The Crystal and Molecular Structure of Di-isothiocyanatolead(II)–Dimethyl Sulphoxide (1/2)

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The title compound has four $Pb[NCS]_2·2Me_2SO$ units in a cell with a = 14.876(3), b = 16.373(7), c = 5.866(1) Å, belonging to space group $P2_1ab$. The absence of a centre of symmetry is supported by the morphology of the crystal. The structure has been refined by the heavy-atom method to R 6.5% for 1 331 observed diffractometer intensities. The lead atom is six co-ordinate with a distorted octahedral co-ordination sphere consisting of two nitrogen atoms [Pb–N 2.45(2), 2.42(5) Å; N–Pb–N 80.2(14)°] and two sulphur atoms [Pb–S 2.19(2) Å; S–Pb–S 121.7(4)°] nearly in a plane with the lead atom, while two oxygen atoms [Pb–O 2.50(2), 2.45(3) Å] of co-ordinated dimethyl sulphoxide molecules subtend an angle of 160.1° at lead(II). The structure is explained in terms of an irregular pentagonal bipyramidal arrangement of six bonded atoms and one lone electron-pair, with the latter directed towards a pentagonal corner between the two sulphur atoms. The 80° angles in the pentagonal plane are attributed to non-bonded repulsions of ligand atoms over-riding the repulsive effect of the lone pair which, however, is thought to be strong enough to distort the O–Pb–O angle from 180 to 160°. Each $Pb[NCS]_2$ unit behaves like a bidentate ligand with a large ' bite ' [S ··· S 4.74(2) Å] to form a planar polymeric chain which extends parallel to c.

CRYSTAL and molecular structures are known for only two complexes of lead(II) thiocyanate, namely dithiocyanatolead(II)–1,7,10,16-tetraoxa-4,14-diazacyclo-octadecane (1/1),[1] $Pb[SCN]_2·C_{12}H_{26}N_2O_4$, and dithiocyanatolead(II)–(4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-[8.8.8]hexacosane) (1/1),[2] $Pb[SCN]_2·C_{18}H_{36}N_2O_6$. The first structure is a hexagonal bipyramid with the cyclic $C_{12}H_{26}N_2O_4$ ligand forming an equatorial plane around lead and the two thiocyanate groups bound through sulphur in the axial positions. In the second structure, lead occupies the cavity of the $C_{18}H_{36}N_2O_6$ bicyclic ligand with one thiocyanate group bonding to lead through sulphur and the other through nitrogen, forming a dodecahedron around lead. For three other complexes, dithiocyanatolead(II)–thiourea (1/4),[3] dithiocyanatolead(II)–2,2′-bipyridine (1/1),[4] and dithiocyanatolead(II)–4,4′-bipyridine (2/1),[4] only i.r. spectra are available. In each case the authors propose that the thiocyanate groups are bound to lead through sulphur atoms.

The crystal and molecular structure of di-isothiocyanatolead(II)–dimethyl sulphoxide (1/2), $Pb[NCS]_2·2dmso$ (dmso = Me_2SO) reported in this paper is part of a series of lead(II) thiocyanate complexes with various ligands now being studied with the purpose of determining the mode of bonding of the thiocyanate group to lead, and whether or not the lone electron-pair in the valence shell of lead(II) is stereochemically important. The crystal structure of the parent $Pb[SCN]_2$ shows no evidence of a localized lone pair.[5] However, the stereochemical importance of the lone pair has been reported in other Pb^{II} compounds such as: $Pb[SCN]_2·C_{12}H_{26}N_2O_4$;[1] lead(II) OO'-di-isopropyl phosphorodithioate,[6] $Pb[(OPr^i)_2PS_2]_2$; tetraethylammonium tris(O-ethyl thiocarbonato)plumbate(II),[7] $[NEt_4][Pb(EtOCS_2)_3]$; and D-penicillaminatolead(II),[8] $Pb[SCMe_2CH(NH_2)CO_2]$.

EXPERIMENTAL

Crystal Data.—$C_6H_{12}N_2O_2PbS_4$, Orthorhombic, M = 479.5, a = 14.876(3), b = 16.373(7), c = 5.866(1) Å, U = 1 428.8 Å^3, D_m = 2.2(1) g cm^{-3} (by flotation), Z = 4, D_c = 2.23 g cm^{-3}, $F(000)$ = 896. Space group $P2_1ab$. Mo-K_α radiation, λ = 0.709 26 Å; μ(Mo-K_α) = 121.6 cm^{-1}.

Data Collection.—Large light pink crystals were obtained when $Pb[SCN]_2$ (3.3 g, 10 mmol) was dissolved in dimethyl sulphoxide (50 ml) at 40 °C and the solution was set aside for several days until crystallization took place. The crystals were filtered off and dried with suction in a nitrogen-filled dry-box (Found: C, 15.2; H, 3.35; N, 5.7; Pb, 42.8. Calc. for $C_6H_{12}N_2O_2PbS_4$: C, 15.02; H, 2.50; N, 5.84; Pb, 43.21%). The complex decomposes slowly to a white powder on exposure to the atmosphere at room temperature, and rapidly at 105—107 °C in a capillary tube filled and sealed under nitrogen.

A detailed examination of crystal morphology revealed that crystals consist of the monohedron {200}, the two dihedra {120} and {$\bar{1}$20}, and the parallelodron {020}. Elongated crystals are biterminated by the parallelohedron {001}. The monohedron {200} was observed on each of the six crystals we measured with the two-circle goniometer and on about twenty others examined under a microscope. This morphology allows us to conclude[9] that there is no centre of symmetry in the crystal and that the point group is $2mm$. These observations are a striking example of the usefulness of morphology in crystal structure determinations.

The diffraction aspect $P{*}ab$ was determined from Weissenberg and rotation films taken with nickel-filtered Cu-K_α radiation, λ = 1.541 8 Å, and from precession photographs

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[1] B. Metz and R. Weiss, *Acta Cryst.*, 1973, **B29**, 1088.

[2] B. Metz and R. Weiss, *Inorg. Chem.*, 1974, **13**, 2094.

[3] D. M. Czakis-Sulkowska and B. Kuznik, *Roczniki Chem.*, 1969, **43**, 1353.

[4] D. M. Czakis-Sulkowska, J. Radwanska-Doczekalska, and A. Gorecka, *Roczniki Chem.*, 1973, **47**, 2345.

[5] J. A. A. Mokuolu and J. C. Speakman, *Acta Cryst.*, 1975, **B31**, 172.

[6] S. L. Lawton and G. T. Kokotailo, *Inorg. Chem.*, 1972, **11**, 363.

[7] W. G. Mumme and G. Winter, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 505.

[8] H. C. Freeman, G. N. Stevens, and I. F. Taylor, *J.C.S. Chem. Comm.*, 1974, 366.

[9] F. C. Phillips, ' Introduction to Crystallography,' The University Press, Glasgow, 4th edn., 1971, p. 3; F. D. Bloss, ' Crystallography and Crystal Chemistry,' Holt, Rinehart, and Winston, New York, 1971, p. 354; D. McKie and C. McKie, ' Crystalline Solids,' Thomas Nelson and Sons, London, 1974, p. 365.

taken with zirconium-filtered Mo-K_α radiation, $\lambda = 0.709\,26$ Å. These photographs showed systematic extinctions: $h00$ and $h0l$ for h odd, $hk0$ for k odd, and $0k0$ for $k \neq 4n$. The last one was recognized as a structural extinction superimposed on the space group extinction $0k0$ absent for k odd which would permit reflections such as $0(4n \pm 2)0$. Of the two space groups $Pmab(D_{2h}^{11})$ and $P2_1ab(C_{2v}^{5})$ consistent with X-ray extinctions, the first centrosymmetric one is ruled out by morphology. In the hemihedry, the general position is $4(a)$ so that Pb is not required to have any particular site symmetry. By selecting $y \simeq 0.125$ for Pb and remembering that Pb represents 37% of the total scattering power, the structural extinction observed for $0k0$ is accounted for.

The crystal used for data collection simulated a rhombic prism, 1.45 mm long and 0.15 mm thick with parallel faces $(120) \cdot (\bar{1}\bar{2}0)$ and $(\bar{1}20) \cdot (1\bar{2}0)$. It was held in a Lindemann glass capillary tube sealed under nitrogen and mounted with the [001] elongation of the crystal making an angle of *ca.* 10° with the rotation axis of the Eulerian cradle.

Intensity measurements were collected with a Picker four-circle automated diffractometer using graphite-monochromated Mo-K_α radiation, $\lambda = 0.710\,7$ Å. The orientation, cell dimensions, and standard deviations were obtained by least-squares fit of χ, ϕ, ω, and 2θ values for twelve general reflections with $2\theta > 35°$. The setting angles were then generated and arranged so as to minimize slewing time.

Intensity data were collected using the θ—2θ scan method, scanning from 0.6° below α_1 to 0.6° above α_2 at $\frac{1}{2}°$ 2θ min^{-1}, and the background was measured for 20 s at each end of the scan. The intensities of three standard reflections remained constant throughout, showing only the deviations from the mean predicted from counting statistics. A total of 1 786 independent reflections was measured in the range $5° \leqslant 2\theta \leqslant 60°$; 1 331 (covering data in the octants hkl and $\bar{h}kl$) having $I > 2\sigma(I)$ were classed as observed. Intensities were corrected for Lorentz and polarization factors by means of the DATRDN program of X-ray 70.[10] The optimum thickness,[11] $t_{\text{opt.}}$ 0.16 mm, was only slightly larger than the thinnest dimension of the crystal. Unfortunately smaller crystals could not be isolated, nor could large crystals be shaped due to their brittleness and tendency to decompose during extended physical handling. The crystal was mounted with its length nearly along the goniometer axis to minimize absorption. An acceptable R of 6.5% was obtained without applying absorption corrections. Atomic scattering factors for neutral atoms were taken from Hanson *et al.*[12] and corrections were made for anomalous dispersion of lead and sulphur.[13]

Structure Determination and Refinement.—The structure was solved by the heavy-atom method after a three-dimensional Patterson function gave the locations of the lead atoms. A series of three-dimensional electron-density and electron-density-difference functions, followed by isotropic full-matrix least-squares refinements of two cycles, led to all other atomic positions except those of hydrogen atoms. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2$. Convergence was reached at R 0.104 for the 1 331 observed reflections used in the refinement. The structure was further refined by full-matrix least-squares methods using anisotropic temperature factors for all atoms but hydrogen and with the 'less-than' reflections, for which $|F_c| > |F_o|$, requiring three cycles for final convergence. The refinement terminated with an unweighted residual R 0.065 for the 1 331 observed reflections; whereas the residual of the 'less than' reflections alone was 18.1%.

RESULTS AND DISCUSSION

Atomic co-ordinates are listed in Table 1, anisotropic temperature factors in Table 2, and bond distances and angles in Table 3. Structure factor amplitudes and phase angles are listed in Supplementary Publication No. SUP 21869 (6 pp., 1 microfiche).* In order to compute the stereoscopic views of the structures (Figures 1 and 2), the low negative U_{22} of C(1) was replaced by a small positive value (0.001).

TABLE 1

Fractional atomic co-ordinates * ($\times 10^3$) with standard deviations in parentheses

Atom	x	y	z
Pb	0	127(1)	176(1)
S(1)	134(1)	287(1)	−053(2)
S(2)	365(1)	037(1)	050(2)
S(3)	166(1)	049(1)	442(3)
S(4)	333(1)	296(1)	440(3)
O(1)	056(2)	269(1)	100(4)
O(2)	443(2)	511(2)	107(4)
C(1)	162(4)	388(1)	−005(7)
C(2)	086(4)	304(3)	672(8)
C(3)	420(3)	063(3)	307(6)
C(4)	130(3)	078(2)	683(6)
C(5)	335(2)	142(3)	−015(8)
C(6)	375(3)	328(3)	689(9)
N(1)	100(2)	100(3)	853(6)
N(2)	400(3)	340(2)	865(8)

* Co-ordinates calculated from x,y,z; $\frac{1}{2} + x, -y, -z$; $\frac{1}{2} + x, \frac{1}{2} - y, z$; $x, \frac{1}{2} + y, -z$.

TABLE 2

Heavy-atom anisotropic temperature factors ($\times 10^3$ for Pb, $\times 10^2$ for all other atoms) *

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{14}
Pb	50(1)	35(1)	40(1)	−4(1)	3(1)	−7(5)
S(1)	4(1)	4(1)	7(1)	−1(1)	1(1)	−1(1)
S(2)	4(1)	4(1)	7(1)	−1(1)	2(1)	−1(1)
S(3)	7(1)	9(1)	8(1)	1(1)	2(1)	−2(1)
S(4)	6(1)	14(1)	6(1)	−2(1)	1(1)	−1(1)
O(1)	8(2)	3(1)	6(1)	−2(1)	1(1)	−1(1)
O(2)	6(2)	7(2)	6(2)	1(1)	1(2)	1(1)
C(1)	22(6)	−4(1)	13(4)	1(1)	−3(4)	1(1)
C(2)	10(4)	9(3)	8(3)	−2(3)	−4(3)	1(3)
C(3)	7(3)	10(3)	3(2)	1(3)	1(2)	−1(2)
C(4)	4(2)	4(1)	4(2)	−1(2)	2(2)	−1(1)
C(5)	1(2)	12(3)	12(4)	2(2)	−3(2)	−2(3)
C(6)	3(2)	7(3)	8(3)	1(2)	3(2)	1(2)
N(1)	5(2)	9(2)	7(2)	1(2)	1(2)	1(2)
N(2)	13(4)	4(2)	9(3)	1(2)	−2(3)	1(2)

* The form of the thermal ellipsoid is $\exp[-2\pi^2(\sum_{i=1}^{3}\sum_{j=1}^{3} h_i h_j a_i^* a_j^* U_{ij})]$.

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue (items less than 10 pp. are supplied as full-size copies).

[10] J. M. Stewart, F. A. Kundell, and J. C. Baldwin, 'The X-Ray 70 System,' University of Maryland, College Park, Maryland.

[11] G. H. Stout and L. H. Jenson, 'X-ray Structure Determination,' The MacMillan Company, New York, 1968, p. 68.

[12] H. P. Hanson, L. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, 1964, **17**, 1040.

[13] 'International Tables for X-ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962, p. 215.

The crystal structure consists of infinite chains of $Pb[NCS]_2{\cdot}2dmso$ units in which the S and N atoms of each thiocyanate group bridge neighbouring lead atoms lying parallel to the *c* axis of the crystal (Figure 1). In fact, the $Pb[NCS]_2$ units form a planar polymeric chain with two dimethyl sulphoxide molecules co-ordinated to each lead atom. Chain axes are parallel but their planes are *ca.* 90° to each other, and sufficiently far apart so that only weak van der Waals interactions occur between them. Each of the four chains passing through the unit cell has a local two-fold axis, but the positions of these chains are not compatible with the centric space group *Pmab*. Lead atoms are six co-ordinate (Figure 2) with two nitrogen atoms [N(1) and N(2)] and two sulphur atoms [S(4) and S(3)] in a plane, as evident from the sum of the angles (360.8°) being almost exactly 360°. Two oxygen atoms [O(1) and O(2)] complete the distorted octahedral configuration by subtending an angle of 160.1(8)° at the lead atom.

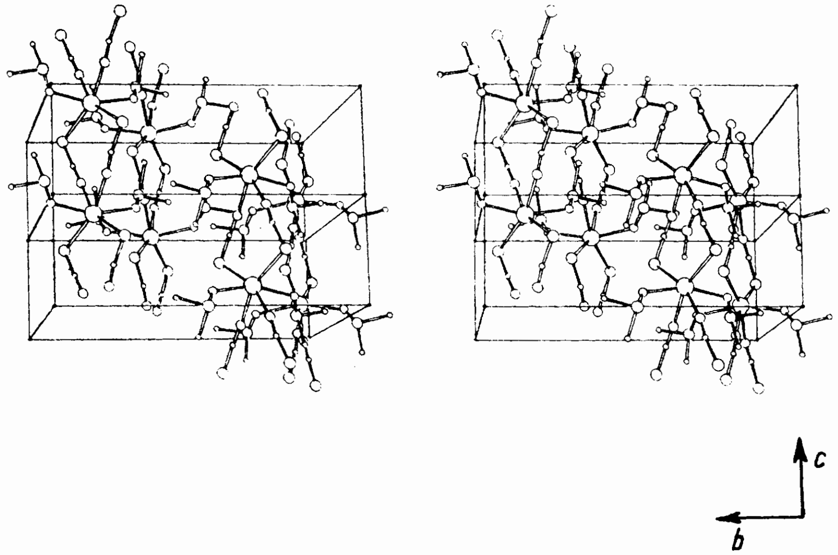

FIGURE 1 ORTEP diagram [14] showing stereoscopically the packing in two unit cells along *c*

TABLE 3

Bond lengths and interatomic approaches (Å) and bond angles (°) with estimated standard deviations in parentheses

Pb–N(1)	2.45(2)	S(1)–C(2)	1.78(3)
Pb–N(2)	2.42(5)	S(2)–O(2)	1.53(3)
Pb–O(1)	2.50(2)	S(2)–C(3)	1.76(4)
Pb–O(2)	2.45(3)	S(2)–C(5)	1.81(5)
Pb–S(3)	3.19(2)	C(4)–N(1)	1.15(5)
Pb–S(4)	3.19(2)	C(4)–S(3)	1.59(4)
S(1)–O(1)	1.50(3)	C(6)–N(2)	1.12(7)
S(1)–C(1)	1.72(2)	C(6)–S(4)	1.67(5)
Pb · · · Pb	5.87(1)	N(1) · · · S(3)	3.69(4)
N(1) · · · N(2)	3.14(6)	N(2) · · · S(4)	3.59(5)
S(3) · · · S(4)	4.74(2)	O(1) · · · S(3)	4.43(3)
N(1) · · · O(1)	3.32(5)	O(1) · · · S(4)	4.00(3)
N(1) · · · O(2)	3.19(5)	O(2) · · · S(3)	3.99(3)
N(2) · · · O(1)	3.23(5)	O(2) · · · S(4)	4.35(3)
N(2) · · · O(2)	3.20(5)		
N(1)–Pb–N(2)	80.2(14)	N(2)–C(6)–S(4)	171.6(41)
O(1)–Pb–O(2)	160.1(8)	O(1)–S(1)–C(1)	106.7(20)
S(3)–Pb–S(4)	121.7(4)	O(1)–S(1)–C(2)	105.4(22)
N(1)–Pb–O(1)	80.1(12)	O(2)–S(2)–C(3)	103.7(19)
N(1)–Pb–O(2)	85.2(12)	O(2)–S(2)–C(5)	108.9(17)
N(2)–Pb–O(1)	82.1(11)	Pb–N(1)–C(4)	163.8(32)
N(2)–Pb–O(2)	82.3(10)	Pb–N(2)–C(6)	161.0(41)
N(1)–Pb–S(3)	80.5(9)	Pb–O(1)–S(1)	123.7(13)
N(2)–Pb–S(4)	78.4(13)	Pb–O(2)–S(2)	128.2(15)
S(3)–Pb–O(1)	101.5(7)	Pb–S(3)–C(4′)	93.0(14)
S(3)–Pb–O(2)	89.1(7)	Pb–S(4)–C(6′)	90.7(16)
S(4)–Pb–O(1)	88.6(7)	C(1)–S(1)–C(2)	95.9(22)
S(4)–Pb–O(2)	100.7(7)	C(3)–S(2)–C(5)	93.7(23)
N(1)–C(4)–S(3)	177.0(35)		

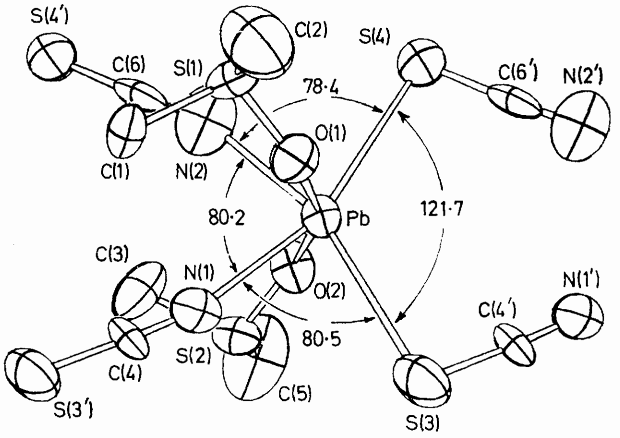

FIGURE 2 ORTEP plot of molecular structure (including NCS from the next unit) showing the atom labelling and the equatorial plane

The presence of appreciable covalent forces is evident from the comparisons of bond distances made in Table 4. Note that the average Pb–N distance of 2.43 Å in $Pb[NCS]_2{\cdot}2dmso$ is only *ca.* 0.1 Å longer than the sum of the covalent radii, and from 0.2 to 0.3 Å shorter than in $Pb[SCN]_2$ and $Pb[SCN]_2{\cdot}C_{18}H_{36}N_2O_6$, both of which are described as having predominantly ionic lead–

[14] C. K. Johnson, ' ORTEP,' Oak Ridge National Laboratory Report ORNL–3794, 1965.

thiocyanate bonds.[2,5] Our average Pb–N distance is also shorter than most distances reported between lead and the nitrogen atoms of co-ordinated ligands (Table 4). Although the average Pb–O distance of 2.48 Å is 0.17 Å longer than the calculated covalent bond distance, it is shorter by 0.25 and 0.50 Å than those in $Pb[SCN]_2\cdot C_{12}H_{26}N_2O_4$ [1] and $Pb[SCN]_2\cdot C_{18}H_{36}N_2O_6$,[2] respectively, both of which have oxygen atoms co-ordinated to a central Pb^{2+} ion. The fact that the average Pb–SCN distance of 3.19 Å in $Pb[NCS]_2\cdot$2dmso is longer than calculated covalent (2.60 Å) and ionic (2.98 Å) bond distances, and almost the same as in $Pb[SCN]_2$, suggests that Pb–SCN donor–acceptor linkages are as weak in the complex as they are thought to be in the parent $Pb[SCN]_2$.[5] Nevertheless, Pb–SCN bonds are strong enough in the complex to account for its insolubility in non-polar solvents, low solubility in polar solvents, and failure to melt sharply.

TABLE 4

Comparison of bond lengths (Å)

Compound	Pb–NCS	Pb–SCN	Pb–O	Pb–N (Ligand)	Pb–S (Ligand)	Ref.
$Pb[NCS]_2\cdot$2dmso	2,45, 2.42	3.19, 3.19	2.50, 2.45			Present work
$Pb[SCN]_2$	2.687, 2.781	2.996, 3.135				5
$Pb[SCN]_2\cdot C_{12}H_{26}N_2O_4$		2.894	2.787, 2.879	2.751		1
$Pb[SCN]_2\cdot C_{18}H_{36}N_2O_6$	2.642	3.121	2.734, 2.829, 2.805 2.980, 2.729, 2.732			2
$Pb[OPr^iPS_2]_2$					2.761, 2.772, 2.985, 3.027, 3.232, 3.175	6
$[NEt_4][Pb(EtOCS_2)_3]$					2.95, 3.13, 2.84, 3.12, 3.68	7
$Pb[SCMe_2CH(NH_2)CO_2]$			2.444, 2.768	2.444	2.716, 3.160, 3.480	8
$Pb(SSCOEt)_2$					2.742, 2.785, 2.838, 2.950	15
$Pb(SSCOBu)_2$					2.82, 2.77, 2.76, 3.03	16
$Pb(SSCOPr)_2\cdot C_5H_5N$				2.55	2.833, 2.896, 2.722, 3.057	17
Sum of covalent radii *	2.33	2.60	2.31			18
Pb^{2+} + ligand van der Waals radii	2.73	2.98	2.68			19, 20
Sum of van der Waals radii	3.55	3.8	3.5			19

* Covalent radii of Pb from ref. 5.

The octahedral geometry around lead is appreciably distorted, as evident from the O(1)–Pb–O(2) angle being 160.1(8)° rather than 180° and the [Pb,N(1),N(2),S(3),S(4)] framework, although planar, being far from a perfect square (Figure 2). One explanation of these distortions is that they are due to the presence of a lone electron-pair in a pentagonal bipyramidal valence-shell-electron-pair-repulsion model.[21] There are six ligand atoms and one valence lone pair around the central lead(II) atom, with the lone pair directed toward a corner of the pentagon located between the sulphur atoms. This location of the lone pair is strongly supported by the in-plane S(3)–Pb–S(4) angle of 121.7(4)° and the axial angle O(1)–Pb–O(2) of 160.1(8)° directed away from the S(3)–Pb–S(4) region. However, the 80° angles in the pentagonal plane are not adequately explained by electron-pair repulsions. This model has also been used to account for the distorted octahedral structures reported, on the basis of *X*-ray data, for $Pb[(OPr^i)PS_2]_2$ [6] and $Pb[SCMe_2CH(NH_2)CO_2]$.[8] In the case of $[NEt_4][Pb(EtOCS_2)_3]$ [7] preliminary *X*-ray data showed a structure based on a pentagonal bipyramidal arrangement of six sulphur atoms and one lone pair around lead, but with the lone pair in an axial rather than an equatorial position.

An alternative explanation of the geometry around lead in $Pb[NCS]_2\cdot$2dmso can be based on a consideration of the non-bonded repulsions of ligand atoms in the co-ordination sphere and the bidentate 'bite' of the sulphur atoms in each $Pb[NCS]_2$ unit of the polymeric chain. All interatomic approaches of the nitrogen and oxygen atoms surrounding the lead atom are either equal to or slightly greater than the sum of the van der Waals radii involved (3.1 Å for N $\cdots$ N and 3.0 Å for N $\cdots$ O).[18] Interatomic approaches of nitrogen and sulphur atoms in the co-ordination sphere are also close to the sum of their van der Waals radii (3.4 Å),[18] but O $\cdots$ S distances are *ca.* 1.0—1.5 Å greater than the sum of their van der Waals radii (3.3 Å).[18] These observations suggest that the three *ca.* 80° angles in the equatorial plane (Figure 2) result primarily from a packing of ligand atoms which minimizes the repulsions between them. These angles are 8° larger than the idealized 72° expected from the seven electron-pair, pentagonal bipyramid model previously discussed. In fact these angles would be less than 72° if (lone-pair)–(bond-pair) repulsions were stronger than (bond-pair)–(bond-pair),[21] and if atomic crowding were not important within the co-ordination sphere.

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[15] H. Hagihara and S. Yamashita, *Acta Cryst.*, 1966, **21**, 350.

[16] H. Hagihara, Y. Watanabe, and S. Yamashita, *Acta Cryst.*, 1968, **B24**, 960.

[17] H. Hagihara, N. Yoshida, and Y. Watanabe, *Acta Cryst.*, 1969, **B25**, 1775.

[18] J. E. Huheey, 'Inorganic Chemistry,' Harper and Row, New York, 1972, p. 184.

[19] A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.

[20] R. D. Shannon and C. T. Prewitt, *Acta Cryst.*, 1970, **B26**, 1076.

[21] R. J. Gillespie, 'Molecular Geometry,' Van Nostrand, London, 1972, p. 71.

The S(3)–Pb–S(4) angle of 121.7(4)° is undoubtedly due to the large bidentate ' bite ' of the bridging sulphur atoms arising from Pb–NCS linkages which are bent at the nitrogen atom [Pb–N(1)–C(4) = 163.8(32)°]. In methyl- and phenyl-tin(IV) isothiocyanates, Sn–NCS linkages with bridging sulphur atoms are also bent at nitrogen to a similar amount.[22] Only preliminary *X*-ray data[23] are available for triphenyl-lead(IV) isothiocyanate; these show that its molecular structure [Pb–N 2.44(2); Pb–S′ 2.90(1); Pb–C 2.20(3) Å; Pb–NCS 172(2); Pb–S′C′N 96(1); N–Pb–S′ 174.9(6)°] is an infinite zig-zag chain similar to that of the corresponding tin compound.[22]

It is also noteworthy that the Pb–S–C angles in $Pb[NCS]_2\cdot$dmso [93.0(14) and 90.7(16)°] are close to the 90° angle characteristic of many *S*-bonded thiocyanate transition metal complexes,[24] as well as of methyl- and phenyl-tin(IV) isothiocyanates.[22] Such 90° angles have been associated with ' head-on overlap between one of the filled π_2 orbitals [of thiocyanate] and a σ-type acceptor orbital on the metal '[24] following molecular orbital descriptions of the thiocyanate ion.[25]

The only observation which the alternative proposal does not account for is the O(1)–Pb–O(2) angle of 160.1(8)°. Since the interatomic approaches between oxygen and sulphur atoms, averaging 4.2 Å, are appreciably longer than the sums of their van der Waals radii (3.3 Å),[18] there is no obvious reason for the observed distortion away from the thiocyanate bridging region unless the lone electron-pair of Pb^{II} were localized in that space. The degree of localization need only be sufficient to produce enough (lone-pair)–(bond-pair) repulsion to distort the O(1)–Pb–O(2) angle until non-bonded repulsions between oxygen and nitrogen atoms come into play and counteract the lone-pair repulsive effect. The possibility of non-bonded repulsions between ligand atoms over-riding the stereochemical effect of a lone pair has already been recognized by Gillespie[21] and applied recently by Lawton *et al.*[26] to account for the molecular structure of the tris-bidentate complex bismuth(III) *OO′*-di-isopropyl phosphorodithioate, $Bi[(OPr^i)_2PS_2]_3$. Perhaps the large bidentate ' bite ' of bridging $Pb[NCS]_2$ units is the factor which provides the space for localization of the lone pair thereby allowing a more even distribution of electron pairs in the co-ordination sphere of lead(II) and a minimization of the energy. Non-bonded repulsions are probably the main effects responsible for the 80° angles in the [Pb,N(1),N(2),S(3),S(4)] plane. Thus, a combination of both explanations gives a plausible account of the structure.

The expected linear geometry of the thiocyanate group is observed and the C–N and C–S distances are in the ranges of distances reported for a variety of thiocyanato- and isothiocyanato-complexes.[24] The fact that C–N and C–S distances are the same in $Pb[SCN]_2$[5] and $Pb[NCS]_2\cdot2$dmso suggests that no major changes have occurred in the thiocyanate units of the latter.

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[22] Y. M. Chow, *Inorg. Chem.*, 1970, **9**, 794; R. A. Forder and G. M. Sheldrick, *J. Organometallic Chem.*, 1970, **21**, 115; **22**, 611; A. M. Domingos and G. M. Sheldrick, *ibid.*, 1974, **67**, 257.

[23] P. H. Bird, personal communication.

[24] J. L. Burmeister in ' The Chemistry and Biochemistry of Thiocyanic Acid and Its Derivatives,' ed. A. A. Newman, Academic Press, London, 1975, p. 68.

[25] L. DiSipio, L. Oleari, and S. DeMichelis, *Co-ordination Chem. Rev.*, 1966, **1**, 7; D. F. Gutterman and H. B. Gray, *J. Amer. Chem. Soc.*, 1971, **93**, 3364.

[26] S. L. Lawton, C. J. Fuhrmeister, R. G. Haas, C. S. Jarman, jun., and F. G. Lohmeyer, *Inorg. Chem.*, 1974, **13**, 135.