Pergamon

PII: S0277-5387(96)00582-7

Polyhedron Vol. 16, No. 15, pp. 2697–2700, 1997

0277–5387/97 $17.00+0.00

Crystal structure of a Pr^{III} complex with a novel macrocyclic ligand

Janfang Ma,[a] Chunji Niu,[a]* Shulan Meng,[a] Yonghua Lin,[a] Yan Xing[a] and Shisheng Ni[b]

[a]Laboratory of Rare Earth Chemistry and Physics, Changchun Institute of Applied Chemistry, Academia Sinica, Changchun 130022, P.R. China

[b]Department of Chemistry, Anhui University, Hefei 230039, P.R. China

(Received 8 January 1996; accepted 27 November 1996)

Abstract—The crystal structure of a novel macrocyclic ligand complex of Pr^{III}, $C_{112}H_{178}O_{52}N_8S_4Pr_2$, $[Pr_2L_2(HL)_2(H_2O)_6]\cdot 22H_2O$ is reported. The macrocyclic ligand has pendant acetic acid through which the ligand is coordinated to the Pr^{III} ion. For the dimeric unit, $[Pr_2L_2(HL)_2(H_2O)_6]$, two Pr^{III} ions are connected by two bridging–chelating carboxyl groups and two bridging carboxyl groups of the ligands, and each Pr^{III} ion is also bonded to a unidentate carboxyl group of the ligand and three water molecules. The dimeric units are bridged by four ligands through their carboxyl groups to form an infinite one-dimensional chain. The coordination number of the Pr^{III} ion is nine, with a distorted tricapped trigonal prismatic configuration. © 1997 Elsevier Science Ltd

Keywords: praseodymium; macrocyclic ligand; complex; crystal structure.

Macrocyclic ligands and their complexes with metals show many potential applications, such as contrast agents for nuclear magnetic resonance imaging, relaxation agents and so on. Many papers concerning macrocyclic ligand complexes have been published [1,2]. In recent years, it has been found that aza(oxa) macrocyclic ligand complexes possess some special properties [3], thereby attracting much attention. As a continuation of our research on macrocyclic ligand complexes, we have investigated syntheses, properties and structures of macrocyclic ligand complexes of lanthanides with 1,15-diaza-3,4 : 12,13-dibenzo-5, 11-dioxa-7,9-(2′,5′-) thiophenecyclononadecane-N, N′-diacetic acid. Here we describe the crystal structure of a Pr^{III} complex with the macrocyclic ligand.

EXPERIMENTAL

The macrocyclic ligand, 1,15-diaza-3,4 : 12,13-dibenzo-5,11-dioxa-7,9-(2′,5′-) thiophenecyclononadecane-N, N′-diacetic acid, ($C_{28}H_{32}O_6N_2S$, H_2L), was synthesized by ourselves, and characterized by spectroscopic and analytical data. The labeling scheme for the macrocyclic ligand is shown in Fig. 1.

Preparation of crystals of the Pr^{III} complex

5 cm^3 of 0.2 mol/L $PrCl_3$ aqueous solution was added to 10 cm^3 of H_2L aqueous solution (1 mmol of the ligand), and the pH of the solution was adjusted to 6.5. The resultant solution was stirred for 1 h, then filtered. The single crystal of the complex was grown from the filtrate in a desiccator over P_2O_5. The green single crystals of the Pr complex were collected by filtering, and washing. After drying, the single crystal ($C_{112}H_{178}O_{52}N_8S_4Pr_2$, $[Pr_2L_2(HL)_2(H_2O)_6]\cdot 22H_2O$, Mr = 2879.04) was used for X-ray diffraction analysis.

X-ray diffraction analysis

Diffraction data collection was performed on a Nicolet R3m/E four-circle diffractometer with MoK_α

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*Author to whom correspondence should be addressed.

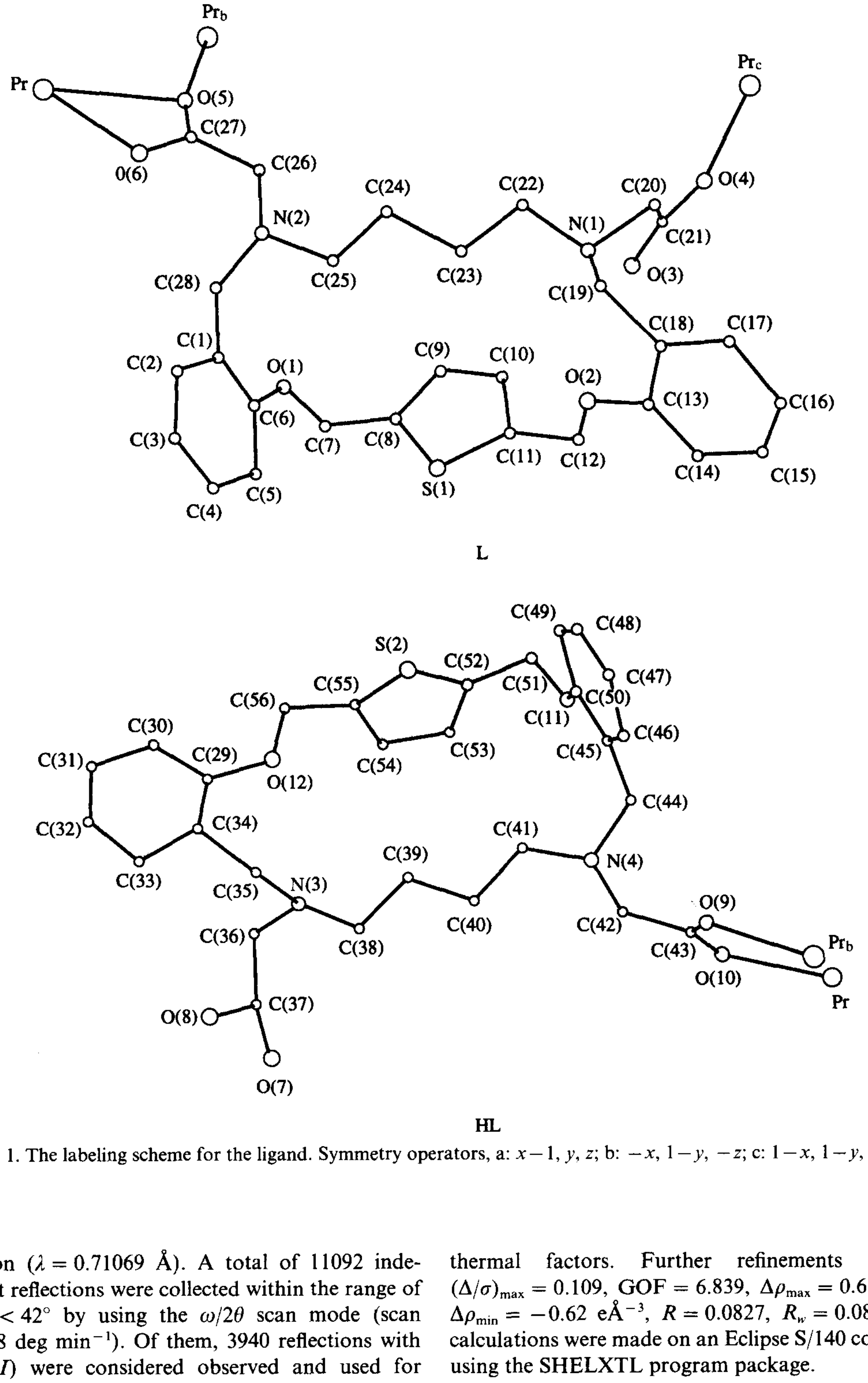

Fig. 1. The labeling scheme for the ligand. Symmetry operators, a: $x-1, y, z$; b: $-x, 1-y, -z$; c: $1-x, 1-y, -z$.

radiation ($\lambda = 0.71069$ Å). A total of 11092 independent reflections were collected within the range of $2 < 2\theta < 42°$ by using the $\omega/2\theta$ scan mode (scan speed, 8 deg min^{-1}). Of them, 3940 reflections with $I > 3\sigma(I)$ were considered observed and used for structure refinement. Correction for LP factors and for absorption effects based on the ψ scan technique was applied. The crystal structure of the complex was solved by heavy-atom methods. All non-hydrogen atoms were refined by block-diagonal least-squares with positional and anisotropic thermal parameters. The coordinates of the hydrogen atoms were fixed by theoretical models and only refined with isotropic thermal factors. Further refinements led to $(\Delta/\sigma)_{\max} = 0.109$, GOF $= 6.839$, $\Delta\rho_{\max} = 0.65$ eÅ^{-3}, $\Delta\rho_{\min} = -0.62$ eÅ^{-3}, $R = 0.0827$, $R_w = 0.0827$. All calculations were made on an Eclipse S/140 computer using the SHELXTL program package.

RESULTS AND DISCUSSION

The crystal of the complex crystallized in the triclinic space group $P\bar{1}$ with the following lattice and other parameters: $a = 14.162(3)$, $b = 18.083(5)$, $c = 21.417(7)$ Å, $\alpha = 112.18(2)$, $\beta = 93.34(2)$, $\gamma =$

97.46(2)°, $V = 5001.4(22)$ Å^3, $Z = 1$, $D_{calc} = 1.22$ g/cm^3, $F(000) = 1900$, $\mu(\text{Mo}K_\alpha) = 10.8$ cm^{-1}.

The ring oxygen, nitrogen and sulfur donors of the ligand do not participate in bonding with the Pr^{III} ion, only the pendant carboxyl groups of the ligand are involved. For the $[Pr_2L_2(HL)_2(H_2O)_6]\cdot 22H_2O$ complex, as shown in Fig. 1, L and HL are coordinated to Pr^{III} in different modes. The two carboxyl groups of the L ligand are deprotonated, so L is coordinated to the Pr^{III} ion through its two carboxylate groups. Moreover, one carboxyl group serves as a tridentate bridging–chelating donor, the other one a unidentate donor. It is interesting to note that one deprotonated carboxyl group of HL ligand serves as a bidentate bridging donor, but the other one which remains protonated is uncoordinated [4].

The selected interatomic distances and bond angles are presented in Table 1. The configuration of the complex is shown in Fig. 2. For a dimeric unit, $[Pr_2L_2(HL)_2(H_2O)_6]$, two bridging-chelating carboxyl groups from two L ligands are coordinated to Pr^{III} and Pr$_b^{III}$. At the same time, Pr^{III} and Pr$_b^{III}$ are bridged by two bidentate carboxyl groups from two HL ligands. Two unidentate carboxyl groups from the other two L ligands are also coordinated to Pr^{III} and Pr$_b^{III}$ ions respectively. In addition, each praseodymium ion is bonded to 3 water molecules. Pr^{III} and Pr$_b^{III}$ ions are connected with adjacent praseodymium ions in neighboring dimeric units respectively by two unidentate carboxyl groups and two bridging–chelating carboxyl groups from the 4 L ligands mentioned above to form an infinite one-dimensional chain. Pr, O(5b), C(27b), O(6b), Pr$_b$, O(5a), C(27a) and O(6a) atoms are essentially coplanar (plane A). Pr, O(10), C(43), O(9), Pr$_b$, O(10a), C(43a) and O(9a) atoms are also essentially coplanar (Plane B). It can be seen from Table 2 that the dihedral angle between plane A and plane B is 87.7°, it indicates that plane B is nearly perpendicular to plane A. The complex containes 28 water molecules. Except for 6 coordinated water molecules, the other 22 water molecules are distributed in the lattice of the crystal of the complex, which makes the crystal structure of the complex more stable [5,6].

The Pr^{III} ion is bonded to 6 oxygen atoms from carboxyl groups of the macrocyclic ligands and 3 oxygen atoms from water molecules giving the coordination number of nine. The coordination polyhedron of the Pr^{III} complex is a distorted tricapped trigonal prism.

The O(5a) atom is coordinated to both Pr^{III} and Pr$_b^{III}$ ions, which makes the bond length of Pr—O(5a) far longer than those of other Pr—O bonds (see Table 1). The average bond length of Pr—O (from carboxyl group) is 2.514 Å (including the Pr—O(5a) bond) and 2.455 Å (except the Pr—O(5a) bond). However, the average bond length of Pr—O (from water molecules) is 2.557 Å. It is obvious that Pr—O bonds (from carboxyl groups) are stronger than Pr—O bonds

Table 1. Selected interatomic distances (Å) and bond angles (°)

Pr—O(4)	2.407(14)	Pr—O(10)	2.420(14)	Pr—O(w1)	2.588(20)
Pr—O(w2)	2.510(20)	Pr—O(w3)	2.572(22)	Pr—C(27a)	3.007(20)
Pr—O(5a)	2.810(15)	Pr—O(5b)	2.423(15)	Pr—O(6a)	2.525(15)
Pr—O(9a)	2.501(16)	C(6)—O(1)	1.363(32)	C(7)—O(1)	1.341(32)
C(12)—O(2)	1.336(32)	C(13)—O(2)	1.332(29)	C(21)—O(3)	1.154(24)
C(21)—O(4)	1.261(23)	C(27)—O(5)	1.187(30)	C(27)—O(6)	1.258(28)
C(29)—O(12)	1.405(33)	C(37)—O(7)	1.275(43)	C(37)—O(8)	1.332(40)
C(43)—O(9)	1.301(34)	C(43)—O(10)	1.201(28)	C(50)—O(11)	1.343(36)
C(51)—O(11)	1.365(34)			C(56)—O(12)	1.398(38)

O(4)—Pr—O(10)	141.1(7)	O(4)—Pr—O(w1)	72.8(6)
O(10)—Pr—O(w1)	135.5(6)	O(4)—Pr—O(w2)	97.3(6)
O(10)—Pr—O(w2)	75.9(6)	O(w1)—Pr—O(w2)	70.5(7)
O(4)—Pr—O(w3)	73.9(6)	O(10)—Pr—O(w3)	67.6(6)
O(w1)—Pr—O(w3)	124.0(7)	O(w2)—Pr—O(w3)	70.8(7)
O(4)—Pr—C(27a)	100.5(5)	O(10)—Pr—C(27a)	73.8(5)
O(w1)—Pr—C(27a)	140.0(7)	O(w2)—Pr—C(27a)	148.4(6)
O(w3)—Pr—C(27a)	89.4(7)	O(4)—Pr—O(5a)	119.6(4)
O(10)—Pr—O(5a)	68.1(5)	O(w1)—Pr—O(5a)	128.6(6)
O(w2)—Pr—O(5a)	141.3(5)	O(w3)—Pr—O(5a)	106.8(6)
O(4)—Pr—O(5b)	145.4(6)	O(10)—Pr—O(5b)	73.0(6)
O(w1)—Pr—O(5b)	75.2(6)	O(w2)—Pr—O(5b)	84.2(7)
O(w3)—Pr—O(5b)	137.2(5)	O(4)—Pr—O(6a)	80.3(5)
O(10)—Pr—O(6a)	81.6(5)	O(w1)—Pr—O(6a)	142.2(5)
O(w2)—Pr—O(6a)	140.5(7)	O(w3)—Pr—O(6a)	70.8(6)
O(4)—Pr—O(9a)	79.8(6)	O(10)—Pr—O(9a)	130.5(6)
O(w1)—Pr—O(9a)	68.7(6)	O(w2)—Pr—O(9a)	138.0(7)
O(w3)—Pr—O(9a)	143.8(5)	C(2)—C(1)—C(6)	118.6(20)

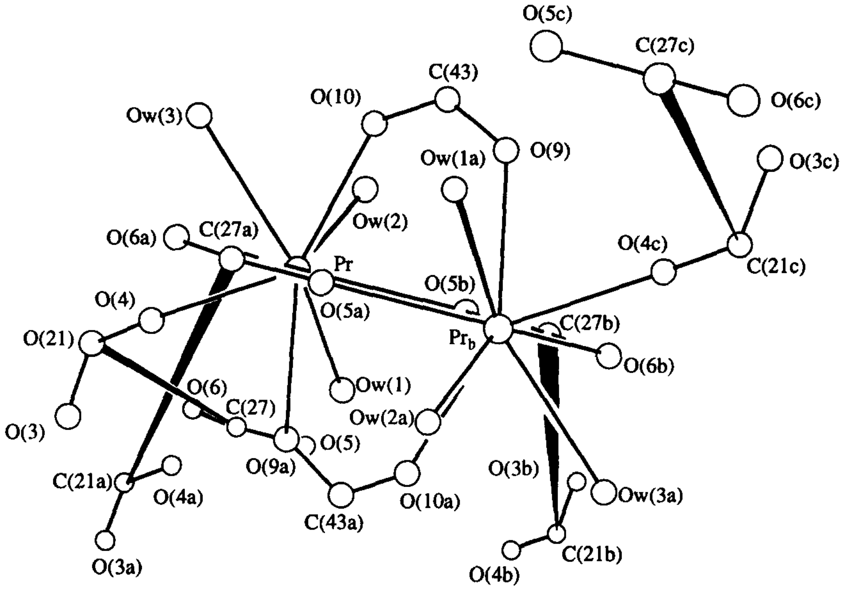

Fig. 2. The configuration of $[Pr_2L_2(HL)_2(H_2O)_6]$.

Table 2. The least-squares planes and dihedral angle

			Planes			Dihedral angle
A	Atoms	Pr	O(5b)	C(27b)	O(6b)	87.7°
	Distances (Å)	−0.0230	0.0250	0.0131	−0.0285	
	Atoms	Pr$_b$	O(5a)	C(27a)	O(6a)	
	Distance (Å)	0.0230	−0.0250	−0.0131	0.0285	
B	Atoms	Pr	O(10)	C(43)	O(9)	
	Distances (Å)	−0.1404	0.1575	−0.0097	−0.1325	
	Atoms	Pr$_b$	O(10a)	C(43a)	O(9a)	
	Distances (Å)	0.1186	−0.0927	−0.0119	0.1109	

(from water molecules). The distance between Pr^{III} and Pr_b^{III} ions is 4.236 Å, showing that there is no Pr—Pr bond in the complex [7].

Acknowledgements—This work was supported by the National Program and the National Natural Science Foundation of China. We appreciate the financial support of this work very much.

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