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Heptadentate Ligands[1] for the Lanthanides. The First Structurally Characterized Example of a Lanthanide Heptadentate Ligand Complex: {Tris(3-aza-4-methyl-6-oxohept-4-en-1-yl)amine}ytterbium(III)

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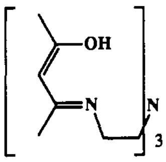
Abstract: Several binary heptacoordinate–N_4O_3–ligand LnL complexes of the lanthanides have been prepared and characterized. The heptadentate ligands are the Schiff base condensation products of tris(2-aminoethyl)amine with 3 equiv of either acetylacetone (to form H_3trac) or a hydroxyacetophenone (to form H_3hatren or H_3datren). The complexes hydrolyze easily but most of the Ln(trac) complexes are stable enough to sublime. Crystals of Yb(trac) were isolated by sublimation, and its structure has been solved; it is the first structurally characterized example of a lanthanide heptadentate ligand complex. Crystals of Yb(trac) are monoclinic, $a = 13.150$ (5) Å, $b = 16.125$ (5) Å, $c = 22.938$ (5) Å, $\beta = 105.83$ (2)°, $Z = 8$, $\rho_c = 1.597$ g cm^{-3}, space group $P2_1/c$. The structure was solved by the Patterson method and was refined by full-matrix least-squares procedures to $R = 0.043$ and $R_w = 0.053$ for 4199 reflections with $I \geq 3\sigma(I)$. The structure contains two crystallographically independent, but virtually identical (one Λ and one Δ), molecules of Yb(trac) having approximate C_3 symmetry. The Yb atoms are coordinated by the three O atoms and four N atoms of the heptadentate trac^{3-} ligand in a capped octahedral arrangement with Yb–O = 2.161(9)–2.199(9) Å and Yb–N = 2.41(1)–2.46(1) Å.

Introduction

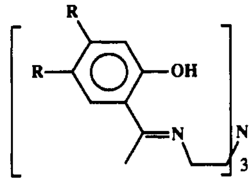
Coordination number seven occupies a special niche in coordination chemistry because it must be forced on all metal ions;[3-6] none adopt it with ease. Most d- and p-block metals can be forced to increase their coordination number to seven with very small or polydentate ligands, while the lanthanide metals (Ln) are usually forced to decrease their coordination number to seven with more sterically demanding ligands. In contrast with higher coordination numbers, crystallographically characterized examples of seven coordination are relatively rare in the lanthanides and are almost always found in the [Ln(bidentate ligand)$_3$(unidentate ligand)] shift reagent complexes.[7,8] There is no structurally characterized example of a lanthanide complex of a heptadentate ligand; this report is the first.

Throughout the Periodic Table, structurally characterized examples of heptadentate ligands coordinating one metal ion are rare. To our knowledge there are only four clear examples: a Co(II) N_2O_5 [2] cryptate,[9] a Cu(II) N_7 Schiff-base,[10] and two In(III) complexes[11] of tricarboxylatotetraazamacrocycles. The first two complexes are pentagonal bipyramidal, and neither ligand contains ionizable protons; the latter two complexes contain tribasic ligands in a trigonal prismatic geometry capped on a square face. Rose's group has reported[12] a series of divalent transition-metal compounds of the N_7 py$_3$tren ligand in which the seventh apical N atom is weakly bonded to Co(II) and Mn(II) and not bonded to other divalent transition metal ions. An extensive review of potentially heptadentate ligands is given in a previous communication.[13]

We recently reported[13] polydentate ligand complexes of the lanthanides wherein the polydentate ligands are from Schiff base condensation reactions of ketones with tris(2-aminoethyl)amine(commonly abbreviated tren). The ketones are 2,4-pentanedione (to give H_3trac), 2′-hydroxyacetophenone (H_3hatren), and 2′-hydroxy-4′,5′-dimethylacetophenone (H_3datren).[1] These ligands are potentially heptadentate and are somewhat analogous to several known ligands which have been examined in an effort to elucidate aspects of seven coordination.[4] H_3trac has been postulated in the literature as a good potentially seven-coordinating ligand.[14-16] In our previous contribution[13] we reported several complexes of H_3trac, H_3hatren, and H_3datren, but we were unsuccessful in crystallizing a complex of the formulation LnL in which L^{3-} was heptadentate; we did however report the crystal structure of a Gd complex (Gd(H_3trac)(NO_3)$_3$) in which H_3trac was tridentate. We have now explored further the chemistry of this family of compounds and can finally report the crystal structure of a LnL complex, Yb(trac).



H_3trac



R = H H_3hatren
CH_3 H_3datren

Experimental Section

Materials and Methods. The ligands were prepared as described previously,[13] except that solid H_3trac (as opposed to an oil) was obtained as follows: the orange oil obtained from the reaction and after extraction

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(1) Abbreviations for the ligands are as follows: H_3trac, tris[(4-hydroxypentenylidene-2-imino)ethyl]amine or tris(3-aza-4-methyl-6-oxo-hept-4-en-1-yl)amine; H_3hatren, tris[(2′-hydroxyphenylethylidene-2-imino)ethyl]amine; H_3datren, tris[(2′-hydroxy-4′,5′-dimethylphenylethylidene-2-imino)ethyl]amine.

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Table I. Physical Properties and Elemental Analyses of the Complexes

	yield[a] (%)	color	mp (°C)	analyzed elements
$\mathrm{PrCl_3(H_3trac)(H_2O)_2}$	57	pale green	190	C, H, N, Pr
$\mathrm{GdCl_3(H_3trac)(H_2O)}$	15	white	194	C, H, Gd, N
$\mathrm{DyCl_3(H_3trac)(H_2O)}$	34	cream	199	C, H, Dy, N
$\mathrm{YbCl_3(H_3trac)(H_2O)}$	47	pale yellow	210	C, H, N, Yb
$\mathrm{YCl_3(H_3trac)}$	18	white	212	C, H, N, Y
La(trac)	81	pale yellow	179	C, H, N
Sm(trac)	35	pale yellow	255	C, H, N
Er(trac)	72	pink	258	C, H, N
Yb(trac)	88	yellow	237	C, H, N
La(hatren)	81	pale yellow	336	C, H, N
Sm(hatren)	58	pale yellow	314	C, H, N
Yb(hatren)	80	pale yellow-green	335	C, H, N
La(datren)	45	pale yellow	341	C, H, N
Sm(datren)	75	cream	327	C, H, N
Yb(datren)	88	pale yellow	358	C, H, N

[a] Recrystallized or sublimed yields.

with hexanes was purified by chromatography on silica gel with ethanol as eluent; this purified yellow oil slowly crystallized during storage over molecular sieves at −10 °C.

Since many of the syntheses were similar, detailed procedures are only given for representative examples. All the complexes which were prepared are listed in Table I. Parent peaks were observed in the EI and FAB mass spectra of all the seven-coordinated Ln(L) complexes (appropriate isotopic ratios were also observed for Er, Yb, and Sm). Proton NMR spectra were recorded on a Bruker AC-200E (200 MHz) or a Bruker WP-80 (80 MHz) spectrometer in DMSO-d_6.

Hydrated lanthanide salts, 2,4-pentanedione, and the hydroxyacetophenones were purchased from Aldrich or Alfa; tren (tris(2-aminoethyl)amine, 99%) was obtained from Aldrich and used without further purification. Anhydrous lanthanide trichlorides were prepared by refluxing the hydrated salts in $\mathrm{SOCl_2}$. Hexamethyldisilazane was distilled from BaO before conversion to the K salt with KH. $\mathrm{Ln[N(SiMe_3)_2]_3}$ was prepared from $\mathrm{KN(SiMe_3)_2}$ and $\mathrm{LnCl_3}$ according to a published procedure.[17] Solvents were distilled from drying agents under Ar immediately prior to use. Air- and moisture-sensitive compounds were prepared and handled by using standard glovebox and Schlenk line techniques as specified in the experimental procedures below. C, H, and N analyses were carried out by Mr. Peter Borda of this department. Lanthanide metal analyses were determined by complexometric titration.[18] Elements which were successfully analyzed (±0.4% for C, H, N; ±0.6% for Ln) are listed in Table I.

$\mathrm{YbCl_3(H_3trac)\cdot H_2O}$. A solution of 3.19 g of $\mathrm{H_3trac}$ (8.11 mmol) in 100 mL of ethanol was added to a solution of 3.14 g of $\mathrm{YbCl_3\cdot 6H_2O}$ (8.11 mmol) in 100 mL of ethanol. The solution became cloudy, and a pale yellow precipitate deposited after stirring for several hours at room temperature. The suspension was cooled at −5 °C, and the product was isolated by filtration. The powder was washed with cold EtOH (50 mL) and dried under vacuum for 24 h at room temperature [infrared spectrum (CsI, Nujol mull) 1605, 1540, 1490 $\mathrm{cm^{-1}}$ (all br vs, $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N}, \mathrm{C}\overset{\cdots}{-}\mathrm{C}, \mathrm{C}\overset{\cdots}{-}\mathrm{O}))$]. The infrared spectra of the $\mathrm{MCl_3(H_3trac)(H_2O)}_x$ complexes are superimposable in the 1400–1700-$\mathrm{cm^{-1}}$ region. The UV spectrum of this complex is identical with that of free $\mathrm{H_3trac}$ (EtOH, 311 nm, $\epsilon = 5.28 \times 10^4\ \mathrm{M^{-1}\ cm^{-1}}$).

La(trac). A solution of 1.27 g of $\mathrm{H_3trac}$ (3.24 mmol) in 60 mL of dry THF was added to a solution of 2.01 g of $\mathrm{La[N(SiMe_3)_2]_3}$ (3.24 mmol) in 60 mL of THF by cannula. The yellow solution was stirred overnight under an argon atmosphere. The solvent was removed under reduced pressure, and the residue was washed with $\mathrm{Et_2O}$ (60 mL) and hexane (2 × 60 mL). Pure La(trac) was isolated as a free-flowing, pale yellow powder [infrared spectrum (CsI, Nujol mull) 1570, 1510, 1400 $\mathrm{cm^{-1}}$ (all br vs, $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N}, \mathrm{C}\overset{\cdots}{-}\mathrm{C}, \mathrm{C}\overset{\cdots}{-}\mathrm{O})$]. The infrared spectra of the Ln(trac) complexes were superimposable with La(trac) in the 1400–1700-$\mathrm{cm^{-1}}$ region [^{1}H NMR δ 4.57 (3 H, s, $\mathrm{C}H$), 3.27 (6 H, m, $\mathrm{C{=}NC}H_2$), 2.80 (6 H, m, $\mathrm{CH_2C}H_2\mathrm{N}$), 1.71 (9 H, s, $\mathrm{C(O)C}H_3$), 1.66 (9 H, s, $\mathrm{C(N)C}H_3$); ^{13}C NMR δ 174.9 ($C{=}\mathrm{O}$), 166.7 ($\mathrm{CH_3}C\mathrm{(N)}$), 98.3($C\mathrm{H}$), 57.9 ($\mathrm{C{=}N}C\mathrm{H_2}$), 49.2 ($\mathrm{CH_2}C\mathrm{H_2N}$), 27.2 ($\mathrm{C(O)}C\mathrm{H_3}$), 21.5 ($\mathrm{C(N)}C\mathrm{H_3}$). This complex decomposed during sublimation. Pure samples of the heavier lanthanide (Sm, Er, Yb) complexes were obtained by sublimation (180 °C, 10^{-2} Torr) or crystallization from THF–$\mathrm{Et_2O}$ mixtures. The crystal of Yb(trac) for X-ray study was prepared by sublimation (180 °C, 10^{-2} Torr).

Table II. Crystallographic Data for Yb(trac)

formula	$\mathrm{C_{21}H_{33}N_4O_3Yb}$
fw	562.56
crystal system	monoclinic
space group	$P2_1/c$
a, Å	13.150 (5)
b, Å	16.125 (5)
c, Å	22.938 (5)
β (deg)	105.83 (2)
V, Å^3	4679 (2)
Z	8
T, °C	21
ρ_c, g/cm^3	1.597
λ, Å	0.71069
μ(Mo Kα) cm^{-1}	40.11
transmission factors	0.67–1.28
R (F_o)	0.043
R_w (F_o)	0.053

La(hatren). $\mathrm{H_3hatren}$ (0.95 g, 1.9 mmol) and $\mathrm{La[N(SiMe_3)_2]_3}$ (1.18 g, 1.90 mmol) were weighed into a Schlenk flask in an argon-filled glovebox. After removal of the flask to a Schlenk line, the solids were dissolved in THF (50 mL). A bright yellow solution was initially formed, but the color rapidly faded and precipitation of a pale yellow solid occurred. The suspension was stirred overnight at room temperature. The reaction mixture was then filtered through a Schlenk frit, and the solid was washed with $\mathrm{Et_2O}$ (4 × 25 mL) and dried under vacuum at room temperature for 3 h. [Infrared spectrum (CsI, Nujol mull) 1600, 1540, 1440 $\mathrm{cm^{-1}}$ (all vs, $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N}, \mathrm{C}\overset{\cdots}{-}\mathrm{C}, \mathrm{C}\overset{\cdots}{-}\mathrm{O})$).] The infrared spectra of the Sm and Yb analogoues were superimposable with La(hatren) in the 1400–1700-$\mathrm{cm^{-1}}$ region: ^{1}H NMR δ 7.21 (3 H, d, C(aryl)–H meta to C(aryl)–O, ortho to $\mathrm{C(aryl){-}C(CH_3){=}N}$), 6.90 (3 H, t, C(aryl)–H meta to C(aryl)–O), 6.26 (3 H, t, C(aryl)–H, para to C(aryl)–O), 6.21 (3 H, d, C(aryl)–H ortho to C(aryl)–O), 3.60 (6 H, m, $\mathrm{C{=}NC}H_2$), 2.89 (6 H, m, $\mathrm{CH_2C}H_2\mathrm{N}$), 2.16 (9 H, s, $\mathrm{C}H_3\mathrm{C{=}N}$). ^{13}C NMR data were not obtained because of the low solubility of this complex.

La(datren). This compound was synthesized by the procedure outlined above for La(hatren) by using $\mathrm{H_3datren}$ (0.84 g, 1.4 mmol) and $\mathrm{La[N(SiMe_3)_2]_3}$ (0.89 g, 1.4 mmol) [infrared spectrum (CsI, Nujol mull) 1618, 1590 (sh), 1520, 1480, 1412, 1400 (all m to vs, $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N}, \mathrm{C}\overset{\cdots}{-}\mathrm{C}, \mathrm{C}\overset{\cdots}{-}\mathrm{O})$)]. The infrared spectra of the Sm and Yb analogues are identical with La(datren) in the 1400–1700-$\mathrm{cm^{-1}}$ region: ^{1}H NMR δ 6.90 (3 H, s, C(aryl)–H meta to C(aryl)–O), 6.00 (3 H, s, C(aryl)–H ortho to C(aryl)–O), 3.56 (6 H, m, $\mathrm{C{=}NC}H_2$), 2.84 (6 H, m, $\mathrm{CH_2C}H_2\mathrm{N}$), 2.10 (9 H, s, $\mathrm{C(C}H_3\mathrm{){=}N}$), 2.02 (9 H, s, C(aryl)–CH_3 meta to C(aryl)–O), 1.99 (9 H, s, C(aryl)–CH_3 para to C(aryl)–O). ^{13}C NMR data were not obtained because of the low solubility of this complex.

X-ray Crystallographic Analysis of Yb(trac). Crystallographic data appear in Table II. The final unit-cell parameters were obtained by least squares on the setting angles for 25 reflections with $2\theta = 27.3–29.2°$. The intensities of three standard reflections, measured every 300 reflections throughout the data collection, remained essentially constant. The data were processed[19] and corrected for Lorentz and polarization effects and absorption (empirical). A total of 11 606 reflections with $2\theta \leq 55°$ was collected on a Rigaku AFC6S diffractometer; of these 11 121 were unique ($R_{\mathrm{int}} = 0.062$), and those 4199 having $I \geq 3\sigma(I)$ were employed in the solution and refinement of the structure. Reflections with $h+k$ odd are systematically weak as a result of the location of the heavy atoms in the unit cell, this being partially responsible for the somewhat low fraction of the data having significant intensity.

The structure was solved by conventional heavy atom methods, the coordinates of the Yb atoms (one from each of the two crystallographically independent molecules) being determined from the Patterson function and those of the remaining non-hydrogen atoms from a subsequent difference Fourier synthesis. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were fixed

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(19) 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.

Table III. Selected Distances (Å) and Angles (deg) Involving Yb for Yb(trac)[a]

	Distances		
Yb(1)–O(1)	2.181 (9)	Yb(2)–O(4)	2.172 (9)
Yb(1)–O(2)	2.161 (9)	Yb(2)–O(5)	2.179 (9)
Yb(1)–O(3)	2.199 (9)	Yb(2)–O(6)	2.180 (9)
Yb(1)–N(1)	2.43 (1)	Yb(2)–N(5)	2.43 (1)
Yb(1)–N(2)	2.46 (1)	Yb(2)–N(6)	2.42 (1)
Yb(1)–N(3)	2.45 (1)	Yb(2)–N(7)	2.41 (1)
Yb(1)–N(4)	2.44 (1)	Yb(2)–N(8)	2.46 (1)
	Angles		
O(1)–Yb(1)–O(2)	86.4 (4)	O(4)–Yb(2)–N(8)	161.5 (4)
O(1)–Yb(1)–O(3)	84.5 (3)	O(5)–Yb(2)–O(6)	85.9 (4)
O(1)–Yb(1)–N(1)	129.1 (4)	O(5)–Yb(2)–N(5)	128.9 (4)
O(1)–Yb(1)–N(2)	75.2 (4)	O(5)–Yb(2)–N(6)	159.9 (4)
O(1)–Yb(1)–N(3)	161.3 (4)	O(5)–Yb(2)–N(7)	76.7 (4)
O(1)–Yb(1)–N(4)	87.1 (4)	O(5)–Yb(2)–N(8)	88.8 (3)
O(2)–Yb(1)–O(3)	86.4 (4)	O(6)–Yb(2)–N(5)	126.8 (4)
O(2)–Yb(1)–N(1)	126.7 (4)	O(6)–Yb(2)–N(6)	88.9 (4)
O(2)–Yb(1)–N(2)	87.8 (4)	O(6)–Yb(2)–N(7)	162.0 (4)
O(2)–Yb(1)–N(3)	75.9 (4)	O(6)–Yb(2)–N(8)	75.8 (4)
O(2)–Yb(1)–N(4)	162.8 (4)	N(5)–Yb(2)–N(6)	68.9 (4)
O(3)–Yb(1)–N(1)	128.8 (4)	N(5)–Yb(2)–N(7)	69.5 (4)
O(3)–Yb(1)–N(2)	159.2 (4)	Yb(1)–N(2)–C(2)	109.7 (8)
O(3)–Yb(1)–N(3)	88.4 (4)	Yb(1)–N(2)–C(3)	129 (1)
O(3)–Yb(1)–N(4)	77.2 (4)		
N(1)–Yb(1)–N(2)	69.8 (3)	Yb(1)–N(3)–C(9)	117.8 (9)
N(1)–Yb(1)–N(3)	68.2 (4)	Yb(1)–N(3)–C(10)	127 (1)
N(1)–Yb(1)–N(4)	69.0 (4)		
N(2)–Yb(1)–N(3)	109.5 (4)	Yb(1)–N(4)–C(16)	117.7 (9)
N(2)–Yb(1)–N(4)	105.9 (4)	Yb(1)–N(4)–C(17)	126 (1)
N(3)–Yb(1)–N(4)	108.2 (4)		
O(4)–Yb(2)–O(5)	83.9 (3)	Yb(2)–N(5)–C(22)	106.6 (9)
O(4)–Yb(2)–O(6)	86.7 (4)	Yb(2)–N(5)–C(29)	106.4 (9)
O(4)–Yb(2)–N(5)	129.4 (4)	Yb(2)–N(5)–C(36)	108.8 (8)
O(4)–Yb(2)–N(6)	76.4 (4)		
O(4)–Yb(2)–N(7)	86.8 (4)		
N(5)–Yb(2)–N(8)	67.7 (4)		
N(6)–Yb(2)–N(7)	105.9 (4)	Yb(2)–N(6)–C(23)	115.9 (9)
N(6)–Yb(2)–N(8)	108.7 (4)	Yb(2)–N(6)–C(24)	127 (1)
N(7)–Yb(2)–N(8)	108.1 (4)		
Yb(1)–O(1)–C(5)	132.2 (9)	Yb(2)–N(7)–C(30)	119 (1)
Yb(1)–O(2)–C(12)	131.2 (9)	Yb(2)–N(7)–C(31)	126 (1)
Yb(1)–O(3)–C(19)	130 (1)		
Yb(2)–O(4)–C(26)	133.8 (9)	Yb(2)–N(8)–C(37)	117.0 (9)
Yb(2)–O(5)–C(33)	129.7 (9)	Yb(2)–N(8)–C(38)	125 (1)
Yb(2)–O(6)–C(40)	129.9 (9)		
Yb(1)–N(1)–C(1)	105.8 (8)		
Yb(1)–N(1)–C(8)	108.0 (8)		
Yb(1)–N(1)–C(15)	107.8 (8)		

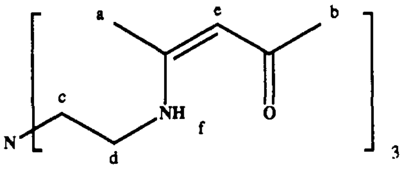
[a] Complete distances and angles are included as supplementary material (Tables SXI and SXI).

in idealized positions (C–H = 0.98 Å, $B_H = 1.2B_{\text{bonded atom}}$). Neutral atom scattering factors and anomalous dispersion corrections for all atoms were taken from the *International Tables for X-ray Crystallography*.[20] Final atomic coordinates and equivalent isotropic thermal parameters, complete bond lengths, and complete bond angles appear in the supplementary material as Tables SX, SXI, and SXII, respectively. An abbreviated list of distances and angles involving Yb appears in Table III. A more detailed table of crystallographic data (Table SI) and tables of hydrogen atom parameters (Table SII), anisotropic thermal parameters (Table SIII), intramolecular distances involving hydrogen atoms (Table SIV), intramolecular bond angles involving hydrogen atoms (Table SV), torsion angles (Table SVI), intermolecular contacts (Table SVII), least-squares planes (Table SVIII), and measured and calculated structure factor amplitudes (Table SIX) are also included as supplementary material.

Results and Discussion

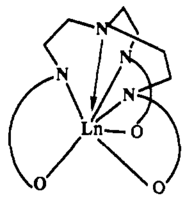
The potentially heptadentate ligands were prepared previously by the Schiff base condensation of tren with 3 equiv of ketone, and several lanthanide complexes of the three new ligands were prepared.[13] Two coordination types had been found (types I and II); type II was structurally characterized, but type I was only postulated, until now.

Table IV. ^{1}H NMR Data[a] (δ in ppm from TMS) for the H_3trac Complexes

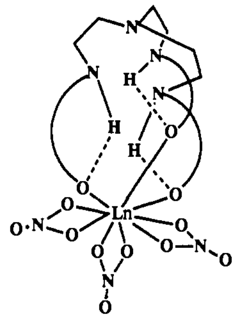


	a	b	c	d	e	f
H_3trac	1.81	1.91	2.55	3.29	4.90	10.60
$PrCl_3(H_3trac)(H_2O)_2$[b]	1.81	1.86	2.59	3.20	4.89	10.54
$DyCl_3(H_3trac)(H_2O)$[b]	1.68	2.67	0.87	2.43	5.73	9.90
$YbCl_3(H_3trac)(H_2O)$[b]	1.61	1.97	3.22	3.80	4.60	10.70
$YCl_3(H_3trac)$	1.80	1.90	2.59	3.26	4.87	10.60

[a] Recorded at 80 MHz in DMSO-d_6. [b] Assignments of a/b and c/d pairs of resonances are tentative.



type I



type II

Type I had proven elusive in our previous work, and it was only with completely anhydrous conditions that it was possible to characterize it unambiguously. When the complexes are prepared from a tris(bis(trimethylsilyl)amido)lanthanide starting material, species which are seven coordinate form (type I). Type I has the formulation LnL and contains the completely coordinated triply deprotonated (trianionic) ligand. Because of the increasing interest in polydentate ligand complexes of the lanthanides as magnetic resonance imaging contrast agents,[21-23] our original intention was to prepare type I neutral complexes with an eighth coordination position open trans to the apical nitrogen atom for the necessary exchange of water molecules. As we reported previously, the complexes hydrolyze in aqueous solution and, therefore, do not represent a new class of contrast agents.

In the work reported here we have again found the two types. The metathesis reaction in ethanol between H_3L (L = trac, hatren, datren) and $LnCl_3$ gave type II complexes $LnCl_3(H_3trac)(H_2O)_x$ in which the ligand was tridentate and three more coordination positions were taken up by Cl^- (Table I); these showed decreasing waters of coordination (x) along the lanthanide series. These compounds gave positive Ag^+ or flame chloride tests; they hydrolyzed slowly over 1 week in aqueous solution, or quickly in refluxing ethanol, to give $LnCl_3(tren)(H_2O)_x$[24] complexes. They were, however, stable for weeks or months in aprotic solvents. The ^{1}H NMR data (Table IV) showed that the H_3trac ligand was off the metal ion in DMSO solution because the paramagnetic shifts[25] were very small (<2 ppm) in the Pr, Dy, and Yb complexes. The chemical shifts for the diamagnetic Y complex and the uncomplexed ligand were essentially identical with and were quite close to those of the paramagnetic lanthanide complexes. If the H_3trac

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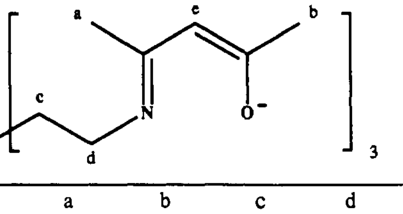
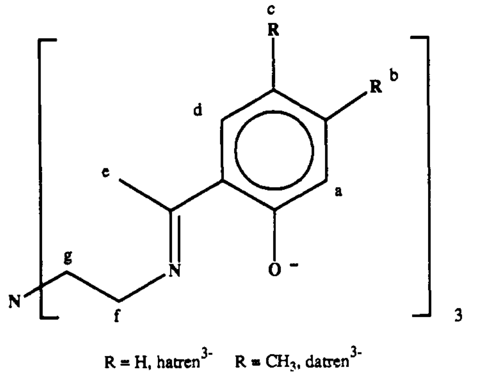
Table V. ^1H NMR Data[a] (δ in ppm from TMS) for the trac^{3-} Complexes



	a	b	c	d	e
La(trac)	1.65	1.70	2.80	3.29	4.57
Sm(trac)[b]	1.99	2.20	2.02	3.42	5.21
Er(trac)[b]	−3.4	−4.4	4.6	4.6	9.0
Yb(trac)[b]	−0.2	−2.5	13.2	5.0	0.3

[a] Recorded at 200 MHz in DMSO-d_6. [b] Assignments of a/b and c/d pairs of resonances are tentative.

Table VI. ^1H NMR Data[a,b] (δ in ppm from TMS) for the hatren^{3-} and datren^{3-} Complexes



	a	b	c	d	e	f	g
La(hatren)	6.21	6.90	6.26	7.21	2.16	3.60	2.89
Sm(hatren)	6.57	6.87	6.50	7.78	2.78	2.93	0.47
Yb(hatren)	7.7	8.0	4.8	3.8	−2.6	7.0	21.1
La(datren)	6.00	2.02	1.99	6.90	2.10	3.56	2.84
Sm(datren)	6.22	2.09	2.01	7.46	2.74	2.95	0.57
Yb(datren)	11.9	3.3	2.8	−0.4	0.5	9.2	−6.5

[a] Recorded at 200 MHz in DMSO-d_6. [b] Assignments of a/d, b/c, and f/g pairs of resonances are tentative.

ligand were tightly bound in these complexes, the paramagnetic shifts should be much greater than those seen in Table IV, and the spectra would be broadened.[25] UV/vis spectra corroborated that the H_3trac was off in ethanol solution.

We were unable to repeat our reported preparations[13] in ethanol of the type I lanthanum ligand complexes. As well, we were unable to remove HCl from the $LnCl_3(H_3trac)(H_2O)_x$ compounds with bases such as pyridine or triethylamine, and addition of $AgBF_4$ gave $[H_3tren][BF_4]_3$ and $Ln(acac)_3$ in addition to AgCl. We therefore chose the highly basic bis(trimethylsilyl)amido ligand to replace chloride in the starting Ln^{3+} salt and dry tetrahydrofuran (THF) as the reaction medium. With these conditions LnL complexes were reproducibly prepared in good yield (Table I). In these LnL complexes the ligands were clearly coordinated firmly to the ion in solution. Tables V and VI illustrate significant paramagnetic shifts in the ^1H NMR spectra of the LnL complexes where Ln is a paramagnetic ion (vs La). The shifts are significant (+18.2 to −9.3 ppm), and there are no N–H protons detected. The type I LnL complexes are thermally robust (Ln(trac) Ln = Sm, Er, Yb sublime intact, X-ray quality crystals of Yb(trac) were grown by sublimation!), but they were immediately hydrolyzed by adding water to (presumably) $Ln(OH)_3(H_3L)(H_2O)_x$. The hatren^{3-} complexes were more soluble than their datren^{3-} analogues, and both series were much less soluble than the trac^{3-} species.

Mass spectral and infrared data for all the compounds were consistent with the indicated formulations. Molecular ions were found in both EI and FAB mass spectra for the type I complexes (attesting to their robustness). There were fragmentation patterns indicative of the respective ligand.[13] The type II chloride complexes had IR spectra superimposable on that of H_3trac and showed ν_{N-H} bands characteristic of the protons bridging the N–O portion of the ligand; these were absent in the type I complexes. The four band infrared spectral pattern (1620–1440 cm^{-1}) characteristic of the Schiff base delocalized C⩦C, C⩦O, C⩦N manifold underwent a general bathochromic shift in both complex types.

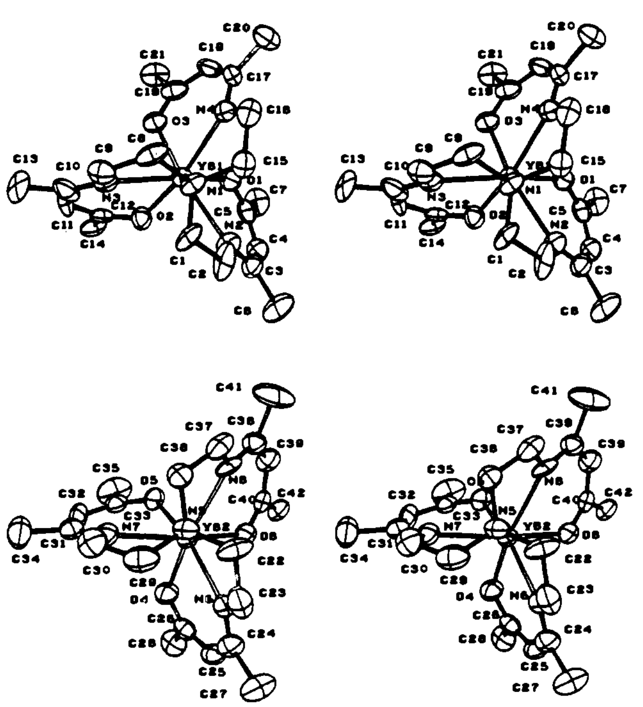


Figure 1. ORTEP stereoviews of the two crystallographically independent Yb(trac) molecules; 50% probability thermal ellipsoids are shown for the non-hydrogen atoms. Hydrogen atoms have been omitted for clarity. Both Λ and Δ enantiomers appear in the asymmetric unit and are, therefore, crystallographically independent.

Single crystals of the LnL complexes proved elusive for several years. La(trac) did crystallize from an ethanol solution containing excess H_3trac; however, the crystals were so unstable that they were never successfully mounted in capillaries, even in the presence of mother liquor (these may in fact have actually been $LaCl_3(H_3trac)(H_2O)_x$). Some crystals were stable at low temperature, but most simply crazed and disintegrated. The preparation of single crystals of a type I complex was (finally) achieved by sublimation of Yb(trac).

The two independent molecules found in the asymmetric unit are shown in Figure 1 with a view roughly down the 3-fold axis (Yb–apical N, N(1), or N(5)) of the molecule. Because trac^{3-} can wrap around Yb^{3+} in either a right-handed (Δ) or left-handed (Λ) screw, both enantiomers are present in the unit cell. They are the two independent molecules; the unit cell is quite large at $Z = 8$. The crystal structure of Yb(trac) consists of discrete Yb(trac) units with four molecules of each enantiomer present in the unit cell. There are no abnormally short intermolecular contacts although there are two contacts between the ligand O atoms and H atoms of neighboring molecules which are less than 2.7 Å: O(2)–methylene H on C(37) = 2.62 Å and O(6)–methylene H on C(9) = 2.69 Å. Every molecule in the unit cell is essentially independent.

The bond lengths (Table SXI) show that the three Schiff base arms of the trac^{3-} ligand are *less* delocalized than in the $Gd(H_3trac)(NO_3)_3$ complex.[13] The methine C–C(N) distances (e.g., C(4)–C(3)) average 1.44 Å, while the methine C–C(O) distances (e.g., C(4)–C(5)) average 1.37 Å. The former distances are longer than in $Gd(H_3trac)(NO_3)_3$ (1.402 Å), while the latter distances are slightly shorter than 1.394 Å. This would suggest a more hydroxyl-like O bonding to Yb. In accordance with this are the Yb–O distances here of 2.18 Å and of 2.23–2.24 Å in various Yb(acac)$_3$L structures;[26-28] however, the carbon–oxygen lengths (av 1.28 Å, and 1.29 Å in the Yb(acac)$_3$L structures[26-28]) are closer to that of the C═O (1.24 Å) in Hacac, rather than the C–O (1.33 Å).[29]

There are three geometries available to a trac^{3-} heptadentate ligand: a trigonal prism capped on a triangular face, a trigonal prism capped on a square face, or a monocapped octahedron.[3-5] It is not surprising that the geometry around the Yb atoms is that of a monocapped distorted octahedron (Figure 1) since trigonal primatic coordination of the three Schiff base arms would leave the apical N atom far removed from Yb. The apical nitrogen atom caps the triangular face formed by the other three coordinating N atoms, and the Yb atoms are displaced 0.63–0.81 Å from the plane of the Schiff base arms. The bond angles suggest that this distortion is a spreading of the N$_3$ face and a shrinking of the O$_3$ face of the octahedron. The trans N–Yb–O angles and the O–Yb–O angles average 161° and 86°, respectively, while the N–Yb–N angles (excluding apical N atoms) average 108°. The chelate N–Yb–O angles and the Yb–O–C angles average, respectively, 77° and 131°. These are very close to those in the Yb(acac)$_3$L structures[26-28] suggesting that the apical N atom and its ethylene arms do not add much strain to the structure.

In the structure of Gd(H$_3$trac)(NO$_3$)$_3$ the capping tertiary nitrogen atom was "tucked in" with its lone pair of electrons pointed at the Gd^{3+} atom but was not bonded to it; however, in the structure of Yb(trac) this bonding interaction is clearly present. We have now characterized structurally both types I and II bonding modes of these heptadentate ligands. The stability of the type I complexes is greater, and the lability less, than their type II analogues. The type I complexes decompose given a competing ligand (hydrolysis, solvent competition), while the type II complexes are stabilized by the other coordinating anions (chloride, nitrate). Imine linkages chelating the lanthanides are unstable, although there are a few rather sketchy reports of them in the literature.[30] The greater stability of the sublimable later Ln complexes of Er and Yb suggests that trac^{3-} fits these metals better than the larger earlier Ln like La; La(trac) could not be sublimed without decomposition. This is contrary to our previous inference[13] about this fit, but the present conclusion is based on considerations which include X-ray data on both types of complex.

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Supplementary Material Available: A more detailed table of crystallographic data (Table SI), tables of hydrogen atom parameters (Table SII), anisotropic thermal parameters (Table SIII), intramolecular distances involving hydrogen atoms (Table SIV), intramolecular bond angles involving hydrogen atoms (Table SV), torsion angles (Table SVI), intermolecular contacts (Table SVII), least-squares planes (Table SVIII), final atomic coordinates and equivalent isotropic thermal parameters (Table SX), and complete tables of distances and angles (Tables SXI and SXII) (32 pages); table of measured and calculated structure factor amplitudes (Table SIX) (72 pages). Ordering information is given on any current masthead page.

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