Synthesis and Structural Characterization of Praseodymium(III) and Neodymium(III) Complexes of Tripodal Tris[2-(salicylideneamino)ethyl]amine

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The preparation and characterization of praseodymium(III) and neodymium(III) complexes of heptadentate (N_4O_3) ligand trensal, tris[2-(salicylideneamino)ethyl]amine (H_3L^1), have been studied. These complexes (PrL^1 and NdL^1) were prepared by the reaction of the praseodymium(III) or neodymium(III) complex of 1,9-bis(2-aminoethyl)-1,4,6,9,12,14-hexaazacyclohexadecane with salicylaldehyde in acetonitrile. Alternatively, the reaction of tris(2-aminoethyl)amine and salicylaldehyde in the presence of praseodymium(III) or neodymium(III) salt in acetonitrile also gave praseodymium(III) and neodymium(III) complexes of trensal. The molecular structures of PrL^1 and NdL^1 were determined by X-ray structural analysis; these are rare examples of lanthanide heptadentate complexes in which the metal ions are coordinated by the four nitrogen atoms and the three oxygen atoms. The crystals of $Pr(C_{27}H_{27}N_4O_3)\cdot 0.5CH_3CN$ and $Nd(C_{27}H_{27}N_4O_3)\cdot 0.5CH_3CN$ are both trigonal, space group $P\bar{3}$, a=13.713(2), c=8.093(3) Å, U=1318.0(7) Å^3, Z=2 for $[PrL^1]\cdot 0.5CH_3CN$, and a=13.724(3), c=8.067(3) Å, U=1315.8(7) Å^3, Z=2 for $[NdL^1]\cdot 0.5CH_3CN$. The structures were solved by heavy-atom Patterson methods and expanded using Fourier techniques; they were then refined by full-matrix least-squares procedures to R=0.033 and R_w=0.043 for 1547 observed reflections with $I \geqq 3\,\sigma(I)$, R=0.028 and R_w=0.039 for 1923 observed reflections with $I \geqq 3\,\sigma(I)$ for $[PrL^1]\cdot 0.5CH_3CN$ and $[NdL^1]\cdot 0.5CH_3CN$, respectively. The individual metal ions and the apical nitrogen atoms lie on a 3-fold axis in each crystal; the molecules possess a C_3 molecular symmetry.

There is a general recognition that the common coordination number for the lanthanides (Ln) is greater than that for the main-transition metals. The existence of complexes of the lanthanides with larger coordination numbers is a natural consequence of their large size, together with the predominantly ionic bonding which they exhibit.[1] In the absence of adverse steric factors, the coordination number of the lanthanides is usually eight or larger. However, there is now a substantial number of complexes known to have a coordination number of seven. Nearly all of them have the basic formulation $[Ln(didentate)_3(monodentate)]^{3+}$ or $[Ln(monodentate)_7]^{3+}$.[2] 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.[3]

Heptadentate ligand trensal, tris[2-(salicylideneamino)ethyl]amine (H_3L^1) (Chart 1), and its substituted ligand, tris[2-(5-chloro-2-hydroxybenzylidene)ethyl]amine, are the condensation products of tris(2-aminoethyl)amine (tren) (Chart 1) with 3 equivalents of salicylaldehyde[4,5] or its 5-substituted derivative.[6] Complexes of V(III),[7] Mn(III),[8,9] and Fe(III)[10] with these ligands have been prepared and characterized. Although these ligands are potentially heptadentate, most of the metal complexes so far studied involve an N_3O_3 donor set of the ligands, with the tertiary nitrogen atom (apical nitrogen atom) remaining uncoordinated. This is because the cavity offered by the N_4O_3 ligand is too large for all seven donor atoms to coordinate to these metal ions.[11] We are interested in the coordination geometry of lanthanide complexes of trensal.

In this paper, we report on the synthesis and character-

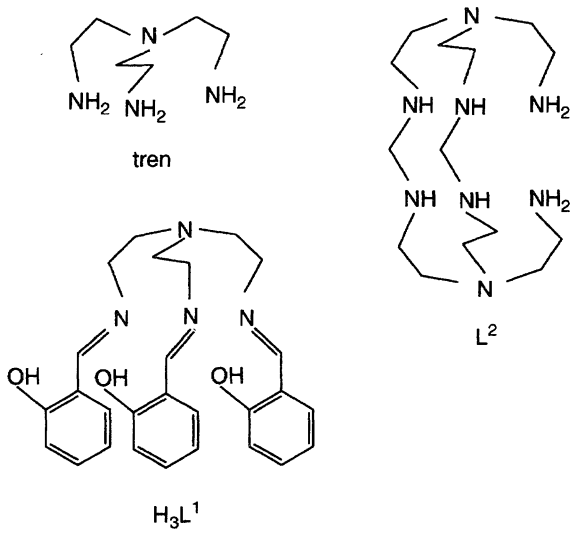

Chart 1.

ization of trensal complexes, PrL^1 and NdL^1, which were derived from the reaction of a Pr(III) or Nd(III) complex of 1, 9-bis(2-aminoethyl)-1,4,6,9,12,14-hexaazacyclohexadecane (L^2) (Chart 1) with salicylaldehyde or the reaction of tren and salicylaldehyde in the presence of Pr(III) or Nd(III) salt. The X-ray crystal structures of PrL^1 and NdL^1 are also reported.

Results and Discussion

Several main-transition metal complexes of trensal, and those of the substituted trensal, have been prepared by the direct reaction of a metal salt with the ligand. However, to our knowledge there has been no report concerning lanthanide complexes with trensal. Attempts to isolate lanthanide complexes of trensal by a direct reaction with lanthanide salt were unsuccessful. During an investigation into the reaction of $[LnL^2](CF_3SO_3)_3$ (Ln=Pr, Nd, and Gd) it was noted that reactions with salicylaldehyde in acetonitrile gave $[LnL^1]\cdot 0.5CH_3CN$ (Ln=Pr, Nd, and Gd[12]). Alternatively, the reaction of tren and salicylaldehyde in the presence of $Ln(CF_3SO_3)_3$ (Ln=Pr, Nd) in acetonitrile also gave $[LnL^1]\cdot 0.5CH_3CN$ (Ln=Pr, Nd). Both Pr(III) and Nd(III) complexes showed similar infrared spectra in which characteristic bands ascribable to $\nu_{C=N}$(1626 cm^{-1}) were observed. The infrared bands corresponding to a primary amine or a trifluoromethanesulfonate anion were not found. Since the product $[LnL^1]\cdot 0.5CH_3CN$ (Ln=Pr, Nd) does not contain a counter anion, the trensal forms an inner-complex in which it functions as a trivalent anionic polydentate ligand.

The starting material, $[LnL^2](CF_3SO_3)_3$ (Ln=Pr, Nd), is a macrocyclic compound. However, the final product, $[LnL^1]\cdot 0.5CH_3CN$ (Ln=Pr, Nd), doesn't contain a macrocyclic ligand. The fact that $[LnL^1]\cdot 0.5CH_3CN$ (Ln=Pr, Nd) was synthesized from $[LnL^2](CF_3SO_3)_3$ (Ln=Pr, Nd) reveals that an intermolecular rearrangement took place between the complex of macrocyclic amine L^2 and salicylaldehyde, forming the trensal complex.

Crystallographic data are presented in Table 1, and the atomic coordinates are given in Tables 2 and 3. The unit cells of PrL^1 and NdL^1 contain two metal complexes and one acetonitrile molecule. Hydrogen atoms, excluding those of acetonitrile, were located. The molecular structures of PrL^1 and NdL^1 are shown in Figs. 1 and 2, respectively, together with atom-labeling schemes. The individual metal ions and the apical nitrogen atoms (N(2)), 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 (Figs. 1 and 2). The metal ions are coordinated

Table 1. Crystallographic Data for $[LnL^1]\cdot 0.5CH_3CN$ (Ln=Pr, Nd)

Compound	$[PrL^1]\cdot 0.5CH_3CN$	$[NdL^1]\cdot 0.5CH_3CN$
Chemical formula	$C_{28}H_{28.5}N_{4.5}O_3Pr$	$C_{28}H_{28.5}N_{4.5}O_3Nd$
Formula weight (M)	616.97	620.30
Crystal color	Green	Pink
Crystal size/mm	0.15 × 0.15 × 0.20	0.20 × 0.20 × 0.35
Crystal system	Trigonal	Trigonal
Space group	$P\bar{3}$	$P\bar{3}$
a/Å	13.713(2)	13.724(3)
c/Å	8.093(3)	8.067(3)
U/Å^3	1318.0(7)	1315.8(7)
Z	2	2
D_{calc}/g cm^{-3}	1.554	1.566
μ(Mo K_α)/cm^{-1}	18.80	20.09
F(000)	622.00	624.00
Absorption correction	Not applied	Applied (trans. factors: 0.9147—1.0000)
2θ range/deg	4—55	4—55
Total number of reflections	2303	2302
Number of unique reflection	2032	2028
Number of observed reflection $[I > 3\,\sigma(I)]$	1547	1923
Number of variables	115	116
R[a)]	0.033	0.028
R_w[b)]	0.043	0.039
Goodness of fit	0.93	0.96
Maximum difference peaks/eÅ^{-3}	0.48	0.63
Minimum difference peaks/eÅ^{-3}	−0.37	−0.69
Extinction correction	None	Secondary
Extinction coefficient		2.98×10^{-7}

a) $R=\Sigma(|F_o|-|F_c|)/\Sigma|F_o|$. b) $R_w=[\Sigma w(|F_o|-F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w=[\sigma^2(F_o)+0.0004|F_o|^2]^{-1}$.

Table 2. Atomic Coordinates for $[PrL^1]\cdot 0.5CH_3CN$

Atom	x	y	z	B_{eq}
Pr(1)	0.6667	0.3333	0.49824(4)	2.834(3)
O(1)	0.7498(2)	0.2549(2)	0.3456(3)	3.64(5)
N(1)	0.8577(2)	0.3775(2)	0.6351(4)	3.50(6)
N(2)	0.6667	0.3333	0.8447(6)	3.57(5)
N(3)	1.0000	0.0000	0.124(2)	7.2(3)
C(1)	0.8444(3)	0.2563(3)	0.3169(4)	3.15(6)
C(2)	0.8548(3)	0.2002(3)	0.1791(5)	3.98(7)
C(3)	0.9532(4)	0.1995(4)	0.1479(6)	5.34(9)
C(4)	1.0446(4)	0.2545(5)	0.2515(6)	5.9(1)
C(5)	1.0356(3)	0.3070(4)	0.3872(6)	5.00(9)
C(6)	0.9377(3)	0.3102(3)	0.4260(5)	3.53(7)
C(7)	0.9363(3)	0.3641(3)	0.5779(5)	3.69(7)
C(8)	0.8737(3)	0.4256(4)	0.8024(5)	4.52(8)
C(9)	0.7743(3)	0.3460(4)	0.9081(5)	4.57(8)
C(10)	1.0000	0.0000	0.267(3)	6.3(3)
C(11)	1.0000	0.0000	0.447(3)	9.2(4)

Table 3. Atomic Coordinates for $[NdL^1]\cdot 0.5CH_3CN$

Atom	x	y	z	B_{eq}
Nd(1)	0.6667	0.3333	0.50105(3)	2.922(4)
O(1)	0.7475(2)	0.2538(2)	0.3469(2)	3.64(4)
N(1)	0.8566(2)	0.3777(2)	0.6365(3)	3.63(5)
N(2)	0.6667	0.3333	0.8481(5)	3.84(5)
N(3)	1.0000	0.0000	0.124(2)	6.5(2)
C(1)	0.8408(2)	0.2547(2)	0.3190(3)	3.14(5)
C(2)	0.8516(3)	0.1976(3)	0.1806(4)	4.04(7)
C(3)	0.9494(3)	0.1972(4)	0.1483(5)	5.35(9)
C(4)	1.0420(3)	0.2524(4)	0.2508(6)	6.1(1)
C(5)	1.0341(3)	0.3069(4)	0.3877(5)	5.14(9)
C(6)	0.9357(3)	0.3103(3)	0.4250(4)	3.61(6)
C(7)	0.9354(2)	0.3641(3)	0.5794(4)	3.79(6)
C(8)	0.8727(3)	0.4266(3)	0.8031(4)	4.63(7)
C(9)	0.7745(3)	0.3477(4)	0.9099(4)	4.87(8)
C(10)	1.0000	0.0000	0.264(3)	6.9(3)
C(11)	1.0000	0.0000	0.454(2)	8.2(3)

by four nitrogen atoms (N(1), N(1′), N(1″), and N(2)) and three oxygen atoms (O(1), O(1′), and O(1″)). As can be seen in Figs. 1 and 2, since the N(1)–C(8)–C(9)–N(2) portions adopt a *gauche* conformation, the molecules are chiral. However, the crystals are racemate, because another isomer of the enantiometric pair exists in the crystal belonging to the centro-symmetrical space group, $P\bar{3}$.

The crystal structures of PrL^1 and NdL^1 are isomorphous, the former of which is shown in Fig. 3. The acetonitrile molecule (N(3), C(10), C(11)), lying on a 3-fold axis at 1, 0, 2, is disordered around an inversion center on the axis. No intermolecular contacts shorter than the sums of the van der Waals radii were found between the complexes and the acetonitrile molecules. Selected bond lengths and angles are presented in Tables 4 and 5.

Trensal is one of the potentially heptadentate ligands. A coordination number of seven, especially heptadentate ligands coordinating one metal ion, is rare in coordination chemistry, because it must be forced on all metal ions; none adopt it with ease. Most main transition metals can be forced

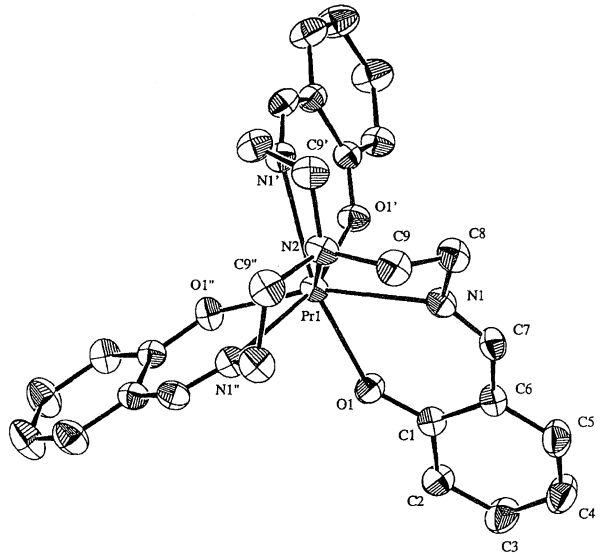

Fig. 1. Molecular structure of PrL^1 in $[PrL^1]\cdot 0.5CH_3CN$. The hydrogen atoms are omitted for clarity.

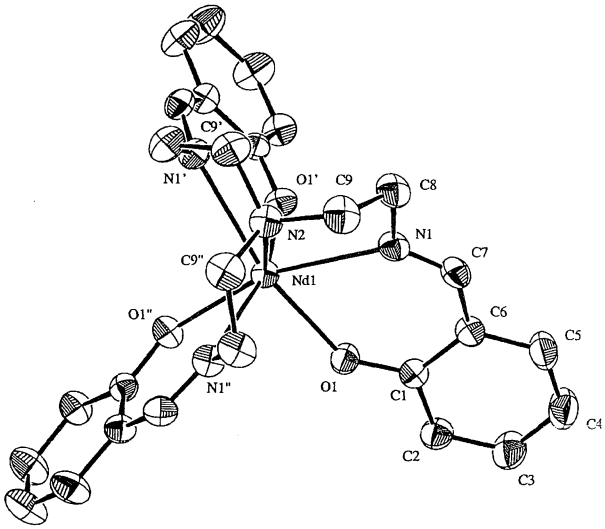

Fig. 2. Molecular structure of NdL^1 in $[NdL^1]\cdot 0.5CH_3CN$. The hydrogen atoms are omitted for clarity.

to increase their coordination number to seven, but with a limited number of ligands. A $Co^{II}N_2O_5$ cryptate[13] and a $Cu^{II}N_7$ Schiff-base[14] complex are structurally characterized examples of this type. The geometry of these complexes is pentagonal bipyramidal. Two In^{III} complexes of macrocycles[15] are also seven coordinate, and their geometry is a trigonal prism capped on a square face. A $Ni^{II}N_7$ complex of tris-[1-(2-pyridyl)-2-azabuten-4-yl]amine[16] is an example of a monocapped octahedron.

In contrast with complexes with higher coordination numbers, structurally characterized examples of a heptadentate ligand coordinating one metal ion are rare in the lanthanides. Yb(trac)[3] is the first example of a structurally characterized lanthanide complex of a heptadentate ligand. It is reported that the geometry around the Yb atoms is that of a monocapped octahedron, since the trigonal primatic coordination of the Schiff-base arms would leave the apical N atom far re-

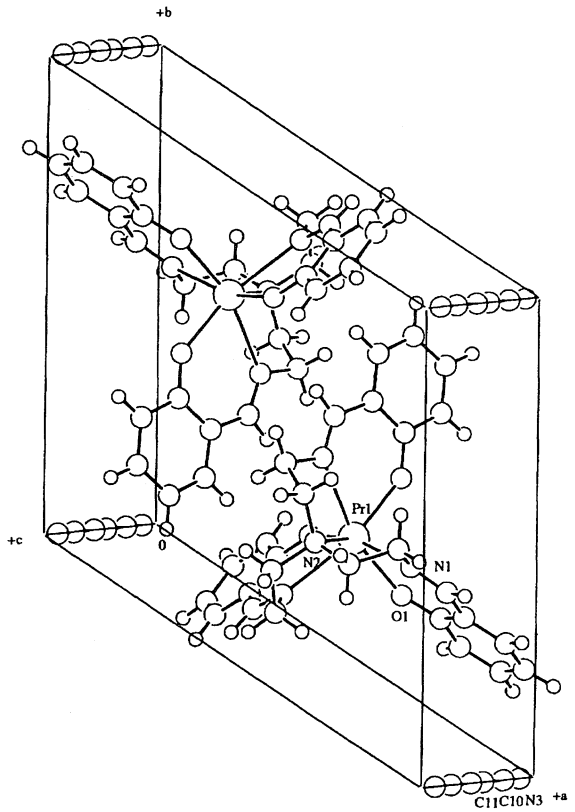

Fig. 3. Molecular packing in the unit cell of the $[PrL^1]\cdot 0.5CH_3CN$ crystal. The acetonitrile molecule (N(3), C(10), C(11)), lying on a 3-fold axis at 1,0,2 is disordered around an inversion center on the axis.

Table 4. Selected Bond Lengths (Å) and Angles (°) with Estimated Standard Deviations (esd's) in Parentheses for $[PrL^1]\cdot 0.5CH_3CN$

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Pr(1)–O(1)	2.282(3)	Pr(1)–N(1)	2.620(3)
Pr(1)–N(2)	2.805(5)	O(1)–C(1)	1.310(4)
N(1)–C(7)	1.268(5)	N(1)–C(8)	1.475(5)
N(2)–C(9)	1.488(4)	C(1)–C(2)	1.403(5)
C(1)–C(6)	1.419(5)	C(2)–C(3)	1.375(6)
C(3)–C(4)	1.378(6)	C(4)–C(5)	1.353(7)
C(5)–C(6)	1.399(6)	C(6)–C(7)	1.441(5)
C(8)–C(9)	1.515(6)	N(3)–C(10)	1.16(3)
C(10)–C(11)	1.44(3)		

O(1)–Pr(1)–O(1′)	93.48(8)	O(1)–Pr(1)–N(1)	70.15(9)
O(1)–Pr(1)–N(1′)	162.31(9)	O(1)–Pr(1)–N(1″)	94.17(9)
O(1)–Pr(1)–N(2)	122.76(6)	N(1)–Pr(1)–N(1′)	103.43(7)
N(1)–Pr(1)–N(2)	65.01(6)	Pr(1)–O(1)–C(1)	144.5(2)
Pr(1)–N(1)–C(7)	129.6(2)	Pr(1)–N(1)–C(8)	113.5(2)
C(7)–N(1)–C(8)	116.9(3)	Pr(1)–N(2)–C(9)	110.2(2)
C(9)–N(2)–C(9′)	108.8(2)	O(1)–C(1)–C(2)	120.3(3)
O(1)–C(1)–C(6)	121.8(3)	C(2)–C(1)–C(6)	117.8(3)
C(1)–C(2)–C(3)	121.3(3)	C(2)–C(3)–C(4)	120.7(4)
C(3)–C(4)–C(5)	119.0(4)	C(4)–C(5)–C(6)	122.9(4)
C(1)–C(6)–C(5)	118.2(4)	C(1)–C(6)–C(7)	123.9(3)
C(5)–C(6)–C(7)	117.8(3)	N(1)–C(7)–C(6)	128.0(3)
N(1)–C(8)–C(9)	108.5(3)	N(2)–C(9)–C(8)	111.8(3)
N(3)–C(10)–C(11)	180.0		

Table 5. Selected Bond Lengths (Å) and Angles (°) with Estimated Standard Deviations (eds's) in Parentheses for $[NdL^1]\cdot 0.5CH_3CN$

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Nd(1)–O(1)	2.275(2)	Nd(1)–N(1)	2.601(3)
Nd(1)–N(2)	2.799(4)	O(1)–C(1)	1.296(3)
N(1)–C(7)	1.273(4)	N(1)–C(8)	1.469(4)
N(2)–C(9)	1.479(4)	C(1)–C(2)	1.413(4)
C(1)–C(6)	1.419(4)	C(2)–C(3)	1.369(5)
C(3)–C(4)	1.383(5)	C(4)–C(5)	1.367(5)
C(5)–C(6)	1.406(5)	C(6)–C(7)	1.449(4)
C(8)–C(9)	1.507(5)	N(3)–C(10)	1.15(2)
C(10)–C(11)	1.50(3)		

O(1)–Nd(1)–O(1′)	93.00(7)	O(1)–Nd(1)–N(1)	70.77(7)
O(1)–Nd(1)–N(1′)	162.76(8)	O(1)–Nd(1)–N(1″)	93.60(8)
O(1)–Nd(1)–N(2)	123.12(5)	N(1)–Nd(1)–N(1′)	103.61(6)
N(1)–Nd(1)–N(2)	65.16(5)	Nd(1)–O(1)–C(1)	143.8(2)
Nd(1)–N(1)–C(7)	129.7(2)	Nd(1)–N(1)–C(8)	113.4(2)
C(7)–N(1)–C(8)	116.9(3)	Nd(1)–N(2)–C(9)	109.7(2)
C(9)–N(2)–C(9′)	109.2(2)	O(1)–C(1)–C(2)	120.6(3)
O(1)–C(1)–C(6)	122.5(3)	C(2)–C(1)–C(6)	116.9(3)
C(1)–C(2)–C(3)	121.8(3)	C(2)–C(3)–C(4)	121.2(3)
C(3)–C(4)–C(5)	118.7(3)	C(4)–C(5)–C(6)	122.1(3)
C(1)–C(6)–C(5)	119.4(3)	C(1)–C(6)–C(7)	123.8(3)
C(5)–C(6)–C(7)	116.7(3)	N(1)–C(7)–C(6)	127.3(3)
N(1)–C(8)–C(9)	108.5(3)	N(2)–C(9)–C(8)	112.2(3)
N(3)–C(10)–C(11)	180.0		

moved from Yb. In the present complexes the coordination geometry around the Pr or Nd atom is a monocapped distorted octahedron (Figs. 1 and 2) in a manner similar to that of the Yb(trac).[3] The apical nitrogen atom caps the triangular face formed by the other three coordinating N atoms.

The Ln–N(2) distances are 2.805(5) Å for PrL^1 and 2.799(4) Å for NdL^1, and the Ln–N(1) distances are 2.620(3) Å for PrL^1 and 2.601(3) Å for NdL^1. Although the apical nitrogens (N(2)) are at greater distances from the metal ions, these nitrogen atoms are coordinated to metal ions, as indicated by the separation of the apical nitrogen atoms (N(2)) from the three nearest nitrogen atoms (N(1)) of 2.92 Å for PrL^1 and 2.91 Å for NdL^1. These values are within twice the van der Waals radius of nitrogen, and are shorter than the distance of N(2)–N(1) [average 3.16 Å][5] in the crystal of free trensal. The difference in the location of N(2) atoms in between the crystals of LnL^1 (Ln=Pr, Nd) and the crystal of free trensal suggests that the apical nitrogen atoms of LnL^1 (Ln=Pr, Nd) have their lone pairs of electrons pointed toward the metal ions.[16] The metal–ligand bond lengths (Ln–N(2)) of the present complexes lie in between those of a Yb(trac)[3] (2.43(1) Å) and a $Ni^{II}N_7$ complex of tris[1-(2-pyridyl)-2-azabuten-4-yl]amine[16] (3.25 Å), in which the coordination of the apical nitrogen atoms to the metal ions was confirmed.

The Ln–N(1) and Ln–O(1) bond distances are 2.620(3) and 2.282(3) Å for PrL^1, and 2.601(3) Å and 2.275(2) Å for NdL^1. These values are consistent with those found in a heptadentate complex Yb(trac)[3] (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.

The Pr and Nd atoms are displaced toward the three nitrogen triangular face from the center of the octahedron. 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–Pr–O angles and the O–Pr–O angles are 162.31(9)° and 93.48(8)°, respectively, while the N–Pr–N angles (excluding apical N atom) are 103.43(7)°. In the case of the Nd(III) complex, the trans N–Nd–O angles and the O–Nd–O angles are 162.76(8)° and 93.00(7)°, respectively, while the N–Nd–N angles (excluding apical N atom) are 103.61(6) °.

The bond lengths and the bond angles of the Pr and Nd complexes of trensal are quite similar to each other, except that the Pr–N(1) distance of 2.620(3) Å is significantly longer than the Nd–N(1) distance of 2.601(3) Å. The Pr–N(2) distance of 2.805(5) Å is slightly longer than the Nd–N(2) distance of 2.799(4) Å and the Pr–O(1) distance of 2.282(3) Å is also slightly longer than the Nd–O(1) distance of 2.275(2) Å. These differences can be attributed to a decrease in the ionic size from Pr(III) to Nd(III).

In conclusion, praseodymium(III) and neodymium(III) complexes of tripodal heptadentate ligand, trensal have been prepared from the complexes of L^2 with salicylaldehyde. The reaction of tren and salicylaldehyde in the presence of a metal salt gave also praseodymium(III) and neodymium(III) complexes of tripodal heptadentate ligand, trensal. The X-ray crystallographic analysis revealed that $[LnL^1]\cdot 0.5CH_3CN$ (Ln=Pr, Nd) are novel examples of heptadentate trensal complexes in which all of the N_4O_3 donor atoms coordinate to the central metal ions.

Further studies on the preparation and characterization of a series of lanthanide complexes of trensal and of substituted trensals are in progress.

Experimental

Materials. The lanthanide trifluoromethanesulfonate salts [$Ln(CF_3SO_3)_3$; Ln=Pr, Nd] were prepared by the addition of trifluoromethanesulfonic acid to a suspension of the oxide in water.[17] After excess oxide was added, the resulting solution was refluxed for approximately 1 h. The undissolved oxide was then removed by filtration, and the water was evaporated on a rotary evaporator. The resulting solid was dried at 200 °C for 24 h and used without further purification.

Preparation of $[PrL^2](CF_3SO_3)_3$. This complex was prepared by the reported method[18] and identified by an elemental analysis and the IR spectra.

Preparation of $[NdL^2](CF_3SO_3)_3$. After a solution of $Nd(CF_3SO_3)_3$ (16.56 g, 28 mmol) in acetonitrile (250 cm^3) was heated to 70—80 °C in an oil bath under N_2, 8.19 g (56 mmol) of tren was added. Bis(dimethylamino)methane (8.58 g, 84 mmol) was then added; the resulting solution was stirred at 75—80 °C for approximately 7 h. The resulting slightly cloudy, orange solution was clarified by filtration, and the acetonitrile was evaporated on a rotary evaporator to give a solid. This crude material was washed with cold acetonitrile and dried. Recrystallization from acetonitrile gave a pale-blue crystalline solid. (9.56 g, 37.6%). IR (KBr disc): $\nu(NH_2)$ 3351 and 3303 cm^{-1}. Found: C, 22.44; H, 3.80; N, 12.08%. Calcd for $C_{17}H_{36}N_8O_9S_3F_9Nd$: C, 22.49; H, 4.00; N, 12.34%.

The Reaction of $[PrL^2](CF_3SO_3)_3$ with Salicylaldehyde. Salicylaldehyde (0.73 g, 6 mmol) was added to a suspension of $[PrL^2](CF_3SO_3)_3$ (1.81 g, 2 mmol) in hot acetonitrile (100 cm^3) and stirred for 30 min at 70—80 °C. The resulting slightly cloudy solution was clarified by filtration, and the volume of the yellow solution was reduced to ca. 15 cm^3 under a vacuum and cooled in a refrigerator overnight. The solution was decanted from the resulting green crystalline product; this solid was washed with cold acetonitrile and dried (0.38 g, 30.8%). IR (KBr): ν(C=N) 1626 cm^{-1}. Found: C, 54.66; H, 4.59; N, 10.20%. Calcd for $C_{28}H_{28.5}N_{4.5}O_3Pr$ ($[PrL^1]\cdot 0.5CH_3CN$): C, 54.51; H, 4.66; N, 10.22%.

The Reaction of Tren and Salicylaldehyde in the Presence of $Pr(CF_3SO_3)_3$. After a solution of $Pr(CF_3SO_3)_3$ (2.35 g, 4 mmol) in acetonitrile (100 cm^3) was heated to 70—80 °C, tren (1.17 g, 8 mmol) was added. The resulting solution was then stirred at 70—80 °C for 10 min, and salicylaldehyde (1.47 g, 12 mmol) was added. The resulting green product was washed with cold acetonitrile and dried. This was confirmed as $[PrL^1]\cdot 0.5CH_3CN$ by a spectroscopic comparison with the above-mentioned authentic sample. (1.02 g, 41.3%). After the mother liquors were cooled for 3 d, crystals suitable for single-crystal X-ray diffraction were obtained.

The Reaction of $[NdL^2](CF_3SO_3)_3$ with Salicylaldehyde. Salicylaldehyde (0.73 g, 6 mmol) was added to a suspension of $[NdL^2](CF_3SO_3)_3$ (1.82 g, 2 mmol) in hot acetonitrile (100 cm^3) and stirred for 15 min at 70—80 °C. After the resulting slightly cloudy solution was clarified by filtration, the volume of the clear yellow solution was reduced to ca. 15 cm^3 under a vacuum and cooled in a refrigerator overnight. The solution was decanted from the resulting pink crystalline product; this sold was washed with cold acetonitrile and dried (0.35 g, 28.2%). IR (KBr disc): ν(C=N) 1626 cm^{-1}. Found: C, 54.24; H, 4.50; N, 10.19%. Calcd for $C_{28}H_{28.5}N_{4.5}O_3Nd$ ($[NdL^1]\cdot 0.5CH_3CN$): C, 54.22; H, 4.63; N, 10.16%.

The Reaction of Tren and Salicylaldehyde in the Presence of $Nd(CF_3SO_3)_3$. After a solution of $Nd(CF_3SO_3)_3$ (2.37 g, 4 mmol) in acetonitrile (100 cm^3) was heated to 70—80 °C, tren (1.17 g, 8 mmol) was added. The resulting solution was stirred at 70—80 °C for 10 min, and then salicylaldehyde (1.47 g, 12 mmol) was added. The resulting pink product was washed with cold acetonitrile and dried. This was confirmed as $[NdL^1]\cdot 0.5CH_3CN$ by a spectroscopic comparison with the above-mentioned authentic sample. (1.58 g, 63.7%). The mother liquors were cooled for 3 d, and crystals suitable for single-crystal X-ray diffraction were obtained.

Crystal Structure Determinations. All measurements were made on a Rigaku AFC7S diffractometer with graphite monochromated Mo $K\alpha$ radiation (λ=0.71069 Å). The cell constants were obtained from a least-squares refinement using 25 centered reflections in the range $22.12 < 2\theta < 24.46°$ for PrL^1 and in the range $22.10 < 2\theta < 36.82°$ for NdL^1. Three standard reflections were monitored every 150 and showed good stability. Data were collected at room temperature in the ω–2θ mode to a maximum 2θ value of 55.0° with an ω scan width of 1.31+0.30 tan θ (PrL^1), with an ω scan width of 1.10+0.30 tan θ (NdL^1), and with a ω scan speed of 16.0° min^{-1}. The data were corrected for both Lorentz and polarization effects. The space group of both crystals was suggested to be $P3$ or $P\bar{3}$, the latter of which was confirmed after the last stage of the refinement. The structure was solved by heavy-atom Patterson methods[19] and expanded using Fourier techniques.[20] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Neutral-atom scattering factors were taken from Cromer and Waber.[21] Anomalous dispersion effects were included in F_C.[22] All of the calculations were performed using

the teXsan[23] crystallographic software package of the Molecular Structure Corporation.

Tables of the atomic coordinates, anisotropic displacement parameters, and observed and calculated structure factors are deposited as Document No. 69022 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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