

DIRECT SYNTHESIS AND CRYSTAL STRUCTURE OF LEAD(II) COMPOUNDS CONTAINING N,N,N',N'- TETRAMETHYLETHYLENEDIAMINE AND ITS CYCLIZATION DERIVATIVE

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Abstract—The complexes $[\text{PbL}]\text{X}_2$ and the mixed salt $\text{L}'\text{PbI}_3$, where L is N,N,N',N'-tetramethylethylenediamine, $(\text{CH}_3)_2\text{N}-\text{CH}_2-\text{CH}_2-\text{N}(\text{CH}_3)_2$, L', its cyclization derivative, $(\text{CH}_3)_2\text{N}^+-\text{CH}_2-\text{CH}_2-(\text{CH}_3)\text{N}-\text{CH}_2$, X = Cl, Br and I, have been synthesized using lead(II) oxide as starting material and characterized by ^1H and ^{13}C NMR spectroscopy and X-ray crystallography. The compounds possess ionic crystal lattices. The lead(II) atoms in $[\text{PbL}]\text{I}_2$ (**1**) are two-coordinated, while in $\text{L}'\text{PbI}_3$ (**2**) the metal atoms are surrounded in an almost regular way by six iodide anions. The structure of the L' cation is supported by NMR spectroscopy.

A number of lead(II) complexes with different aminoalcohols were prepared from components in common organic solvents (Solv) and studied by X-ray diffraction.¹⁻³ Following upon these investigations we were successful in synthesizing the new compounds $[\text{PbL}]\text{X}_2$ and $\text{L}'\text{PbI}_3$, and herein report the details of their preparation and structural features.

EXPERIMENTAL

Materials

All chemicals were commercial products of reagent grade; N,N,N',N'-tetramethylethylenediamine, lead(II) oxide and ammonium salts were used without further purification; N,N-dimethylformamide (DMF), dimethyl sulphoxide (DMSO), acetonitrile (MeCN) and isopropanol (i-PrOH) were purified according to the conventional methods.⁴

NMR spectra

^1H NMR spectra were obtained in $(\text{CD}_3)_2\text{SO}$ and CD_3CN solutions with a Bruker WP-200 spectrometer (200 MHz), while ^{13}C NMR spectra were obtained in $(\text{CD}_3)_2\text{SO}$ solutions with a Varian Gemini-200 spectrometer (50.289 MHz). All measurements were carried out at room temperature.

Chemical shifts are expressed in ppm relative to internal $\text{Si}(\text{CH}_3)_4$; $J(\text{HH})$ values are given in Hz; order of citation for proton signals in braces: {i} number of equivalent nuclei (by integration), {ii} multiplicity (s—singlet, t—triplet), {iii} coupling constant, {iv} assignment.

Synthesis of $[\text{PbL}]\text{X}_2$

For the preparation of compound **1** the following method was used: PbO (2.23 g, 10 mmol), NH_4I (2.90 g, 20 mmol), DMSO (15 cm^3) and L (10 mmol, 1.16 g) were placed in the flask in the above order. The mixture was heated in air up to 80°C and stirred until total dissolution of PbO was observed (8–10 min). The clear colourless solution obtained was allowed to stand at room temperature for 2 h; then crystals separated from the solution. The crystals were filtered, washed with i-PrOH, and finally dried

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in vacuo at room temperature; yield 4.73 g (82%). Found: H, 2.7; C, 12.4; N, 4.8; I, 43.9; Pb, 36.0. Calc. for [PbL]I₂: H, 2.8; C, 12.5; N, 4.9; I, 44.0; Pb, 35.9%. $\delta_{\text{H}}(\text{CD}_3\text{CN})$: 2.56 {12 H, s, CH₃}, 2.82 {4 H, s, CH₂}.

The same product was also obtained on heating (80°C) both in DMF under argon flux and in DMSO in air using a lead oxide to ammonium iodide ratio of 1:3.

The [PbL]Cl₂ and [PbL]Br₂ compounds were obtained in the similar way {yield 3.15 g (80%) and 3.82 g (79%), respectively}. Found: H, 4.2; C, 18.7; N, 8.0; Cl, 18.1; Pb, 52.7. Calc. for [PbL]Cl₂: H, 4.1; C, 18.3; N, 7.1; Cl, 18.0; Pb, 52.6%. $\delta_{\text{H}}[(\text{CD}_3)_2\text{SO}]$ for [PbL]Cl₂: 2.41 {12 H, s, CH₃}, 2.59 {4 H, s, CH₂}.

Found: H, 3.4; C, 14.7; N, 5.9; Br, 33.5; Pb, 43.0%. Calc. for [PbL]Br₂: H, 3.3; C, 14.9; N, 5.8; Br, 33.1; Pb, 42.9%. $\delta_{\text{H}}[(\text{CD}_3)_2\text{SO}]$ for [PbL]Br₂: 2.49 {12 H, s, CH₃}, 2.65 {4 H, s, CH₂}.

The complexes prepared are the colourless crystals which are sparingly soluble in water and organic solvents at room temperature.

Synthesis of compound 2

The compound 2 was prepared like previous one: PbO (2.23 g, 10 mmol), NH₄I (4.35 g, 30 mmol), DMF or MeCN (10 cm³) and L (10 mmol, 1.16 g) were used; yield 5.62 g (80%). The compound obtained is the colourless crystalline substance which is sparingly soluble in water and organic solvents at room temperature. Found: H, 2.3; C, 10.2; N, 3.9; I, 54.3; Pb, 29.4. Calc. for L'PbI₃: H, 2.2; C, 10.3; N, 4.0; I, 54.2; Pb, 29.5%. $\delta_{\text{H}}[(\text{CD}_3)_2\text{SO}]$: 2.42 {3 H, s, CH₃-N}, 3.02 {2 H, t, *J*(HH) 7 Hz, CH₂-N}, 3.18 {6 H, s, (CH₃)₂-N⁺}, 3.62 {2 H, t, *J*(HH) 7 Hz, CH₂-N⁺}, 4.03 {2 H, s, N-CH₂-N⁺}. $\delta_{\text{C}}[(\text{CD}_3)_2\text{SO}]$: 38.42 [s, CH₃-N], 51.76 [s, CH₃-N], 52.36 [s, broad, (CH₃)₂-N⁺], 63.56 [s, CH₂-N⁺], 85.59 [s, N-CH₂-N⁺].

The same compound was also obtained analogously both in DMF and MeCN using a lead oxide to ammonium iodide ratio of 1:2.

Crystal structure determination

Crystallographic measurements were made using an Enraf-Nonius CAD-4 diffractometer (graphite-monochromatized Mo-K_α radiation, $\lambda = 0.71073$ Å) operating in the $\omega/2\theta$ scan mode with a ratio of the scanning rates of $\omega/\theta = 1/2$. The accurate unit cell parameters and the orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 24 reflections

in the range $13 < \theta < 15^\circ$. The structures were solved by direct methods (MULTAN) and refined by full-matrix least-squares techniques in the anisotropic approximation. Crystal data, details of data collection and structure refinement parameters are summarized in Table 1. The positions of the hydrogen atoms were idealized and included in the structure factor calculations. Each hydrogen atom was assigned an isotropic thermal parameter of 1.3 times that of the attached atom. Convergence was reached at the agreement factors listed in Table 1. Corrections for Lorentz and polarization effects as well as an empirical correction for absorption using DIFABS⁵ were applied. All calculations were carried out on a PDP-11/23+ computer using the SDP-PLUS program package.⁶

The coordination environment of the lead atoms with the atomic labelling schemes and the perspective views of the packing in the unit cells of the crystal lattices are shown in Figs 1 and 2.

Selected bond distances and angles are given in Tables 2 and 3. Observed and calculated structure factors, anisotropic thermal parameters and final fractional atomic coordinates are given in the supplementary material.

The compounds [PbL]Cl₂ and [PbL]Br₂ are isostructural. No suitable crystals of these substances for data collection could be found {accurate unit cell parameters were obtained for [PbL]Cl₂ only: $a = 17.829(3)$, $b = 8.093(2)$, $c = 18.330(5)$ Å, $\beta = 117.74(2)^\circ$; space group $P2_1/n$ }.

RESULTS AND DISCUSSION

Synthetic and spectroscopic features

On formation of the [PbL]X₂ complexes both CH₃ (2.25 ppm) and CH₂ (2.40 ppm) proton signals found in the spectrum of the free ligand shift downfield *ca* 0.15–0.30 and 0.20–0.40 ppm, respectively. Therefore the coordination of the amino group to the metal results in higher acidity of methyl and methylene protons adjacent to such a group by virtue of an electron-withdrawing effect, i.e. the metal ion acts as "super acid" and causes a polarization of the ligand.⁷

The possible route of formation of the compound 2 in DMF (or MeCN) on heating is:

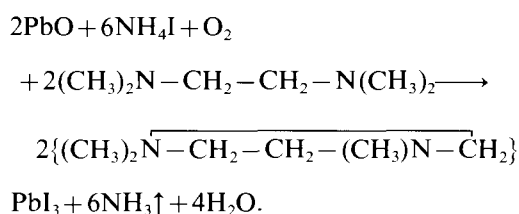


Table 1. Crystallographic data

Formula	$[\text{PbI}_3]_w [\text{C}_6\text{H}_{15}\text{N}_2]^+$	$[\text{C}_6\text{H}_{16}\text{N}_2\text{Pb}]^{2+} 2\text{I}^-$
Formula weight	703.10	577.21
Colour	Colourless	Colourless
Crystal size (mm)	$0.20 \times 0.20 \times 0.20$	$0.15 \times 0.20 \times 0.15$
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	10.782(1)	8.484(1)
b (Å)	17.775(3)	9.205(2)
c (Å)	7.958(2)	17.264(2)
α (°)	90	90
β (°)	99.38(1)	91.05(1)
γ (°)	90	90
Volume (Å ³)	1504.7(1)	1348.0(1)
Z	4	4
Temperature (K)	296	295
D_x (g cm ⁻³)	3.104	2.844
Absorption coefficient (cm ⁻¹)	173.6	170.6
$F(000)$	1224	1016
θ_{max} (°)	25	25
Data measured	2893	2585
Unique data with $I > 3\sigma(I)$	1556	1807
R	0.039	0.044
R_w^a	0.062	0.056

^a Weighting scheme $w^{-1} = \sigma^2(F) + 0.0016 F^2$.

Supporting evidence for this reaction comes from the interaction of the same components in DMF under argon that gives compound 1.

The reducing action of iodine anions to O₂ differ in DMSO, DMF and MeCN due chiefly to differ-

ences in the strength of solvation of these solvents to the iodide anions.⁸ Because of sulphur atom polarization properties, DMSO possesses more effective solvation and stabilization abilities of iodide ions than DMF and MeCN. In addition due to

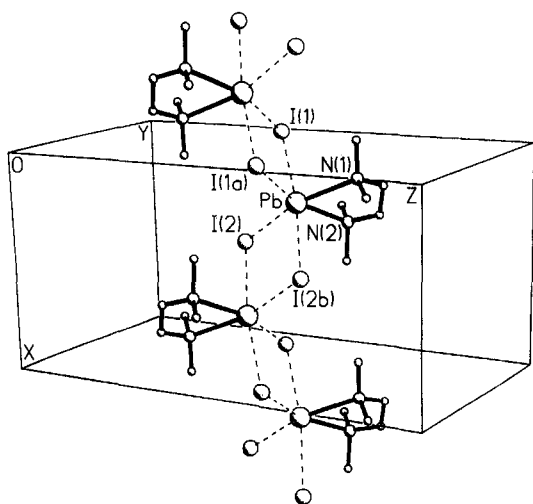


Fig. 1. Fragment of the crystal structure of $[\text{PbL}]\text{I}_2$ ("a" and "b" denote the following equivalent positions $\langle 2-x, -y, 2-z \rangle$ and $\langle 1-x, -y, 2-z \rangle$, respectively; the carbon atoms are unlabelled for clarity; hydrogen atoms are omitted; mainly ionic interaction of lead and iodine atoms is shown as dashes).

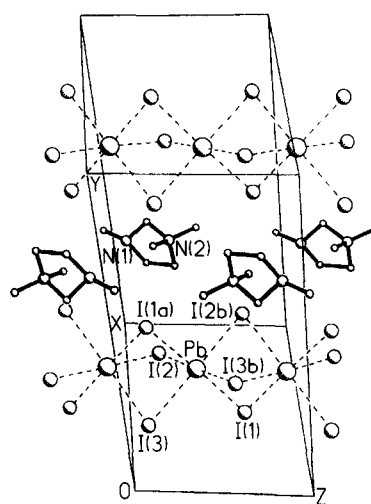


Fig. 2. Fragment of the crystal structure of L/PbI_3 ("a" and "b" denote the following equivalent positions $\langle x, 0.5-y, -0.5+z \rangle$ and $\langle x, 0.5-y, 0.5+z \rangle$, respectively; the carbon atoms are unlabelled for clarity; hydrogen atoms are omitted; mainly ionic interaction of lead and iodine atoms is shown as dashes).

Table 2. Selected interatomic distances (Å) and angles (°) for $[\text{PbI}_3]_n[\text{C}_6\text{H}_{15}\text{N}_2]^+([\text{PbL}]_2)^a$

Interatomic distances			
Pb—I(1)	3.2156	Pb—I(2b)	3.2170(9)
Pb—I(1a)	3.3240(9)	Pb—N(1)	2.630(9)
Pb—I(2)	3.3109(9)	Pb—N(2)	2.627(9)
Angles			
I(1)—Pb—I(1a)	89.81(2)	I(1a)—Pb—N(2)	156.9(2)
I(1)—Pb—I(2)	87.62(2)	I(2)—Pb—I(2b)	87.2(2)
I(1)—Pb—I(2b)	172.42(2)	I(2)—Pb—N(1)	157.1(2)
I(1)—Pb—N(1)	92.4(3)	I(2)—Pb—N(2)	87.2(2)
I(1)—Pb—N(2)	93.9(2)	I(2b)—Pb—N(1)	94.5(2)
I(1a)—Pb—I(2)	115.81(2)	I(2b)—Pb—N(2)	91.7(2)
I(1a)—Pb—I(2b)	87.31(2)	N(1)—Pb—N(2)	70.0(3)
I(1a)—Pb—N(1)	87.1(2)		

^a“a” and “b” refer to atoms related by the symmetry operations $\langle 2-x, -y, 2-z \rangle$ and $\langle 1-x, -y, 2-z \rangle$, respectively.

Table 3. Selected interatomic distances (Å) and angles (°) for $[\text{C}_6\text{H}_{16}\text{N}_2\text{Pb}]^{2+}2\text{I}^- (\text{L}'\text{PbI}_3)^a$

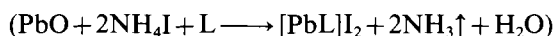
Interatomic distances			
Pb—I(1)	3.225(1)	Pb—I(2b)	3.214(1)
Pb—I(1a)	3.204(1)	Pb—I(3)	3.239(1)
Pb—I(2)	3.268(1)	Pb—I(3b)	3.196(1)
Angles			
I(1)—Pb—I(1a)	176.27(4)	I(1a)—Pb—I(3a)	92.05(4)
I(1)—Pb—I(2)	95.77(4)	I(2)—Pb—I(2b)	93.30(3)
I(1)—Pb—I(2b)	87.27(4)	I(2)—Pb—I(3)	84.61(3)
I(1)—Pb—I(3)	92.28(4)	I(2)—Pb—I(3b)	178.70(3)
I(1)—Pb—I(3b)	85.50(4)	I(2b)—Pb—I(3)	177.81(4)
I(1a)—Pb—I(2)	86.80(4)	I(2b)—Pb—I(3b)	86.20(4)
I(1a)—Pb—I(2a)	95.40(4)	I(3)—Pb—I(3b)	95.91(4)
I(1a)—Pb—I(3)	85.10(4)		

^a“a” and “b” refer to $\langle x, 0.5-y, -0.5+z \rangle$ and $\langle x, 0.5-y, 0.5+z \rangle$ equivalent positions, respectively.

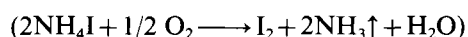
vacant *d*-orbitals the sulphur atom can act as electrophile for the iodide anion.

It also worth noting that by treating compound **1** with a solution of NH_4I in DMF in air (80°C; molar ratio of the complex to NH_4I was 1 : 1) the compound **2** was obtained, while in the case of heating of the DMF solution of L and NH_4I (same conditions; molar ratio 1 : 3) and in the systems $\text{PbO-NH}_4\text{Cl}$ (or NH_4Br)—Solv there was no evidence for the formation of the cyclization derivative.

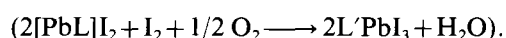
Summing up the above data, the proposed route of the interaction of the components involves the initial compound **1** formation



and oxidation of iodide ions



followed by oxidation cleavage of the CH_3 group, five-membered ring closure and the mixed salt formation



The structure of the cyclization derivative was identified on the basis of the above mentioned NMR spectroscopic properties.

Crystal structure of compound 1

The crystal is formed by complex ions $[\text{PbL}]^{2+}$ and iodide anions (Fig. 1).

The coordination of the lead atom is far from regular: the Pb atom forms two quite short bonds with the nitrogen atoms; hence, a rather rare "bent" two-coordinate geometry occurs, in other words, the environment of the lead atom possesses a pseudo-trigonal coordination with the lone pair of electrons in an unoccupied apex.^{9,10} This unsymmetrical coordination is likely to be caused by geometrical constraints of the chelating ligand and the influence of the stereochemically active lone pair of electrons. Such geometry leaves space for additional close contacts with iodine anions (Table 2); these interatomic separations are too long for strong interactions, exceeding the sum of single bond covalent radii of iodine and lead.^{11,12}

The Pb atom has only standard van der Waals contacts^{11,12} with the neighbouring lead atoms, namely $\text{Pb} \cdots \text{Pb} \langle 1-x, -y, 2-z \rangle 4.722(1)$ and $\text{Pb} \cdots \text{Pb} \langle 2-x, -y, 2-z \rangle 4.635(1) \text{ \AA}$.

The chelating ligand is structurally normal,^{11,12} the puckered five-membered $\overline{\text{Pb}-\text{N}-\text{C}-\text{C}-\text{N}}$ ring has a gauche conformation.

Crystal structure of compound 2

The compound possesses an ionic crystal lattice (Fig. 2).

The lead atom has an almost regular octahedral environment (Table 3), with the non-bonding pair of electrons, apparently occupying the isotropic valence level *s*-orbital.¹⁰ The values of $\text{Pb} \cdots \text{Pb} \langle x, 0.5-y, -0.5+z \rangle$ and $\text{Pb} \cdots \text{Pb} \langle x, 0.5-y, 0.5+z \rangle$ separations [*ca* 3.979(1) Å] allow us to postulate the existence of the weak additional interaction (the van der Waals' radius of the lead atom¹² is *ca* 2.3 Å, while the nearest interatomic distance in the crystal lattice of lead¹¹ is *ca* 3.48 Å).

The lead-iodine interatomic distances (Table 3) exceed the average length of the single covalent bond of these atoms and therefore these contacts have very little covalent character.^{11,12} The compound comprises chains of the (PbI_6) distorted octahedra sharing three iodine atoms. These chains are held together by the cyclic cations (Fig. 2). The atoms of the C—C—N fragment of the L' cyclic cation, where N is the quaternary N(2) atom (Fig.

2), are disordered and have partial occupancy of 50% in two positions.

In spite of the fact that the accuracy of the final fractional coordinates of the light atoms is not high, examination of the available bond parameter data reveals that the L' cation geometry (in accord with general theoretical predictions^{11,12}) is quite normal. As mentioned above the structure of this cation is supported by NMR spectroscopy.

The $\text{N}(1) \cdots \text{N}(2) \langle x, y, z-1 \rangle$ interatomic distances [2.32(3) Å] are significantly less than the doubled van der Waals' radius of the nitrogen atom^{11,12} (*ca* 2 × 1.6 Å) and allow the postulation of an essential electrostatic interaction of these atoms.

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