Inorg. Chem. **1995,** *34,* 4921−4925

Complexation of the Potentially Heptadentate Ligand $\mathrm{H_3dha_3tren}$ with Lanthanides: Architecture of a $\mathrm{[Nd(NO_3)_3(H_3dha_3tren)]}_n$ Polymer with Profuse Modes of Nitrate Coordination

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Received March 2, 1995

Introduction

We have been interested in linear and tripodal tetraamine-based potentially heptadentate N_4O_3 ligands (Chart 1) because the ease of synthesis of these polydentate Schiff base ligands and their ready reduction to amine phenols have led to a rich lanthanide coordination chemistry.[2−6] The facility with which one can vary the preorganization, cavity size, coordination geometry, and rigidity of the ligand makes possible the synthesis of a series of lanthanide complexes with different geometries, a series in which five coordination modes have thus far been found.[2−6] The goal of this work is to understand the coordination chemistry of lanthanide complexes of N_4O_3 ligands and to enable the design of specific metal chelates for a variety of applications based on water solubility and stability, as well as lipophilicity. $\mathrm{H_3dha_3tren}$ (see Scheme 1) is a tribasic ligand which contains both lipophilic hydrocarbon chains and polar carbonyl groups; the conjugated ring preserves some aromaticity. The oxygen-rich nature of the arms can potentially induce electronic changes and alter the metal-binding properties of the nitrogens and the exocyclic oxygen atoms. $\mathrm{H_3dha_3tren}$ can be readily synthesized from the condensation reaction of tris(2-aminoethyl)amine (tren) with dehydroacetic acid (dha);[7] in this paper, we report some properties of its lanthanide complexes as part of an effort to prepare multinuclear, and possibly polymeric, arrays of rare earth ions.

Experimental Section

Materials and Methods. Hydrated lanthanide salts, tris(2-aminoethyl)amine (tren), and dehydroacetic acid were purchased from Aldrich or Alfa and used without further purification. Ethanol was dried over 4 Å molecular sieves. Infrared spectra were recorded as KBr disks in the range 4000−400 cm^{-1} on a Perkin-Elmer PE 783 spectrometer and were referenced to polystyrene. NMR spectra (200 and 400 MHz) were recorded on Bruker AC-200E and WH-400 spectrometers, respectively. NMR data are reported as δ (ppm) downfield of external TMS. Mass spectra were obtained with either a Delsi Nermag R10-10C (desorption chemical ionization, DCI) or a Kratos Concept II HQ (liquid secondary ion mass spectrometry, LSIMS) instrument. UV/vis spectra were recorded on a Shimadzu UV-2100 spectrometer. Melting points were measured on a Mel-Temp apparatus and were uncorrected. Analyses for C, H, and N were carried out by Mr. Peter Borda in this department.

Preparations of Ligand and Complexes. $\mathbf{H_3dha_3tren}$. This synthesis is simpler than the reported preparation.[7] To a suspension of 10 g (60 mmol) of dehydroacetic acid in 100 mL of anhydrous ethanol was added a solution of 2.92 g (20 mmol) of tren in 10 mL of ethanol. The mixture was heated at 60 °C for 20 min and then poured into 500 mL of diethyl ether. A yellow powder formed immediately. The suspension was kept in an ice-bath for approximately 1 h, and the solid was then filtered out, washed with diethyl ether, and dried in air. The yield was 12.0 g (86%). Anal. Calcd (found) for $C_{30}H_{36}N_4O_9\cdot 0.5H_2O$: C 59.50 (59.64), H 6.16 (6.08), N 9.25 (9.19). Mass spectrum (DCI): *m/z* = 597 ($M^+ = \mathrm{H_4dha_3tren^+}$). IR (cm^{-1}, KBr disk): 1700, 1662, 1640−1560, 1478 (all vs or s, $\upsilon_{C=C}$, $\upsilon_{C=O}$). ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.0 (s, 9H, CH_3), 2.5 (s, 9H, CH_3), 2.9 (t, 6H, $N\mathit{CH_2}CH_2N$), 3.6 (q, 6H, $NCH_2\mathit{CH_2}N$), 5.5 (s, 3H), 13.9 (br s, 3H, NH).

The ligand $\mathrm{H_3dha_3tren}$ can be hydrolyzed, losing one arm, to form $\mathrm{(H_3dha_2tren)NO_3}$ in a wet methanol solution of $Yb(NO_3)_3$. Anal. Calcd (found) for $C_{22}H_{31}N_5O_9\cdot H_2O$: C, 50.09 (50.29); H, 6.26 (6.23); N, 13.28 (13.11). Mass spectrum (LSIMS): *m/z* = 447 ($M^+ = \mathrm{H_3dha_2tren^+}$). IR (cm^{-1}, KBr disk): 1710, 1660, 1630−1575 (all vs or s, $\upsilon_{C=O}$, $\upsilon_{C=C}$). ^{1}H NMR (400 MHz, D_2O): δ 1.9 (s, 6H, CH_3), 2.3 (s, 6H, CH_3), 2.65 (t, 4H, $N\mathit{CH_2}CH_2N$), 2.75 (t, 2H, $N\mathit{CH_2}CH_2NH_3^+$), 3.0 (t, 2H, $NCH_2\mathit{CH_2}NH_3^+$), 3.4 (t, 4H, $NCH_2\mathit{CH_2}N$), 5.4 (s, 2H).

$\mathbf{Nd(dha_3tren)\cdot 0.5NaNO_3\cdot 1.5H_2O}$. A solution of $\mathrm{H_3dha_3tren}$ (0.35 g, 0.5 mmol) in 5 mL of chloroform was added to a solution of $Nd(NO_3)_3\cdot 5H_2O$ (0.22 g, 0.5 mmol) in 20 mL of anhydrous ethanol, and a white precipitate formed immediately. Upon gradual addition of sodium acetate (0.12 g, 1.5 mmol) in 10 mL of methanol, the precipitate dissolved to give a pink solution from which pink crystals formed slowly. Most of the crystals cracked after a few days. A crystal suitable for the X-ray diffraction was mounted in its mother liquor (however, the elemental formula of the X-ray structure sample picked from the same bulk product was not the same as that of the bulk product, *vide infra*). The yield was 0.21 g (48%). Anal. Calcd (found) for $C_{30}H_{33}N_4NdO_9\cdot 0.5NaNO_3\cdot 1.5H_2O$: C, 44.63 (44.67); H, 4.49 (4.73); N, 7.81 (7.56). Mass spectrum (LSIMS): *m/z* = 597 ($M^+ = \mathrm{H_4dha_3tren^+}$). IR (cm^{-1}, KBr disk): 1712 s, 1690 s, 1662 m, 1640−1530 br s, 1478 s ($\upsilon_{C=O}$, $\upsilon_{C=C}$), 1387 (υ_{NO}). Because of decomposition, UV spectra in MeOH, $CHCl_3$ and DMSO, as well as the ^{1}H NMR spectrum in methanol, were similar to those of the ligand. A sodium flame test was positive.

$\mathbf{Pr(dha_3tren)\cdot 0.5NaNO_3\cdot 1.5H_2O}$. The green crystals were synthesized by the same procedure as for the Nd analog. The yield was 0.23 g (55%). Anal. Calcd (found) for $C_{30}H_{33}N_4O_9Pr\cdot 0.5NaNO_3\cdot 1.5H_2O$: C, 44.81 (45.00); H, 4.51 (4.64); N, 7.84 (7.73). Mass spectrum (LSIMS): *m/z* = 735 ($M^+ = \mathrm{HPrdha_3tren^+}$); 597 ($M^+ = \mathrm{H_4dha_3tren^+}$). IR (cm^{-1}, KBr disk): 1702, 1692, 1660, 1640−1540, 1475 (all s, $\upsilon_{C=O}$, $\upsilon_{C=C}$), 1390 (υ_{NO}).

X-ray Crystallographic Analyses of $\mathbf{(H_3dha_2tren)(NO_3)\cdot H_2O}$ and $\mathbf{[Nd(NO_3)_3(H_3dha_3tren)]_n}$. Selected crystallographic data appear in Table 1. The final unit-cell parameters were obtained by least-squares on the setting angles for 25 reflections with $2\theta = 25.9-55.0°$ for $\mathrm{(H_3dha_2tren)(NO_3)\cdot H_2O}$ and 10.4−20.9° for $\mathrm{[Nd(NO_3)_3(H_3dha_3tren)]}_n$. The intensities of three standard reflections, measured every 200 reflections throughout the data collections, remained constant for both complexes. The data were processed[8] and corrected for Lorentz and polarization effects, and absorption (empirical, based on azimuthal scans for three reflections).

The structure of $\mathrm{(H_3dha_2tren)(NO_3)\cdot H_2O}$ was solved by direct methods and that of $\mathrm{[Nd(NO_3)_3(H_3dha_3tren)]}_n$ was solved by conventional heavy atom methods. The structure analysis of $\mathrm{(H_3dha_2tren)(NO_3)\cdot H_2O}$ was initiated in the centrosymmetric space group $P\bar{1}$ on the basis of the *E*-statistics, this choice being confirmed by subsequent

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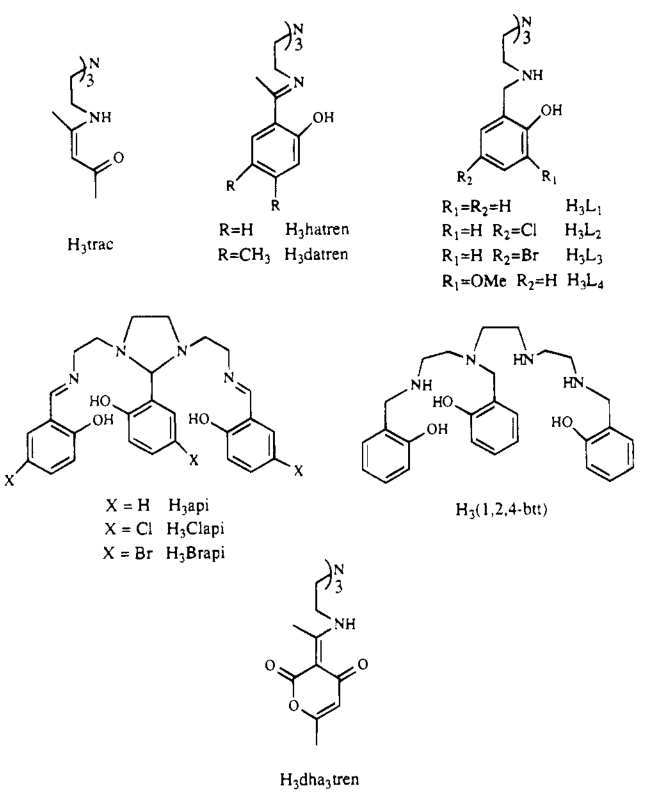
Chart 1



Scheme 1

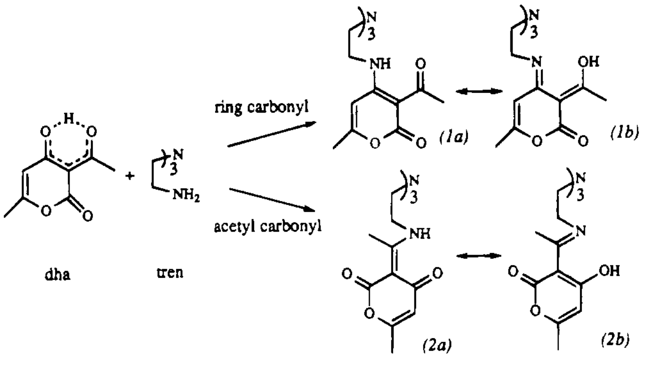


Table 1. Crystallographic Data for the Two Structures

	$(H_3dha_2tren)(NO_3)\cdot H_2O$	$[Nd(NO_3)_3(H_3dha_3tren)]_n$
formula	$C_{22}H_{33}N_5O_{10}$	$C_{30}H_{36}N_7NdO_{18}$
fw	527.53	926.89
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
a, Å	11.483(2)	10.488(3)
b, Å	11.775(3)	20.047(4)
c, Å	9.691(4)	18.587(4)
α, deg	98.70(3)	90
β, deg	97.90(2)	96.17(2)
γ, deg	77.22(2)	90
V, Å^3	1255.8(7)	3885(1)
Z	2	4
R^a	0.054	0.052
$R_w{}^a$	0.048	0.044

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

calculations. All non-hydrogen atoms of both structures were refined with anisotropic thermal parameters. Hydrogen atoms were fixed in calculated positions (N−H/C−H = 0.98 Å, $B_H = 1.2B_{\text{bonded atom}}$). Difference maps suggested that the hydrogen atoms of the C(20) methyl group of $(H_3dha_2tren)(NO_3)\cdot H_2O$ was (1:1) disordered with respect to a rotation about the C(17)-C(20) bond. A 2-fold split-atom model was employed. A correction for secondary extinction (Zacharaisen type) was applied for $(H_3dha_2tren)(NO_3)\cdot H_2O$, the final value of the extinction coefficient being 1.21(13) × 10^{-6}. Neutral atom scattering factors for all atoms[9] and anomalous dispersion corrections for the non-hydrogen atoms[10] were taken from the *International Tables for X-Ray Crystallography*. Selected bond lengths and bond angles for the two structures appear in Tables 2 and 3, respectively. Complete tables of final atomic coordinates and equivalent isotropic thermal parameters, crystallographic data, hydrogen atom parameters, anisotropic thermal parameters, bond lengths, bond angles, torsion angles, intermolecular contacts, and least-squares planes for both structures are included as supporting information.

Table 2. Selected Bond Lengths (Å) and Angles (deg) in $(H_3dha_2tren)NO_3\cdot H_2O$ with Estimated Standard Deviations

Bond Lengths			
O(3)−C(9)	1.257(5)	O(6)−C(19)	1.256(4)
N(2)−C(3)	1.309(5)	N(3)−C(13)	1.306(5)
C(3)−C(5)	1.425(6)	C(13)−C(15)	1.433(6)
C(5)−C(9)	1.440(6)	C(15)−C(19)	1.428(6)
Bond Angles			
N(2)−C(3)−C(4)	118.8(5)	N(3)−C(13)−C(14)	118.3(4)
N(2)−C(3)−C(5)	118.3(4)	N(3)−C(13)−C(15)	118.0(4)
O(3)−C(9)−C(5)	123.8(5)	O(6)−C(19)−C(15)	124.2(4)
C(3)−C(5)−C(9)	120.6(5)	C(13)−C(15)−C(19)	121.4(4)

Results and Discussion

Synthesis and Properties of H_3dha_3tren. Because of the resonance forms available to dehydroacetic acid (dha), reaction of tren with dha raises two questions. Which is the condensation site: the carbonyl of the ring (to give *1a/1b* in Scheme 1) or the carbonyl of an acetyl group at the side-chain (to give *2a/2b*)? What is the conformation of the Schiff base ligand: the enol−imine (*1b/2b*) or keto−amine (*1a/2a*) form?

It has recently been shown, on the basis of an X-ray structure and NMR spectra,[11] that in 2-acetylcyclohexanone (where both a ring carbonyl and an acetyl group are present) ethylenediamine reacts preferentially with the carbonyl of the ring, rather than with the acetyl group, as had been originally proposed.[12] In the reaction of tren with dha, we found, however, that the carbonyl of the acetyl group at the side chain was the preferred reaction site. Crystal structures of both $(H_3dha_2tren)NO_3$, and the ligand H_3dha_3tren in the Nd complex, proved conclusively that the condensation reaction did occur at the acetyl side chain, excluding the possible existence of ring carbonyl derivatives *1a* and *1b* in Scheme 1. The X-ray structures showed conclusively that the arms were in the tautomeric enamine−ketone form *(2a)*, as are most Schiff bases which are derived from β-diketones and aliphatic amines.[13,14] The preference of the Schiff base for the keto-enamine over the enol−imine structure was confirmed in solution ($CDCl_3$) by the ^1H NMR CH_2−NH coupling which showed a multiplet at 3.6 ppm for the α-hydrogen atoms of the secondary amine fragment coupled with hydrogen atoms on both the adjacent methylene carbon and the neighboring nitrogen atoms. On treatment with D_2O, this signal simplified to a triplet as a result of $NH_2 \leftrightarrow ND_2$ exchange. The crystal structure, as well as the ^1H NMR spectrum in $CDCl_3$, confirmed that H_3dha_3tren has the same

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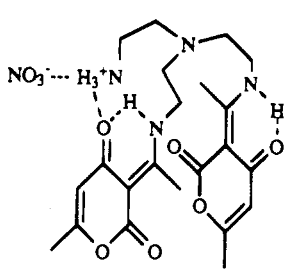
Table 3. Selected Bond Lengths (Å) and Angles (deg) in $[Nd(NO_3)_3(H_3dha_3tren)]_n$ with Estimated Standard Deviations[a]

	Bond Lengths (Å)		
Nd(1)−O(3)	2.481(8)	Nd(1)−O(13)*	2.419(7)
Nd(1)−O(6)′	2.486(7)	Nd(1)−O(14)	2.541(7)
Nd(1)−O(10)	2.36(1)	Nd(1)−O(16)	2.603(8)
Nd(1)−O(11)*	2.418(9)	Nd(1)−O(17)	2.545(8)
Nd(1)−O(13)	2.594(7)		
	Bond Angles (deg)		
O(3)−Nd(1)−O(6)′	70.5(3)	O(3)−Nd(1)−O(14)	71.9(2)
O(3)−Nd(1)−O(10)	142.3(3)	O(13)−Nd(1)−O(14)	52.0(2)
O(3)−Nd(1)−O(11)*	78.9(2)	O(13)−Nd(1)−O(16)	135.7(3)
O(3)−Nd(1)−O(13)	121.1(2)	O(13)−Nd(1)−O(17)	147.6(3)
O(3)−Nd(1)−O(13)*	143.7(2)	O(13)*−Nd(1)−O(14)	121.7(2)
O(3)−Nd(1)−O(14)	71.9(2)	O(13)*−Nd(1)−O(16)	73.5(3)
O(3)−Nd(1)−O(16)	75.9(3)	O(13)*−Nd(1)−O(17)	83.5(2)
O(3)−Nd(1)−O(17)	91.2(3)	O(14)−Nd(1)−O(16)	138.0(3)
O(6)′−Nd(1)−O(10)	71.8(3)	O(14)−Nd(1)−O(17)	154.2(3)
O(6)′−Nd(1)−O(11)*	145.3(3)	O(16)−Nd(1)−O(17)	49.2(3)
O(6)′−Nd(1)−O(13)	111.7(2)	O(10)−Nd(1)−O(14)	101.5(3)
O(6)′−Nd(1)−O(13)*	140.4(3)	O(10)−Nd(1)−O(16)	120.4(3)
O(6)′−Nd(1)−O(14)	81.1(2)	O(10)−Nd(1)−O(17)	79.8(3)
O(6)′−Nd(1)−O(16)	112.6(3)	O(11)*−Nd(1)−O(13)	70.7(2)
O(6)′−Nd(1)−O(17)	74.8(2)	O(11)*−Nd(1)−O(13)*	74.2(3)
O(10)−Nd(1)−O(11)*	136.3(3)	O(11)*−Nd(1)−O(14)	73.9(3)
O(10)−Nd(1)−O(13)	72.9(3)	O(11)*−Nd(1)−O(16)	74.0(3)
O(10)−Nd(1)−O(13)*	72.0(3)	O(11)*−Nd(1)−O(17)	122.9(3)
O(10)−N(5)−O(11)	130(1)	O(14)−N(6)−O(15)	121(1)
O(10)−N(5)−O(12)	119(1)	O(16)−N(7)−O(17)	117(1)
O(11)−N(5)−O(12)	112(1)	O(16)−N(7)−O(18)	119(1)
O(13)−N(6)−O(14)	122(1)	O(17)−N(7)−O(18)	124(1)
O(13)−N(6)−O(15)	116(1)		

[a] Symmetry operations: (∗) $2 - x, 1 - y, 1 - z$; (′) $^1/_2 + x, {}^1/_2 - y, -{}^1/_2 + z$.

ketone−enamine conformation in the solid state as in the solution, even though this conformation may have slightly less resonance stablization.[15] This is, however, favored by N−H- - -O hydrogen bonding which is generally stronger than N- - -H−O hydrogen bonding.[14] In this compound, the ^{1}H NMR spectrum in $CDCl_3$ showed a broad peak at 13.9 ppm, indicative of strong intramolecular hydrogen bonding.

Crystal Structure of $(H_3dha_2tren)NO_3$. In our first attempts to investigate the coordination properties of the tripodal ligand H_3dha_3tren with various metal ions, we discovered that it is hydrolyzed easily to form $(H_3dha_2tren)^+$ in wet methanol. In order to examine bond parameters in the uncomplexed ligand, the nitrate salt $(H_3dha_2tren)NO_3$ was crystallized, and its crystal structure was determined. Selected bond lengths and bond angles for $(H_3dha_2tren)NO_3$ are listed in Table 2 while an ORTEP diagram is illustrated in Figure 1. The two arms were found in the tautomeric enamine-keto form with the hydrogen located on the nitrogen atom. The two arms are parallel (dihedral angle within 6°) with the methyl groups on the exocyclic double bonds (C(4) and C(14)) oriented in opposite directions. Since the exocyclic keto-oxygen has greater electron density than the exocyclic ester-oxygen, it is not unexpected that all three intramolecular hydrogen bonds form between the exocyclic keto-oxygen and hydrogen atoms on the primary or secondary amines. The H-bond length of H(2)- - -O(6) is 1.76 Å, longer than that of H(1)- - -O(3) (1.71 Å). This is because O(6) forms a second weaker H-bond with a primary amine hydrogen (H(4)- - -O(6) = 1.93 Å, N(4)−H(4)- - -O(6) = 159°). The nitrate group hydrogen bonds to the ligand through one of the primary amine hydrogens (H(3)- - -O(9) = 1.90 Å, O(9)- - -H(3)−N(4) = 162°). The bond lengths (Table 2) show that the two Schiff base arms of the ligand are quite delocalized. The C−O lengths (average 1.26 Å) are much closer to that of a C=O double bond (1.24 Å) than a C−O single bond (1.33 Å); the C−N bond lengths are the same as those found in another averaged structure (1.31 Å).[6]



$H_3dha_2tren \cdot NO_3$

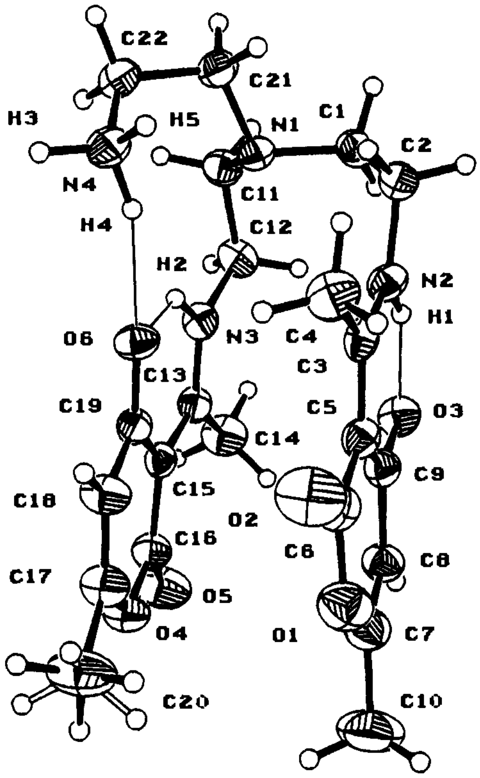


Figure 1. Structural and ORTEP drawings of $(H_3dha_2tren)NO_3$ with the numbering scheme. Thermal ellipsoids for the non-hydrogen atoms are drawn at the 33% probablity level.

Metal Complexes $Ln(dha_3tren)\cdot 0.5NaNO_3\cdot 1.5H_2O$ (Ln = Pr, Nd). Synthesis of these complexes was finally achieved with great difficulty. The dryness of the solvents, as well as the selection of the metal ion was found to be crucial to the preparation. Only the Pr^{3+} and Nd^{3+} complexes could be prepared from the reaction of $Ln(NO_3)_3\cdot nH_2O$ with H_3dha_3tren and 3 equiv of anhydrous sodium acetate in a mixture of absolute ethanol, chloroform, and methanol. (Reactions of $La(NO_3)_3$, $Gd(NO_3)_3$, and $Yb(NO_3)_3$ with H_3dha_3tren under the same conditions gave final products containing no ligand visible in the infrared spectra.) Elemental analyses suggested the formulation $Ln(dha_3tren)\cdot 0.5NaNO_3\cdot 1.5H_2O$, while infrared spectra showed strong nitrate peaks around 1380 cm^{-1}, and both complexes gave positive sodium flame tests. The complexes demetallated in methanol and DMSO, as evinced in the UV and ^{1}H NMR spectra, demonstrating the instability of these complexes over periods of time in donor solvents. Our inability to prepare other lanthanide complexes, and the instability of the Pr and Nd complexes are consistent with a lack of flexibility

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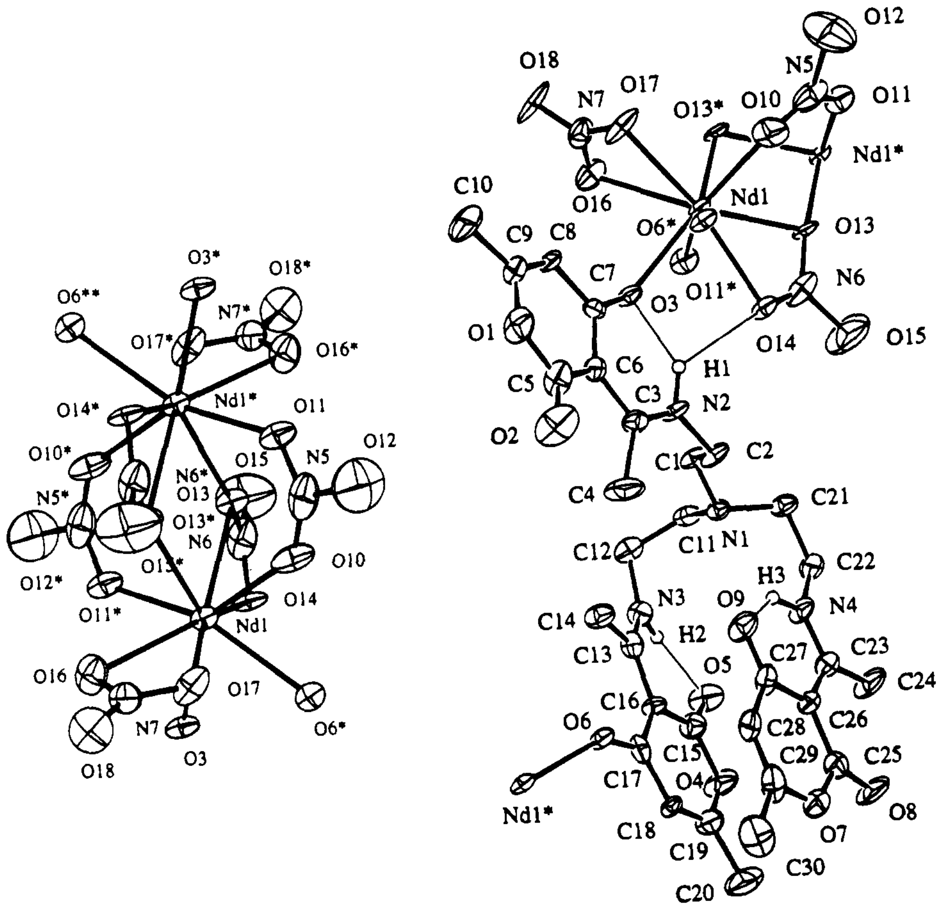


Figure 2. ORTEP drawings of the coordination environment of Nd in $[Nd(NO_3)_3(H_3dha_3tren)]_n$ (left) and of one $[Nd(NO_3)_3(H_3dha_3tren)]$ unit, both with the numbering scheme. Thermal ellipsoids for the non-hydrogen atoms are drawn at the 33% probablity level.

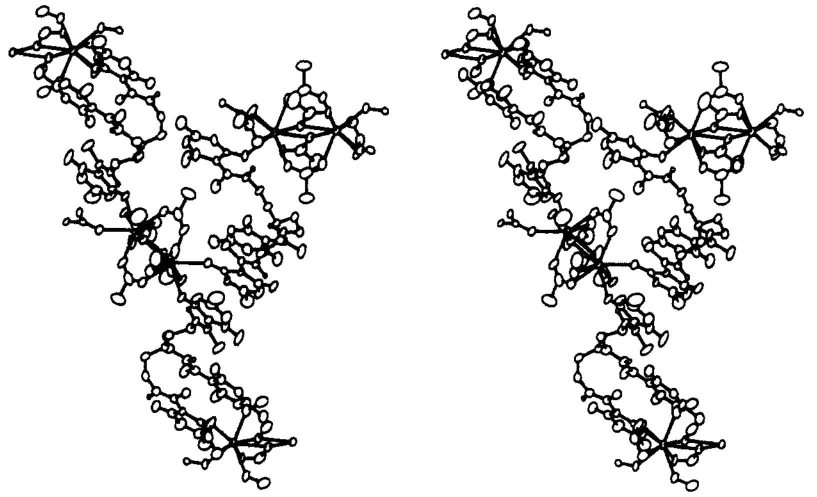


Figure 3. ORTEP stereoview of the polymer $[Nd(NO_3)_3(H_3dha_3tren)]_n$.

in the ligand backbone due to the exocyclic ring double bond, and the weaker basicity of the exocyclic keto-oxygen on the conjugate chelate ring as compared with a phenolate oxygen, for example.[2-4]

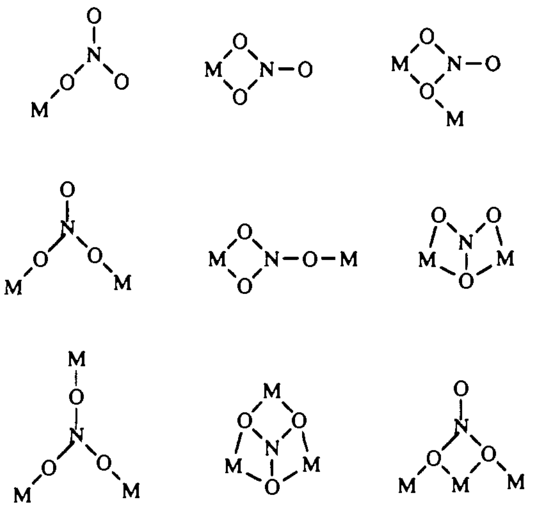
Crystal Structure of $[Nd(H_3dha_3tren)(NO_3)_3]_n$. Although characterization of the bulk samples of the lanthanide complexes gave the formulation $Ln(dha_3tren)\cdot 0.5NaNO_3\cdot 1.5H_2O$, the single crystal picked gave the polymeric structure with the empirical formulation $Nd(H_3dha_3tren)(NO_3)_3$. Selected bond lengths and bond angles of the coordination sphere in $[Nd(H_3dha_3tren)(NO_3)_3]_n$ are listed in Table 3 while the ORTEP diagrams of the coordination environment around the metal ion and the three dimensional polymer (in stereo) are illustrated in Figures 2 and 3, respectively. The two neodymium atoms form a dinuclear center through four bridging nitrate groups, and these neighboring dinuclear centers are linked together by the ligands to build a polymer in a three dimensional array. Each neodymium atom is coordinated by nine oxygens, and the geometry around each of the metal ions is a monocapped square antiprism and the Nd−Nd distance is 4.06 Å.

As is shown in Figure 2, among the nine oxygen atoms coordinated to the neodymium atom, two exocyclic keto-oxygen atoms are from two separate ligands with an average Nd-O distance of 2.49 Å, similar to that found in an eight-coordinate neodymium acetylacetonate complex[16] and a nine-coordinate neodymium oxalate complex.[17] The other seven oxygen atoms are from three kinds of nitrate ligands, classified in terms of their coordination modes to each of (Nd(1), Nd(1)*). One is the bridging (unidentate, unidentate) mode—the N(5) nitrate spans two Nd atoms through the two oxygen atoms O(10) and O(11). The Nd−O distances are Nd(1)−O(10) = 2.36(1) and Nd(1)−O(11)* = 2.418(9) Å, and the corresponding N−O distances are 1.23(1) and 1.30(1) Å, respectively, with the enlarged O−N−O angle of 130(1)°. A second mode is the simple bidentate nitrate (N(7))—the nitrate group forms a four-membered chelate ring incorporating one neodymium atom with Nd(1)−O(17) = 2.545(8) Å and Nd(1)−O(16) = 2.603(8) Å, consistent with those found in the 10-coordinated aquonitratoneodymium complex[18] and 11-coordinated (bipyridyl)(nitrato)neodymium complex.[19] The corresponding N−O distances are 1.23(1) and 1.29(1) Å, respectively, and the O−N−O angle is 117(1)°. (The atoms of the four-membered ring Nd(1), Nd(1)*, O(13), and O(13)* are all in the same plane, which is almost perfectly perpendicular to the eight-membered ring composed of Nd(1), O(10), O(11), N(5), Nd(1)*, O(10)*, O(11)*, and N(5)*.) The third mode is the bridging (bidentate, unidentate) nitrate (N(6))—the nitrate ligand bridges the two Nd atoms with one oxygen atom (O(13)), while the other oxygen atom (O(14)) is only coordinated to one Nd. Generally, when bridging oxygen atoms form two strong M−O bonds, their basicity should be lowered from that of a singly bonded oxygen atom and their bond lengths are accordingly longer. However, the Nd−O distances (Nd(1)−O(14) = 2.541(7) Å and Nd(1)−O(13) = 2.594(7) Å) coordinated to one Nd atom are much longer than that to another Nd atom (Nd(1)−O(13)* = 2.418(7) Å). The N−O distances in this unusual nitrate are as to be expected; the N−O related to the unbridging oxygen (N(6)−O(14)) is 1.24(1) Å, much shorter than N(6)−O(13) of related to the bridging oxygen (1.34(1) Å).

The nitrate group can coordinate to the metal ion in many ways. The common coordination modes are shown in Chart 2. Most nitrate complexes contain only one or two coordination modes; it is very rare to have many nitrate modes within one compound. To our knowledge, only one complex, $[\{Ph_2Te(NO_3)\}_2O]_2$-$Ph_2Te(NO_3)(OH)$,[20] has more than two modes. The $[Nd(H_3dha_3tren)(NO_3)_3]_n$ structure is the first lanthanide compound that contains so many nitrate modes in one three dimensional polymeric molecule.

Coordination of the ligand to the metal ion results in three distinct hydrogen bonds. In one arm, the hydrogen H(1) on the secondary amine N(2) intramolecularly hydrogen bonds with the coordinated exocyclic keto-oxygen O(3), and with the nearby coordinated oxygen of the nitrate group. The H(1)- - -O(3) and H(1)- - -O(14) distances are 1.84 and 2.28 Å respectively, and the corresponding N−H- - -O angles are 136 and 131°. The H-bond also causes lengthening of the corresponding C−O bond (C(7)−O(3) = 1.27(1) Å) compared to the non-H-bonded C−O length (C(17)−O(6) = 1.24(1) Å). In the second arm, after coordination of the exocyclic keto-oxygen O(6) to the Nd atom, an intramolecular H-bond forms between the exocyclic ester-oxygen O(5) and the hydrogen H(2) on the secondary amine (H(2)- - -O(5) = 1.79 Å, N(3)−H(2)- - -O(5) = 134°). The H-bond of H- - -O (ester) is a bit weaker than that of H- - -O (keto). In the third free arm, the hydrogen bonding is unchanged from that in the free ligand.

Chart 2. Common Nitrate Coordination Modes



In conclusion, a new complex which contains three distinct nitrate coordination modes in one three dimensional polymer has been structurally characterized. H_3dha$_3$tren was found to be a relatively weakly chelating ligand but, in conjunction with nitrate, to be most suitable for building polymeric arrays of lanthanide ions. The yield of this polymer is being optimized, and variations in the stoichiometry studied.

Acknowledgment is made to the Natural Sciences and Engineering Research Council for an operating grant (C.O.) and a postdoctoral fellowship (S.L.). We also thank Professor J. Trotter for the very kind use of his crystallographic facilities.

Supporting Information Available: Detailed tables of final atomic coordinates and equivalent isotropic thermal parameters, crystallographic data, hydrogen atom parameters, anisotropic thermal parameters, bond lengths, bond angles, torsion angles, intermolecular contacts, and least-squares planes (44 pages). Ordering information is given on any current masthead page.

IC950229T

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