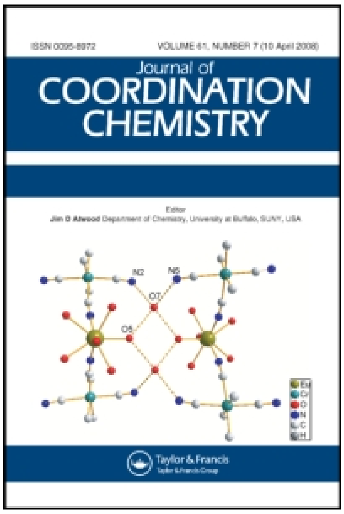

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DIRECT SYNTHESIS AND CRYSTAL STRUCTURE OF DIIODOETHYLENDIAMINELEAD(II) DIMETHYLSULFOXIDE

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DIRECT SYNTHESIS AND CRYSTAL STRUCTURE OF DIIODOETHYLENDIAMINELEAD(II) DIMETHYLSULFOXIDE

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A direct method of obtaining $PbEnI_2 \cdot DMSO$ is reported. The crystal structure of the compound was determined by X-ray techniques. $PbEnI_2 \cdot DMSO$ is triclinic, space group $P\bar{1}$, $C_4H_{14}I_2N_2PbS$, $a = 10.225(3)$, $b = 10.132(3)$, $c = 6.900(2)$ Å; $\alpha = 90.83(2)$, $\beta = 88.30(2)$, $\gamma = 106.35(4)^\circ$; $V = 685.6(4)$ Å^3; $z = 2$, calculated density 2.92 g cm^{-3}. Neutral $PbEnI_2$ complexes are associated with DMSO molecules *via* H-bonds. The lead(II) ion is covalently linked with a chelated En molecule (Pb–N 2.46–2.48 Å) and I^- anions (Pb–I 3.087–3.343 Å). Covalently bonded atoms form an umbrella-like coordination Pb(II) polyhedron. The side containing the lone electron pair of the lead(II) ion has coordination completed by two I^- anions of neighbouring molecules with the Pb–I 3.621–3.627 Å.

KEY WORDS: Lead(II), X-ray crystal structure, ethylendiamine, iodide, DMSO adduct

INTRODUCTION

Complexes of lead are of special interest because of their unusual crystal chemistry.[1] Coordination in lead complexes is determined principally by the electronic configuration of the lead ion, *viz*., by the dominating influence of the lone electron pair.[2,3] With these points in mind, we have undertaken a structural investigation of the iodo complex $PbEnI_2 \cdot DMSO$ prepared by a direct method of synthesis.

EXPERIMENTAL

For the preparation of the complex the following method was used. Some 2.23 g (0.01 mol) of PbO, 2.90 g (0.02 mol) of NH_4I, 20 cm^3 of DMSO and 1.34 cm^3 (0.02 mol) of ethylendiamine (En) were placed in a flask and the mixture was stirred for four hours at 50–60°C. The resulting colourless solution was allowed to stand at room temperature. This resulted in crystals separating from the solution. They were filtrated, washed with dry isopropanol, and finally dried *in vacuo* at room temperature (yield 3.7 g (61.7%)). Calcd. for $PbEnI_2 \cdot DMSO$: Pb, 34.6; I, 42.4; N = 4.67; C = 8.01; H = 2.33%. Found: Pb, 34.6; I, 41.9; N, 4.6; C, 8.2; H, 2.3%.

The complex is colorless and insoluble in water. $PbEnI_2 \cdot DMSO$ dissolves in DMF and DMSO on heating.

Infrared spectra were recorded on a UR-10 spectrophotometer in the 4000–400 cm^{-1} region using conventional techniques. Absorptions were found in the 3130–3310 cm^{-1} region that could be attributed to vibrational modes of coordinated En.[4] It is however emphasized that the observation of considerably overlapped bands in the 1000–1100 cm^{-1} region makes the interpretation of the DMSO modes impossible.

Diffraction data were collected from a colourless single crystal of prismatic habit of size of 0.15 × 0.15 × 0.60 mm on a computer-controlled RED-4 four-circle diffractometer (graphite crystal monochromated MoKα radiation, $\mu = 167.9\ cm^{-1}$, with background and Lp corrections). The unit cell dimensions and crystal orientation matrix were obtained from least-squares refinement of 20 carefully centred high angle reflections. The reflections were measured using the θ–2θ scan technique, with an ω-scan rate of 8 degrees per minute.

The compound crystallizes in the triclinic space group $P\bar{1}$ with the cell $a = 10.225(3)$, $b = 10.132(3)$, $c = 6.900(2)$ Å, $\alpha = 90.83(2)$, $\beta = 88.30(2)$, $\gamma = 106.35(4)°$ $V = 685.6(4)$ Å^3; a density of 2.92 g cm^{-3} was calculated for two formula units ($C_4H_{14}I_2N_2PbS$) per cell.

A total of 1670 reflections with $5° \leqslant 2\theta \leqslant 55°$ were measured; of these, 1185 were crystallographically independent and had $I > 3\delta(I)$.

The structure was solved by the heavy-atom method and difference Fourier syntheses. Least-squares refinement in the isotropic approximation led to an R factor of 0.11, which was decreased to 0.06 using the Diffabs absorption correction program.[5]

Further least-square refinement with anisotropic thermal parameters for non-hydrogen atoms (isotropic for hydrogen atoms) gave values $R = 0.049$, $R_w = 0.048$, with $w = (\delta^2 + 0.007F^2)^{-1}$.

The positions of the hydrogen atoms of NH_2 and CH_2 groups were calculated using conventional geometries. The positions of the hydrogen atoms of CH_3 groups were located unambiguously in a difference Fourier synthesis.

The calculations were carried out on a CM-4 computer using the SHELX-86[6] in the SHELX-CM version.[7] Positional and thermal parameters (B_{eq}) derived from the last cycle of least-square refinement, along with their associated standard deviations are presented in Table 1. Bond lengths and angles are listed in Tables 2 and 3.

DISCUSSION

The crystal comprises neutral $PbEnI_2$ complexes and DMSO molecules. These components are united in the framework through hydrogen bonds and electrostatic interactions. Figure 1 shows a projection of the structure on the *xz* plane.

In the complex, the $PbEnI_2$ (Figure 2) umbrella-like coordination polyhedron is formed by the N atoms of ethylendiamine and two crystallographically independent I^- ions. The Pb–N distances are close to the sum of the covalent radii of Pb (1.50 Å) and N (0.74 Å)[8] (2.48 and 2.46 Å, Table 2). Anion I(2) is at a distance (3.087 Å) that is slightly longer than the sum (2.90 Å) of the radii of Pb and I. The Pb–I(1) bond (3.343 Å) is substantially longer.

TABLE 1
Final coordinates and standard deviations (in parentheses)* for non-hydrogen atoms

	X/a	y/b	z/c	B eq**
Pb	3584 (1)	553 (1)	2544 (1)	2.95 (4)
I(1)	5596 (2)	−1540 (2)	2475 (2)	3.67 (9)
I(2)	1162 (2)	1813 (2)	2739 (3)	4.89 (10)
S	6235 (11)	4002 (8)	2335 (12)	6.8 (5)
O	6688 (20)	2741 (15)	2359 (2)	4.6 (8)
N(1)	2164 (21)	−1307 (18)	4636 (25)	3.3 (8)
N(2)	2050 (23)	−1129 (19)	419 (25)	3.9 (9)
C(1)	4169 (33)	−2519 (30)	3524 (35)	5.4 (14)
C(2)	997 (31)	−2144 (24)	1615 (36)	4.8 (12)
C(3)	7106 (56)	5147 (39)	4026 (51)	13.0 (31)
C(4)	7004 (53)	5015 (39)	539 (59)	12.2 (26)

* All values have been multiplied by 10^4.
** The temperature factors have the form $B_{eq} = 4/3\{B_{11}a^2a^{*2} + \cdots + 2B_{23}bcb^*c^* \cos\alpha\}$.

TABLE 2
Internuclear distances (Å) and angles (deg.)

(1) Coordination polyhedron of Pb(II)			
Pb-N(1)	2.48 (2)	Pb-I(1)*	3.627 (2)
Pb-N(2)	2.46 (2)	Pb-I(1)**	3.621 (2)
Pb-I(1)	3.343 (2)	Pb-S	3.774 (9)
Pb-I(2)	3.087 (2)		
(2) En			
N(1)-C(1)	1.42 (3)	PbN(1)C(1)	112.2 (16)
N(2)-C(2)	1.49 (3)	PbN(2)C(2)	110.0 (15)
C(1)-C(2)	1.50 (4)	N(1)C(1)C(2)	111.8 (23)
		N(2)C(2)C(1)	115.6 (22)
(3) DMSO			
S-O	1.47 (2)	OSC(3)	104.9 (18)
S-C(3)	1.71 (4)	OSC(4)	110.5 (18)
S-C(4)	1.65 (4)	C(3)SC(4)	91.4 (22)

* Symmetry code $1 - x, -y, -z$.
** Symmetry code $1 - x, -y, 1 - z$.

TABLE 3
H-bond data

Donor, A	Acceptor, B	Symmetry code for B	Dist., Å		angle, deg.
			A···B	H···B	A-H···B
N(2)	O	$1 - x, -y, -z$	2.99	1.92	165°
N(1)	O	$1 - x, -y, 1 - z$	2.99	1.99	156°
N(1)	I(2)	$-x, -y, 1 - z$	3.71	2.82	141°
N(1)	I(2)	$-x, -y, -z$	3.88	3.15	100°

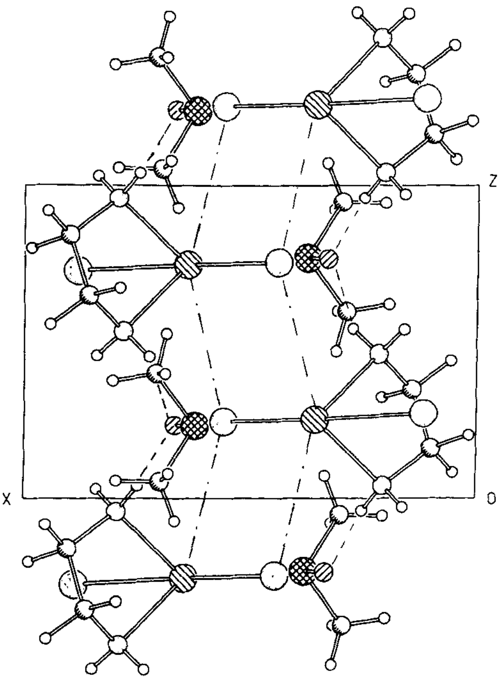

FIGURE 1 Projection of the crystal structure on the *xz* plane. H-bonds—dashed lines; intermolecular Pb–I interactions—dotted-dashed lines.

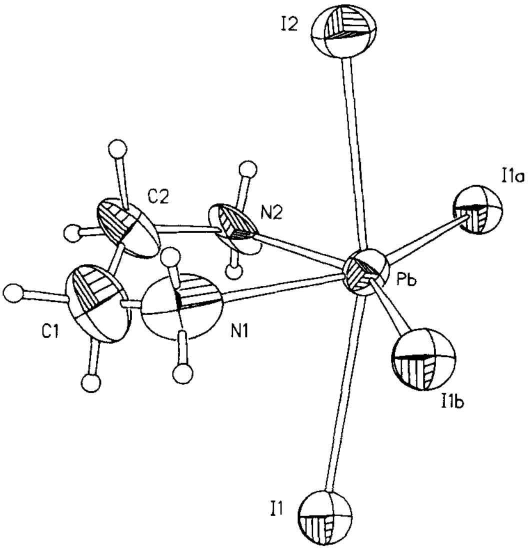

FIGURE 2 ORTEP diagram of the molecular structure, $PbEnI_2$. Iodine atoms (1a and 1b) of neighbouring complexes are included.

The geometry of $PbEnI_2$ is similar to that reported for PbO[9] where an AX_4E configuration (E is the lone electron pair, X the donor atom, *viz*, O) is realized. In PbO the lead atom is surrounded by four oxygen atoms at the base of a pyramid with the lone electron pair at the apex.

We wish to stress the difference in Pb–I distances for the two covalently coordinated I atoms. Similar differences in PbX distances were found for $NH_4Pb_2Br_5$ (Ref. 10) and $[Co(NH_3)_6](Pb_4Cl_{11})$.[11] The I(1)-Pb-I(2) angle is 165.8° and the N(1)-Pb-N(2) angle, 72.5°, is typical for the chelate. On the side of the lone electron pair the coordination of lead is supplemented by two iodine ions (1a and 1b) of neighbouring complexes. The corresponding Pb–I distances are 3.621 and 3.627 Å (Figure 2, Table 2). They complete coordination of lead to give a distorted octahedral configuration. The I–Pb–I angles vary in the range 80.9–87.4°. Different structural functions of I(1) and I(2) ions should be noted: if I(2) is connected with only one Pb atom, I(1) forms a μ_3-bridge between the lead atom and others with symmetry codes $1-x$, $-y$, $1-z$ and $1-x$, $-y$, $-z$. One could suppose that the Pb–I(1) distance is stipulated by the specific character of I(1) bonding in the structure.

The nearest non-bonded atom to lead is the sulfur atom of DMSO (3.774 Å). The five membered En–Pb ring possesses the *gauche* conformation with a dihedral angle of 49.8°.

The geometry of DMSO in this complex is quite ordinary: the S–O distance is 1.47 Å, and S–C distances are 1.65 and 1.71 Å. The angles are approximately tetrahedral.

Figure 1 shows the arrangement of $PbEnI_2$ and DMSO groups and the network of hydrogen bonding in the unit cell. Table 3 lists close internuclear distances. Hence, using the criterion of Hamilton and Ibers[12] that a hydrogen bond exists if both the A–H and H ··· B separations are less than the sum of their van der Waals radii, it is concluded that a hydrogen bond exists between N and I.

SUPPLEMENTARY DATA

Tables of anisotropic thermal parameters, H atom coordinates and observed and calculated structure factors are available from V.N.K.

REFERENCES

1. J.A. Simonov, V.V. Skopenko, V.N. Kokozay, S.R. Petrusenko and A.A. Dvorkin, *J. Inorg. Chem. (Russ.)*, **36**, 625 (1991).
2. R.J. Gillespie, *J. Am. Chem. Soc.*, **82**, 5978 (1960).
3. R.J. Gillespie and R.S. Nyholm, *Quart. Rev. Chem. Soc.*, **11**, 339 (1957).
4. Ch.J. Pouchert, "The Aldrich Library of FT-IR Spectra", Edition 1–3 (Aldrich Chem. Corp., USA, 1985).
5. N. Walter and D. Stuart, *Acta Cryst.*, **A39**, 158 (1983).
6. G.M. Sheldrick, "SHELX86. Program for Crystal Structure Determination" (Univ. of Cambridge, England, 1986).
7. V.K. Pechearskii, P.Yu. Zavalli and L.G. Aksel'rud, *Vestnik L'vov Univ.*, **25**, 9 (1984).
8. "International Tables for X-ray Crystallography", **3** (Birmingham, Kynoch Press, 1954).
9. A.F. Wells, "Structural Inorganic Chemistry" (Clarendon Press, Oxford, 1986).
10. F.G. Ras, D.J.W. Ijdo and G.C. Verschoor, *Acta Cryst.*, **B33**, 259 (1977).
11. P. Mauersberger, H.J. Haupt and F. Huber, *Acta Cryst.*, **B35**, 295 (1979).
12. W.C. Hamilton and J.A. Ibers, "Hydrogen Bonding in Solids" (Benjamin, New York, 1968).