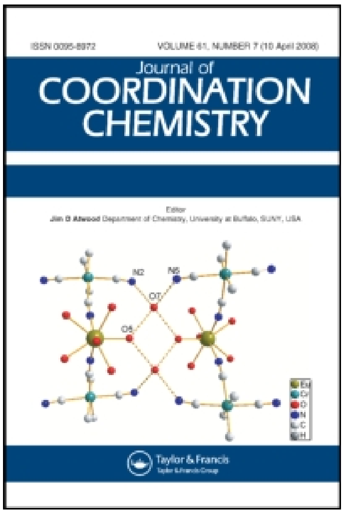

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SYNTHESIS AND CRYSTAL STRUCTURE OF A LEAD THIOCYANATE COMPLEX WITH 1,10-DITHIA-4,7,13,16-TETRAOXACYCLOOCTADECANE

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SYNTHESIS AND CRYSTAL STRUCTURE OF A LEAD THIOCYANATE COMPLEX WITH 1,10-DITHIA-4,7,13,16-TETRAOXACYCLOOCTADECANE

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The macrocyclic lead complex [Pb(1,10-dithia-18-crown-6)(NCS)(μ-NCS)] was isolated and characterized spectroscopically. The compound crystallizes in orthorhombic space group $P2_12_12_1$, with a = 10.986, b = 13.823, c = 14.160, the structure was solved and refined to R = 0.044. The lead atom is coordinated in a distorted, capped, tetragonal antiprismatic arrangement (coordination number 9) forming by 4O atoms (Pb....O distances are 2.83-2.92 Å), 2S and N atoms (Pb....S and Pb....N distances are 3.02, 3.05 and 2.43, 2.46Å) and a bridging S atom in the apical position (Pb....S, 3.59Å).

KEYWORDS: lead, thiacrown ethers, X-ray structure

INTRODUCTION

The ability of crown ethers to form stable complexes with lead ion is well known. It has[1,2] been shown that 18-membered macrocycles such as 18-crown-6(18C6) and dicyclohexano-18-crown-6 form most stable compounds. These facts point to the interest being paid to the structures of such compounds.[3,4] The crystal structures of two [Pb(dicyclohexano-18-crown-6)$(NO_3)_2$] complexes with *cis-syn-cis* and *cis-anti-cis* isomers of the crown ether,[5,6] [Pb(18C6)$(CCl_3COO)_2$]$\cdot 2CCl_3COOH$[7] and [Pb(18C6)$(CH_3COO)_2$]$\cdot 3H_2O$[8] were reported earlier. Recently, a study of [Pb(18C6)$(NO_3)_2$] appeared.[9] In all of these compounds one might expect 10-coordination for the lead atom because of the bidentate character of the anion. It was of special interest to study similar compounds with potentially monodentate ions.

Halogenide lead complexes with 18-membered crown ethers show a distorted, hexagonal bipyramidal arrangement around the lead ion with coordination number 8.[10] Two thiocyanate complexes of 18-membered macrocycles ([Pb(18C6)(NCS)-(SCN)] and [Pb(*cis-anti-cis*-dicyclohexano-18-crown-6)$(SCN)_2$] were studied by

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means of X-Ray diffractometry.[11] A distorted D_{3d} geometry for the macrocycle was observed in all cases. The same coordination number was observed in Pb(15-crown-5)$(NCS)_2$ complex with a bridging thiocyanate group.[12]

Several metal ion complexes with 1,10-dithia-4,7,13,16-tetraoxacyclooctadecane (1,10-dithia-18-crown-6) were investigated.[13-15] With soft metals (Ag, Pt, Hg), this thiamacrocycle form compounds with short M-S separations and practically non-coordinated oxygen atoms. The thermodynamic properties of lead dithia-18-crown-6 complexes were studied in methanol solutions.[16] From the significant decrease of log K and enthalpy values in comparison with 18-crown-6 it was suggested that interactions between Pb^{2+} and the sulphur atoms are negligible. The situation in the crystal state seem to be uncertain. To our knowledge no structures of lead thiocyanate with 18-membered dithiacrown ethers has been reported. We present that of the title complex here.

EXPERIMENTAL

Preparation of complex

Commercial $Pb(SCN)_2$ was purified by recrystallization from hot water. Dithia-18-crown-6 (Institute of Organic Chemistry, Kiev) was used without further purification. The title compound was obtained by reaction of a hot aqueous solution of $Pb(SCN)_2$ with an equimolar amount of crown ether in boiling water solution. Colorless crystals of the desired compound gave satisfactory elemental analyses.

IR spectra were recorded as Nujol mulls on UR-20 spectrometer.

Crystal and molecular structure determination

Suitable crystals were obtained by recrystallization from aqueous solution. Crystal data and data collection parameters are summarized in Table 1. Lattice parameters were obtained from least-squares refinement of the setting angles of 24 reflections

Table 1 Crystal data and structure refinement details.

Empirical formula	$C_{14}H_{24}N_2O_4Pb\ S_4$
Formula weight	619.78
Wavelength Mo Kα	0.71073 A
Space group	$P2_12_12_1$
Unit cell dimensions	a = 10.986(3)Å b = 13.823(7)Å c = 14.160(3)Å
Volume	2150.3(13)$Å^3$
Z	4
Density (calculated)	1.914
Absorption coefficient	8.254 mm^{-1}
$F(000)$	1200
Theta range for data collection	2.06 to 25.96 deg.
Index ranges	$0 \leq h \leq 13$, $0 \leq k \leq 17$, $0 \leq l \leq 17$
Reflections collected	2393
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.117
Final R indices [I>2sigma (I)]	R = 0.044, $wR2$ = 0.106

with $22 < 2\theta < 28$. Reflections were measured on Enraf-Nonius CAD-4 diffractometer at room temperature in the θ-2θ scan mode using MoKα radiation (graphite monochromator). The structure was solved using the heavy atom method with succeeding Fourier syntheses.[17,18] Full-matrix least-squares refinement with anisotropic temperature factors for all non-hydrogen atoms of the molecule converged to the agreement factors shown in Table 1. All hydrogen atoms were placed at calculated positions. A selection of bond distances and angles is given in Table 3.

Hydrogen atom coordinates, thermal parameters, full lists of bond angles and lengths, and Fo and Fc values are available from the authors upon request.

RESULTS AND DISCUSSION

Description of the structure

The lead ion is surrounded by two *cis*-coordinated thiocyanate groups and all donor atoms of the macrocycle (Figure 1). In the crystal Pb(dithia-18-crown-6)$(NCS)_2$ complexes from a chain connected *via* NCS bridges (Figure 2). Another thiocyanate group remains *N*-coordinated, in agreement with the larger thermal parameter for the S(4) atom.

Pb-O distances in both complexes range from 2.84 to 2.92 Å, only slightly longer than for Pb(18-crown-6) complexes with D_{3d} geometry (2.7-2.88 Å), and similar to lead acetate with *C*2 geometry (2.87-3.15 Å). The Pb-S separations (see Table 3) are

Table 2 Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2$ × 10^3).

Atom	*x/a*	*y/b*	*z/c*	*U(eq)*
Pb	-3989(1)	-700(1)	3271(1)	35(1)
S(1)	-1611(4)	-815(3)	-2207(3)	47(1)
S(2)	-6222(4)	204(3)	-4205(3)	53(1)
S(3)	-6328(4)	1759(3)	-1266(3)	51(1)
S(4)	-658(6)	1647(6)	-3631(5)	101(2)
O(1)	-4067(12)	-1637(8)	-1488(8)	56(3)
O(2)	-6263(11)	-1358(10)	-2576(9)	62(3)
O(3)	-4138(9)	-757(7)	-5334(6)	41(2)
O(4)	-2038(8)	-1444(7)	-4360(6)	37(2)
N(1)	-4674(13)	510(9)	-2141(9)	50(3)
N(2)	-2892(15)	751(10)	-3811(11)	58(4)
C(1)	-1898(17)	-1514(12)	-1182(11)	52(4)
C(2)	-2959(16)	-2171(13)	-1247(13)	54(4)
C(3)	-5118(18)	-2155(15)	-1362(15)	72(6)
C(4)	-6211(17)	-1596(15)	-1582(14)	70(6)
C(5)	-7351(19)	-876(22)	-2827(15)	93(9)
C(6)	-7314(14)	-762(20)	-3886(14)	86(8)
C(7)	-6063(16)	-3(13)	-5466(11)	57(4)
C(8)	-5323(14)	-864(13)	-5718(10)	49(4)
C(9)	-3289(13)	-1429(12)	-5722(10)	45(4)
C(10)	-2061(14)	-1211(11)	-5345(10)	44(4)
C(11)	-877(17)	-1333(12)	-3959(12)	54(4)
C(12)	-886(13)	-1687(11)	-2967(11)	46(4)
C(21)	-5374(13)	1035(10)	-1779(10)	40(3)
C(22)	-2007(18)	1106(13)	-3745(11)	54(4)

U(eq) is defined as one third of the trace of the orthogonalized *Uij* tensor.

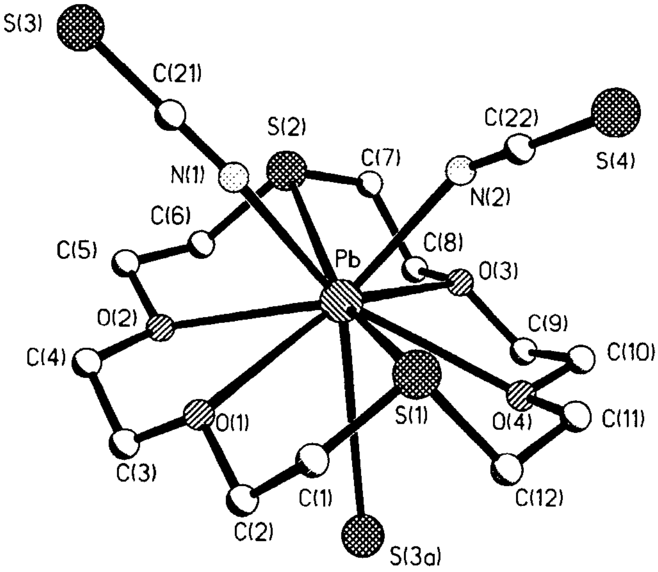

Figure 1 Molecular structure of [Pb(dithia-18-crown-6)(NCS)(μ-NCS).

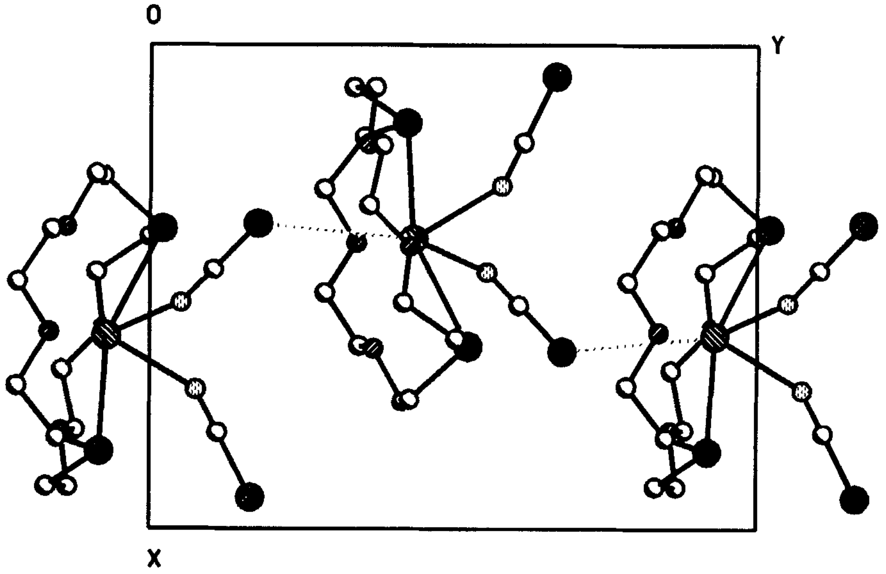

Figure 2 Packing of molecules in the cell.

Table 3 Selected bond lengths [Å] and angles [deg].

Pb-N(1)	2.433(12)	Pb-N(2)	2.461(14)
Pb-O(1)	2.838(11)	Pb-O(3)	2.927(9)
Pb-O(2)	2.835(11)	Pb-O(4)	2.834(9)
Pb-S(1)	3.019(4)	Pb-S(2)	3.055(4)
Pb-S(3a)	3.59		
	N(1)-Pb-N(2)		78.2(5)
	C(22)-N(2)-Pb		140.8(14)
	N(1)-C(21)-S(3)		179.1(13)
	C(21)-N(1)-Pb		156.0(12)
	N(2)-C(22)-S(4)	179(2)	
	N(2)-Pb-O(4)		75.9(4)
	N(1)-Pb-O(2)		73.7(4)
	N(1)-Pb-O(1)		73.7(4)
	O(2)-Pb-O(1)		61.2(4)
	N(2)-Pb-O(3)		74.9(4)
	O(4)-Pb-O(3)		59.3(3)
	N(1)-Pb-S(1)		88.6(3)
	N(2)-Pb-S(1)		77.0(4)
	O(4)-Pb-S(1)		66.3(2)
	O(1)-Pb-S(1)		63.8(3)
	N(1)-Pb-S(2)		75.8(3)
	N(2)-Pb-S(2)		85.7(4)
	O(2)-Pb-S(2)		64.8(3)
	O(3)-Pb-S(2)		62.2(2)
	S(1)-Pb-S(2)		158.83(11)

nearly the same as in [La(dithio-18-crown-6)(ClO_4)$_2$] (3.032 and 3.045 Å, but La^{3+} is significantly smaller than Pb^{2+}), but much longer than in silver and mercury complexes (2.5-2.6 Å). The comparatively short Pb-S and Pb-N distances allow suggest a partly covalent nature for these bonds. A long distance between Pb and the bridging sulphur atom may be a result of electrostatic repulsion between the thiocyanate ion and oxygen atoms of the macrocycle.

One may describe the coordination polyhedron as a very distorted, capped, tetragonal antiprism (Figure 3). Two 'planes', 4O and 2S + 2N, are above and under the lead atom. Deviations of oxygen atoms from their mean plane are less than 0.15Å; Pb is shifted from this plane towards the thiocyanate groups (0.86Å). The mean 'plane' formed by nitrogen and sulphur atoms is parallel to the previous one but with deviations of 0.67Å for sulphur and nitrogen atoms.

The intermediate behaviour of lead between soft and hard acids would allow NCS group to coordinate either by N or by S. The two sulphur atoms in the macrocycle forces the coordination of thiocyanate anion *via* the nitrogen atom. In contrast to behaviour in methanol solution,[16] in the crystal state Pb-S binding is important part. All thiocyanate groups are practically linear.

The C-O and C-C distances (1.43(2) and 1.49(2) A) in the macrocycle are typical of other macrocyclic polyether complexes (1.43(1) and 1.49(2)Å, respectively[4]). Also typical[4] are C-O-C angles (112.6-114.0^0). C-S (1.81(4) A) separations are comparable with those reported for organic sulphides. As usual, C-S-C angles are smaller (101.7 and 100.9^0) than C-O-C ones.

Torsion angles of the C-C bonds correspond to a *gauche* conformation and C-O bonds to *trans*. The C-S torsion angles of each sulphur atom are -164^0

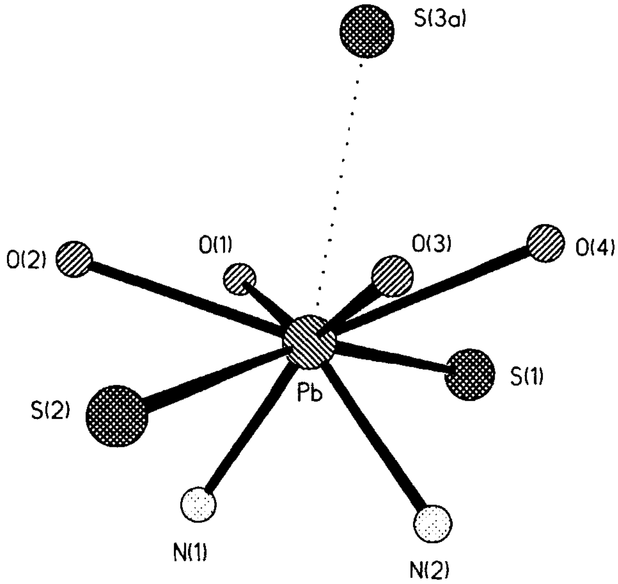

Figure 3 The Pb $O_4N_2S_3$ coordination polyhedron.

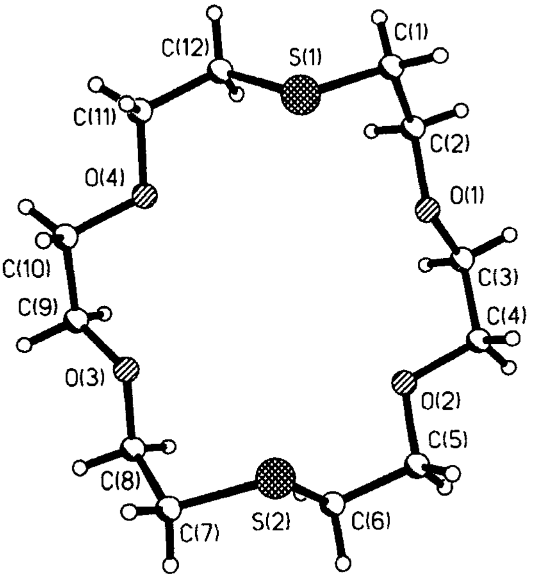

Figure 4 Macrocyclic ligand geometry.

(C(11)C(12)S(1)C(1)) and -78^0 (C12)S(1)C(1)C(2), 167^0(C(5)C(6)S(2)C(7) and $-74°$(C(6)S(2)C(7)C(8)), respectively. The macrocycle molecule has a distorted C_2 symmetry with two-fold axes orthogonal to the mean plane (Figure 4). This conformation is similar to that observed for $[Pb(18C6)(CH_3COO)_2]3H_2O$.[8] Its energy is higher than for D_{3d} in the case of 18-crown-6,[4] but for dithio ethers with long C-S distances it can be optimal.

IR spectra

The DT18C6 IR frequencies are similar to those of 18C6, but more complicated because of loss of symmetry. Two different CN bands are observed at 2040 and 2070 cm^{-1}, similar to those in Pb(dicyclohexano-18-crown-2)$(NCS)_2$. It is known[19] that *S*-coordination of thiocyanate causes an increased frequency of the CN band. This allows us to assign the band at 2040 cm^{-1} to *N*-coordinated NCS and that at 2070-to the bridged ion. The structure confirms this assignment. A strong band at 1095 cm^{-1} and two weaker ones at 1080 cm^{-1} and 1125 cm^{-1} can be attributed to ν_{as}(C-O-C) + ν(CC) vibrations whereas bands at 920 and 1030 are due to ν_s(C-O-C) + ν (CC) modes.[4]

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