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THE CRYSTAL AND MOLECULAR STRUCTURES OF DIPHENYLDI(ISOTHIOCYANATO)-BIS(HEXAMETHYLPHOSPHORAMIDE)-TIN(IV) AND -LEAD(IV)

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Summary

The compound diphenyldi(isothiocyanato)bis(hexamethylphosphoramide)tin(IV) is triclinic, space group $P\bar{1}$, a 9.832(3), b 11.401(12), c 16.735(17) Å, α 89.46(7), β 76.59(6), γ 85.81(5)° and $Z = 2$. The structure was refined on 3741 nonzero Mo-$K_{\bar{\alpha}}$ reflections collected at 173 K to $R = 0.036$. The analogous lead(IV) compound is also triclinic, space group $P\bar{1}$, a 10.031(1), b 12.427(2), c 15.292(5) Å, α 86.97(2), β 77.78(2), γ 85.66(1)°, $Z = 2$. This structure was refined on 2886 Mo-$K_{\bar{\alpha}}$ reflections collected at room temperature to $R = 0.031$. These two compounds are isomorphous with unit cells containing two symmetry-independent $Ph_2M(NCS)_2 \cdot 2HMPA$ (M = Sn or Pb; HMPA = hexamethylphosphoramide) molecules occupying crystallographic inversion centers. The two molecules have very similar geometries, with an *all-trans* arrangement of ligands around the metal.

Introduction

Diphenyltin dihalides Ph_2SnX_2 are known to form 1 : 2 complexes with various monodentate Lewis bases [1,2]. These compounds usually possess octahedral coordination, but there are no strict rules to predict which of the possible stereoisomers is formed. The phenyl groups show some preference for a mutually *trans* arrangement [3], but this is not strictly obeyed [4–6]. Similar considerations seem to hold for the corresponding Ph_2PbX_2 systems [7–9], although sound structural data are scarce for lead(IV) systems. Furthermore, that structural information from tin(IV) compounds should not be lightly transferred to lead(IV) systems is exemplified by the different structures obtained for the Ph_2MCl_2 compounds: Ph_2SnCl_2 is best described as monomeric and tetrahedral [10], whereas Ph_2PbCl_2 has a polymeric

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arrangement of *trans*-Ph_2PbCl_4 units with all chlorine atoms bridging the octahedra to form infinite chains [11].

The two complexes discussed in the present report are addition compounds of the pseudohalides $Ph_2M(NCS)_2$. In the only thiocyanate-containing tin(IV) complex for which X-ray results are available, the pseudohalide group is monodentate and *N*-bonded [6]. That the sulphur atom in this group does not lack affinity for tin is shown by the polymeric structures of $Me_3Sn(NCS)$ [12], $Ph_3Sn(NCS)$ [13] and $Me_2Sn(NCS)_2$ [14] which use bridging thiocyanate groups. No crystallographic studies appear to have been reported as yet on Pb^{IV} thiocyanate compounds.

Vibrational spectra, particularly when both infrared and Raman data are available, can also provide stereochemical information although solid-state results must be interpreted with caution. In benzene, differing Raman and infrared ν(CN) values for $Ph_2Sn(NCS)_2 \cdot 2HMPA$ [2] and $Ph_2Pb(NCS)_2 \cdot 2HMPA$ [9] were taken as consistent with a *trans*-$M(NCS)_2$ structure for the adducts in solution. However, solid-state data show some differences for the two adducts. For $Ph_2Sn(NCS)_2 \cdot 2HMPA$ [2], although infrared and Raman ν(CN) values coincide, differing ν(CS) frequencies (783 and 825 cm^{-1}, respectively) and the one strong infrared absorption assigned to ν(Sn–NCS) which does not completely coincide with the Raman peak, were taken to indicate that the *trans*-structure is retained in the solid state. For the lead analogue, the doubling of Raman peaks (ν(CN) 2052, 2043 cm^{-1}; ν(CS) 808, 797 cm^{-1}) with coincident infrared values (2040 and 795 cm^{-1}, respectively) [8] together with the splitting of ν(Pb–NCS) (Raman 155, 135 cm^{-1}, infrared 160, 145 cm^{-1}) [9], suggested a *cis*-$Pb(NCS)_2$ arrangement in the solid state, although crystal lattice effects might account for the splitting. It is the need to remove this ambiguity which has prompted this X-ray diffraction study of $Ph_2Pb(NCS)_2 \cdot 2HMPA$. The structure of the tin analogue has also been determined both to assist in the solution of the lead adduct structure and to provide more comparative data on analogous tin and lead systems.

Experimental

Crystallographic data for the tin compound

$C_{26}H_{46}N_8O_2P_2S_2Sn$, FW = 747.46. Triclinic, $P\bar{1}$, a 9.832(3), b 11.401(12), c 16.735(17) Å, α 89.46(7), β 76.59(6), γ 85.81(5)°, V 1819.8 Å^3, D_{cal} 1.364 g cm^{-3}, $Z = 2$, λ(Mo-$K_{\bar{\alpha}}$) 0.71069 Å (graphite monochromator), μ(Mo-K_α) 9.33 cm^{-1}, T 173 K.

Crystals suitable for X-ray work were obtained by slow evaporation at room temperature of a solution of an earlier sample [2] in CH_2Cl_2 (m.p. 230–232° C). A specimen of dimensions $0.23 \times 0.41 \times 0.12$ mm^3 was used for the X-ray study. It was mounted on an Enraf–Nonius CAD-4 diffractometer and a set of 25 reflections randomly distributed in the Laue sphere was generated by the search procedure. After centring, the indexing routine yielded the above triclinic reduced cell, which was checked by recording long-exposure oscillation photographs about each of the axes. The Niggli coefficients clearly indicated that no symmetry higher than triclinic was present. Therefore, the compound had to belong to one of the triclinic space groups, $P1$ or $P\bar{1}$.

A set of 4716 unique hkl, $hk\bar{l}$, $h\bar{k}l$ and $h\bar{k}\bar{l}$ reflections ($2\theta \leqslant 45°$) was collected as described elsewhere [15]. The fluctuation of the six standard reflections remained within ±2.8% during the experiment. The 3741 reflections with $I \geqslant 3\sigma(I)$ were retained for structure determination. These data were corrected for the Lorentz effect, polarization and absorption (Gaussian integration, grid $8 \times 8 \times 8$, transmission range: 0.21–0.76).

The structure was solved in space group $P\bar{1}$ by the heavy-atom method and refined on $|F_o|$ by full-matrix least-squares in the early stages. The Patterson map showed a single strong peak at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, which would normally correspond to two tin atoms in general position at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ and $(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$. Attempts to solve the structure from this starting point led to apparent disorder of all the atoms in the unit cell. However, the structure could be solved when the tin atoms were positioned on crystallographic inversion centers $1d$ $(\frac{1}{2}, 0, 0)$ and $1g$ $(0, \frac{1}{2}, \frac{1}{2})$. The difference Fourier (ΔF) map phased on tin showed pseudo-symmetry as expected, since the phasing model was I-centered. Several peaks had the correct height and distance from tin to be assigned to phosphorus atoms. One of these positions was arbitrarily selected. From this point, the remaining non-hydrogen atoms were progressively located by the usual procedure of structure factor and ΔF map calculations.

Isotropic refinement of all non-hydrogen atoms converged to $R = \Sigma \| F_o| - |F_c\| / \Sigma |F_o| = 0.089$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{\frac{1}{2}} = 0.099$. After a few cycles in which the Sn, P and S atoms were anisotropically refined, a ΔF map revealed the positions of all the phenyl hydrogens and of at least one hydrogen for each methyl group. The phenyl and methyl hydrogens were fixed at idealized positons (C–H 0.95 Å, B 4.0 Å^2 (phenyl), 5.0 Å^2 (methyl)). The hydrogen parameters were not refined, but the coordinates were recalculated after each least-squares cycle. The final cycles of refinement were carried out by block-diagonal least-squares. Anisotropic refinement of all non-hydrogen atoms converged to $R = 0.036$, $R_w = 0.053$ and a goodness-of-fit ratio of 2.06 for 373 parameters varied. The highest residual peak and deepest valley in the final ΔF map were +0.85 and −0.77 e/Å^3, respectively, both near a tin atom. The general background was below $\pm |0.5|$ e/Å^3. There was no apparent disorder that could indicate that the space group might be $P1$ instead of $P\bar{1}$.

Crystallographic data for the lead compound

$C_{26}H_{46}N_8O_2P_2S_2Pb$ FW = 835.97. Triclinic, $P\bar{1}$, a 10.031(1), b 12.427(2), c 15.292(5) Å. α 86.97(2), β 77.78(2), γ 85.66(1)°, V 1856.4 Å^3, D_{cal} 1.496 g cm^{-3}, $Z = 2$, λ(Mo-$K_{\bar{\alpha}}$) 0.71069 Å (graphite monochromator), μ(Mo-K_α) 48.05 cm^{-1}, T 293 K.

Crystals suitable for X-ray work were selected from those prepared earlier [8] and recrystallized from benzene (m.p. 228–230 °C). A specimen of dimensions $0.11 \times 0.33 \times 0.40$ mm^3 was used. The cell dimensions and intensity data were obtained as described above. A set of 5145 unique hkl, $h\bar{k}l$, $hk\bar{l}$ and $h\bar{k}\bar{l}$ reflections ($2\theta \leqslant 46°$, fluctuations of standards $< \pm 5.6\%$) was collected, of which 2886 ($I > 3\sigma(I)$) were retained for structure determination. These data were corrected for the Lorentz effect, polarization and absorption (Gaussian integration, grid $10 \times 10 \times 10$, transmission range = 0.23–0.45).

The procedure used above revealed that the lead and tin complexes were actually isomorphous. Refinement (anisotropic for lead, isotropic for the remaining atoms) by full-matrix least-squares converged to $R = 0.084$ and $R_w = 0.090$. Anisotropic refinement of all non-hydrogen atoms led to $R = 0.036$ and $R_w = 0.041$. All hydrogen atoms were introduced at idealized positions. Block-diagonal least-squares were used for the last cycles of refinement. At convergence, $R = 0.031$ and $R_w = 0.036$, whereas the goodness-of-fit ratio was 1.27 for 373 parameters varied. In the final ΔF map, the highest residual peaks ($\pm|0.35\text{–}0.45|$ e/Å^{-3}) were located 1.0–1.2 Å from Pb, S or P. The general background was below ± 0.25 e/Å^{-3}.

TABLE 1

REFINED COORDINATES ($\times 10^4$) AND EQUIVALENT TEMPERATURE FACTORS ($\times 10^3$) [a]

Atom	x	y	z	U_{eq}
$Sn(C_6H_5)_2(NCS)_2 \cdot 2HMPA$				
Sn(1)	5000	0	0	33
Sn(2)	0	5000	5000	30
P(1)	7199(2)	1980(1)	708(1)	37
P(2)	−2522(1)	7205(1)	4686(1)	33
S(1)	7108(2)	−3183(2)	1531(1)	63
S(2)	−2344(2)	1768(2)	3985(1)	64
O(1)	6364(4)	1314(3)	246(2)	44
O(2)	−1921(3)	6018(3)	4903(2)	35
N(10)	6120(6)	−1442(5)	572(3)	53
N(11)	7689(5)	1173(4)	1420(3)	49
N(12)	8567(5)	2417(5)	32(3)	51
N(13)	6271(5)	3152(4)	1152(3)	49
N(20)	−933(6)	3451(4)	4594(3)	53
N(21)	−3640(5)	6951(4)	4121(3)	43
N(22)	−1479(5)	8134(4)	4140(3)	37
N(23)	−3192(5)	7908(4)	5565(3)	41
C(10)	6529(5)	−2176(5)	958(3)	37
C(11)	6685(8)	556(6)	2030(4)	58
C(12)	9074(8)	1231(8)	1625(5)	78
C(13)	9418(7)	1583(7)	−587(5)	68
C(14)	9251(9)	3491(7)	141(5)	79
C(15)	5527(8)	3936(6)	656(5)	66
C(16)	6390(9)	3645(7)	1939(4)	72
C(20)	−1536(5)	2765(5)	4336(3)	32
C(21)	−4020(7)	5767(6)	3965(5)	62
C(22)	−4528(7)	7905(6)	3879(4)	55
C(23)	−532(6)	8795(5)	4509(4)	45
C(24)	−1069(7)	8133(5)	3223(4)	48
C(25)	−3770(6)	9149(5)	5607(4)	41
C(26)	−3880(6)	7216(5)	6270(4)	45
C(31)	6402(5)	−352(6)	−1161(3)	38
C(32)	6974(6)	−1511(6)	−1401(4)	51
C(33)	7877(7)	−1725(7)	−2165(4)	59
C(34)	8245(7)	−831(7)	−2718(4)	65
C(35)	7700(7)	307(6)	−2505(4)	59
C(36)	6795(6)	553(6)	−1728(4)	49
C(41)	−903(6)	4661(5)	6269(3)	38
C(42)	−300(7)	4905(6)	6931(3)	48
C(43)	−869(8)	4690(7)	7728(4)	63
C(44)	−2099(8)	4124(7)	7940(4)	68
C(45)	−2766(6)	3851(6)	7332(4)	56
C(46)	−2185(6)	4080(5)	6508(4)	46

TABLE 1 (continued)

Atom	x	y	z	U_{eq}
$Pb(C_6H_5)_2(NCS)_2 \cdot 2HMPA$				
Pb(1)	5000	0	0	86
Pb(2)	0	5000	5000	77
P(1)	7219(2)	1840(2)	833(2)	81
P(2)	−2677(2)	6924(2)	4368(2)	78
S(1)	7066(5)	−3604(3)	772(3)	198
S(2)	−1807(4)	1460(3)	4468(3)	185
O(1)	6335(6)	1283(5)	399(4)	119
O(2)	−1978(5)	5983(4)	4735(4)	93
N(10)	6403(8)	−1466(6)	533(5)	122
N(11)	7657(8)	1147(7)	1642(5)	128
N(12)	8572(8)	2139(8)	139(6)	145
N(13)	6439(9)	2957(6)	1236(6)	131
N(20)	−1173(8)	3421(6)	4856(6)	125
N(21)	−3801(7)	6513(6)	3892(5)	114
N(22)	−1774(7)	7699(7)	3639(5)	122
N(23)	−3352(8)	7738(6)	5163(5)	113
C(10)	6653(9)	−2357(7)	629(6)	99
C(11)	6756(14)	536(11)	2272(8)	183
C(12)	9116(14)	1094(15)	1763(10)	239
C(13)	9269(13)	1455(15)	−500(10)	235
C(14)	9044(21)	3157(22)	−6(22)	521
C(15)	5493(14)	3572(10)	838(13)	230
C(16)	6760(28)	3437(14)	1974(11)	370
C(20)	−1430(8)	2593(7)	4682(6)	88
C(21)	−4036(14)	5429(11)	3817(10)	192
C(22)	−4753(12)	7275(11)	3514(10)	190
C(23)	−796(12)	8367(12)	3898(11)	224
C(24)	−1331(15)	7374(13)	2735(9)	215
C(25)	−3917(13)	8856(8)	5027(10)	181
C(26)	−3888(14)	7292(10)	6064(8)	171
C(31)	6339(8)	−39(7)	−1327(6)	94
C(32)	6952(9)	−1037(8)	−1585(7)	118
C(33)	7794(10)	−1078(9)	−2435(7)	134
C(34)	7966(10)	−197(11)	−2985(7)	144
C(35)	7350(10)	775(10)	−2720(6)	141
C(36)	6528(10)	887(8)	−1862(7)	123
C(41)	−870(8)	5017(7)	6394(6)	101
C(42)	−353(11)	5531(9)	6992(7)	137
C(43)	−1007(13)	5522(12)	7898(7)	177
C(44)	−2133(11)	4976(11)	8176(7)	161
C(45)	−2674(11)	4464(12)	7596(8)	161
C(46)	−1992(10)	4472(8)	6695(6)	118

[a] Estimated standard deviations in parentheses.

The refined parameters for the two compounds are listed in Table 1. The scattering factors used were from standard sources [16]. Anomalous dispersion was taken into account for Pb, Sn, P and S [17].

Results and discussion

Complete structure determination shows that $Ph_2Sn(NCS)_2 \cdot 2HMPA$ and $Ph_2Pb(NCS)_2 \cdot 2HMPA$ are isomorphous, even though they show large differences

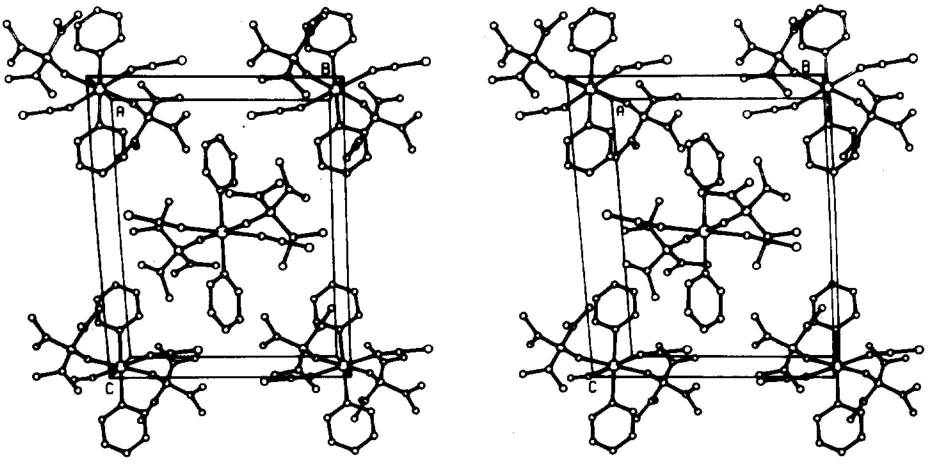

Fig. 1. Stereoview of the unit cell of $Ph_2Pb(NCS)_2 \cdot 2HMPA$. The atoms represented by spheres of arbitrary size, can be identified from Fig. 2.

in their *b* and *c* cell edges. In both cases, the $P\bar{1}$ unit cell contains two molecules. However, in contrast to the usual case of two equivalent molecules related by the crystallographic inversion centre, the present unit cell contains two symmetry-independent molecules, each sitting on a crystallographic inversion centre (Fig. 1). Therefore, the molecules possess C_i point symmetry. These two molecules, shown for the lead compound in Fig. 2, are very similar. They both have the *all-trans* ligand distribution around the roughly octahedrally coordinated metal center. Deviations from the ideal 90° angles are all small ($< 3.4°$ for Sn, $< 4.4°$ for Pb), whereas the 180° angles are imposed by crystallographic symmetry. The HMPA ligands are bonded through oxygen as expected, and the thiocyanate groups are unidentate *N*-bonded.

The tin–phenyl distances (mean 2.138, σ 0.006 Å) compare well with those found for other *trans*-Ph_2Sn units in the octahedrally coordinated compounds $Ph_2SnCl_2(DMSO)_2$ (mean 2.125(8) Å) [18] and Ph_2SnCl_2(bipy) (mean 2.152(8) Å) [19]. Binding of the unidentate NCS^- groups takes place with a Sn–N–C angle of 170.1(5)°, identical for the two independent molecules. The Sn–N distances (2.242(6) and 2.229(5) Å) are slightly less than for the seven-coordinate $Me_2Sn(NCS)_2$(terpy) (2.282(4) Å) [20], but longer than for the bridging group in $Me_2Sn(NCS)_2$ (2.139(13) Å) [14]. Comparison with the other known Sn^{IV} thiocyanate compounds [3] is not possible because of the larger errors in these studies.

As to the HMPA molecule, it is found to be oxygen-bonded as anticipated, with a tin–oxygen distance of 2.184(4) Å, corresponding to the average distance reported for a series of tin-HMPA complexes [21]. The Sn–O–P angles are 158.9(3) and 144.5(2)°. For the above series of Sn^{IV} compounds, it was in the 147.6–164.3° range. This angle is probably not a restricted parameter and could be readily changed by steric constraints.

This structure further confirms the generalization that in hexacoordinate diorgano-tin complexes with monodentate ligands, the organic groups occupy *trans* positions. It is hard to know the contribution of electronic factors to this situation,

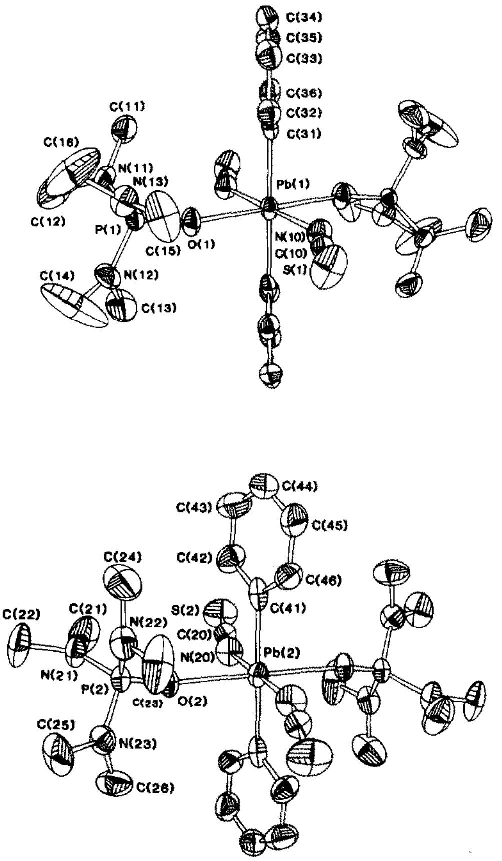

Fig. 2. ORTEP drawings of the two independent $Ph_2Pb(NCS)_2 \cdot 2HMPA$ molecules. The Pb atoms occupy crystallographic inversion centers. Ellipsoids correspond to 30% probability.

but for $Ph_2Sn(NCS)_2 \cdot 2HMPA$, the phenyl groups are most likely the substituents imposing the greatest steric constraint, tending to avoid being at 90°. The isothiocyanato ligands are end-on coordinated and occupy very little space at the metal surface, whereas the wide range of acceptable M–O–P angles with HMPA and the presumably free rotation about the Sn–O and P–O bonds imparts a flexibility to this ligand which is expected to adjust to neighbouring steric constraints. Therefore, it is the phenyl rings that impose the greatest steric requirements. However, there are exceptions. In the bipyridyl complex $Ph_2Sn(NCS)_2 \cdot$ bipy, the Ph groups occupy *cis* positions in the distorted octahedron [6]. It is interesting that this geometry is attained at the expense of some Sn–Ph bond strength (Sn–C 2.183(5) and 2.161(5) Å) and is favoured by the presence of the NCS and bipy groups, leaving more space at the metal surface for the phenyl rings and giving a Ph–Sn–Ph angle of 106.3(2)°. The same behavior is also observed for the diethyldithiocarbamate complex $Ph_2SnS_2CNEt_2$ (Sn–C 2.180(17) and 2.173(13) Å, Ph–Sn–Ph 101.4(6)°) [5]. The *trans,trans* arrangement in the equatorial plane is more difficult to rationalize. Two varieties of the related $Ph_2SnCl_2(DMSO)_2$ compound show a *cis,cis*-$(DMSO)_2SnCl_2$

TABLE 2

INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) FOR $M(C_6H_5)_2(NCS)_2 \cdot 2HMPA$ [a]

	M = Sn	M = Pb
M(1)–O(1)	2.185(4)	2.341(6)
M(1)–N(10)	2.242(6)	2.430(8)
M(1)–C(31)	2.128(5)	2.184(9)
N(10)–C(10)	1.158(8)	1.126(12)
C(10)–S(1)	1.643(6)	1.589(10)
O(1)–P(1)	1.498(4)	1.448(7)
M(2)–O(2)	2.182(4)	2.348(5)
M(2)–N(20)	2.229(5)	2.406(8)
M(2)–C(41)	2.147(6)	2.126(10)
N(20)–C(20)	1.159(8)	1.138(11)
C(20)–S(2)	1.621(6)	1.554(9)
O(2)–P(2)	1.512(4)	1.465(6)
O(1)–M(1)–N(10)	92.6(2)	91.2(2)
O(1)–M(1)–C(31)	89.3(2)	89.3(3)
O(1)–M(1)–O(1) [b]	180.0	180.0
O(1)–M(1)–N(10) [b]	87.4(2)	88.8(2)
O(1)–M(1)–C(31) [b]	90.7(2)	90.7(3)
N(10)–M(1)–C(31)	90.5(2)	90.5(3)
N(10)–M(1)–N(10) [b]	180.0	180.0
N(10)–M(1)–C(31) [b]	89.5(2)	89.5(3)
C(31)–M(1)–C(31) [b]	180.0	180.0
M(1)–N(10)–C(10)	170.2(5)	149.8(7)
N(10)–C(10)–S(1)	178.0(5)	177.6(9)
M(1)–O(1)–P(1)	158.9(3)	163.8(4)
O(2)–M(2)–N(20)	86.6(2)	85.6(2)
O(2)–M(2)–C(41)	90.1(2)	88.6(3)
O(2)–M(2)–O(2) [c]	180.0	180.0
O(2)–M(2)–N(20) [c]	93.4(2)	94.4(2)
O(2)–M(2)–C(41) [c]	89.9(2)	91.4(3)
N(20)–M(2)–C(41)	91.8(2)	90.8(3)
N(20)–M(2)–N(20) [c]	180.0	180.0
N(20)–M(2)–C(41) [c]	88.2(2)	89.2(3)
C(41)–M(2)–C(41) [c]	180.0	180.0
M(2)–N(20)–C(20)	170.1(5)	163.8(7)
N(20)–C(20)–S(2)	178.0(5)	178.5(8)
M(2)–O(2)–P(2)	144.5(2)	152.1(4)

[a] Estimated standard deviations in parentheses. [b] $1-x, -y, -z$. [c] $-x, 1-y, 1-z$.

arrangement [18]. This probably results from subtle balance between steric and electronic factors.

X-ray data on six-coordinate Pb^{IV} compounds remain scanty. Excepting Ph_2PbCl_2 which contains bridging chlorines [11], the compound reported here is the first example of a crystal structure for a monomeric six-coordinate organo-Pb^{IV} compound. The overall structure is the same as that of the tin complex above. Distances and angles are given in Table 2. Interestingly, whereas the Pb–O and Pb–N distances are all ~ 0.17 Å greater than the corresponding tin bonds, the length of the Pb–Ph bonds (mean 2.155 Å) is not much more than the Sn–Ph bonds (2.138 Å). This is similar to the Pb–Ph distance of 2.12(2) Å in Ph_2PbCl_2 [11] and within the range of 2.17–2.19 Å in Ph_3PbX (X = Cl, Br and OH) [22]. Probably to maintain the overall structure in spite of these irregular changes in bond lengths, several rather large changes have occurred in some of the bond angles compared with the Sn compound (Table 2). The NCS groups have appreciably changed their orientations, the Pb–N–C angles being 149.8(7) and 163.8(7)° here, whereas the Sn–N–C angles were both equal to 170.1(5). Changes in the M–O–P angles are also important: 158.9(3) and 144.5(2)° for Sn vs. 163.8(4) and 152.1(4)° for Pb.

The geometries of the substituents are normal. The individual values of distances and angles not listed in Table 2 are given in the supplementary material. In the phenyl rings, the C–C distances average 1.383 Å and the angles average 120.0°. The rings are planar within 1.8σ (0.017 Å). Departure from linearity for the thiocyanate groups is small (178.0°), and the C–N and C–S bond lengths (mean values 1.145 and 1.602 Å, respectively) are normal for *N*-bonded groups [6,14]. The following mean values for the distances and angles in HMPA are similar to those found earlier [21]: P–O 1.481, P–N 1.626, N–C 1.453 Å; O–P–N 111.0, N–P–N 107.9, P–N–C 122.1 and C–N–C 113.4°. The environment of the nitrogen atoms is roughly planar, but half of the groups show significant pyramidal distortions displacing the nitrogen atom by as much as 0.25 Å above the P–C–C plane.

The accuracy on light-atom positions for the tin compound is somewhat better than for the lead compound. One of the reasons is that the presence of heavy Pb atoms is expected to increase the standard deviations on light atom parameters, compared with those of the tin compound. However, the structure of the tin complex is also better defined because the data were collected at 173 K, whereas they were obtained at room temperature for the lead compound, resulting in much greater thermal motion in the peripheral groups of the molecule and probably mild disorder in some of the NMe_2 groups of HMPA. Attempts were made to obtain data for $Ph_2Pb(NCS)_2 \cdot 2HMPA$ at 173 K, but before this temperature was reached, a phase transition occurred, and the crystal usually broke apart. The low-temperature phase was not studied, because the original question was raised by vibrational spectra taken at room temperature. Polymorphism is probably related to conformational changes in the HMPA region. A similar case is that of $Ph_2SnCl_2 \cdot 2DMSO$, which was isolated as two forms depending on reaction conditions [18]. The structures of the molecules in these two forms differ mainly in the orientation of the SMe_2 portion of DMSO with respect to the rest of the molecule. These orientations are interconnected by changes in torsion angles about the Sn–O and O–S bonds of DMSO, and by a change in the Sn–O–S angle. The same broad range of angles can be spanned here for Pb–O–P angles and for the torsions about the Pb–O and O–P bonds. It is therefore likely that at low temperature, the stresses imposed by the rather large departure from linearity in the Pb–N–CS region are relieved by conformational or orientational change of the nearby HMPA ligand, accompanied by some reorientation of the molecules to maximize space filling.

Lastly, the fact that the tin and lead compounds are isostructural with both having *all-trans* centrosymmetric molecular structures, provides another example of the pitfalls often encountered when deducing stereochemistry for the solid state from vibrational spectra even when both Raman and infrared data are available. For $Ph_2Sn(NCS)_2 \cdot 2HMPA$, the *all-trans* solid state structure was correctly predicted since the two independent molecules do not differ sufficiently to have different ν(CN), ν(CS) or ν(Sn–NCS) values while the molecular center of symmetry causes mutual exclusion for ν(CS) and ν(Sn–NCS). In contrast, the two independent

$Ph_2Pb(NCS)_2 \cdot 2HMPA$ molecules differ enough to cause splitting of ν(CN), ν(CS) and ν(Pb–NCS) in the infrared spectrum of this compound while ν(Pb–NCS) is split in the Raman spectrum also. Unfortunately, these data are equally consistent with equivalent *cis*-$Pb(NCS)_2$ units related by a lattice center of symmetry causing the splitting and mutual exclusion observed, particularly for ν(Pb–NCS). Thus while solid state vibrational data can often demonstrate the presence of a center of symmetry, they do not always show whether this symmetry element is molecular or lattice in nature.

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References

1 A.G. Davies and P.J. Smith, in G. Wilkinson, F.G.A. Stone, and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Pergamon, Oxford, 1982, Chap. 11.
2 I. Wharf, M. Onyszchuk, D.M. Tallett, and J.M. Miller, Can. J. Spectr., 24 (1979) 123.
3 J.A. Zubieta and J.J. Zuckerman, Prog. Inorg. Chem., 24 (1978) 251; P.J. Smith, Adv. Inorg. Chem. Radiochem., 23 (1980) 1; J. Organomet. Chem. Libr., 12 (1981), 97, and references therein; Cambridge Crystallographic Database of Organics and Organometallics, National Research Council, Ottawa, Canada, August 1986.
4 M.A. Mullins and C. Curran, Inorg. Chem., 7 (1968) 2584; A.J. Crowe, R. Hill, P.J. Smith, V.G.K. Das, and J.S. Brooks, J. Organomet. Chem., 182 (1979) 345.
5 P.F. Lindley and P. Carr, J. Cryst. Mol. Struct., 4 (1974) 173.
6 E.J. Gabe, L. Prasad, Y. LePage, and F.E. Smith, Acta Crystallogr., B38 (1982) 256.
7 P.G. Harrison, in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Pergamon, Oxford, Chap. 12.
8 R. Makhija and M. Onyszchuk, J. Organomet. Chem., 135 (1977) 261.
9 I. Wharf, M. Onyszchuk, J.M. Miller, and T.R.B. Jones, J. Organomet. Chem., 190 (1980) 417.
10 P.T. Greene and R.F. Bryan, J. Chem. Soc., (A) (1971) 2549.
11 M. Mammi, V. Busetti, and A. Del Pra, Inorg. Chim. Acta, 1 (1967) 419.
12 R.A. Forder and G.M. Sheldrick, Chem. Commun., (1969) 1125; J. Organomet. Chem., 21 (1970) 115.
13 A.M. Domingos and G.M. Sheldrick, J. Organomet. Chem., 67 (1974) 257.
14 Y.M. Chow, Inorg. Chem., 9 (1970) 794. R.A. Forder and G.M. Sheldrick, J. Organomet. Chem., 22 (1970) 611.
15 F. Bélanger-Gariépy and A.L. Beauchamp, J. Am. Chem. Soc., 102 (1980) 3461.
16 D.T. Cromer and J.T. Waber, Acta Crystallogr., 18 (1965) 104; R.F. Stewart, E.R. Davidson, and W.T. Simpson, J. Chem. Phys., 42 (1965) 3175.
17 D.T. Cromer, Acta Crystallogr., 18 (1965) 17.
18 L. Coghi, M. Nardelli, C. Pelizzi, and G. Pelizzi, Gazz. Chim. Ital., 105 (1975) 1187.
19 P.G. Harrison, T.J. King, and J.A. Richards, J. Chem. Soc., Dalton Trans., (1976) 1723.
20 D.V. Naik and W.R. Scheidt, Inorg. Chem., 12 (1973) 272.
21 L.A. Aslanov, V.M. Ionov, V.M. Attiya, A.B. Permin, and V.S. Petrosyan, Zh. Strukt. Khim., 18 (1977) 1103; Engl. Transl., 876.
22 C. Glidewell and D.C. Liles, Acta Crystallogr., B34 (1978) 129; H. Preut and F. Huber, Z. Anorg. Allgem. Chem., 435 (1977) 234.