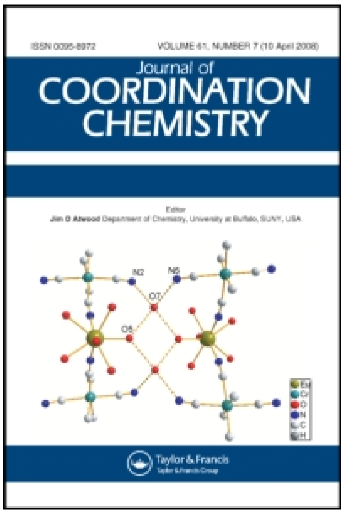

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DIRECT SYNTHESIS OF LEAD(II) COMPLEXES WITH TRIETHANOLAMINE USING LEAD(II) OXIDE AS STARTING MATERIAL

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NOTE

DIRECT SYNTHESIS OF LEAD(II) COMPLEXES WITH TRIETHANOLAMINE USING LEAD(II) OXIDE AS STARTING MATERIAL

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A number of lead(II) complexes containing triethanolamine (L) is reported. The compounds were identified and characterized by chemical analyses and IR investigations. The crystal structure of bis(triethanolamine)lead(II) acetate was determined by X-ray crystallographic analysis. The compound crystallizes in space group $C2/c$ with $a = 10.373(2)$, $b = 16.079(2)$, $c = 13.707(3)$ Å, $\beta = 99.36(2)°$, $V = 2255.7$ Å^3, $Z = 4$, d(calculated) = 1.84 g cm^{-3}. The structure was refined by least-squares methods to a final value of the R of 0.025 for 3185 reflections with $I > 3\sigma(I)$. The complex consists of eight coordinated $[PbL_2]^{2+}$ cations and two CH_3COO^- anions joined together by hydrogen bonds between the oxygen atoms of the carboxyl groups and the hydroxyl hydrogens of ligands. The lead atom lies on a two-fold rotation axis and the structure of the coordination polyhedron is a distorted trigonododecahedron.

KEYWORDS: lead(II), direct synthesis, X-ray crystal structure

INTRODUCTION

It is possible to explain the biological activity of aminoalcohol complexes[1] by the participation of these compounds in biosynthesis. As reported,[2,3] application of aminoalcohols in direct syntheses of coordination compounds, using metallic powders and oxides of metals as starting material, gives a number of advantages. Thus, for instance, in case of ethanolamine (HE), complexes containing both neutral and deprotonated ethanolamine are obtained,

$$MO + 2NH_4X + (n + 1)HE \xrightarrow{\text{solvent}} M(E)X(HE)_n + 2NH_3 + H_2O,$$

where M is a metal; X = Cl, Br, I, NO_3. It is clear that aminoethanol may be used at the same time as solvent.

Continuing our investigations of direct synthesis of aminoehtanol complexes, we have studied the interaction of lead(II) oxide with methanol, acetonitrile, *N,N*-dimethylformamide (DMFA) and dimethylsulfoxide (DMSO) solutions of ammonia salts (halides, thiocyanate, acetate) and triethanolamine, and have prepared a number of complexes with aminoalcohols.

EXPERIMENTAL

Preparations of starting compounds, and methods of isolation and investigation of complexes were as described previously.[2,3]

As is clear from Table 1, in the studied systems, only two types of complexes formed. Compounds obtained do not depend on solvent, ratio of starting reagents and conditions of synthesis, but mainly by the nature of the anion. Thus, $PbNCS \cdot 0.5L_1$ was obtained using a lead oxide to ligand ratio of 1:4 and the analogous iodide complex using a lead oxide to ligand ratio of 1:3.

It is worth noting that triethanolamine is not very useful as a solvent in the direct synthesis of lead complexes because of its poor solvating ability (unlike ethanolamine), in pure triethanolamine only $PbL_2(CH_3COO)_2$ was obtained in high yield.

On coordination, changes in absorption frequencies of $N(CH_2CH_2OH)_3$ occurred; namely, the mode found in spectra of the free ligand[4] at $1150\,cm^{-1}$ shifts $50\,cm^{-1}$ to lower energy and the band at $880\,cm^{-1}$ shifts approximately $40\,cm^{-1}$ to higher energy. The ionic nature of chemical bonding in $PbL_2(CH_3COO)_2$ is peculiar for the acetate group as its absorptions are identical with those observed in $NaCH_3COO$.[4] IR data for the other compounds present no opportunity to make reliable conclusions about the nature of bonding of halogen atoms and the thiocyanate group.

In view of current interest in the chemistry of lead and the lack of structural data on lead-aminoalcohol complexes we decided to undertake structural studies of a number of the reported compounds. The first choice for this kind of work was the complex with $PbL_2(CH_3COO)_2$. It is noted that the abovementioned compound forms with high yield in all investigated systems containing ammonium acetate and dissolves well in water, forming stable solutions. According to preliminary data, toxic properties of this complex are to a marked degree less than those of other reported lead compounds.[5]

For the preparation of this compound the following method was used: 2.23 g (0.01 mol) of PbO, 1.44 g (0.02 mol) of NH_4CH_3COO, $15\,cm^3$ of DMFA and

Table 1 Compositions of Obtained Compounds of Lead(II) (X = Br, I, NCS).

Systems	Analytical Results, %*					Assumed Composition**
	Pb	X	N	C	H	
$PbO\text{-}NH_4I\text{-}L\text{-}DMFA$	$\frac{49.9}{50.7}$	$\frac{31.0}{31.1}$	$\frac{1.6}{1.7}$	$\frac{8.7}{8.8}$	$\frac{1.6}{1.7}$	$PbI \cdot 0.5\,L_1$
$PbO\text{-}NH_4NCS\text{-}L\text{-}CH_3CN$	$\frac{61.0}{60.9}$	$\frac{16.9}{17.1}$	$\frac{6.5}{6.2}$	$\frac{14.2}{14.3}$	$\frac{2.1}{1.9}$	$PbNCS \cdot 0.5\,L_1$
$PbO\text{-}NH_4Br\text{-}L\text{-}DMSO$	$\frac{30.7}{31.1}$	$\frac{23.7}{24.0}$	$\frac{4.1}{4.2}$	$\frac{22.0}{21.7}$	$\frac{4.5}{4.6}$	$PbBr_2 \cdot 2L$
$PbO\text{-}NH_4CH_3COO\text{-}L\text{-}CH_3OH$	$\frac{33.0}{33.2}$		$\frac{4.1}{4.5}$	$\frac{30.1}{30.8}$	$\frac{5.7}{5.8}$	$Pb(CH_3COO)_2 \cdot 2L$
$PbO\text{-}NH_4CH_3COO\text{-}L\text{-}DMFA$	$\frac{33.1}{33.2}$		$\frac{4.5}{4.5}$	$\frac{30.5}{30.8}$	$\frac{5.6}{5.8}$	$Pb(CH_3COO)_2 \cdot 2L$

* Numerator is found value; denominator is value calculated for marked formula. ** L_1 is twice deprotonated L.

2.66 cm^3 (0.02 mol) of $N(CH_2CH_2OH)_3$ were heated to boiling and stirred until total dissolution was observed (3–5 min). The colorless solution obtained was allowed to stand at room temperature, when crystals separated from the solution. The product was filtered, washed with dry isopropanol and dried *in vacuo* at room temperature. Yield: 4.56 g (80%).

Crystallographic measurements were made at 20°C using an Enraf Nonius CAD-4 diffractometer operating in the $\omega/2\theta$ scan mode (the ratio of the scanning rates was $\omega/\theta = 1.2$). The intensity data were collected in the range $1 \leq \theta \leq 32°$ using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Intensities of 3729 unique reflections were measured. The structure was solved by direct methods and refined by full-matrix least-squares techniques in the anisotropic approximation. In the refinement, 3185 reflections with $I > 3\sigma(I)$ were used. All hydrogen atoms were located in difference Fourier maps and were included in the final refinements with fixed positional and thermal parameters (only H{O(1)}, H{O(2)} and H{O(3) atoms were refined isotropically). Convergence was obtained at $R = 0.025$ and $R_\omega = 0.032$, GOF = 1.07 (144 refined parameters; largest shift/esd after final cycle < 0.02; largest peak in the final difference map = 0.76 e/Å^3). The weighting scheme $w = (\sigma^2 F + 0.0016 F^2)^{-1}$ was used. Correction for Lorentz and polarization effects as well as for absorption (using DIFABS program[6]) were applied. All structural calculations were carried out with a PDP-11/23+ computer using the CDP-PLUS program package.[7] Full crystallographic data have been deposited at the Cambridge Crystallographic Data Center.

Crystal data $C_{16}H_{36}N_2O_{10}Pb$, $FW = 623.7$, monoclinic, $a = 10.373(2)$, $b = 16.079(2)$, $c = 13.707(3)$ Å, $\beta = 99.36(2)$, $V = 2255.7$ Å^3, $Z = 4$, d(calculated) = 1.84 g cm^{-3}, space group $C2/c$, $\mu = 75.8$ cm^{-1}, $F(000) = 1232$.

RESULTS AND DISCUSSION

Atomic coordinates, selected bondlengths and angles are given in Tables 2 to 4.

The structure is formed by associates of monomeric complex ions $[PbL_2]^{2+}$ connected to a pair of acetate ions by hydrogen bonding (Figure 1). As the lead atom lies on a two-fold rotation axis parallel to y, the point group of the complex ion must not be higher than C_2. The coordination polyhedron of the lead atom is formed by two nitrogen and six oxygen atoms of two tetradentate molecules of the ligand and represents a distorted trigonododecahedron (Figure 2). Hence, distortion of the coordination polyhedron is evidently caused by crystal packing of the complex ions in conjunction with space group demands and its distortion is evident in the non-collinearity of the Pb-N bonds (Table 4). The geometry of the chelate ligands is similar (Tables 3–5). All six puckered, five-membered Pb-OCCN rings have an unsymmetrical *gauche* conformation. The acetate ions are structurally normal.

Hydrogen atoms of hydroxyl groups of the ligand form a network of unsymmitrical hydrogen bonds with aceate ions: O(1)–H[O(1)]. . .O(5) $\{1 - x, y, 0.5 - z\}$ – $r <$ O(1) – H[O(1)] $>$ = 0.97 Å, $r <$ H[O(1)]. . .O(5) $>$ = 1.70 Å, $r <$ O(1). . . O(5) = 2.63 Å, angle O(1) – H[O(1)] – O(5) = 159.1°; O(2) – H[O(2)] . . . O(4) $\{-0.5 + x, 0.5 - y, -1.5 + z\}$ – $r <$O(2) – H[O(2)] $>$ = 0.85 Å, r <

H[O(2)]...O(4) > = 1.79 Å, r < O(2)...O(4)> = 2.64 Å, angle O(2) - H[O(2)] - O(4) = 178.5^0;O(3) - H[O(3)]... O(4){x,y,z} - r<O(3) - H[O(3)]> = 1.10 Å, r < H[O(3)]...O(4) > = 1.52 Å, r < O(3)...O(4) > = 2.61 Å, angle O(3) -H[O(3)] - O(4) = 167.2^0.

Table 2 Atomic Coordinates and Thermal Parameters (B_{eq}, Å^2).

Atom	*x/a*	*y/b*	*z/c*	B_{eq}
Pb	0.500	0.14873(1)	0.250	2.183(2)
O(1)	0.3702(3)	0.0217(2)	0.1753(2)	3.56(5)
O(2)	0.3050(3)	0.2596(2)	0.2243(2)	3.90(5)
O(3)	0.5390(3)	0.1623(2)	0.4437(2)	4.17(6)
O(4)	0.7612(3)	0.1485(2)	0.5630(2)	3.88(6)
O(5)	0.8333(3)	0.0755(2)	0.4478(2)	4.77(6)
N	0.2886(3)	0.1114(2)	0.3419(2)	2.75(5)
C(1)	0.2143(3)	0.0425(2)	0.2881(3)	3.51(7)
C(2)	0.3024(4)	-0.0180(2)	0.2449(3)	3.76(7)
C(3)	0.2058(3)	0.1862(3)	0.3418(3)	3.51(7)
C(4)	0.1837(4)	0.2310(2)	0.2439(3)	3.66(7)
C(5)	0.3404(4)	0.0845(3)	0.4439(3)	3.62(7)
C(6)	0.4390(4)	0.1425(2)	0.4994(3)	3.62(8)
C(7)	0.8516(3)	0.1138(2)	0.5268(3)	2.91(6)
C(8)	0.9882(4)	0.1192(3)	0.5829(3)	4.10(8)
H(01)	0.310(4)	0.044(3)	0.120(3)	1.9(9)
H(02)	0.290(3)	0.289(2)	0.172(3)	0.7(7)
H(03)	0.636(8)	0.150(3)	0.487(6)	5(2)

Table 3 Bond Lengths (Å) for the Complex.

Pb—O(1)	2.567(3)	O(2)—H(02)	0.85(5)	N—C(5)	1.479(4)
Pb—O(2)	2.676(3)	O(3)—C(6)	1.420(5)	C(1)—C(2)	1.520(6)
Pb—O(3)	2.629(3)	O(3)—H(03)	1.11(8)	C(3)—C(4)	1.507(5)
Pb—N	2.767(3)	O(4)—C(7)	1.260(5)	C(5)—C(6)	1.497(6)
O(1)—C(2)	1.424(5)	O(5)—C(7)	1.233(4)	C(7)—C(8)	1.502(6)
O(1)—H(01)	0.97(5)	N—C(1)	1.477(5)		
O(2)—C(4)	1.406(5)	N—C(3)	1.478(5)		

Table 4 Bond angles (°) for the Complex.

O(1)—Pb—O(1′)	74.5(1)	O(3)—Pb—N′	118.34(9)	C(1)—N—C(3)	110.8(3)
O(1)—Pb—O(2)	98.13(9)	N—Pb—N′	154.9(1)	C(1)—N—C(5)	109.4(3)
O(1)—Pb—O(2′)	156.81(9)	Pb—O(1)—C(2)	111.9(2)	C(3)—N—C(5)	111.1(3)
O(1)—Pb—O(3)	116.97(9)			N—C(1)—C(2)	112.1(3)
O(1)—Pb—O(3′)	71.27(9)			O(1)—C(2)—C(1)	111.7(3)
O(1)—Pb—N	66.77(9)	Pb—O(2)—C(4)	115.9(3)	N—C(3)—C(4)	113.2(4)
O(1)—Pb—N′	92.81(9)			O(2)—C(4)—C(3)	108.4(3)
O(2)—Pb—O(2′)	96.5(1)			N—C(5)—C(6)	114.3(4)
O(2)—Pb—O(3)	93.81(9)	Pb—O(3)—C(6)	121.3(2)	O(3)—C(6)—C(5)	111.4(3)
O(2)—Pb—O(3′)	79.80(9)			O(4)—C(7)—O(5)	123.4(3)
O(2)—Pb—N	64.30(9)			O(4)—C(7)—C(8)	118.3(3)
O(2)—Pb—N′	136.28(9)	Pb—N—C(1)	108.9(2)	O(5)—C(7)—C(8)	118.4(4)
O(3)—Pb—O(3′)	170.5(1)	Pb—N—C(3)	109.0(3)		
O(3)—Pb—N	64.0(1)	Pb—N—C(5)	107.5(3)		

Table 5 Torsion Angles (°) for the Complex.

Atom 1	Atom2	Atom3	Atom4	Angle		Atom1	Atom2	Atom3	Atom4	Angle	
O(2)	Pb	O(1)	C(2)	- 83.03	(0.23)	O(3)	Pb	N	C(5)	- 25.83	(0.21)
O(3)	Pb	O(1)	C(2)	15.48	(0.26)	Pb	O(1)	C(2)	C(1)	55.17	(0.35)
N	Pb	O(1)	C(2)	- 25.58	(0.22)	Pb	O(2)	C(4)	C(3)	47.64	(0.35)
O(1)	Pb	O(2)	C(4)	40.76	(0.25)	Pb	O(3)	C(6)	C(5)	22.77	(0.41)
O(3)	Pb	O(2)	C(4)	- 77.18	(0.25)	Pb	N	C(1)	C(2)	33.30	(0.33)
N	Pb	O(2)	C(4)	- 18.51	(0.23)	C(3)	N	C(1)	C(2)	153.18	(0.30)
O(1)	Pb	O(3)	C(6)	- 40.36	(0.29)	C(5)	N	C(1)	C(2)	- 83.94	(0.36)
O(2)	Pb	O(3)	C(6)	60.77	(0.27)	Pb	N	C(3)	C(4)	44.43	(0.33)
N	Pb	O(3)	C(6)	1.84	(0.25)	C(1)	N	C(3)	C(4)	- 75.34	(0.37)
O(1)	Pb	N	C(1)	- 4.94	(0.20)	C(5)	N	C(3)	C(4)	162.76	(0.31)
O(1)	Pb	N	C(3)	- 125.89	(0.22)	Pb	N	C(5)	C(6)	50.34	(0.35)
O(1)	Pb	N	C(5)	113.52	(0.23)	C(1)	N	C(5)	C(6)	168.43	(0.32)
O(2)	Pb	N	C(1)	107.24	(0.22)	C(3)	N	C(5)	C(6)	- 68.91	(0.40)
O(2)	Pb	N	C(3)	- 13.71	(0.20)	N	C(1)	C(2)	O(1)	- 61.20	(0.41)
O(2)	Pb	N	C(5)	- 134.30	(0.23)	N	C(3)	C(4)	O(2)	- 63.09	(0.40)
O(3)	Pb	N	C(1)	- 144.29	(0.23)	N	C(5)	C(6)	O(3)	- 50.54	(0.44)
O(3)	Pb	N	C(3)	94.77	(0.22)						

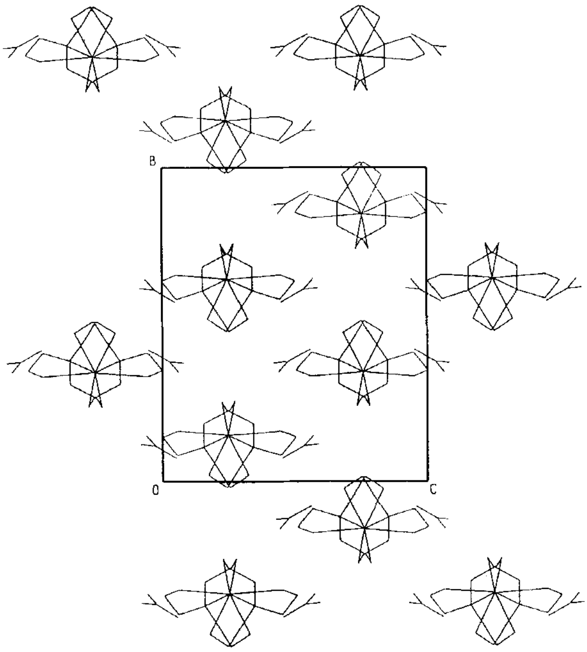

Figure 1 View of the crystal structure projected on the *bc* plane.

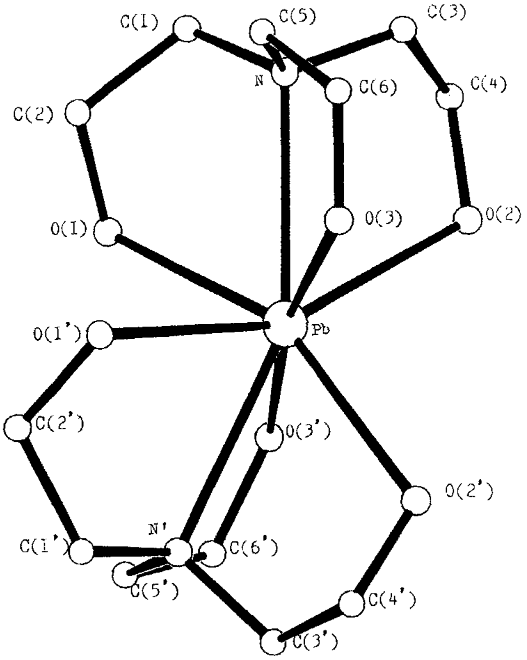

Figure 2 Geometry of the $[PbL_2]^{2+}$ cation.

The compounds PbI·0.5 L_1 and PbNCS·0.5 L_1 possess more difficult and, to our mind, interesting strucures. Results of X-ray investigations of these species will be reported later.

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