Synthesis and Structural Characterization of Ln(III) Complexes (Ln = Eu, Gd, Tb, Er, Tm, Lu) of Tripodal Tris[2-(salicylideneamino)ethyl]amine

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The preparation and characterization of Ln(III) complexes (Ln = Eu, Gd, Tb, Er, Tm, Lu) of heptadentate (N_4O_3) ligand trensal, tris[2-(salicylideneamino)ethyl]amine (H_3L^1), have been studied. The molecular structures of [LnL^1] were determined by X-ray structural analysis ; these are heptadentate complexes in which the metal ions are coordinated by the three oxygen atoms and the four nitrogen atoms.

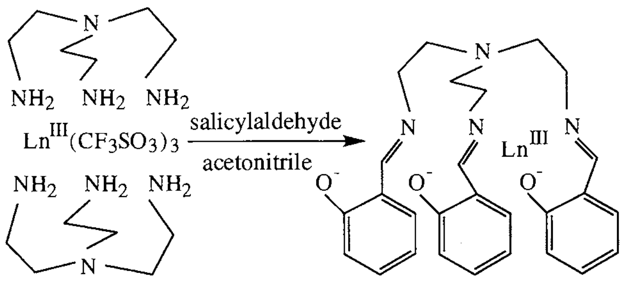
There is now a substantial number of lanthanide complexes known to have a coordination number of seven. Nearly all of them have the basic formulation [Ln(bidentate)$_3$(unidentate)]$^{3+}$.[1] On the contrary, structurally characterized examples of a heptadentate ligand coordinating one metal ion are scarce. The first example of this type of complex in lanthanides is [tris(3-aza-4-methyl-6-oxohept-4-en-1-yl)amine]ytterbium(III) (Yb(trac)), reported by D. J. Berg and et al.[2]

We have reported Pr(III) and Nd(III) complexes of tripodal heptadentate (N_4O_3) ligand trensal, tris[2-(salicylideneamino) ethyl]amine (H_3L^1).[3] The X-ray crystallographic analysis revealed that [LnL^1] (Ln = Pr, Nd) are examples of heptadentate complexes in which all the N_4O_3 donor atoms coordinate to the central metal ions. We have now explored further the chemistry of this family of compounds and can report the crystal structures of [LnL^1] (Ln = Eu, Gd,[4] Tb, Er, Tm, Lu).

Tris(2-aminoethyl)amine (8 mmol) was added to a solution of 4 mmol of $Ln(CF_3SO_3)_3$ (Ln = Eu, Gd, Tb, Er, Tm, Lu)[5] in acetonitrile (100 cm^3) and stirred for 10 min at 70-80 °C. Then salicylaldehyde (12 mmol) was added to this solution and stirred for 2 min at 70-80 °C. The product was precipitated on cooling for 5 h. This product was clarified by filtration and washed with cold acetonitrile and dried. After the mother liquors were cooled for 3 days, single crystals suitable for single-crystal X-ray diffraction were obtained. These products (Ln = Eu, Gd, Tb, Er, Tm, Lu) gave IR bands at 1626-1631 cm^{-1} due to C=N stretching vibration, but no bands corresponding to a primary amine nor to a trifluoromethanesulfonate anion were observed. The metal ion concentration of each crystals was determined by an ICP-atomic emission spectrometer.[6-11] This information together with the elemental analysis[6-11] suggested that the compounds formed were [LnL^1] · $0.5CH_3CN$ (Ln = Eu, Gd, Tb) and [LnL^1] (Ln = Er, Tm, Lu). No intermolecular contacts were found between the complexes and the acetonitrile molecules (Ln = Eu, Gd, Tb).

The structures of **2** were determined by X-ray structural analysis.[12-17] All measurements were made on a Rigaku AFC7S diffractometer with graphite monochromated Mo-K_α radiation (λ = 0.71069 Å).

The molecular structure of [LuL^1] is shown in Figure 1 together with atom-labelling schemes. The individual metal ions and the apical nitrogen atoms (N2) lie on a 3-fold axis in each crystal ; the molecules possess a C_3 molecular symmetry. The symmetrically related atoms are represented by the primed and double-primed numbers of the corresponding atoms. The structures of the other complexes of [LnL^1] (Ln = Eu, Gd, Tb, Er, Tm) were found to be similar to that of [LuL^1], i.e., the metal ions are coordinated by the three oxygen atoms (O1, O1', and O1") and four nitrogen atoms (N1, N1', N1", and N2).



1 $Ln(tren)_2(CF_3SO_3)_3$
Ln = Eu,Gd,Tb,Er,Tm,Lu

2 [LnL^1]
Ln = Eu,Gd,Tb,Er,Tm,Lu

There is a general recognition that the coordination number of lanthanide complexes decreases with increase in the atomic number. This coordination number change may be a major cause of the irregularities observed for the properties of the lanthanide complexes.[18] There are numerous examples in which the solvent molecules contained in the formula are coordinated and thereby change the coordination number.[19] In addition it is quite often found that some of the anions are coordinated. Both of these factors severely complicate the determination of the coordination number of lanthanide complexes.

In this respect, [LnL^1] is a novel example because the coordination number of the lanthanide complexes dose not change in the wide range of the series of [LnL^1] (Ln = Pr, Nd, Eu, Gd, Tb, Er, Tm, Lu). It has become possible to compare the correlation between the ionic radii and the interatomic distances in the lanthanide members under the same coordination number.

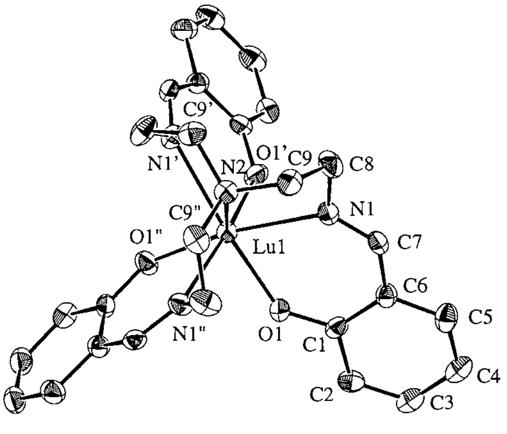


Figure 1. Molecular structure of [LuL^1]. The hydrogen atoms are omitted for clarity.

Table 1. The bond distances of [LnL^1] (Ln = Pr, Nd, Eu, Gd, Tb, Er, Tm, Lu)

	[PrL^1] ^{3}	[NdL^1] ^{3}	[EuL^1]	[GdL^1]	[TbL^1]	[ErL^1]	[TmL^1]	[LuL^1]
Ln-O1/Å	2.282(3)	2.275(2)	2.238(4)	2.233(4)	2.219(3)	2.188(5)	2.167(5)	2.162(5)
Ln-N1/Å	2.620(3)	2.601(3)	2.538(5)	2.534(5)	2.502(4)	2.455(6)	2.449(6)	2.426(6)
Ln-N2/Å	2.805(5)	2.799(4)	2.776(8)	2.758(9)	2.740(7)	2.716(8)	2.713(8)	2.722(8)

Additionally, metal to ligand bond distances of each complex are classified into three groups (Ln-O1, Ln-N1, and Ln-N2) because the complexes have a C_3 molecular symmetry.

Table 1 shows the bond distances of Ln-O1, Ln-N1, and Ln-N2 of [LnL^1]. The bond distances decrease with decrease in the ionic radii of the central metal ions. The metal-ligand bond distances of Ln-N2 of the present complexes lie in between those of a Yb(trac)^2 (2.43(1) Å) and a Ni^{II} N$_7$ complex of tris[1-(2-pyridyl)-2-azabuten-4-yl]amine^{20} (3.25 Å), in which the coordination of the apical nitrogen atoms to the metal ions was confirmed. The Ln-N1 bond distances lie in between 2.620(3) Å ([PrL^1]) and 2.426(6) Å ([LuL^1]). The Ln-O1 bond distances lie in between 2.282(3) Å ([PrL^1]) and 2.162(5) Å ([LuL^1]). These values are consistent with those found in a heptadentate complex Yb(trac)^2 (Yb-N = 2.41(1)-2.46(1) Å, Yb-O = 2.161(9)-2.199(9) Å) after correcting for the ionic radii differences of these metal ions.

In conclusion, lanthanide complexes ([LnL^1]) of tripodal heptadentate ligand, trensal have been prepared from the reaction of tris(2-aminoethyl)amine and salicylaldehyde in the presence of a metal salt. The X-ray crystallographic analysis revealed that [LnL^1] is a example of heptadentate trensal complexes in which all of the N_4O_3 donor atoms coordinate to the central metal ions. The bond distances of Ln-O1, Ln-N1, and Ln-N2 were found to be decreased with increase in the atomic number.

References and Notes

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6 **2** (Ln = Eu) : Anal. Found : C, 53.46 ; H, 4.40 ; N, 9.97 ; Eu, 23.50%. Calcd for $C_{27}H_{27}N_4O_3Eu \cdot 0.5CH_3CN$: C, 53.55 ; H,4.57 ; N, 10.04 ; Eu, 24.20%.

7 **2** (Ln = Gd) : Anal. Found : C, 52.72 ; H, 4.47 ; N, 9.83 ; Gd, 24.48%. Calcd for $C_{27}H_{27}N_4O_3Gd \cdot 0.5CH_3CN$: C, 53.10 ; H,4.54 ; N, 9.95 ; Gd, 24.83%.

8 **2** (Ln = Tb) : Anal. Found : C, 52.90 ; H, 4.40 ; N, 9.60 ; Tb, 24.51%. Calcd for $C_{27}H_{27}N_4O_3Tb \cdot 0.5CH_3CN$: C, 52.96 ; H,4.52 ; N, 9.93 ; Tb, 25.03%.

9 **2** (Ln = Er) : Anal. Found : C, 52.10 ; H, 4.37 ; N, 9.24 ; Er, 26.91%. Calcd for $C_{27}H_{27}N_4O_3Er$: C, 52.07 ; H,4.37 ; N, 9.00 ; Er, 26.86%.

10 **2** (Ln = Tm) : Anal. Found : C, 51.93 ; H, 4.36 ; N, 8.97 ; Tm, 26.67%. Calcd for $C_{27}H_{27}N_4O_3Tm$: C, 51.85 ; H,4.40 ; N, 9.18 ; Tm, 27.05%.

11 **2** (Ln = Lu) : Anal. Found : C, 51.27 ; H, 4.28 ; N, 8.98 ; Lu, 27.22%. Calcd for $C_{27}H_{27}N_4O_3Lu$: C, 51.43 ; H,4.32 ; N, 8.90 ; Lu, 27.75%.

12 Crystal data for **2** (Ln = Eu) : $C_{27}H_{27}N_4O_3Eu \cdot 0.5CH_3CN$, M = 628.68, trigonal, space group $P\bar{3}$, a=13.832(2) Å, c=7.922(2) Å, Z=2, V=1312.7(4) Å^3, D_c=1.589 g/cm^3.
The structure was solved by heavy-atom Patterson methods and expanded using Fourier techniques and was refined by full-matrix least-squares procedures to R = 0.034 and R_w=0.037 for 1323 observed reflections with $I \geqq 3\sigma(I)$.

13 Crystal data for **2** (Ln = Gd) : $C_{27}H_{27}N_4O_3Gd \cdot 0.5CH_3CN$, M = 633.31, trigonal, space group $P\bar{3}$, a=13.767(2) Å, c=7.973(3) Å, Z=2, V=1308.6(4) Å^3, D_c=1.607 g/cm^3.
The structure was solved by direct methods and expanded using Fourier techniques and was refined by full-matrix least-squares procedures to$R$ =0.034andR_w=0.046 for 1369 observed reflections with $I \geqq 3\sigma(I)$.

14 Crystal data for **2** (Ln = Tb) : $C_{27}H_{27}N_4O_3Tb \cdot 0.5CH_3CN$, M = 634.99, trigonal, space group $P\bar{3}$, a=13.872(2) Å, c=7.858(1) Å, Z=2, V=1309.6(2) Å^3, D_c=1.610 g/cm^3.
The structure was solved by direct methods and expanded using Fourier techniques and was refined by full-matrix least-squares procedures to$R$ = 0.031 andR_w=0.032 for 1373 observed reflections with $I \geqq 3\sigma(I)$.

15 Crystal data for **2** (Ln = Er) : $C_{27}H_{27}N_4O_3Er$, M = 622.80, trigonal, space group $P\bar{3}c1$, a=12.977(1) Å, c=16.573(3) Å, Z=4, V=2417.2(6) Å^3, D_c=1.711 g/cm^3.
The structure was solved by direct methods and expanded using Fourier techniques and was refined by full-matrix least-squares procedures to$R$ =0.029 and R_w=0.032 for 1019 observed reflections with $I \geqq 3\sigma(I)$.

16 Crystal data for **2** (Ln = Tm) : $C_{27}H_{27}N_4O_3Tm$, M = 624.47, trigonal, space group $P\bar{3}c1$, a=12.963(2) Å, c=16.556(2) Å, Z=4, V=2409.3(3) Å^3, D_c=1.721 g/cm^3.
The structure was solved by direct methods and expanded using Fourier techniques and was refined by full-matrix least-squares procedures to R = 0.028 and R_w=0.030 for 975 observed reflections with $I \geqq 3\sigma(I)$.

17 Crystal data for **2** (Ln = Lu) : $C_{27}H_{27}N_4O_3Lu$, M = 651.30, trigonal, space group $P\bar{3}c1$, a=12.906(1) Å, c=16.684(3) Å, Z=4, V=2406.6(4) Å^3, D_c=1.797 g/cm^3.
The structure was solved by direct methods and expanded using Fourier techniques and was refined by full-matrix least-squares procedures to R = 0.029 and R_w=0.031 for 968 observed reflections with $I \geqq 3\sigma(I)$.

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