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Reaction of lead halides with 18-crown-6 and dicyclohexano-18-crown-6: Solvent extraction, synthesis and crystal structure of [Pb(18-crown-6)I_2]

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Solvent extraction of lead halides with 18-crown-6 (18C6), dicyclohexano-18-crown-6 (DC18C6, cis-syn-cis and cis-anti-cis isomers) in chloroform was studied, and the extraction constants corrected for side reactions and ionic strength effects were obtained. The compounds of the same composition as those being extracted were also isolated in crystal form. The molecular structure of the [Pb(18C6)I_2] complex has been determined. Crystals are monoclinic, $P2_1/n$, a=11.237(2), b=10.992(2), c=8.139(2)Å, β=97.32(3)°, V=997.1(7)Å^3, D_{calc}=2.416(2)gcm^{-3}, Z=2 for the composition $C_{12}H_{24}O_6PbI_2$. The final R-factor is 0.043 for 558 unique reflections. The lead atom is coordinated to six oxygen atoms of the crown ether and two iodine atoms forming a hexagonal bipyramidal coordination polyhedron. The 18C6 molecule and the two halogen atoms form a hydrophobic coating for the lead atom which may be assumed to be the main reason of high extraction constants of the iodine complexes. For 10-coordinate lead ion (bidentate counter ions) the cis-syn-cis isomer of DC18C6 appears to be the best extraction reagent, while for 8-coordinate lead ion (monodentate halide anion) no difference between isomers was observed.

INTRODUCTION

The ability of crown ethers to form stable complexes with lead ion is well known. Crown ethers were also used for solvent extraction of lead with 18-crown-6(18C6) or dicyclohexano-18-crown-6 (DC18C6), and nitrate[1,2], trichloroacetate[2], picrate[3], Orange-2[4] as the counter ions. The possibility of lead bromide sorption on crown ether-loaded polyurethane foams was also shown[5]. These clarify the interest being paid to the structure of such compounds. The crystal structures of two [Pb(DC18C6)$(NO_3)_2$] complexes with cis-syn-cis and cis-anti-cis isomers[6,7], [Pb(18C6)$(CCl_3COO)_2$] x $2CCl_3$ COOH[8], and [Pb(15C5)$(CCl_3COO)_2(H_2O)$][9], were studied earlier using X-ray diffractometry. Recently the study of [Pb(18C6)$(NO_3)_2$ was performed simultaneously by independent groups,[10,11] as well as of [Pb(18C6) $(CH_3COO)_2$] x $3H_2O$[12].

The possibility of extracting p-block elements from chloride solutions was reported in several publications[13,14]. Crystal structures of Bi and Sb halides with 18-membered crown ethers have also been described[15,16]. To our knowledge no structure of lead halides with crown ethers has been reported.

We have observed an effective solvent extraction of lead halides by crown ethers 18C6 and DC18C6 (cis-syn-cis isomer, 'A', and cis-anti-cis isomer, 'B'). The more detailed investigation of this phenomenon was a goal of this study.

EXPERIMENTAL

Lead halides were of analytical grade and were recrystallized from water before use. Chloroform (Pharmaceutical grade) was purified by 6-times stepwise shaking with equal volumes of water. Triply distilled water was used in all experiments. 18-crown-6 ('Aldrich'), and isomers of DC18C6 (Moscow Institute of Chemical Technology, ca. 98% purity) were used without purification.

IR spectra (UR-20, 'Karl Zeiss Jena') were recorded in nujol mulls (the same being *measured in KBr disks*

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were very similar). Some IR experiments were performed in $CHCl_3$ saturated with appropriate compound in 0.04 mm cells vs pure solvent.

SOLVENT EXTRACTION

An aqueous solution contained lead nitrate (0.05-0.1 mmol/L) and appropriate lithium halide. The chloroform phase contained crown ether (0.5-6 mmol/L). Equal volumes (10/10) of the two phases were shaken for 15 min at 20°C. After the phase separation the lead concentration was determined by simple atomic absorption techniques and the distribution ratio D_{Pb} was calculated. The concentration of lead in the organic phase in blank tests (pure chloroform without any crown ether, or crown ether solution without lithium halide addition) at our experimental conditions was less than 1% of total lead nitrate concentration in aqueous phase.

SYNTHESIS

Equimolar amounts of hot saturated aqueous solutions of the appropriate lead salt and crown ether were mixed and slowly cooled. Slow evaporation at laboratory temperature afforded crystals of the lead complexes.

X-RAY DATA COLLECTION AND STRUCTURE DETERMINATION

Crystals of $[Pb(18C6)I_2]$ suitable for diffraction analysis were obtained by recrystallization from water.

The crystal of size 1.0 x 0.15 x 0.10 mm was mounted on a RED-4 four-circle diffractometer controlled by a M-6000 computer. Lattice parameters were obtained from least-squares refinement of the setting angles of 15 reflections with $15<2\theta<20°$. The independent reflections were measured in the $\theta/2\theta$ scan mode up to $(\sin\theta/\lambda)_{max}=0.53 Å^{-1}$ using MoKα-radiation (graphite monochromator). The structure solution was obtained by heavy atom method in CSD-complex[17]. Coordinates of Pb and I atoms were found from Patterson function, all the others were localized at Fourier-map. After structure refinement in isotropic approximation the absorption

Table 1 Data collection and structure analysis parametres

Molecular formula	$C_{12}H_{24}O_6PbI_2$
Space group	$P2_1/n$
Unit cell	
a, Å	11.237(2)
b, Å	10.992(2)
c, Å	8.139(2)
β, °	97.32(3)
V, Å^3	997.1(7)
Z	2
F(000)	664
D_{calc}(gcm^{-3})	2.416(2)
μ(cm^{-1})	114.91
Radiation	$MoK_\alpha(\lambda=0.71069)$
Number of unique reflections measured	604
Reflections included $I>3\sigma(I)$	558
R(hkl)	0.043
R_w	0.048
w	$1/(s(F)^2+0.005F^2)$

Table 2 Final fractional coordinates (x10^4) and mean temperature factors B for non-hydrogen atoms of $[PbI_2(18\text{-crown-}6)]$

Atom	*x/a*	*y/a*	*z/a*	*B, Å^2*
Pb	0	0	0	2.25
I	-2627(1)	000(2)	1033(2)	4.22
O(1)	-0785(15)	-1697(14)	-2375(20)	2.49
C(2)	-1155(26)	-1381(21)	-4064(14)	5.29
C(3)	-1767(18)	-0187(17)	-3890(32)	2.59
O(4)	-0957(15)	0752(14)	-3198(20)	3.07
C(5)	-1419(24)	1972(17)	-3309(30)	4.40
C(6)	-0582(27)	2748(28)	-2195(16)	6.19
O(7)	-0516(17)	2378(17)	-0513(21)	3.23
C(8)	-0048(32)	3327(19)	0573(25)	5.47
C(9)	0135(27)	2818(19)	2290(28)	4.86

Table 3 Bond distances (Å) and angles (°) in $[Pb(18\text{-crown-}6)I_2]$

Atoms	*Distance*	*Atoms*	*Angle*	*Atoms*	*Angle*
Pb-I	3.17(1)	C2-O1-C9*	110(2)	C9*-O1-C2-C3	-178
O1-C2	1.42(2)	O1-C2-C3	102(2)	O1-C2-C3-O4	66
C9*-O1	1.42(3)	C2-C3-O4	113(2)	C2-C3-O4-C5	168
C2-C3	1.49(3)	C3-O4-C5	116(2)	C3-O4-C5-C6	167
C3-O4	1.44(3)	O4-C5-C6	108(2)	O4-C5-C6-O7	-62
O4-C5	1.43(3)	C5-C6-O7	112(2)	C5-C6-O7-C8	-161
C5-C6	1.48(4)	C6-O7-C8	111(2)	C6-O7-C8-C9	-173
C6-O7	1.42(3)	O7-C8-C9	108(2)	O7-C8-C9-O1*	50
O7-C8	1.42(3)	O1*-C9-C8	121(2)	C8-C9-O1*-C2*	168
C8-C9	1.49(3)				
Pb-O1	2.75(2)				
Pb-O2	2.81(2)				
Pb-O3	2.69(2)				

correction was made using DIFABS programme[18]. Non-hydrogen atoms were refined anisotropically by block-diagonal least squares approach. The geometrically constrained hydrogen atoms were placed in calculated positions 0.95Å from the bonded carbon atoms and allowed to ride on these atoms with isotropic temperature factors fixed at 5Å^2. A summary of data collection parameters is given in Table 1. The final values of the atom positional parameters are given in Table 2, bond distances, endocyclic and torsion angles, in Table 3.

RESULTS AND DISCUSSION

Extraction Properties

Selected solvent extraction data as log D vs. log $[X]_t$ are shown in Fig. 1. The subscript 't' denotes the total concentration.

The experiments confirmed the composition $PbLX_2$ for all compounds being formed in the organic phase (where L is crown ether and X is an anion).

The overall extraction constant can be written as:

$$K_{ex} = [PbLX_2]_o/[Pb^{2+}]_w[L]_o[X^-]_w^2 \qquad (1)$$

where 'o' and 'w' indices indicate the chloroform and aqueous phases, respectively.

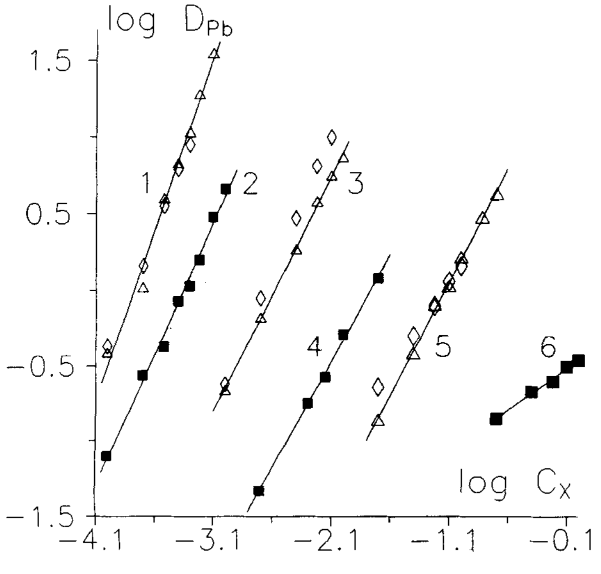

Figure 1 Plots of log D vs log $[X]_t$ for $PbLX_2$ system. $[DC18C6]_t$ = 1 mmol/l, $[18C6]_t$ = 2 mmol/l 1-Pb(DC18C6)I_2, 2-Pb(18C6)I_2, 3-Pb(DC18C6)Br_2, 4-Pb(18C6)Br_2, 5-Pb(DC18C6)Cl_2, 6-Pb(18C6)Cl_2, Triangles - cis-syn-cis ("A") isomer of DC18C6, rhomb- cis-anti-cis ("B") isomer

The equilibrium constants of some other important processes in the two-phase system may be defined by the following equations:

$$P = [L]_o/[L]_w \qquad (2)$$
$$P = 6.1 (18C6),\ 10^{3.35} (DC18C6"A") \qquad (Ref. 19, 20)$$

$$K_{PbL} = [PbL^{2+}]_W/[Pb^{2+}]_W[L]_W \qquad (3)$$
$$K_{PbL} = 10^{4.27} (18C6),\ 10^{4.95} (DC18C6"A"),\ 10^{4.43} (DC18C6"B") \qquad (Ref. 21)$$

$$K_{PbLCl} = [PbLCl^+]_W/[PbL^{2+}]_W[Cl^-]_W \qquad (4)$$
$$K_{PbX} = 10^{1.6}(Cl^-, \mu=0),\ 10^{1.6} (Br^-, \mu=0),\ 10^{1.3}(I^-, \mu=1)$$

$$K_{PbLCl} = [PbLCl^+]_W/[PbL^{2+}]_W[Cl^-]_W \qquad (5)$$
$$K_{PbLCl} = 10^{1.7} (18C6) \qquad (Ref. 22)$$

$$K_{ex}' = [PbLX_2]_o/[PbL^{2+}]_W[X^-]_W^2 \qquad (6)$$

$$K_{ex} = K_{ex}'\ K_{PbL}/P \qquad (7)$$

High distribution coefficient P of DC18C6[20] allows one to neglect the its binding into complex compounds in the aqueous phase under the experimental conditions. The absence of DC18C6 in the aqueous phase was confirmed by separate experiments. Thus, $[L]_o = [L]_t - [Pb\ LX_2]_o$. In this case PbX^+ complexes and free Pb^{2+} ion are the only species in the aqueous phase. For iodide compounds correction on PbI^+ concentration is less than the standard deviation of the experiment.

Special attention must be paid to Pb18C6^{2+} complex formation in the aqueous phase. Under conditions of our experiment ($[18C6]_t$ = 2-6 mmol/L) a cationic complex [Pb18C6^{2+}] was the main form of lead in the aqueous phase. [Pb(18C6)Cl$^+$] complexes in chloride-containing solutions have been also observed[22]. Extraction constants K_{ex}' were calculated and then corrected on the partial dissociation of [Pb18C6^{2+}] using Eq.2 and 3. K_{ex} were obtained from K_{ex}' using Eq.7.

Further correction on activity coefficients of Pb^{2+} and X^- ions in aqueous solutions was performed using the Davies equation. The resulting extraction constants are collected in Table 4.

The extraction constants increase with anion is in the usual order Cl<Br<I, which is in a good agreement with the increase of anion hydrophobicity.

The difference in extraction constants between 18C6 and DC18C6 complexes with the same anion is significantly high in the cases of the small and comparatively hydrophilic chloride anion. This effect is reduced with the increase of ion radii and completely disappears in the case of a large organic dye anion (e.g. Orange 2). There is no difference in extraction constants for halide lead complexes of the two (A and B) isomers of DC18C6.

Table 4 Extraction constants of lead complexes with 18C6, and A & B isomers of DC18C6 of $PbLX_2$ composition (T = 20 °C)

Anion	*log K_{ex}*		
	18C6	*A-isomer*	*B-isomer*
Cl	5.7	6.1	6.2
nitrate[a]	5.82	6.6	6.2
Br	7.7	8.4	8.5
I	10.7	11.4	11.4
Trichloroacetate[a]	8.0	8.2	7.8
Orange-2	13.2[b]	13.1[b]	

Each constant is a mean from 6 – 10 separate measurements. Standard deviation was of the order of 0.05-0.1.
a) Ref. 2 b) Ref. 4

These results strictly differ from those for nitrate and trichloroacetate which both are bidentate ligands[6 – 11]. The high extraction constants of $PbLI_2$ compounds are of special practical interest.

SELECTED PROPERTIES OF SOLID PBLX$_2$ COMPLEXES

The solubility of $PbLX_2$ in water (Cl>Br>I) changes in the opposite order to extractability confirming the significant role of complex hydratation in extraction equilibria.

The selected IR spectral data are presented in Table 5. A small shift was observed for the C-O-C band in 18C6 compounds. The differences in IR data for 18C6 are connected mostly not with complex formation but perhaps with the conformation change from C_2 (free molecule) to distorted D_{3d} in all the complexes. The IR bands of the DC18C6 complexes are very similar to those of 18C6, which confirms the similarity in structure.

The dissolution of a complex in chloroform causes a very small shift of band position: e.g. υ_{as} (COC) of $[Pb(18C6)I_2]$ was observed at 1102 cm^{-1}. The position of this bond in chloroform solution of uncomplexed 18C6 remains the same as in pure compound: 1120 cm^{-1}.

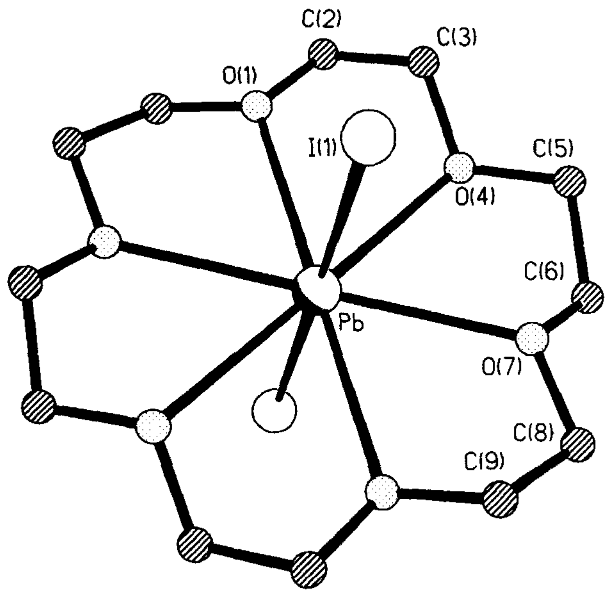

Figure 2 Molecular structure of $[Pb(18\text{-crown-}6)I_2]$

[PB(18-CROWN-6)I$_2$] MOLECULAR STRUCTURE

The structure can be described as a molecular one. The individual complex $[Pb(18C6)I_2]$ is shown in Fig. 2. It is centrosymmetric; the lead entity occupies the position on the inversion center and is coordinated by six crown ether oxygen atoms and two iodide ions. The coordination polyhedron is a distorted hexagonal bipyramid.

Pb-O distances are in the range 2.69 – 2.81Å, which is similar to the trichloroacetate complex[8]. Both may be explained by ion-dipole rather than covalent character of the Pb-O bonds. The Pb-I distance is less than sum of ionic radii and is similar to that for PbI_2 which confirms the partly covalent character of it.

Geometric parameters of the 18-crown-6 moiety are presented in Table 3. In general they are in accordance with the average characteristics for this molecule in complex compounds. The average C-O and C-C bond

Table 5 Selected IR data for crown ethers and their lead complexes

Compound	*$\tau(CH_2)$*	*$\upsilon_{as}(COC)$*	*$\upsilon_s(COC)$+ $\upsilon(CC)+\rho(CH_2)$*	*$\upsilon(CO)$+ $\rho(CH_2)$*
18C6		1120	987	857
$PbCl_2$·18C6	1297,1259	1097	969	832
$PbBr_2$·18C6	1291,1251	1097	970	834
PbI_2·18C6	1291,1251	1098	968	837
DC18C6		1101	992	844
$PbBr_2$·DC18C6	1290,1242, 1272,1205,	1088, 1116	991, 940	835, 847
PbI_2·DC18C6	1290,1245, 1272,1205	1090, 1114	991, 942	835 843

Assignments similar to those in Ref. 23.

distances are 1.42 and 1.49 Å, respectively; C-C-O and C-O-C endocyclic bond angles are 109 and 112°, correspondently. Being centrosymmetric, 18-crown-6 has a pseudo-D_{3d}-conformation. The torsion angles along the heterocyclic framework are usual for gauche (O-C-C-O, 50 – 65°), and trans (C-C-O-C, 161 – 178°) conformations (Table 3). The deviation of the O atoms from the mean plane of the macrocycle donor atoms (±0.16 Å) is slightly lower than usually.

CONCLUSIONS

The macrocycle molecule and two iodine atoms form a well-defined coating for the lead ion, preventing the possible additional hydratation of the complex, in contrast to trichloroacetate and nitrate. The hydratation of iodine atoms and methylene groups of the complex in water is expected to be very low. It may be assumed as a main reason for the comparatively high extraction constant of $PbLI_2$ as well as for the easy formation of the complex in the solid state.

In general, for 10-coordinate lead ion (bidentate counter ions) the cis-syn-cis isomer of DC18C6 appears to be the best extraction reagent, while for 8-coordinate lead ion (monodentate halide anion) no difference between isomers was observed. It allows one to propose the technical mixture of isomers instead of pure ones for extraction of lead in different separation procedures with the use of monodentate counterion ligands.

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