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LEWIS BASE ADDUCTS OF LEAD(II) COMPOUNDS III* SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF $LPb(ClO_4)_2$ AND $LPb(NCS)_2$, (L= *MESO*-5,7,7,12,14,14-HEXAMETHYL-1,4,8,11-TETRA-AZACYCOTETRADECANE)

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Abstract

The reactions of $Pb(ClO_4)_2$ and $Pb(SCN)_2$ with *meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11,tetra-azacyclotetradecane ($C_{16}H_{36}N_4$= L) yielded colorless crystals of $LPb(ClO_4)_2$ (**1**) and $LPb(NCS)_2$ (**2**), respectively. Their structures were determined by X-ray crystallography. Crystal data: **1** monoclinic, $P\,2_1/c$, a =11.293 (4)Å, b = 16.382 (6) Å, c = 21.518(4)Å, β = 92.14(2)°, Z = 4, MoKα, 1824 observed ($I>2.5\sigma(I)$) data (20°C), R = 0.044; **2**, orthorombic, $P\,cab$, a = 15.861(2) Å, b = 10.436(8) Å, c = 20.347(4) Å, β = 90.00(3)°, Z = 4, MoKα, 1763 observed ($I>2.5\sigma(I)$ data (20°C), R= 0.051. In both molecules, lead(II) cation is situated above the plane of the macrocyclic ring.

Introduction

A number of synthetic and structural studies have been undertaken on complexes of the N_4-quadridentate macrocyclic L^1 and L^2 with lead(II) salts [1-3]. In spite of the large size of the central lead atom, and a tendency in such complexes to high coordination numbers, the adduct stoichiometries are 1:1 rather than 2:1 (as in $[Pb(tren)_2]Cl_2$ (tren= $N(CH_2CH_2NH_2)_3$ [4]. With ligands such as these, amino hydrogen atom dispositions and ligand conformations are dependent on metal size, ligand size and substitution pattern. Thus in $[Pb(L^1)Cl]^+$ and $[Pb(L^1)(NO_3)_2]$, all the hydrogen atoms are disposed on the same side of the macrocyclic plane, within its "cup", while in $[Pb(L^2)(NO_3)_2]$ they are alternatively disposed on either side. In continuing the studies of lead(II) systems, here the synthesis and structural characterization of 1:1 adducts of lead(II) perchlorate and thiocyanate with the macrocyclic ligand *meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane (L) is reported.

Keywords: Synthesis and molecular structures of $LPbX_2$ (L= macrocyclic tetramine, X= ClO_4, SCN)

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Experimental Section

Materials

The macrocyclic ligand (L) was prepared as described in the literature [5]. $Pb(ClO_4)_2.6H_2O$ was obtained from Aldrich, and $Pb(SCN)_2$ was synthesized by the addition of

a hot aqueous solution of NaSCN to a boiling aqueous solution of $Pb(NO_3)_2$.

Physical Measurements

Elemental analysis was carried out on a Heraeus elemental analyser, CHN-O-RAPID. Infrared spectra were obtained as KBr disks (4000-600 cm^{-1}) with a Perkin-Elmer IR-297 spectrophotometer. X-ray crystallographic data were collected with an Enraf-Nonius CAD4 diffractometer.

Preparation of $LPb(ClO_4)_2$ (1) and $LPb(NCS)_2$ (2)

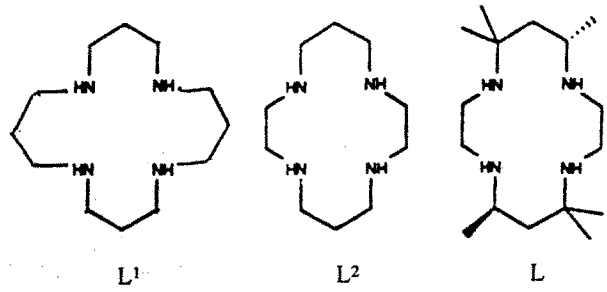
A mixture of $Pb(ClO_4)_2$. $6H_2O$ (0.5 g, 1.0 mmol) or $Pb(SCN)_2$ (0.32 g, 1.0 mmol) with the ligand L (0.61 g, 1.0 mmol) was placed at the bottom of a branched glass tube and 25 ml of ethanol was poured into the tube. The end of the tube containing lead(II) salt and the ligand was kept in an oil bath at 333 K and the other end kept at ambient temperature (*ca.* 292-294 K). After a few days, crystals formed in the lower temperature region were filtered off and washed with ethanol and ether and air dried (yield 80-90%). Anal. calcd. for $C_{16}H_{36}N_4O_8Cl_2Pb$(1): C, 27.82; H, 5.22; N, 8.12. Found: C, 27.80; H, 5.19: N, 8.13%.
Calcd. for $C_{16}H_{36}N_6S_2Pb$(2): C, 35.57; H, 5.93; N, 13.84%. Found: C, 35.60; H, 5.90; N, 13.86%.

X-ray Structural Determinations

Colorless crystals of **1** and **2** were attached to the end of a glass fiber and mounted on the diffractometer, employing graphite-monochromated MoKα radiation. Unit cell dimensions of **1** and **2** at 20°C were obtained by least-squares fits of the setting angles of 30 reflections, respectively. The structures were solved via the Patterson heavy-atom method using SHELXS86 [6]. Hydrogen atoms were found from different Fourier maps calculated after isotropic refinement. Refinement was by full-matrix least-square techniques based on F to minimize the quantity of $\Sigma_w(|F_o| - |F_c|)^2$ with $w = 1\sigma^2(F)$ using XTAL program [7] and scattering factors for all atoms were taken from reference 8. Crystallographic data, selected bond lengths and angles are given in Tables I and II, respectively.

Results and Discussion

The reaction of the macrocyclic ligand (L) with $Pb(ClO_4)_2$ and $Pb(SCN)_2$ in ethanolic solution (1:1) produced colorless crystals of **1** and **2**, respectively (Figure 1). The infrared spectra of **1** and **2** clearly show that in the solid state the perchlorate and thiocyanate anion, respectively, are also coordinated. Thus, Cl-O stretching frequencies are observed for **1** at 1130(s), 1110(s), 1090(w) and 1080(s) cm^{-1}, indicating ClO_4^- coordination [9]. NCS bending vibrations at 483 cm^{-1} in **2** were observed, which indicates monodentate N-coordination of the SCN anion to the



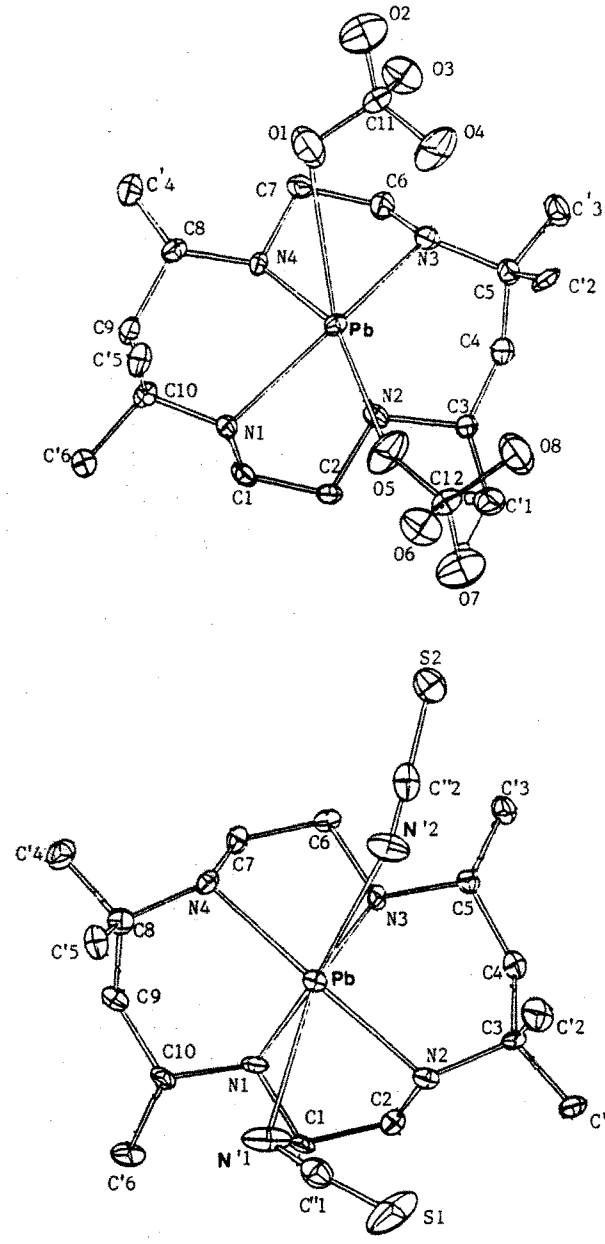


Figure 1. Prospective view and atom numbering of **1**(top) and **2** (bottom)

Table I. Crystallographic data

formula	$C_{16}H_{36}N_4O_8Cl_2Pb$(**1**)	$C_{16}H_{36}N_6S_2Pb$(**2**)
fw	690.1	607.3
crystal system	monoclinic	orthorombic
space group	$P2_1/c$	*Pcab*
a, Å	11.293(4)	15.861(2)
b, Å	16.382(6)	10.436(8)
c, Å	21.518(4)	20.347(4)
β, deg	92.14(2)	90.00(3)
V, Å^3	3981(6)	3368(8)
Z	4	4
^{d}calcd, g/cm^3	1.68	1.60
cryst size, mm^3	0.34 × 0.31 × 0.83	0.31 × 0.26 × 0.90
temp.°C	20	20
μ(MoKα), cm^{-1}	142.3	131.2
radiation (graphite monochromated)	MoKα (λ= 0.71070Å)	MoKα (λ= 0.71070Å)
range of transmission factors	0.24-0.48	0.25-0.52
scan method	θ-2θ	θ-2θ
data collcn range (2θ), deg	2-49	3-58
no. of reflcns measd	1452	1623
no. of unique data (I>2.5σ (I))	1824	1763
R, R_w	0.044, 0.053	0.051, 0.042

Table II. Selected bond lengths (Å) and angles (deg) for **1** and **2**

	1		**2**	
(a)	Lengths			
	Pb-N1	2.48 (2)	Pb-N1	2.44 (3)
	Pb-N2	2.46 (1)	Pb-N2	2.47 (1)
	Pb-N3	2.50 (4)	Pb-N3	2.58 (4)
	Pb-N4	2.48 (2)	Pb-N4	2.49 (2)
	Pb-O1	2.84 (5)	Pb-N′1	2.80 (2)
	Pb-O5	2.86 (1)	Pb-N′2	2.85 (4)
	N1-C1	1.46 (2)	N1-C1	1.49 (1)
	C1-C2	1.51 (6)	C1-C2	1.53 (4)
	C3-C′1	1.54 (5)	C3-C′1	1.53 (3)
(b)	Angles			
	N1-Pb-N2	73.6 (5)	N1-Pb-N2	71.8 (5)
	N1-Pb-N3	79.4 (2)	N1-Pb-N3	78.2 (1)
	N1-Pb-N4	76.9 (4)	N1-Pb-N4	75.6 (2)
	N2-Pb-O5	80.3 (1)	N1-Pb-N′1	81.2 (4)
	N2-Pb-O1	121.9 (6)	N1-Pb-N′2	123.8 (3)
	C1-N1-Pb	112.2 (2)	C1-N1-Pb	113.3 (1)
	C1-N1-C10	113.1 (2)	C1-N1-C10	112.8 (6)
	O1-Pb-O5	89.6 (6)	N′1-Pb-N′2	91.5 (2)
	C′6-C10-C9	109.8 (2)	C′6-C10-C9	109.6 (4)

metal [10].

Both complexes studied have strong underlying similarities as far as the macrocycle is concerned. In both cases, the structure approximates to the predicted *cis*-octahedral geometry [2]. However, there is considerable distortion from ideal octahedral geometry in the nitrogen positions of L.

In complex **1**, perchlorate anions are coordinated to LPb^{2+} moiety via one oxygen atom each, i.e. 01 and 05 (Pb-01 2.84(5)Å), and may best be described as monodentate ClO_4^- ligands [11]. Complex **2** has an average Pb-NCS distance of 2.82Å and Nl-Pb-N2= 91.5(2)°. The Pb is 1.40 and 1.37Å out of the mean N_4 plane in **1** and **2**, respectively.

In **1** and **2**, the N-H bonds alternate up and down, which is similar to the structure of $PbL^2(NO_3)_2$ [2]. The two lead complexes of **1** and **2** have similar Pb-N (macrocycle) distances of 2.48 and 2.49Å, respectively. The lead centres in both cases attain a coordination number of 6 (four Pb-N and two Pb-0 or Pb-N with anions, respectively). Attempts to prepare L_2PbX_2 complexes were not successful. This may be due to the active lone pair in the Pb^{2+} cation and steric hindrance of the macrocycle in 1:1 complexes of this type.

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