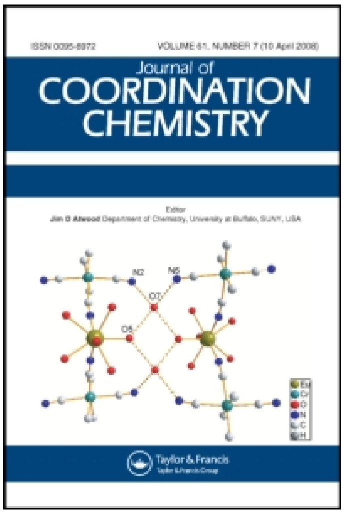

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DIRECT SYNTHESIS OF LEAD(II) COMPLEXES OF 2-DIMETHYLAMINOETHANOL

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DIRECT SYNTHESIS OF LEAD(II) COMPLEXES OF 2-DIMETHYLAMINOETHANOL

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A number of new lead(II) complexes of composition PbLX, where L is the 2-dimethylaminoethoxo ligand and X = Cl, Br, I, NCS and NO_3, have been prepared. The crystal structure of PbLBr has been determined by X-ray methods. $(PbLBr)_3$ is monoclinic, space group *C2/c*, with $a = 28.573$, $b = 9.249$, $c = 19.104$ Å, $\gamma = 107.72(1)^\circ$, $V = 4805.4$ Å^3, Z = 8 d(calc) = 3.11 g cm^{-3}, $F(000) = 3984$, $\mu = 260.9$ cm^{-1} (MoKα). The structure was refined by least-squares methods to a final R factor of 0.024 for 2433 reflections having $I > 3\sigma(I)$. Trimer, $(PbLBr)_3$, are joined by bridging bromine atoms in endless "ribbons" along [010]. The 2-dimethylaminoethoxo group is coordinated *via* oxygen and nitrogen atoms.

KEYWORDS: Lead(II), 2-dimethylaminoethanol, direct synthesis, X-ray structure

INTRODUCTION

In the light of our efforts to elaborate methods of direct synthesis of coordination compounds, the interaction of lead(II) oxide with non-aqueous (methanol, acetonitrile, *N,N*-dimethylformamide, dimethylsulfoxide) solutions of ammonium salts (halides, thiocyanate, nitrate) and 2-dimethylaminoethanol was investigated. Complexes PbLX were isolated and the bromide was structurally characterized. Results are presented below.

EXPERIMENTAL

Preparations of starting compounds, and general experimental methods were as described previously.[1] Reactions are similar to those in aminoethanol solutions, but because of the low solubility of the products in methanol, acetonitrile and 2-dimethylaminoethanol, yields are poor if they are used as solvents.

In contrast to complexes of ethanolamine[1] (Table 1) the stoichiometry of compounds obtained does not depend on the nature of the solvent or the ammonium salt: in all cases only substances of composition PbXL were obtained. These are colourless, crystalline powders which are poorly soluble in water and organic solvents.

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Table 1 Compositions of obtained compounds of lead(II).

Investigated system	Analytical results, %*					composition**
	Pb	X	N	C	H	
$PbO-NH_4Cl-HL$	63.7	11.5	3.8	13.4	2.7	PbLCl
	62.64	10.72	4.24	14.52	3.05	
$PbO-NH_4Br-HL-CH_3CN$	55.2	20.9	3.6	12.7	2.2	PbLBr
	55.22	21.29	3.73	12.80	2.69	
$PbO-NH_4I-HL-DMSO$	48.3	29.5	3.2	11.2	2.4	PbLI
	49.07	30.05	3.32	11.38	2.39	
$PbO-NH_4NCS-HL-DMFA$	58.2		7.8	16.4	2.5	PbL(NCS)
	58.63		7.93	16.99	2.86	
$PbO-NH_4NO_3-HL-CH_3OH$	57.3		7.4	11.6	2.3	$PbL(NO_3)$
	57.98		7.84	13.44	2.83	

* Numerator is found value; denominator is value calculated. ** L is the 2-dimethylaminoethoxo group.

For the preparation of the bromide complex a mixture of 2.23 g (0.01 mol) of PbO, 2.0 g (0.01 mol) of NH_4Br, 15 cm^3 of DMF and 10 cm^3 of 2-dimethylaminoethanol was refluxed and stirred until all solids had dissolved (3–5 min). The resulting colourless solution was allowed to stand at room temperature. Crystals separated from solution; these were filtered, washed with dry isopropanol and dried *in vacuo* at room temperature. Yield: 3.0 g (80%). Other complexes were prepared similarly (Table 1).

Crystallographic measurements were made at 20°C using an Enraf-Nonius CAD-4 diffractometer operating in the $\omega/2\theta$ scan mode (ratio of scanning rates $\omega/2\theta = 1.2$). Intensities were collected in the range $1 \leq \theta \leq 24°$ using graphite monochromated MoKα radiation ($\lambda = 0.71073$ Å). Intensities of 3328 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, 2433 significant reflections with $I > 3\sigma(I)$ were used. About 40% of the hydrogen atoms were located in Fourier maps; the positions of the remaining atoms were calculated. All hydrogen atoms were included in the final refinement with fixed positional and thermal ($B_{iso} = 5$ Å^2) parameters. Convergence obtained at $R = 0.036$ and $R_w = 0.036$; goodness of fit 1.13; largest shift/esd in final cycle less than 0.16; largest peak in final difference map 1.06 e/Å^3; weighting scheme $w = (\delta^2 F + 0.0016F^2)^{-1}$. Corrections for Lorentz and polarization effects as well as an empirical correction for absorption using the DIFABS program[3] were applied. All structural calculations were carried out using a PDP 11/23+ computer and the CDP-PLUS program package.[3]

Crystal data for $C_{12}H_{30}Br_3N_3O_3Pb_3$: $M = 1125.7$ (the trimer) monoclinic, space group $C2/c$, $a = 28.573$, $b = 9.249$, $c = 19.104$ Å, $\beta = 107.72(1)°$; $V = 4805.4$ Å^3, $Z = 8$, $d(calc) = 3.11$ g cm^{-3}, $F(000) = 3984$, $\mu = 260.9$ cm^{-1} (MoKα).

Atomic coordinates, bond distances and angles are listed in Tables 2–4. Observed and calculated structure factors, anisotropic thermal parameters, torsion angle data and H atom coordinates are available from the authors on request.

Table 2 Positional and equivalent isotropic thermal parameters of the heavy atoms in PbLBr.

Atom	*x*/*a*	y/*b*	z/*c*	B_{eq}, Å^2
Pb(1)	0.83654(2)	0.14904(5)	0.03169(2)	2.470(9)
Pb(2)	0.92501(2)	0.41880(5)	-0.02044(2)	2.50(1)
Pb(3)	0.79350(2)	0.54495(5)	-0.02784(2)	2.460(9)
Br(1)	0.75069(5)	0.2503(2)	-0.10866(6)	3.70(3)
Br(2)	0.96419(5)	0.6807(2)	-0.09449(8)	4.37(3)
Br(3)	0.85211(6)	0.7867(2)	0.04955(8)	4.86(4)
O(1)	0.8581(3)	0.3891(8)	0.0512(4)	2.4(2)
O(2)	0.8947(3)	0.1831(8)	-0.0244(4)	3.3(2)
O(3)	0.8473(3)	0.5008(9)	-0.0897(4)	2.8(2)
N(1)	0.9031(3)	0.166(1)	0.1549(5)	2.9(2)
N(2)	0.9469(4)	0.267(1)	-0.1202(5)	3.8(3)
N(3)	0.7687(3)	0.705(1)	-0.1457(5)	3.1(2)
C(1)	0.8769(5)	0.418(1)	0.1307(6)	3.4(3)
C(2)	0.9186(5)	0.321(1)	0.1645(6)	3.2(3)
C(3)	0.9439(5)	0.072(2)	0.1545(7)	4.6(4)
C(4)	0.8801(5)	0.121(2)	0.2123(7)	4.4(3)
C(5)	0.9025(6)	0.080(1)	-0.0757(9)	5.4(4)
C(6)	0.9478(5)	0.118(2)	-0.0952(7)	5.0(4)
C(7)	0.9127(7)	0.288(2)	-0.1957(8)	6.7(5)
C(8)	0.9982(5)	0.300(2)	-0.1229(9)	5.6(4)
C(9)	0.8347(5)	0.552(2)	-0.1627(7)	3.9(3)
C(10)	0.8126(5)	0.702(2)	-0.1707(7)	4.1(3)
C(11)	0.7259(5)	0.638(2)	-0.2002(7)	4.1(3)
C(12)	0.7565(6)	0.857(1)	-0.1359(7)	4.5(4)

Table 3 Selected bond lengths (Å) for PbLBr.

Pb(1)—Br(1)	3.174(1)	Pb(2)—N(2)	2.60(1)	N(1)—C(4)	1.51(2)
Pb(1)—Br(1)*	3.387(1)	Pb(3)—Br(1)	3.185(1)	N(2)—C(6)	1.45(2)
Pb(1)—Br(3)**	3.382(1)	Pb(3)—Br(3)	2.911(1)	N(2)—C(7)	1.49(2)
Pb(1)—O(1)	2.302(7)	Pb(3)—O(1)	2.462(7)	N(2)—C(8)	1.52(8)
Pb(1)—O(2)	2.256(7)	Pb(3)—O(3)	2.244(7)	N(3)—C(10)	1.47(1)
Pb(1)—N(1)	2.541(9)	Pb(3)—N(3)	2.603(9)	N(3)—C(11)	1.48(2)
Pb(2)—Br(2)	3.174(1)	O(1)—C(1)	1.47(1)	N(3)—C(12)	1.49(2)
Pb(2)—Br(2)***	3.385(1)	O(2)—C(5)	1.43(1)	C(1)—C(2)	1.48(2)
Pb(2)—O(1)	2.683(7)	O(3)—C(9)	1.41(1)	C(5)—C(6)	1.49(2)
PB(2)—O(2)	2.338(7)	N(1)—C(2)	1.49(1)	C(9)—C(10)	1.52(2)
PB(2)—O(3)	2.339(7)	N(1)—C(3)	1.45(2)		

Symmetry codes: *3/2 - *x*, 1/2 - *y*, - *z*; ***x*, - 1 + *y*, *z*; ***2 - *x*, 1 - *y*, - *z*.

DISCUSSION

The structure of the crystallographically indepedent fragment of PbLBr is shown in Figure 1. These trimers of PbLBr, are joined by bromine atoms to form "ribbons" along [010] (Figure 2). Three fragments also are linked by bromine atoms along [001]; these serve to define the width of the "ribbon".

Coordination polyhedra of lead(II) atoms in the trimer are rather different. By taking into consideration hypothetical bond lengths, calculated[5,6] using atomic radii, and experimental data given in Tables 2 and 3 one may conclude that trigonal pyramidal and bisphenoid (idealized C_{2v} symmetry of the distorted tetrahedron)

Table 4 Selected bond angles (°) for PbLBr (symmetry codes as for Table 3).

Br(1)	—Pb(1)—Br(1)*	78.70(3)	O(1)—Pb(2)—O(3)	67.7(2)	Pb(3)—O(1)—C(1)	119.6(6)
Br(1)	—Pb(1)—Br(3)**	114.90(4)	O(1)—Pb(2)—N(2)	133.6(3)	Pb(1)—O(2)—Pb(2)	115.7(4)
Br(1)	—Pb(1)—O(1)	87.3(2)	O(2)—Pb(2)—O(3)	90.3(3)	Pb(1)—O(2)—C(5)	121.5(8)
Br(1)	—Pb(1)—O(2)	92.8(2)	O(2)—Pb(2)—N(2)	69.1(3)	Pb(2)—O(2)—C(5)	120.6(8)
Br(1)	—Pb(1)—N(1)	158.8(2)	O(3)—Pb(2)—N(2)	99.2(3)	Pb(2)—O(3)—Pb(3)	116.5(3)
Br(1)*	—Pb(1)—Br(3)**	108.66(4)	Br(1)—Pb(3)—Br(3)	168.23(4)	Pb(2)—O(3)—C(9)	125.5(7)
Br(1)*	—Pb(1)—O(1)	82.1(3)	Br(1)—Pb(3)—O(1)	84.4(2)	Pb(3)—O(3)—C(9)	116.8(8)
Br(1)*	—Pb(1)—O(2)	156.0(2)	Br(1)—Pb(3)—O(3)	79.3(3)	Pb(1)—N(1)—C(2)	106.5(6)
Br(3)*	—Pb(1)—N(1)	91.3(2)	Br(1)—Pb(3)—N(3)	95.9(2)	Pb(1)—N(1)—C(3)	109.4(7)
Br(3)**	—Pb(1)—O(1)	156.6(2)	Br(3)—Pb(3)—O(1)	86.0(2)	Pb(1)—N(1)—C(4)	106.8(6)
Br(3)**	—Pb(1)—O(2)	95.3(2)	Br(3)—Pb(3)—O(3)	91.5(2)	C(2)—N(1)—C(3)	111(1)
Br(3)**	—Pb(1)—N(1)	86.0(2)	Br(3)—Pb(3)—N(3)	88.1(3)	C(2)—N(1)—C(4)	111(1)
O(1)	—Pb(1)—O(2)	75.1(3)	O(1)—Pb(3)—O(3)	73.2(3)	C(3)—N(1)—C(4)	112(2)
O(1)	—Pb(1)—N(1)	72.8(3)	O(1)—Pb(3)—N(3)	144.9(3)	Pb(2)—N(2)—C(6)	104.7(8)
O(2)	—Pb(1)—N(1)	88.9(3)	O(3)—Pb(3)—N(3)	72.4(3)	Pb(2)—N(2)—C(7)	114.2(9)
Br(2)	—Pb(2)—Br(2)***	96.26(4)	Pb(1)—Br(1)—Pb(3)	76.03(3)	Pb(2)—N(2)—C(8)	111.9(8)
Br(2)	—Pb(2)—O(1)	135.1(2)	Pb(1)—Br(3)—Pb(3)	132.15(5)	C(6)—N(2)—C(7)	112(2)
Br(2)	—Pb(2)—O(2)	150.9(2)	Pb(1)—O(1)—Pb(2)	102.3(3)	C(6)—N(2)—C(8)	106(2)
Br(2)	—Pb(2)—O(3)	84.5(3)	Pb(1)—O(1)—Pb(3)	110.6(3)	C(7)—N(2)—C(8)	107(1)
Br(2)	—Pb(2)—N(2)	83.5(3)	Pb(1)—O(1)—C(1)	109.9(7)	Pb(3)—N(3)—C(10)	103.5(6)
Br(2)***	—Pb(2)—O(1)	108.2(1)	Pb(2)—O(1)—Pb(3)	98.3(2)	Pb(3)—N(3)—C(11)	108.8(8)
Br(2)***	—Pb(2)—O(2)	91.8(2)	Pb(2)—O(1)—C(1)	114.5(7)	Pb(3)—N(3)—C(12)	116.5(8)
Br(2)***	—Pb(2)—O(3)	174.1(2)	O(2)—C(5)—C(6)	110(2)	C(10)—N(3)—C(11)	112(1)
Br(2)***	—Pb(2)—N(2)	86.7(2)	N(2)—C(6)—C(5)	112(1)	C(10)—N(3)—C(12)	108(2)
O(1)	—Pb(2)—O(2)	66.8(3)			C(11)—N(3)—C(12)	108.1(9)
O(1)	—C(1)—C(2)	109(2)			O(3)—C(9)—C(10)	112(1)
N(1)	—C(2)—C(1)	111.2(9)			N(3)—C(10)—C(9)	111(1)

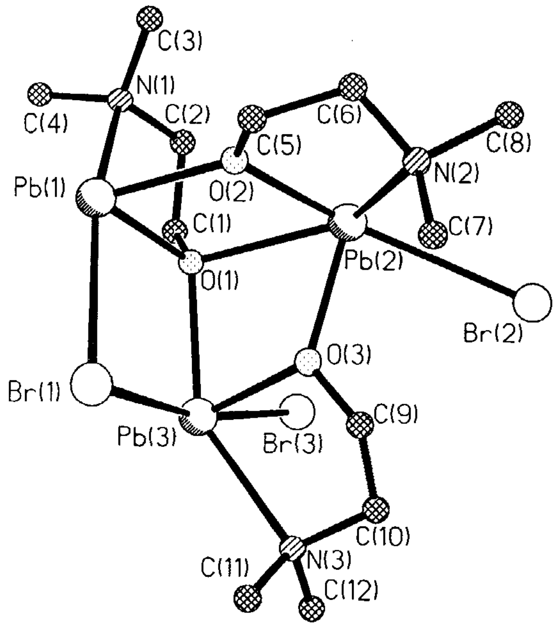

Figure 1 Structure of the crystallographically independent fragment (hydrogen atoms omitted for clarity) of $(PbLBr)_3$.

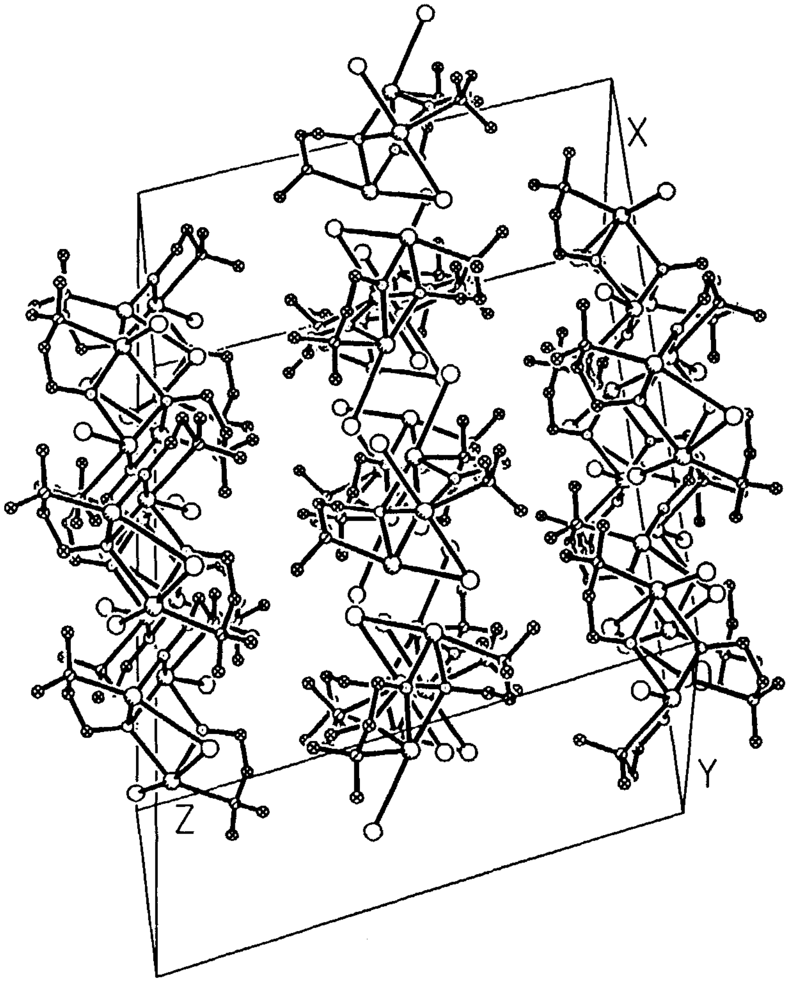

Figure 2 Packing of the ribbon chains in the unit cell (hydrogen atoms omitted for clarity).

with rather short interatomic distances are the basic structural units of lead coordination. Donor atoms of neighboring molecules transform these coordination polyhedra into different configurations.

Pyramidal coordination is peculiar to the Pb(1) atom; nitrogen and oxygen atoms form three, rather short bonds with bond angles at the metal ranging from 75–89°. Br(1), Br(1) {3/2-x, 1/2-y, -z} and Br(3) {x, -1+y, z}, complete a distorted octahedron. Close contacts to Pb(2) and bond angles at this atom are evidence of formation of another basic polyhedron, the bisphenoid. However, additional close contacts with Br(2) and Br(2) {2-x, 1-y, -z} complete another distorted octahedron.

Trigonal pyramidal, Pb(3)O(1)O(3)N(3), covalent interactions, form the basic structural unit of Pb(3), but in this case Br(1) and Br(3) atoms (Figure 1) alter this shape to a tetragonal pyramid with O(3) in the apical site. The lead atom is displaced from the least-squares plane of atoms Br(1)O(1)Br(3)N(3) by approximately 0.5 Å away from the oxygen.

Consequently, in all cases, the lead atoms in fact display coordination spheres, partly because of steric effects associated with their lone pairs of electrons.

This circumstance mainly explains the observed distortions in the complex. Thus in the case of the trigonal coordination of Pb(1), the influence of lone pair results in a decrease of bond angles at the central atom in comparison with the ideal tetrahedral angle. Considering the metal atom as formally being octahedral, one can conclude that the same reason causes the trigonal distortion of the octahedron.

Taking into consideration the lone pair, Pb(2) possesses a distorted *pseudo*-trigonal bipyramidal coordination geometry with the maximum lone pair electron density in the equatorial plane. This results in quite obvious distortion of bond angles and decrease of the bond lengths (equatorial) Pb(2)-O(2) and Pb(2)-O(3), as compared with axial Pb(2)-O(1) and Pb(2)-N(2) contacts.

In addition to angle distortions in the Pb(3) polyhedron, metal-ligand bonds disposed in the pyramid base are influenced to a marked degree by the lone pair, located beyond the polyhedron. Thus these bonds are longer than the apical interatomic distance Pb(3)-O(3).

In five-membered metal rings (PbNCCO), 2-dimethylaminoethoxo groups possess a *gauche* configuration with torsion angles (NCCO) in the range 53–61°. Angles at nitrogen atoms are tetrahedral. Carbon—carbon distances are somewhat shorter than normal aliphatic C—C bond lengths[4] but this is a common property of chelated complexes containing five-membered rings. The tetradentate, bridging oxygen atom O(1) possesses a distorted tetrahedral shape. Bond angles at the bidentate bridging oxygen atoms O(2) and O(3) are consistent with trigonal planar geometry.

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