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A Short Pb···Pb Separation in the Polymeric Compound Bis(pyrrolidinecarbodithioato)lead(II) and a Conformational Pathway Interconversion for the “$Pb^{II}S_4$” Framework

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The X-ray structure of bis(pyrrolidinecarbodithioato)lead(II), $Pb^{II}(pdtc)_2$, $C_{10}H_{16}N_2S_4Pb$, shows the metal to be on a crystallographic 2-fold axis. The primary Pb−S bonds are equal, 2.89 Å; this is a unique feature of this compound compared to other Pb(II) dithiocarbamate structures. The crystal structure consists of polymeric Pb(pdtc)$_2$ units stacked along the *c* axis in two antiparallel columns; successive Pb(pdtc)$_2$ units are staggered. There are weaker Pb−S bonding interactions with the unit above (secondary Pb−S bonds) such that the coordination polyhedron formed by the eight S atoms bound to the Pb atom is a distorted square antiprism. Successive antiprisms share the pyramidal base, and the Pb···Pb distance between neighboring Pb(pdtc)$_2$ units is 3.886(1) Å. We analyze the structures of other PbS_4 compounds and find that the Pb lone pair is important in defining their geometry. The large variety of Pb configurations results from peripheral changes in the ligand. This is due to a compromise between the efficient use of space in the crystal and the tendency of lead to have different coordination numbers. These configurations can be described by a pathway of conformational interconversion from a 4-sided pyramidal geometry to an octahedral system. The title compound crystallizes in the orthorhombic space group *Pccn* with $z = 4$; cell constants are $a = 13.839(14)$ Å, $b = 14.058(16)$ Å, $c = 7.763(6)$ Å.

Introduction

In general, environmental pollution is now the major source of heavy-metal poisoning. The metal lead is widely distributed in the environment due to its natural occurrence and its broad industrial use since it is both very workable and very durable. With reductions both in tetraethyllead as a gasoline additive in many countries and in the use of lead in soldered cans used for food storage, the major sources of lead exposure are lead from gasoline accumulated over the years in dust and soil, lead-containing paints, and lead leeched into drinking water from old lead solder and pipes.[1] Lead poisoning varies greatly among persons, affecting children the most. Toxicity varies greatly as well, ranging from death to very subtle effects such as learning and behavioral disorders in children. The half-life of lead in blood is 1−2 months, and the body generally excretes lead although some is accumulated, mainly in bone and baby teeth. Lead can be removed from the body using nonspecific chelating agents, such as ethylenediaminetetraacetic acid, EDTA.[2] Among the undesirable side effects of EDTA are kidney damage[2] and mobilization of naturally occurring cations (Mn^{2+}, Zn^{2+}, Cu^{2+}, etc.).[3] 2,3-Dimercaptopropanol (BAL) is another nonspecific lead chelator,[2] and 2,3-dimercaptans, a family of compounds closely related to dithiocarbamates (dtc), have been administered to children suffering from Pb poisoning.[2b] The lack of a therapeutic and specific oral chelator for lead poisoning and the fact that lead interacts primarily with enzyme sulfhydril groups in biological systems[4] make the design of detoxifying lead−thiolate complexes of interest.

Dtc form complexes with many metals and are used frequently. For example, in medicine, diethyldithiocarbamate (ddtc) has been used to combat nickel poisoning from intake of nickel carbonyl,[5] and the ligand has been examined for its ability to extract other soft acids.[6] Also, pretreatment with ddtc lowers the nephrotoxicity due to the administration of the anticancer drug cisplatin.[7] Ammonium pyrrolidinecarbodithioate (also known as pyrrolidinedithiocarbamate), NH_4(pdtc), has been used for some years in lead analysis, *i.e.*, in blood[8] and hair.[9] The standard method for the determination of lead in water and food analysis when using atomic absorption spectrometry is to extract the lead by chelating it with pdtc.[10] We are therefore interested in the structure of lead pyrrolidinecarbodithioate, $Pb^{II}(pdtc)_2$, and report its X-ray structure determination below.

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Table 1. Crystallographic Data

formula	$C_{10}H_{16}N_2S_4Pb$
fw	499.70
a, Å	13.839(14)
b, Å	14.058(16)
c, Å	7.763(6)
V, Å^3	1510.3(3)
Z	4
space group (No.)	*Pccn* (56)
T, °C	23
F(000)	944
λ, Å	1.54178
ρ^{calc}, g/cm^3	2.196
ρ^{obsd} (flotation methods, CH_3I), g/cm^3	2.189(3)
μ, cm^{-1}	264.80
transm coeff	0.796/1
R^a	0.0354
$R_w{}^b$	0.0413

^{a} $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w(F_o) = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Table 2. Atomic Coordinates and Isotropic Displacement Parameters with Their Esd's in Parentheses

	x	y	z	b(eq)
Pb	0.2500	0.2500	0.58529(9)	2.47(2)
S1	0.1636(2)	0.1029(2)	0.3749(6)	3.5(1)
S2	0.0760(3)	0.2966(3)	0.3970(6)	3.0(1)
N1	−0.0202(7)	0.1407(8)	0.309(2)	2.7(3)
C1	0.063(1)	0.174(1)	0.352(2)	2.6(4)
C2	−0.034(1)	0.041(1)	0.250(3)	3.7(4)
C3	−0.131(1)	0.047(1)	0.158(4)	7.3(8)
C4	−0.183(1)	0.126(1)	0.237(4)	6.0(6)
C5	−0.1085(9)	0.198(1)	0.288(2)	3.3(4)

^{a} $b(\text{eq}) = (4/3)\sum_{ij}[a(i)\ a(j)\ b(ij)]$.

Table 3. Selected Bond Distances and Angles in the Asymmetric Unit with Esd's in Parentheses

Distances (Å)			
Pb−S1	2.895(4)	S1−C1	1.73(1)
Pb−S2	2.893(4)	S2−C1	1.76(2)
Angles (deg)			
S2−Pb−S1	62.1(1)	S2′−Pb−S2	119.2(1)
S1′−Pb−S1	111.2(1)	C1−S1−Pb	88.7(5)
S1′−Pb−S2	84.0(1)	C1−S2−Pb	88.0(5)

Lead has many complexes with a high coordination number (CN), a remarkable diversity in the geometry adopted by the central lead atom, and ambiguous metal−metal interactions.[11,12] We document some structural features of $Pb^{II}S_4$ complexes since we are interested in understanding some of the peculiar stereochemistry that occurs in PbS_4 complexes. Sometimes we reinterpret the structure reports by considering the crystal structure and not simply the molecular structure. In this manner, newly considered molecular associations establish a higher CN for the metal. This approach was used recently by Haiduc et al.[13] where it was shown that the structures of $Pb[S_2PR_2]_2$, bis(dithiophosphinato)lead(II), and $Pb[S_2P(OR)_2]_2$, bis(dithiophosphato)lead(II), needed reinterpretation by incorporating additional, weaker Pb−S bonds that increased the CN of lead.

The lone pair of electrons on the metal in the $Pb^{II}S_4$ complexes obviously affects the geometry of these complexes,[12] and we wish to clarify the mechansim. In the compounds we have analyzed, the lone pair seems to play a role in determining the geometry and the degree of intermolecular interactions such that monomeric, dimeric, and polymeric $Pb^{II}S_4$ species are among those found. In light of this, we present here a structural analysis of compounds of the type "PbS_4".

Experimental Section

The title compound was synthesized according to the literature.[14] Sixty mL of aqueous 1.6×10^{-1} M ammonium pyrrolidinecarbodithioate (Aldrich reagent grade) and 6 mL of aqueous 4×10^{-3} M lead nitrate (Baker reagent grade) were mixed. $CHCl_3$ was added so that the $Pb^{II}(pdtc)_2$ compound could be extracted from the yellowish organic layer. Microcrystals formed upon standing. IR spectroscopy confirmed the existence of the desired product since the features were in agreement with previously described results.[15] Crystals suitable for X-ray diffraction analysis were obtained from a 1:10 $CHCl_3$−DMSO solution. Colorless, needle-like crystals formed in 2−3 days; one was chosen for data collection at the Molecular Structure Corporation (The Woodlands, TX 77381). Crystallographic data are in Table 1, and full data collection details are in Table S4 (Supporting Information).

The structure was solved and refined using the CAOS system of programs.[16] An initial Patterson map revealed the position of the lead atom on a special position of a 2-fold rotation axis. Other non-hydrogen atoms were found from subsequent Fourier analyses and difference Fourier analyses. Hydrogen atoms were calculated at idealized positions at a C−H distance of 0.96 Å and refined as riding on their parent atoms. All non-hydrogen atoms were refined anisotropically, and least squares refinement continued until convergence was reached. Atomic parameters are listed in Table 2, and selected bond distances and angles between atoms are in Table 3. More complete data are in the Supporting Information.

Results and Discussion

The metal is on a crystallographic 2-fold axis of symmetry, and so the asymmetric unit consists of one pdtc ligand and half the metal atom (see Figure 1 for atomic numbering). The $Pb(pdtc)_2$ units are obtained, then, by applying the 2-axis ($^1/_2 - x$, $^1/_2 - y$, z). The title compound is pyramidal with the Pb^{2+} ion at the apex covalently bound to the four S atoms making up the base of the pyramid. The primary Pb−S bonds are Pb−S1 = Pb−S1′ = 2.895(4) Å and Pb−S2 = Pb−S2′ = 2.893(4) Å. The fact that these distances are equal (within esd) is a unique feature of this structure as compared to other (dithiocarbamato)lead(II) structures (see Table 4). The stereochemical approach of the four S atoms is distorted square pyramidal and is described by the trans angles S1−Pb−S1′ = 111.2(1)° and S2−Pb−S2′ = 119.2(1)°, and the sides of the base defined by the separations S1−S2 = S1′−S2′ = 2.985(5) Å and S1−S2′ = S2−S1′ = 3.873(5) Å. Deviations of the individual atoms from the least squares plane of the base are S1, −0.06 Å; S2, 0.14 Å; S1′, −0.10 Å; S2′, 0.03 Å. The bite angle is 62.1(1)°.

The pyrrolidine ring is in the envelope conformation. This is generally characterized by four atoms that lie approximately in a plane and the fifth one, the flap atom, at ca. 0.5 Å from the plane. In our case, C3 is the flap atom and its distance to the plane is 0.44 Å. The deviation of the other individual atoms from the plane is ±0.04 Å.

To determine the geometry of compounds whose lone pair component can cause significant distortion, VESPR theory[17] is usually invoked, and it predicts that the lone pair of electrons should be situated where the Pb−S bonds are longest and the S−Pb−S bond angle is larger than expected, while the S−Pb−S

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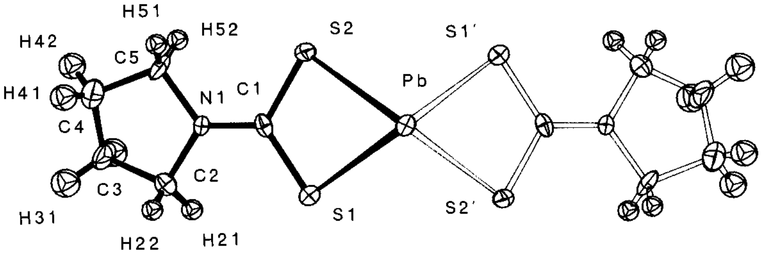

Figure 1. The pyramidal Pb(pdtc)$_2$ unit with the primary Pb−S bonds. The asymmetric unit is indicated by filled bonds. Displacement ellipsoids are shown at the 30% probability level.

angle on the opposite side of the lone pair should be smaller than predicted. Another method proposed by Andersson[18] uses the volume occupied by the lone pair to locate its position in the complex since the Pb−lone pair interaction is shorter than a Pb−S bonding interaction and the Pb is forced off center in a regular polyhedron. The geometry so far described in our compound is in keeping with the metallic lone pair located on the apical part of the pyramid, opposite the S atoms and stereochemically active.

From a literature search using the Cambridge Structural Database,[19] we formulated Table 4 which summarizes pertinent geometrical information of $Pb^{II}(XS_2)_2$ compounds where the ligand is a bidentate anionic species. The structure of the title compound resembles most that of Hummel-1[20] (see Table 4), where the pyramid is described by equal trans angles: 113.3(3)° and 113.6(3)°, respectively, and with the separations S1−S2 = S3−S4 = 2.97(2) Å and S1−S4 = S2−S3 = 3.79(2) Å. Other similarities between this species and the title compound exist as well and are the Pb−S primary bonds (2.88(1) Å) and the bite angle of the chelating ligands 62.0(3)°. Other related "PbS$_4$" complexes have a greater distortion of the 4-sided pyramidal geometry as will be discussed later.

Analysis of the three-dimensional packing of the title compound shows additional features responsible for the crystal structure that consists of Pb(pdtc)$_2$ units stacked along the *c* axis. The stacking can be described by two antiparallel columns of linked Pb(pdtc)$_2$ units, one with the pyramidal Pb(pdtc)$_2$ unit going up (+*c*) and the other column made up of centrosymmetrically related linked Pb(pdtc)$_2$ units going down (−*c*). Successive Pb(pdtc)$_2$ units are staggered (as shown in Figure S1, Supporting Information). The separation of the metal from the next unit is described by the distances: Pb−S1″(=S6) = Pb−S1‴(=S8) = 3.283(4) Å and Pb−S2″(=S5) = Pb−S2‴(=S7) = 3.478(4) Å, which are shorter than the corresponding sum of the Pb and S van der Waals[30] radii (3.80 Å). Therefore, an additional weaker bonding interaction on the metal by these "secondary Pb−S bonds" exists. The coordination polyhedron formed by the eight S atoms bound to Pb is a distorted square antiprism where the pyramidal base is not square but rectangular and one pyramid is shorter than the other. The crystal structure is polymeric with the successive antiprisms sharing the pyramidal bases as shown in Figure 2. The bonding in such a coordination polyhedron formed from eight sulfur atoms linked to a Pb(II) ion can be explained as being made up of hybrid orbitals derived from the empty metallic 5p and 5d orbitals as described by Lippard.[31] The Pb(II) lone pair is apparently responsible for the longer Pb−S secondary bond distances, since it is presumably located on the side of the Pb(II) ion facing the secondary bonds.

Two examples of 8-coordination in lead compounds are PbF$_2$ and diaboleite, Cu(OH)$_4$Pb$_2$Cl$_2$. The former[32] crystallizes as an ionic arrangement in the fluorite (CaF$_2$) fashion and, therefore, is not related to our compound. Diaboleite[33] most resembles the title compound as the lead atom is at the center of a square antiprism, rotated 45° and coordinated to four oxygen atoms at 2.57(1) Å on one side of the antiprism, and four Cl atoms with two sets of two Cl atoms at 3.01(5) and 3.18(5) Å on the other side. Since the sum of the covalent radii[34] (Pauling) of Pb (1.54 Å) and O (0.66 Å) or Cl (0.99 Å) is 2.20 Å (Pb−O) or 2.53 Å (Pb−Cl), all the experimental bonds are longer than covalent. The Pb lone pair seems distributed in a symmetrical fashion and not directed preferentially toward one side of the square antiprism polyhedron. This interpretation has the lone pair occupying a 5s^2 orbital and stereochemically inactive; this differs from the disposition of the lone pair in our compound.

Nine-coordination for lead is found[35] in PbCl$_2$, where each Pb is surrounded by nine Cl atoms and no Pb−Pb interaction is seen. It is classified as an ionic crystal and does not appear related to our compound.

Examination of the neighboring unit in the title compound shows a Pb−Pb distance of 3.886(1) Å. As the corresponding van der Waals[30] parameter is 4.04 Å, this could imply weak bonding involving the lead lone pair which is directed toward the next Pb unit. However since a marked difference between primary (2.89 Å) and secondary (3.28 and 3.48 Å) Pb−S bond lengths is seen in our compound, complete donation of the lone pair to the next metal is excluded. It is therefore interesting to explore the possibility of metallic bonding in this structure, which would implicate the Pb(II) lone pair along the stacking axis of the Pb(pdtc)$_2$ units and lead to a higher CN for lead. In the literature,[36] there is discussion as to whether Pb−Pb bonds, albeit weak, exist in Pb compounds or if these close contacts can be described as van der Waals interactions. Lead monoxide exists in two solid state modifications, α-PbO and *β*-PbO, both having close Pb−Pb distances, and with α-PbO having a Pb−

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Table 4. Geometrical Parameters in Pb(XS$_2$)$_2$ Compounds

X	bite, deg	Pb−S1, Å	Pb−S2, Å	Pb−S3, Å	Pb−S4, Å	S1−Pb−S3, deg	S2−Pb−S4, deg	Pb−Pb, Å	ref
C═C(CN)$_2$	62.0(3)	2.88(1)	2.88(1)	2.88(1)	2.88(1)	113.3(3)	113.6(3)	4.07	20 Hummel-1
NCC═CCN	75.5(2) 79.3(2)	2.694(6)	2.903(6)	2.706(6)	2.875(6)	94.9(2)	152.6(2)	3.92	21 Hummel-2
C═C(CN)$_2$	64.7 66.8	2.689(4)	2.978(4)	2.735(5)	2.845(4)	90.9	143.8	3.72	22 Hummel-3
CN(CH$_2$)$_4$	62.1(1)	2.895(4)	2.893(4)	2.895(4)	2.893(4)	111.2(1)	119.2(1)	3.89	this work[g]
CN(CH$_3$)$_2$	63.3(1)	2.779(5)	2.873(6)	2.779(5)	2.873(6)	105.5(1)	126.8(2)	4.21	23
CN-*i*-Pr$_2$	63.9(2) 64.0(2)	2.673(4)	2.843(5)	2.681(4)	2.859(5)	97.7(2)	138.6(2)	4.34	24
CNEt$_2$	64.1(3) 61.9(2)	2.744(9)	2.88(1)	2.786(9)	2.94(1)	96.2(4)	133.2(4)	4.68	25
P(OEt)$_2$	71.1(2) 70.6(2)	2.754(6)	2.996(5)	2.790(6)	3.022(6)	94.1(2)	138.2(2)	5.23	26
P(O-*i*-Bu)$_2$	68.1 73.1	2.755(5)	3.127(5)	2.768(5)	2.762(6)	93.0(2)	156.2(2)	4.02	27
P(OPh)$_2$	71.9 65.6	2.753(5)	3.323(5)	2.896(7)	2.732(6)	91.0(2)	151.6(3)	4.17	27
COEt	64.4 61.3	2.74(3)	2.84(3)	2.79(3)	2.95(3)	98.2	136.7	4.26	28
COCH$_3$	62.3(2) 62.3(2)	3.01(2)	2.92(1)	3.01(2)	2.92(1)	90.3(2)	137.6(2)	4.26	29

X	S13,[a] Å	S14, Å	S23, Å	S24, Å	S12, Å (bite)	S34, Å (bite)	PL S1,[b] Å	PL S2, Å	PL S3, Å	PL S4, Å	PL Pb, Å	PL$_1$∧PL$_2$,[c] Å	PbS(sec),[d] Å	S(pr)−Pb−S(sec),[e] deg
C═C(CN)$_2$	4.81	3.79	3.79	4.81	2.97	2.97	0.00	0.00	0.00	0.00	1.58	79.6	3.47 3.47 3.46 3.46	167
NCC═CCN	3.98	4.11	3.58	5.61	3.43	3.44	0.50	−0.62	0.69	−0.55	−1.23	95.6	3.61	174
C═C(CN)$_2$	3.86	4.03	3.83	5.53	3.04	3.07	−0.48	0.51	−0.52	0.49	1.39	91.3	3.35 3.70	165
CN(CH$_2$)$_4$	4.78	3.87	3.87	4.99	2.98	2.98	−0.06	0.14	−0.10	0.03	1.55	77.7	3.48 3.48 3.28 3.28	152
CN(CH$_3$)$_2$	4.42	3.81	3.81	4.42	2.97	2.97	−0.20	0.20	−0.20	0.20	1.48	79.1	3.36 3.36	168
CN-*i*-Pr$_2$	4.05	3.84	3.89	5.33	2.92	2.94	−0.38	0.38	−0.38	0.38	1.39	83.0	3.56 3.53	173
CNEt$_2$	4.11	3.70	4.03	5.35	2.99	2.95	0.36	−0.33	0.33	−0.36	−1.49	84.6	3.44 3.55	154
P(OEt)$_2$	4.06	3.74	3.77	5.62	3.35	3.36	0.41	−0.41	0.41	−0.41	−1.48	88.2	3.47 3.48 3.00[f] 3.04[f]	151
P(O-*i*-Bu)$_2$	4.00	3.87	4.54	5.76	3.31	3.29	0.80	−0.64	0.54	−0.71	−1.22	86.8	3.44 3.60	149
P(OPh)$_2$	4.03	3.77	4.79	5.87	3.33	3.31	0.83	−0.59	0.45	−0.69	−1.31	88.3	3.12 3.49	155
COEt	4.17	4.16	3.77	5.40	2.98	2.94	0.35	−0.39	0.42	−0.37	−1.43	82.3	3.32 3.37 3.49 3.65	158
COCH$_3$	4.27	4.10	4.10	5.45	3.07	3.06	0.53	−0.53	0.53	−0.53	−1.59	89.8	3.02 3.02	180

[a] S_{ij} denotes the separation between the atoms S*i* and S*j*. [b] PL denotes the least-squares plane made by the atoms S1, S2, S3, and S4; PL S represents the relative distance to the S atom. [c] PL$_1$ and PL$_2$ are the chelating planes S1−Pb−S2 and S3−Pb−S4. The dihedral angle between these two planes is reported. [d] Denotes Pb−S(secondary) lengths. [e] Denotes the maximum S(primary)−Pb−S(secondary) bond angle. [f] Pb−O bonds. [g] For consistency with other structures, S1′ = S3 and S2′ = S4. [h] In a recent article by I. Haiduc[13] *et al.*, dithiophosphinato−Pb complexes, (R$_2$PS$_2$)$_2$Pb, were discussed, and so this family of compounds is not treated in this table.

Pb separation of 3.87 Å: the same as that observed in the title compound. Hoffman has calculated, using molecular orbital techniques for the two solid PbO crystalline modifications, a weak covalent Pb−Pb bonding interaction.[36] In contrast, PbS[37] is a cubic (NaCl-type) structure with a Pb−S distance of 2.97 Å and a stereochemically inactive lone pair; therefore, it is not pertinent to our discussion.

In order to rationalize the geometry and effective coordination number of Pb, we analyze similar structures for metal−metal bonding. (*n*-Propyldithiocarbamato)silver(I)[38] shows Ag−Ag bonds of 2.905(5), 3.199(6), and 3.446(5) Å. This species is a hexamer with the metal atoms occupying the central part and the alkyl groups shielding the hexanuclear unit; thus this geometry is dissimilar from that of our compound. In PbS$_4$ structures (see Table 4), the title compound, Hummel-2,[21] and Hummel-3[22] are the only examples with Pb−Pb lengths shorter than 4.04 Å. The compound Hummel-1 does not show Pb−Pb interaction as the separation between the metals is 4.07 Å. Hummel-1 and Hummel-3 differ only by the cation used, K$^+$

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(37) Wells, A. F. *Structural Inorganic Chemistry*; Clarendon Press: Oxford, England, 1962; p 527.

(38) Hesse, R.; Nilson, R. *Acta Chem. Scand.* **1969**, *23*, 825.

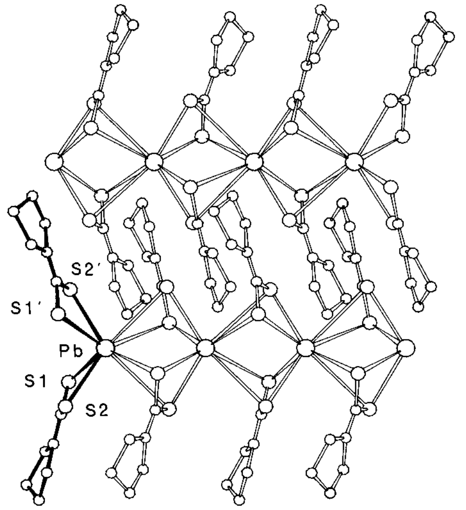

Figure 2. The polymeric crystal structure along *c* composed of two antiparallel and centrosymmetric chains. The shortest separation between the Pb atoms in different chains is 9.952(1) Å. Filled bonds indicate all of the atoms shown in Figure 1. Pb atoms on the bottom of the figure have coordinates $^{1}/_{4}$, $^{1}/_{4}$, z with $z = 0.58529$; 1.08529; 1.58529 and 2.08529. Those on top are $-^{1}/_{4}$, $-^{1}/_{4}$, z with $z = 0.41471$; 0.91471; 1.41471 and 1.91471.

and $AsPh_4^+$, respectively. The presence of the bulky cation in Hummel-3 induces a stronger approach between metal-containing anion units (the Pb−S(sec) lengths in Hummel-3 are shorter than in Hummel-1). This feature is certainly uncommon, and whether these short Pb···Pb distances imply bonding has not been discussed.[21,22] Structural analysis of PbS_4 compounds in Table 4 helps us to address this question later.

Data in Table 4 are ordered according to decreasing angle S1−Pb−S3 for each family (Hummel compounds, carbamates, phosphates, and xanthates). Also angle S1−Pb−S3 < S2−Pb−S4. Generally, Pb−S1 and Pb−S3 are the shortest of the four primary Pb−S bonds. We have calculated the least squares plane of the S1−S2−S3−S4 group of atoms and the relative deviation of each sulfur atom and the Pb atom from the plane. The table also includes a column describing "secondary" Pb−S interactions. In addition, large angles of S(pr)−Pb−S(sec) are reported since these angles help in identifying trends in the coordination geometry. We also report the dihedral angles between the chelating planes.

From Table 4, we can see the following trends:

1. The most obvious correlation is that the bite angles (S1−Pb−S2 and S3−Pb−S4) depend on the atom that links both S atoms. Thus for C, there is a range of 61.3° (for C−OEt) to 66.8° (in $C{=}C(CN)_2$, Hummel-3), while for P, the range of the bite angle is 65.6−73.1°. Bite distances S1···S2 (S12) and S3···S4 (S34) show a range for C of 2.92−3.07 Å and, for P, of 3.31−3.35 Å.

2. The geometry of the rectangular base of the pyramid is such that, the smaller the S1−Pb−S3 angle, the wider the S2−Pb−S4 angle. If these two angles are equal, then there is no deviation of the sulfur atoms from the plane of the base (Hummel-1). In contrast, $Pb(S_2P(O\text{-}i\text{-}Bu)_2)_2$ has the greatest difference between these two angles[27] and shows the largest deviations for the sulfur atoms. Concomitantly, the distance of the least squares plane to Pb becomes shorter (it is 1.22 Å for the latter case and 1.58 Å in Hummel-1), thus demonstrating that as Pb approaches the base, there is a stronger deformation of the rectangular base.

3. The decreasing S1−Pb−S3 angle is generally associated with an increasing dihedral angle between the planes of the two bite angles (S1−Pb−S2 and S3−Pb−S4).

4. Equal S1−Pb−S3 and S2−Pb−S4 angles are associated with equal Pb−S(pr) distances (Hummel-1). However, equal Pb−S(pr) bond distances do not imply equal S1−Pb−S3 and S2−Pb−S4 angles as seen in our case (111.2°, 119.2°).

5. Although xanthates show greater pyramidal deformation than carbamates, the range of deformation as shown by S1−Pb−S3 and S2−Pb−S4 angles is larger in carbamates (111.2−96.2° and 119.2−138.6°, respectively) than for xanthates (98.2−90.3° and 136.7−137.6°, respectively). Since the volume of carbamates is larger than for the equivalent xanthates, one could imagine that the role of the substituent might be understood in terms of occupation of space. However, the change of S1−Pb−S3 and S2−Pb−S4 in dithiocarbamates shows no such trend, as the sequence of pyramidal deformation is $X = CN(CH_3)_2 < CN\text{-}i\text{-}Pr_2 < CNEt_2$.

6. Among carbamates, phosphates, and xanthates, the greatest deformation of the pyramid is observed for phosphate derivatives as indicated by the range of S1−Pb−S3 (94.1−91.0°) or S2−Pb−S4 (138.2−156.2°). The base of the pyramid shows greater deviation of the S atoms from planarity.

In addition, the following features in Table 4 are noted. In a highly symmetric system as Hummel-1, the metal shows four equal primary bonds (Pb−S1, Pb−S2, Pb−S3, Pb−S4) plus four equal secondary weaker bonds (Pb−S5, Pb−S6, Pb−S7, Pb−S8). In this system, the Pb lone pair then can be considered to be located on the prismatic half of the polyhedron containing the secondary bonds and acting to push the weaker bound sulfur atoms away. Our compound is also highly symmetric (all Pb−S(pr) bonds are equal) but less so than Hummel-1, as a closing of S1−Pb−S3 and a widening of S2−Pb−S4 is found (our angles are 111.2(1) and 119.2(1)°, while for Hummel-1 they are 113°). In addition, the four equal secondary bonds in Hummel-1 (3.47 Å) are split in our compound into two couples at 3.48 and 3.28 Å from the metal. A closer approach of two of the secondary S atoms in our case induces higher deformation of the Pb polyhedron. In Hummel-1, the primary and secondary S atoms bonded to the Pb atom are eclipsed while our compound with distorted square antiprism geometry (Figure S1) has the two groups staggered.

Table 4 shows that, in the other dithiocarbamates, fewer secondary bonds are present and so the CN becomes smaller, to primarily octahedral geometry. Three of these compounds ((dimethyl-, diisopropyl-, and diethyldithiocarbamato)lead(II)) show more deformation in comparison with Hummel-1 and the title compound; this is in keeping with the trend described earlier. Also the shortening of the Pb−S primary bonds in the three latter dithiocarbamates is to be noted. The dimethyldithiocarbamate species is characterized by an eclipsed geometry and a shortening of the Pb−S secondary bonds, 3.36 Å; the diethyldithiocarbamate compound has a similar structure which shows lengthening of these Pb−S secondary bonds (3.44 and 3.55 Å). The octahedron is more deformed since the four S atoms lying in between Pb atoms are not coplanar as in the dimethyl compound. Hummel-1 and the three dithiocarbamates (the title compound and the dimethyl- and diethyl complexes) have the stereochemically active Pb lone pair directed toward the next Pb atom of the linear chain and are polymeric. In bis(isopropyldithiocarbamato)lead(II) the metal is still surrounded by six S atoms associated with four primary and two secondary Pb−S bonds. The increasing deformation of the four-sided pyramid in this case is also accompanied by the loss of linearity among Pb atoms as each metal receives secondary bonds from different units and the angle Pb···Pb···Pb is 157°. In addition, the lone pair is not directed toward the next Pb atom but rather is in between the two Pb−S secondary bonds.

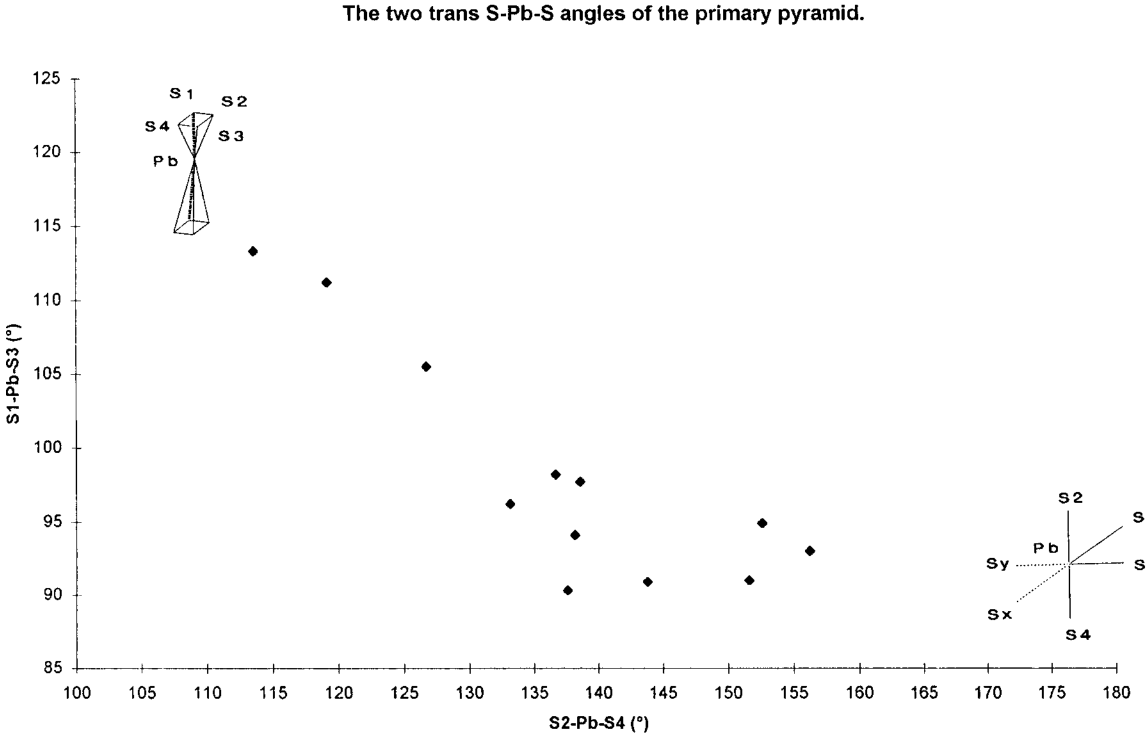

Figure 3. Conformational pathway from a pyramidal four-sided PbS_4 moiety toward an octahedral system (data taken from Table 4).

A parallel trend is seen in the case of phosphates where CN tends to decrease as the structure becomes more deformed. Higher coordination number (CN = 8) is present for a very distorted system (X = $P(OEt)_2$), but in addition to two Pb−S secondary bonds, two weak Pb−O bonds are present. Nonetheless, a decrease in the CN for phosphates is found in X = $P(O$-*i*-$Bu)_2$ and X = $P(OPh)_2$ species; this results in increased deformation of the PbS_4 moeity. Dithiophosphates have been discussed recently by I. Haiduc[13] along with dithiophosphinates; therefore, no further discussion will be given here.

As mentioned above, xanthates have more deformed PbS_4 pyramids and somewhat resemble the trend shown by the phosphates. High CN exists in ethyl xanthate with two couples of secondary Pb−S bonds from two different Pb units. The nonbonding Pb···Pb···Pb angle is 68°, and the Pb lone pair is stereochemically active as it is in between these two couples. Methyl xanthate is unique because its octahedral arrangement contains Pb−S bonds from the next unit of the same order as the primary bonds, 3.02 and 3.01 Å, respectively. This is the most symmetrical octahedron found in the literature for this family of polymers as there is no significant distortion from 90° in the S−Pb−S *cis*-octahedral angles. It also was concluded that the lone pair is stereochemically inactive and the deviation of S−Pb−S angle of 137.6(2)° from 180° was related to the restricted bite distance of the xanthate ligand.[29]

The series of compounds described by Hummel and coworkers deserves special attention because in addition to the highly symmetric Hummel-1 (which is an anion crystallized as the potassium salt, $K_2[Pb(S_2C{=}C(CN)_2)_2]$) other species, where the cation is changed, show interesting features. Hummel-1 has the anion displayed as a polymeric chain with the cation K^+ arranged on the sides of the chain so that neutralization of the electric charge is sufficiently reached. Hummel-3 is a dinuclear complex, $[AsPh_4]_2[Pb(S_2C{=}C(CN)_2)_2]$, probably because the bulky cation $AsPh_4^+$ cannot pack in a similar efficient manner as the K^+. The dinuclear arrangement therefore may be a way to avoid a buildup of large negative charge in the Pb anionic species. Thus, replacing K^+ by the large cation $AsPh_4^+$ forces the polymer to arrange as a dinuclear unit where the Pb···Pb separation is 3.72 Å. A similar dinuclear structure is obtained keeping the counterion ($AsPh_4^+$) and changing the XS_2 moiety in the compound Hummel-2, $[AsPh_4]_2[Pb(S(CN)C{=}C(CN)S)_2]$. Both $AsPh_4^+$ compounds are much more deformed than Hummel-1 (see Table 4) and show the dinuclear anion as a centrosymmetric species with the lone pair *not* in between the two Pb atoms. Thus, in Hummel-2, the metal has octahedral electronic structure defined by the Pb lone pair opposite S1 (Pb−S1 is the shortest Pb−S bond); Hummel-3 shows a similar arrangement with an additional very weak Pb−S(sec) interaction of 3.70 Å (Pb−S van der Waals[30] sum = 3.80 Å) that can be neglected. Both compounds have the Pb atom displaced off center by the stereochemically active lone pair.

These analyses on Table 4 show that the "PbS_4" moiety is a pyramidal arrangement which is subjected to progressive deformation. Using the data collected in Table 4, we represent the S1−Pb−S3 and S2−Pb−S4 bond angles in Figure 3. This figure demonstrates that deformation of the regular pyramidal shape is strongly favored (only Hummel-1, the most symmetric pyramid, and the title compound are not deformed). Because deformed pyramids approach octahedral geometry, the limit of this pathway for conformational interconversion should be S2−Pb−S4 = 180° and S1−Pb−S3 = 90°, but since the maximum value of S2−Pb−S4 is 156.2°, in $Pb(S_2P(O$-*i*-$Bu)_2)_2$, it appears that the 180° limit is not favored.[41] The stereochemically active lone pair and the chelating ligand properties probably preclude this option. On the other hand, the S1−Pb−S3 angle seems less suited for deformation as 10 of the 13 data in Figure 3 are in the range 90−98°, with three of them having values in the

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(39) Lawton, S. L.; Kokotailo, G. T. *Inorg. Chem.* **1972**, *11*, 363.

(40) Bharadwaj, P. K.; Arbuckle, B. W.; Musker, W. K. *Inorg. Chim. Acta* **1988**, *142*, 243.

(41) In formulating Table 4, we did not consider the compounds bis(isopropyldithiophosphato)lead(II)[39] and (dipropyldithiocarbamato)lead(II).[40] Reference 39 has a pentagonal bipyramidal electronic geometry with the Pb lone pair occupying an equatorial position; it is not octahedral. Reference 40 is a tetramer that shows two 5-coordinate Pb atoms with a bridging carbamate linking the two metal centers. Both compounds do not fit the trend shown in Figure 3.

range 90.3−91.0°, that is, typical for regular octahedral *cis*-bond angles.

Conclusion

From analyses of $Pb(XS_2)_2$ polymeric species (for a given family of ligands), we have found that increasing deformation in the PbS_4 primary pyramidal moiety is associated with the following:

1. loss of linearity of the polymer, and even breakup of the polymer chain (in the case of ionic species, the counterion effect must be considered; for example, less distorted PbS_4 units yield polymeric systems, as in the title compound, although not all polymers are composed of undistorted species); 2. decreasing CN; 3. the Pb lone pair shifting away from the next Pb atom in the polynuclear complex; 4. shortening of some Pb−S primary bonds; 5. shortening of some Pb−S secondary bonds. These effects combine to show an interconversion toward primarily octahedral geometry as shown in Figure 3.

Further, a remarkable variation in coordination geometries arises from a decrease in the coordination number of lead: besides the several distorted octahedral species shown in Figure 3, a pentagonal bipyramidal configuration[39] is found. The Pb lone pair appears to be of great importance in determining the geometry of these compounds. In our case, this lone pair is directed toward the next Pb unit, but in ref 39 it is in the equatorial plane of the bipyramid, and in ref 22 it occupies one octahedral position, whereas in ref 29 it is stereochemically inactive.

The effects of peripheral changes in the ligand are responsible for a large variety of Pb configurations as already noted by Haiduc[13] et al. on lead dithiophosphinate and dithiophosphate structures. This result is a compromise between an efficient use of space in the crystal (packing forces) and the tendency of lead to have different coordination numbers. Harrison et al. concluded that, for Pb(II) complexes containing *O,O′*-di-R-dithiophosphate ligands,[27] with small substituents (R = Et, *i*-Pr), 8-coordination is achieved via formation of chain structures, while for sterically demanding groups (R = *i*-Bu, Ph), dimeric octahedral species predominate. This does not seem to apply to dithiocarbamates: the pyrrolidine substituent in our complex stabilizes a polymeric species that is more symmetric than those obtained for smaller groups such as dimethyl-[23] and diethyldithiocarbamate.[25]

In summary, compounds of the type $Pb(XS_2)_2$ in the literature do not show Pb···Pb bonding. As a marked difference between primary (2.89 Å) and secondary Pb−S bond lengths (3.28 and 3.48 Å) is found in our compound, complete donation of the Pb lone pair to the next metal is excluded. Support for weak or partial metal interaction among the lead atoms in our compound comes from the molecular orbital calculations of Hoffman on α−PbO, where the Pb−Pb separation is equal to that found in the title compound, 3.89 Å.

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Supporting Information Available: Tables S1−S4 containing full geometrical data, anisotropic displacement parameters, hydrogen coordinates, and full crystallographic data and Figure S1 depicting a PbS_8 staggered and distorted square antiprism moiety (6 pages). Ordering information is given on any current masthead page. Calculated and experimental structure factors can be obtained by writing to the authors (e-mail: Rossi@Vassar.edu).

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