Synthesis and Crystal Structure of a Dinuclear Praseodymium Nitrate Complex¹

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Abstract—Dinuclear supramolecular complex of praseodymium nitrate with an unsymmetrical tipodal ligand benzyl-N,N-bis[(2'-benzylaminoformyl)phenoxyl)ethyl]-amine (L), have been prepared. The X-ray single-crystal diffraction analysis indicates that this complex was crystallized in the monoclinic system, space group $P2_1/c$ with parameters a = 16.736(3), b = 14.042(3), c = 19.782(4) Å, $\beta = 101.823^\circ$, V = 4550.50(16) Å³, Z = 4. The structure was refined to the final $R_1 = 0.0473$. The complex units are linked by the intermolecular hydrogen bonds to form a three-dimensional (3D) netlike supramolecuar structure. **DOI:** 10.1134/S1070328413100102

INTRODUCTION

Tripodal ligands have the advantage of the selective coordinating capacity and hard binding sites, therefore stabilizing their complexes, acquiring novel coordination structure and shielding the encapsulated ion from interaction with the surroundings [1-6]. Most of these ligands are symmetrical with three identical arms while the unsymmetrical tripodal organic ligands are rare [7-15]. In this research, we designed and prepared a conformationally flexible unsymmetrical benzyl- and (2'-benzylaminoformyl)phenoxyl-containing amide type tripodal ligand benzyl-N,N-bis[(2'-benzyl-aminoformyl)phenoxyl)ethyl]-amine (L)



and investigated its reaction with praseodymium nitrate. Ligands containing one or more amide functionality have proved to be useful in self-assembly because they give predictable patterns of hydrogen bonding that can add extra dimensionality and helicity to the supramolecular structures [16]. The preorientation of L should favor the formation of a dinuclear complex on coordination to Pr^{3+} . And the structure analyses of the praseodymium complex shows that it forms interesting dinuclear [2 + 2] rectangular macrocyclic structures.

EXPERIMENTAL

Material and methods. N-Benzylsalicylamide was prepared according to the literature methods [17], β , β '-dichlordiethylamine hydrochloride salt [18] and lanthanide nitrates [19] were prepared according to the literature methods, respectively. Other chemicals were obtained from commercial sources and used without further purification. Carbon, nitrogen and hydrogen were determined using an Elementar Vario EL. The IR spectra were recorded in the 4000– 400 cm⁻¹ region using KBr pellets and a Nicolet Nexus 670 FTIR spectrometer. ¹H NMR spectra were measured on a Varian Mercury 300 spectrometer in *d*-chloroform solutions, with TMS as internal standard.

Synthesis of the ligand. The β , β '-dichlordiethylamine hydrochloride salt (1 mmol) and potassium carbonate (2 mmol) were refluxed in acetone (25 cm³) for 30 min, and then the benzyl bromide (1 mmol) was added to the solution. The reaction mixture was refluxed for 12 h and the hot solution was filtered off. The collected organic phase was evaporated in vacuum. Then the obtained product was added to a mixture

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Table 1. Crystal data and structure refinement for complex I

Parameter	Value
Empirical formula	$C_{84}H_{94}N_{14}O_{28}Pr_2$
Formula weight	2029.55
Wavelength, Å	0.71073
Crystal system; space group	Monoclinic; $P2_1/c$
<i>a</i> , Å	16.7358(3) Å
b, Å	14.0425(3) Å
<i>c</i> , Å	19.7825(4) Å
β, deg	101.8230(10)
Volume, Å ³	4550.50(16)
Ζ	2
$\rho_{calcd},mg\;m^{-3}$	1.481
Absorption coefficient, mm ⁻¹	1.143
<i>F</i> (000)	2076
Crystal size, mm	$0.30 \times 0.23 \times 0.14$
θ Range for data collection, deg	1.91–27.53
Limiting indices <i>h</i> , <i>k</i> , <i>l</i>	$-21 \le h \le 21, -16 \le k \le 18, \\ -20 \le l \le 25$
Reflections collected/unique (R_{int})	27506/10279 (0.0264)
Data/restraints/parameters	10279/973/606
Goodness-of-fit on F^2	1.026
Final <i>R</i> indices $(I > 2\sigma(I))$	$R_1 = 0.0362, wR_2 = 0.0962$
Largest diff. peak and hole, $e \text{ Å}^{-3}$	0.594 and -0.594

of N-benzylsalicylamide (2.0 mmol), potassium carbonate (4 mmol) and DMF (20 cm³) which was warmed to ~90°C. And the reaction mixture was stirred at 90–95°C for 8 h. After cooling down, the mixture was poured into water (100 cm³). The resulted solid was treated with column chromatography on silica gel (petroleum ether : ethyl acetate (3 : 2)) to get the ligand L, the yield was 80%, m.p. 124–125°C.

For $C_{39}H_{39}N_3O_4$			
anal. calcd., %:	C, 76.32;	Н, 6.40;	N, 6.58.
Found, %:	C, 76.39;	Н, 6.18;	N, 6.51.

¹H NMR (CDCl₃; 300 MHz): 2.65–2.69 (t., 4H), 3.47–3.49 (s., 2H), 3.88–3.92 (t., 4H), 4.60–4.62 (d., 4H), 6.63–7.38 (m., 23H), 8.21–8.27 (q., 2H).

IR spectrum (KBr; v, cm⁻¹): 3330 m, 1636 s, 1600 m, 1531 m, 1488 m, 1449 m, 1307 m, 1237 m, 1106 w, 822 w, 753 s, 697 m.

Synthesis of the praseodymium nitrate complex (I). An ethyl acetate solution (5 cm^3) of $Pr(NO_3)_3 \cdot 6H_2O$ (0.1 mmol) was added dropwise to a solution of 0.1 mmol ligand L in the ethyl acetate (5 cm³). The mixture was stirred at room temperature for 8 h. And then the precipitated solid complex was filtered off, washed with ethyl acetate, dried in vacuo over P₄O₁₀ for 48 h and submitted for elemental analysis, the yield was 75%. Single-crystals of complex I were obtained by slow diffusion of diethyl ether to a dilute DMF solution of this complex at room temperature.

X-ray diffraction. Single crystal with dimensions of $(0.30 \times 0.23 \times 0.14)$ mm was chosen. Determinations of unit-cell parameters and data collections were performed with Mo K_{α} radiation ($\lambda = 0.7107$ Å) at 294(2) K on a Bruker SMART diffractometer. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods on F^2 . Primary non-hydrogen atoms were solved by direct method, and secondary non-hydrogen atoms were added geometrically and not refined. All calculations were performed using the programs SHELXS-97 and SHELXL-97 [20].

Crystal data and refinement parameters for complex I are listed in Table 1. Selected bond lengths and angles are given in Table 2. Supplementary material for the complex has been deposited with the Cambridge Crystallographic Data Centre (no. 788729; deposit@ ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Bond	d, Å	Bond	<i>d</i> , Å	Bond	d, Å
Pr(1)–O(1)	2.535(3)	Pr(1)–O(4)	2.554(3)	Pr(1)–O(9)	2.364(2)
Pr(1)–O(2)	2.583(3)	Pr(1)–O(6)	2.573(3)	Pr(1)–O(10)	2.382(2)
Pr(1)–O(3)	2.414(3)	Pr(1)–O(7)	2.563(3)	Pr(1)–O(11)	2.535(3)
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
O(1)Pr(1)O(2)	49.67(10)	O(2)Pr(1)O(9)	80.45(9)	O(4)Pr(1)O(10)	75.36(11)
O(1)Pr(1)O(3)	79.49(10)	O(2)Pr(1)O(10)	76.39(9)	O(4)Pr(1)O(11)	49.98(10)
O(1)Pr(1)O(4)	143.73(10)	O(2)Pr(1)O(12)	152.40(9)	O(6)Pr(1)O(7)	49.49(9)
O(1)Pr(1)O(6)	73.72(10)	O(3)Pr(1)O(4)	72.21(10)	O(6)Pr(1)O(9)	125.83(9)
O(1)Pr(1)O(7)	70.70(10)	O(3)Pr(1)O(6)	74.77(10)	O(6)Pr(1)O(10)	150.73(10)
O(1)Pr(1)O(9)	87.79(10)	O(3)Pr(1)O(7)	121.68(9)	O(6)Pr(1)O(11)	89.65(10)
O(1)Pr(1)O(10)	126.00(10)	O(3)Pr(1)O(9)	151.64(10)	O(7)Pr(1)O(9)	76.40(9)
O(1)Pr(1)O(11)	148.72(10)	O(3)Pr(1)O(10)	87.14(9)	O(7)Pr(1)O(10)	150.47(8)
O(2)Pr(1)O(3)	71.97(10)	O(3)Pr(1)O(11)	122.16(10)	O(7)Pr(1)O(11)	78.32(10)
O(2)Pr(1)O(4)	134.90(11)	O(4)Pr(1)O(6)	77.25(11)	O(9)Pr(1)O(10)	79.97(9)
O(2)Pr(1)O(6)	117.78(10)	O(4)Pr(1)O(7)	105.57(11)	O(9)Pr(1)O(11)	80.70(9)
O(2)Pr(1)O(7)	116.22(10)	O(4)Pr(1)O(9)	127.31(9)	O(10)Pr(1)O(11)	80.62(9)

Table 2. Selected bond distances (Å) and angles (deg) for complex \boldsymbol{I}

Table 3. Geometric parameters of hydrogen bonds in crystal packing of structure I

Contact D–H…A	Distance, Å			Angle DHA deg	Summatry
	D-H	Н…А	D…A	Aligie DHA, deg	Symmetry
N(5)-H(5A)····O(14)	0.86	2.54	3.123(8)	126	x, 1/2 - y, 1/2 + z
C(33)–H(33 <i>B</i>)…O(12)	0.97	2.56	3.193(7)	148	x, -1 + y, z
N(5)-H(5A)····O(13)	0.86	2.00	2.632(2)	130	
N(7)-H(7A)····O(15)	0.86	1.96	2.630(5)	133	
$C(7) - H(7B) \cdots O(10)$	0.93	2.45	2.769(8)	100	
C(9)-H(9A)····O(10)	0.97	2.46	2.800(8)	100	
C(13)–H(13 <i>A</i>)…O(2)	0.93	2.57	3.361(7)	144	
C(13)-H(13A)····O(9)	0.93	2.41	2.746(8)	101	
C(17)–H(17 <i>A</i>)…O(9)	0.97	2.40	2.786(3)	103	
C(23)-H(23 <i>A</i>)····O(4)	0.97	2.59	3.183(6)	120	
$C(23) - H(23B) \cdots O(6)$	0.97	2.55	3.160(7)	121	



Fig. 1. ORTEP drawing of the dinuclear complex. The thermal ellipsoid for the image represent a 30% probability limit. Hydrogen atoms were omitted for clarity.

RESULTS AND DISCUSSION

An X-ray structural analysis established that the praseodymium complex I consists of a $[Pr_2L_2(NO_3)_6(DMF)_2]$ fragment. An ORTEP plot (Fig. 1) shows that the central Pr^{3+} is coordinated with nine donor atoms, six of which belong to the three bidentate nitrate groups and two oxygen atoms from carbonyl groups from two bridging ligands and the remaining one to carbonyl group of DMF molecule. As shown in Fig. 1, two ligands adopt a faceto-face orientation and are joined together by two Pr^{3+} ions to generate a discrete binuclear rectangular macrocycle structure. The unit consists of two independent enantiomeric Pr^{3+} centers bridged by two ligands [21].

As shown in Fig. 2, the dinuclear complexes exhibit intra- and intermolecular hydrogen bonding which assemble a three-dimensional (3D) netlike supramolecular structure. In the complex, atom C(33) of the ligand L acts as hydrogen bond donors to form bifurcated hydrogen bonds C-H-O with the oxygen atoms O(12) of a neighboring molecule, thus generating a two-dimensional (2D) supramolecular layer [22]. In addition, the layers are linked by intermolecular hydrogen bond N(5)- $H(5A)\cdots O(14)$ to form a three-dimensional (3D) netlike supermolecule as shown in Fig. 2. Hydrogen bonding parameters of the complex are given in Table 3.



Fig. 2. 3D supramolecular network generated by intermolecular hydrogen bonds.

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