	N(4)–C(17)	1.310 (5)
Gd–O(10)	2.472 (3)	C(1)–C(2)	1.520 (5)
Gd–O(11)	2.527 (2)	C(3)–C(4)	1.406 (5)
O(1)–C(5)	1.274 (4)	C(3)–C(7)	1.505 (5)
O(2)–C(12)	1.274 (3)	C(4)–C(5)	1.394 (5)
O(3)–C(19)	1.280 (4)	C(5)–C(6)	1.496 (6)
O(4)–N(5)	1.263 (4)	C(8)–C(9)	1.531 (7)
O(5)–N(5)	1.267 (4)	C(10)–C(11)	1.392 (5)
O(6)–N(5)	1.218 (4)	C(10)–C(14)	1.506 (4)
O(7)–N(6)	1.267 (3)	C(11)–C(12)	1.392 (4)
O(8)–N(6)	1.267 (4)	C(12)–C(13)	1.498 (5)
O(9)–N(6)	1.210 (3)	C(15)–C(16)	1.529 (6)
O(10)–N(7)	1.260 (5)	C(17)–C(18)	1.407 (6)
O(11)–N(7)	1.261 (5)	C(17)–C(21)	1.494 (5)
O(12)–N(7)	1.221 (4)	C(18)–C(19)	1.397 (5)
N(1)–C(1)	1.471 (4)	C(19)–C(20)	1.494 (6)
N(1)–C(8)	1.464 (5)		

Table V. Bond Angles (deg) with Estimated Standard Deviations in Parentheses

O(1)–Gd–O(2)	79.78 (8)	Gd–O(11)–N(7)	95.0 (2)
O(1)–Gd–O(3)	79.76 (8)	C(1)–N(1)–C(8)	113.7 (3)
O(1)–Gd–O(4)	148.33 (8)	C(1)–N(1)–C(15)	113.0 (3)
O(1)–Gd–O(5)	151.04 (9)	C(8)–N(1)–C(15)	113.7 (3)
O(1)–Gd–O(7)	72.12 (7)	C(2)–N(2)–C(3)	125.3 (3)
O(1)–Gd–O(8)	123.02 (8)	C(9)–N(3)–C(10)	125.8 (3)
O(1)–Gd–O(10)	94.50 (11)	C(16)–N(4)–C(17)	126.0 (3)
O(1)–Gd–O(11)	82.34 (9)	O(4)–N(5)–O(5)	116.1 (3)
O(2)–Gd–O(3)	79.71 (8)	O(4)–N(5)–O(6)	122.0 (4)
O(2)–Gd–O(4)	80.86 (8)	O(5)–N(5)–O(6)	121.9 (3)
O(2)–Gd–O(5)	86.19 (9)	O(7)–N(6)–O(8)	115.0 (2)
O(2)–Gd–O(7)	148.19 (7)	O(7)–N(6)–O(9)	122.5 (3)
O(2)–Gd–O(8)	152.13 (10)	O(8)–N(6)–O(9)	122.5 (3)
O(2)–Gd–O(10)	127.64 (9)	O(10)–N(7)–O(11)	116.3 (3)
O(2)–Gd–O(11)	77.01 (9)	O(10)–N(7)–O(12)	121.6 (4)
O(3)–Gd–O(4)	72.28 (8)	O(11)–N(7)–O(12)	122.1 (4)
O(3)–Gd–O(5)	122.60 (9)	N(1)–C(1)–C(2)	110.9 (3)
O(3)–Gd–O(7)	80.88 (8)	N(2)–C(2)–C(11)	110.3 (3)
O(3)–Gd–O(8)	88.42 (9)	N(2)–C(3)–C(4)	122.4 (3)
O(3)–Gd–O(10)	150.95 (9)	N(2)–C(3)–C(7)	118.9 (3)
O(3)–Gd–O(11)	152.75 (9)	C(4)–C(3)–C(7)	118.7 (4)
O(4)–Gd–O(5)	50.54 (8)	C(3)–C(4)–C(5)	125.2 (3)
O(4)–Gd–O(7)	116.51 (8)	O(1)–C(5)–C(4)	123.6 (3)
O(4)–Gd–O(8)	71.50 (9)	O(1)–C(5)–C(6)	119.2 (3)
O(4)–Gd–O(10)	117.17 (11)	C(4)–C(5)–C(6)	117.2 (3)
O(4)–Gd–O(11)	117.16 (10)	N(1)–C(8)–C(9)	113.0 (3)
O(5)–Gd–O(7)	125.58 (8)	N(3)–C(9)–C(8)	110.3 (3)
O(5)–Gd–O(8)	79.10 (9)	N(3)–C(10)–C(11)	122.2 (3)
O(5)–Gd–O(10)	74.26 (11)	N(3)–C(10)–C(14)	119.2 (3)
O(5)–Gd–O(11)	69.81 (10)	C(11)–C(10)–C(14)	118.5 (3)
O(7)–Gd–O(8)	50.94 (8)	C(10)–C(11)–C(12)	125.5 (3)
O(7)–Gd–O(10)	70.31 (9)	O(2)–C(12)–C(11)	122.8 (3)
O(7)–Gd–O(11)	112.79 (10)	O(2)–C(12)–C(13)	119.3 (3)
O(8)–Gd–O(10)	70.77 (11)	C(11)–C(12)–C(13)	117.9 (3)
O(8)–Gd–O(11)	118.65 (10)	N(1)–C(15)–C(16)	111.9 (3)
O(10)–Gd–O(11)	50.73 (10)	N(4)–C(16)–C(15)	111.1 (3)
Gd–O(1)–C(5)	139.5 (2)	N(4)–C(17)–C(18)	122.5 (3)
Gd–O(2)–C(12)	148.4 (2)	N(4)–C(17)–C(21)	119.1 (4)
Gd–O(3)–C(19)	140.5 (2)	C(18)–C(17)–C(21)	118.3 (4)
Gd–O(4)–N(5)	96.7 (2)	C(17)–C(18)–C(19)	125.4 (3)
Gd–O(5)–N(5)	96.6 (2)	O(3)–C(19)–C(18)	122.4 (3)
Gd–O(7)–N(6)	94.8 (2)	O(3)–C(19)–C(20)	118.2 (3)
Gd–O(8)–N(6)	98.7 (2)	C(18)–C(19)–C(20)	119.4 (3)
Gd–O(10)–N(7)	97.7 (2)		

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(24) The computer programs used include locally written programs for data processing and locally modified versions of the following: ORFLS, full-matrix least-squares, and ORFFE, function and errors, by W. R. Busing, K. O. Martin, and H. A. Levy; FORDAP, Patterson and Fourier syntheses, by A. Zalkin; ORTEP II, illustrations, by C. K. Johnson; AGNOST, absorption corrections, by J. A. Ibers.

(25) *International Tables for X-Ray Crystallography*. Kynoch: Birmingham, UK, 1974 (present distributor D. Reidel: Dordrecht, The Netherlands); Vol. IV, pp 99–102 and 149.

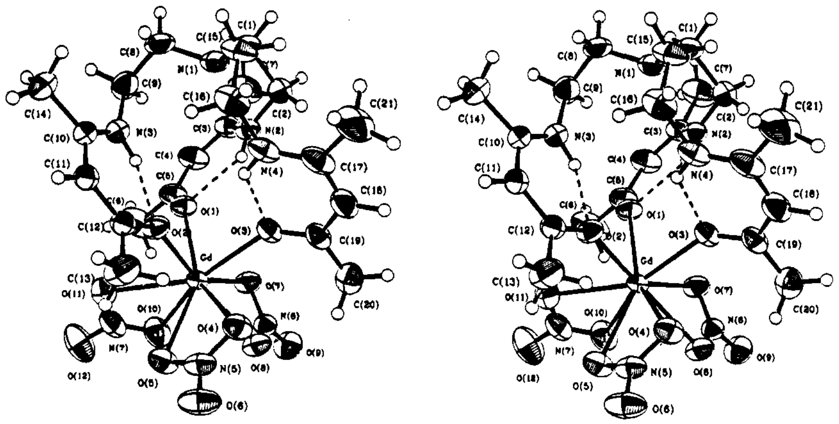
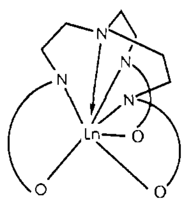


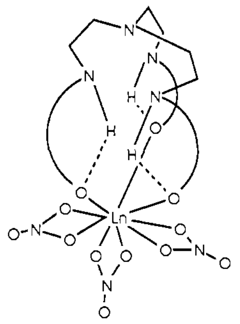
Figure 1. ORTEP stereoview of $Gd(H_3trac)(NO_3)_3$.

Results and Discussion

Three new potentially heptadentate ligands have been prepared by the Schiff base condensation of tren with 3 equiv of ketone. Several lanthanide complexes of the three new ligands have been prepared, and two coordination types have been found. When the complexes are prepared from a starting lanthanide salt that contains a poorly coordinating anion, such as Cl^-, species that are presumably seven-coordinate result (type I). Type I has the formulation Ln(L) and contains the completely coordinated triply deprotonated (trianionic) ligand, and Ln is six- or seven-coordinated, with a further possible coordination position open trans to the tertiary nitrogen atom. These complexes are labile and lose the ligand in solvents that coordinate Ln well, such as DMSO or pyridine.



Type I



Type II

When a starting lanthanide nitrate salt is employed, a different, nine-coordinate geometry results (type II). The type II complexes are quite stable in solution and in the solid state—they contain three bidentate nitrate ligands, each of which is trans to a coordinating oxygen atom from the ligand. Unlike the type I case, the ligand has not been deprotonated and the three protons are found bridging the N and O atoms of each of the three acetylacetonimine arms of the ligand. Type II has the formulation $Ln(H_3L)(NO_3)_3$.

The synthesis of the ligands and compounds was accomplished without great difficulty; however, there was a tendency for the preparation of type I Ln(L) complexes to become more difficult for smaller Ln (to the right of the series). Table I shows analyses for type I complexes of La and Pr only. The opposite trend was observed for the type II $Ln(H_3L)(NO_3)_3$ species, which were more tractable as Ln became smaller. The lesser lability of the latter series of complexes meant that they were accessible for all Ln. Addition of bases to convert type II to type I resulted in the partial hydrolysis of the ligand. For all the compounds, except the H_3trac ligand, which is an oil, satisfactory elemental analyses were obtained. Mass spectral and infrared data for all the ligands and complexes were completely consistent with the indicated formulations. Often, in the mass spectra of the type II complexes, peaks for the type I formulation were observed as the molecular ion and were more intense than in the type I complexes themselves.

Type II complexes show IR (N–H) stretches characteristic of the protons bridging the N–O portion of the ligand. These are absent in the type I complexes. The four-band infrared spectral pattern (1620–1440 cm^{-1}), which is characteristic of the Schiff base delocalized $C{=}C$, $C{=}O$, $C{=}N$ manifold (see for example ref 17 and 19) undergoes a general bathochromic shift in both the complex types, and there may be an energy reordering upon complexation. New bands appear below 400 cm^{-1} in the spectrum of each complexed ligand, and these are more likely ν(Ln–O); however, assignments are very difficult in this region because of the low energies associated with these vibrations.[17]

The IR bands associated with the nitrate groups suggested the presence of bidentate linkages in many of the type II complexes, based on the correlation suggested by Lever et al.[26] A splitting of the NO_3^- combination bands in the 1700–1800-cm^{-1} region of 20–66 cm^{-1} is indicative of bidentate binding, while a smaller splitting (5–26 cm^{-1}) suggests monodentate nitrate. For the type II H_3trac complexes this splitting was 40 cm^{-1}, the bands appearing at 1780 and 1740 cm^{-1}. In compounds where crystals are unobtainable, this criterion is often used to determine the nitrate binding mode, especially in lanthanide nitrate complexes where the higher coordination requirements of the metals favor bidentate ligation of these anions.[27]

NMR data were recorded for the ligands; however, the La complexes were too labile for the acquisition of spectra. ^1H NMR spectral studies of analyzed samples showed chemical shifts of the free ligand or broad peaks; both results suggested that the exchange was extremely rapid. In solvents such as pyridine and DMSO, spectra and reactions showed that ligand exchange was occurring to form the multisolvated Ln^{3+} in solution.

Single crystals of the complexes proved elusive in most cases, especially for the Ln(L) species. La(trac) did crystallize from an ethanol solution containing excess H_3trac; however, the crystals were so unstable that they could not be mounted in capillaries, even in the presence of mother liquor. Some crystals were stable at low temperature, but most simply cracked and disintegrated. Efforts to prepare single crystals of a type I complex continue.

Concomitant with their increased stability, crystals of the type II complexes were considerably easier to grow reproducibly. The crystal structure of $Gd(H_3trac)(NO_3)_3$ consists of discrete molecules linked along the *c* axis by C–H···O hydrogen bonds [C(8)–H(8b)···O(8) (*x*, *y*, 1 + *z*); H···O = 2.31 Å, C···O = 3.275 (4) Å, and C–H···O = 168°]. These chains are cross-linked by weak C–H···O interactions [C(16)–H(16b)···O(4) (*x*, 1 – *y*, $^1/_2$ + *z*); H···O = 2.53 Å, C···O = 3.438 (5) Å, and C–H···O = 155°] to give a three dimensional array. The three "acidic" protons that are removed in the type I complexes are found in three intramolecular N–H···O hydrogen bonds, between the nitrogen and the oxygen atoms on each acetylacetone imino arm of the H_3trac ligand. These six-membered rings are nearly planar (Figure 1)

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(26) Lever, A. B. P.; Mantovani, E.; Ramaswamy, B. S. *Can. J. Chem.* **1971**, *49*, 1957–1964.

(27) Sakamoto, M. *Inorg. Chim. Acta* **1987**, *131*, 139–142 and references therein.

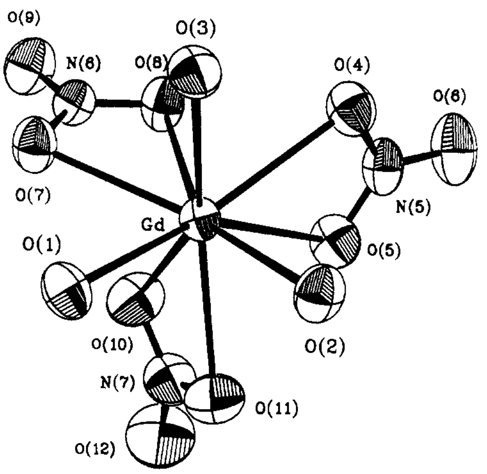

Figure 2. ORTEP view of the tricapped trigonal prismatic GdO_9 coordination polyhedron in $Gd(H_3trac)(NO_3)_3$.

(mean parameters: H···O = 2.05 Å, N···O = 2.727 Å, N–H···O = 130°). In this structure the capping tertiary nitrogen atom is "tucked in" with its lone pair of electrons pointed at the Gd^{3+} atom. This suggests that the type I complexes may indeed contain heptadentate ligands. The three arms of the ligand form a left-handed screw in approaching the metal ion, although the three nitrates form a right-handed screw in their orientation around the Gd^{3+}.

Two of the three nitrate groups show statistically (not chemically) significant deviations from planarity, N(5) and N(6) being displaced 0.010 (3) and 0.014 (3) Å from their respective O_3 planes. Otherwise, the three coordinated nitrates are quite normal in their dimensions.[28] The Gd atom is significantly displaced from the NO_3 mean planes (by 0.1201 (1), 0.3047 (1), and 0.1670 (1) Å from the N(5), N(6), and N(7) nitrate planes, respectively).

Bond lengths show that the three Schiff base arms of the H_3trac ligand are quite delocalized; however, the protons are definitely located on the N atoms. The carbon–oxygen lengths (average 1.28 Å) are much closer to that of the C=O bond (1.24 Å) in Hacac, rather than the C—O bond (1.33 Å).[29] The C—O lengths are also less than the average of those values found in eight metal structures of the acacen ligand (average 1.29 Å).[30] ($H_2acacen$ is formed from 2 equiv of acac and 1 equiv of ethylenediamine). A similar situation is found in the tris(acac)(acetylacetone imine)Yb^{III} structure where the acetylacetone imine ligand is O-coordinated and N-protonated.[31] Within experimental error, the C=N and C–N bond lengths are the same as those found in the averaged acacen structures (1.31 Å); however, the two C=C distances are the same in this structure, and they are much more delocalized than those found in the acacen structures.[30]

The Gd is displaced from the delocalized portions of the Schiff base ligands (by 0.9616 (1), 0.7090 (1), and 0.9381 (1) Å from N(2)–C(3)–C(4)–C(5)–O(1), and corresponding planes containing O(3) and O(4), respectively). The delocalized portions of H_3trac in the structure show deviations from planarity of up to 0.211 (4) Å for C(16) (with respect to the O(3), N(4), C(16)–C(21) mean plane), probably a result of intra- and intermolecular steric forces.

The complex crystallizes as a pseudo-*fac* isomer (Figure 1), if each nitrate is considered to occupy a single coordination position. The bond angles verify this description of the coordination sphere around the Gd atom (e.g. O(3)–Gd–O(10) = 151°, O(3)–Gd–O(11) = 153°, O(10)–Gd–O(11) = 51°; the three angles total 354°). An alternative depiction is that of the tricapped trigonal prism that is characteristic of [M(bidentate)$_3$(monodentate)$_3$] complexes.[32,33] The three H_3trac O atoms (O(1), O(2), O(3)) and three of the nitrate O atoms (O(5), O(8), O(10)) form a distorted trigonal prism while the other nitrate atoms (O(4), O(7), O(11)) are the caps (Figure 2). This geometry is quite common for Ln complexes of this form, many of which have bidentate = nitrate.[33]

The stability of the type I complexes is significantly less and the lability is greater than the corresponding tris(acac) complexes. Substituted-acac complexes of the lanthanides are often used as NMR shift reagents because of the ability of these paramagnetic species to form stable adducts in solution,[34] and Schiff base complexes of the transition metals are notoriously stable.[35] The type I complexes decompose given any opportunity (hydrolysis, solvent competition), while the type II complexes are stabilized by the chelating nitrates. Imine linkages chelating to the lanthanides are obviously unstable, although there are a number of sketchy reports of them in the literature.[36]

It seems, from the great difficulty which we found in preparing type I complexes of Ln smaller than Pr^{3+}, that the hole size in the ligands will only accommodate the larger members of the rare earth series. The type I complexes are formed only with the largest of the lanthanides; the smaller Ln are too small to fit in the hole of the potentially seven-coordinating ligand. This fits the available information; however, the conclusive result will be the X-ray crystal structure of a type I complex, and this is being actively sought.

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Registry No. H_3trac, 116670-22-5; tren, 4097-89-6; $H_3hatren$, 116670-23-6; $H_3datren$, 116670-24-7; La(trac), 116699-29-7; Pr(H_3trac)$(NO_3)_3$, 116699-33-3; Nd(H_3trac)$(NO_3)_3$, 116699-34-4; Gd(H_3trac)$(NO_3)_3$, 116699-35-5; Dy(H_3trac)$(NO_3)_3$, 116699-36-6; Yb(H_3trac)$(NO_3)_3$, 116699-37-7; La(hatren), 116699-30-0; Pr(hatren), 116699-31-1; La($H_3hatren$)$(NO_3)_3$, 116699-38-8; Pr($H_3hatren$)$(NO_3)_3$, 116699-39-9; Nd($H_3hatren$)$(NO_3)_3$, 116699-40-2; Gd($H_3hatren$)$(NO_3)_3$, 116724-32-4; Dy($H_3hatren$)$(NO_3)_3$, 116699-41-3; Yb($H_3hatren$)$(NO_3)_3$, 116699-42-4; La(datren), 116699-32-2; La($H_3datren$)$(NO_3)_3$, 116699-43-5; Pr($H_3datren$)$(NO_3)_3$, 116699-44-6; Nd($H_3datren$)$(NO_3)_3$, 116699-45-7; Gd($H_3datren$)$(NO_3)_3$, 116724-47-1; Dy($H_3datren$)$(NO_3)_3$, 116699-46-8; Yb($H_3datren$)$(NO_3)_3$, 116699-47-9; 2,4-pentanedione, 123-54-6; 2′-hydroxyacetophenone, 582-24-1; 2′-hydroxy-4′,5′-dimethylacetophenone, 36436-65-4.

Supplementary Material Available: Intraannular torsion angles for the four-membered chelate rings, hydrogen atom parameters, anisotropic thermal parameters, and torsion angles (Tables VI–IX) (6 pages); measured and calculated structure factor amplitudes (Table X) (24 pages). Ordering information is given on any current masthead page.

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