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**X-ray structural study of Ph<sub>2</sub>PbCl<sub>2</sub>(DMSO)<sub>2</sub>, Ph<sub>2</sub>PbCl<sub>2</sub>(HMPT)<sub>2</sub> and Ph<sub>3</sub>PbCl(HMPT)**

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## X-RAY STRUCTURAL STUDY OF $\text{Ph}_2\text{PbCl}_2(\text{DMSO})_2$ , $\text{Ph}_2\text{PbCl}_2(\text{HMPT})_2$ AND $\text{Ph}_3\text{PbCl}(\text{HMPT})$

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**Abstract**—An X-ray structural investigation of  $\text{Ph}_2\text{PbCl}_2(\text{DMSO})_2$  (**I**),  $\text{Ph}_2\text{PbCl}_2(\text{HMPT})_2$  (**II**) and  $\text{Ph}_3\text{PbCl}(\text{HMPT})$  (**III**) was carried out (DMSO = dimethylsulphoxide, HMPT = hexamethyltriamide phosphoric acid). Complexes **I** and **II** have octahedrally coordinated  $\text{Pb}^{\text{IV}}$ , but in **III** the coordination is trigonal-bipyramidal. Comparison with the analogous tin compounds indicates the relative shortening of Pb—C bonds and lengthening of Pb—Cl, Pb—N and Pb—O bonds. This phenomenon can be explained in terms of rehybridization of orbitals of the central atom.

In our previous work the X-ray structures of  $\text{Ph}_2\text{PbCl}_2$  complexes with nitrogen-donor ligands such as imidazole<sup>1</sup> and dipyrindine<sup>2</sup> were described and some manifestations of the mutual influence of ligands in lead(IV) complexes were discussed. As a continuation of this study, an X-ray structural investigation of organolead chloride complexes with oxygen-donor ligands,  $\text{Ph}_2\text{PbCl}_2(\text{DMSO})_2$  (**I**),  $\text{Ph}_2\text{PbCl}_2(\text{HMPT})_2$  (**II**) and  $\text{Ph}_3\text{PbCl}(\text{HMPT})$  (**III**), was carried out (DMSO = dimethylsulphoxide, HMPT = hexamethyltriamide phosphoric acid).

### EXPERIMENTAL

#### *Synthesis and crystal preparation*

$\text{Ph}_2\text{PbCl}_2\text{D}_2$  [D = DMSO (**I**) and HMPT (**II**)].  $\text{Ph}_2\text{PbCl}_2$  (0.5 g) was boiled in 25 cm<sup>3</sup> of chloroform with a three-fold excess of ligand with complete

dissolution in accordance with known procedure.<sup>3</sup> Single crystals were grown by slow cooling.

$\text{Ph}_3\text{PbCl}(\text{HMPT})$ . A five-fold excess of HMPT was added to a benzene solution of  $\text{Ph}_3\text{PbCl}$ . After evaporation single crystals were obtained.

#### *Data collection and structure determination*

For data collection a CAD-4 diffractometer (Mo- $K_\alpha$  radiation, graphite monochromator,  $\omega$ -scanning) was used. Crystal data and structure determination conditions are listed in Table 1. For structures **I** and **III**, only the independent part of the reciprocal space was investigated. In the case of structure **II** reflections in a hemisphere were collected and their intensities were averaged after correction crystal decomposition (50% loss of intensity of standard reflections). Empirical absorption corrections were made.<sup>4</sup> Coordinates of the lead atoms were determined by the Patterson method and other non-hydrogen atoms were located from Fourier and difference Fourier maps. All non-hydrogen atoms were refined anisotropically, positions of

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Table 1. Crystallographic data for I–III

	I	II	III
Compound	Ph <sub>2</sub> PbCl <sub>2</sub> (DMSO) <sub>2</sub>	Ph <sub>2</sub> PbCl <sub>2</sub> (HMPT) <sub>2</sub>	Ph <sub>3</sub> PbCl(HMPT)
Formula	C <sub>16</sub> H <sub>22</sub> Cl <sub>2</sub> O <sub>2</sub> PbS <sub>2</sub>	C <sub>24</sub> H <sub>46</sub> Cl <sub>2</sub> N <sub>6</sub> O <sub>2</sub> P <sub>2</sub> Pb	C <sub>24</sub> H <sub>33</sub> ClN <sub>3</sub> OPb
Crystal dimensions (mm)	0.15 × 0.2 × 0.25	0.15 × 0.15 × 0.4	0.25 × 0.25 × 0.3
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> (Å)	9.680(2)	11.667(3)	9.449(3)
<i>b</i> (Å)	15.944(3)	16.472(4)	15.563(4)
<i>c</i> (Å)	13.159(4)	17.403(6)	18.322(6)
$\beta$ (°)	92.89(2)	98.59(3)	93.70(2)
<i>Z</i>	4	4	4
<i>D</i> <sub>c</sub> (g cm <sup>-3</sup> )	1.927	1.588	1.614
$\mu$ (cm <sup>-1</sup> )	88.5	54.3	65.0
$\theta_{\max}$ (°)	25	25	25
Number of reflections with <i>I</i> > 3 $\sigma$ ( <i>I</i> )	2767	5416	3625
<i>R</i>	0.028	0.044	0.038
<i>R</i> <sub>w</sub>	0.032	0.049	0.043

hydrogen atoms were calculated geometrically and these atoms were used for structure factor calculations, but not refined. All calculations were performed using the SDP package.<sup>5</sup> Scattering factors were taken from the *International Tables of X-ray Crystallography*.<sup>6</sup> Full supplementary material has been deposited.

For Ph<sub>3</sub>PbCl(HMPT), parameters of the monoclinic unit cell *a* = 9.43, *b* = 15.62, *c* = 18.35 Å,  $\beta$  = 93.3° and space group *P*2<sub>1</sub>/*n* have been re-

ported (the structure determination was not carried out),<sup>7</sup> which are very close to our results.

## RESULTS AND DISCUSSION

### Structure description

Molecular structures of the investigated compounds are displayed in Figs 1–3; the important

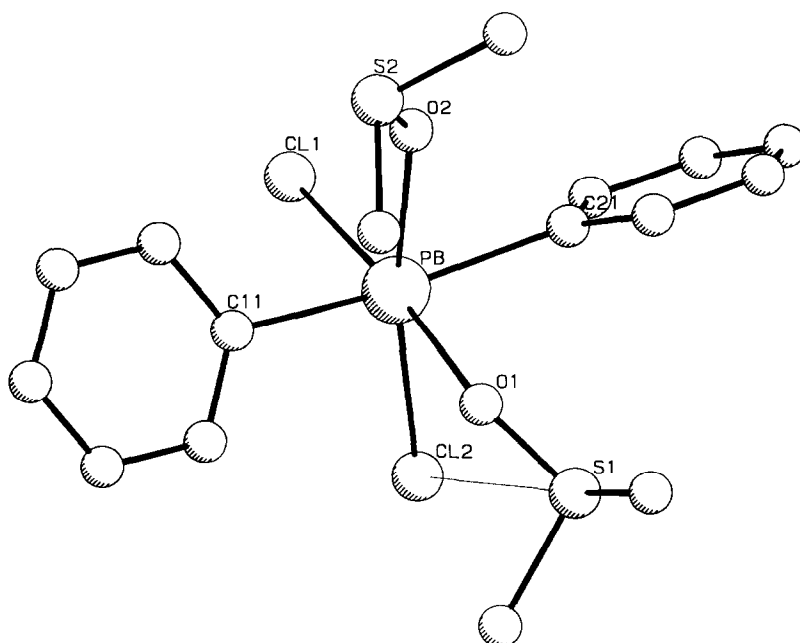


Fig. 1. A perspective view of I showing the atom labelling scheme.

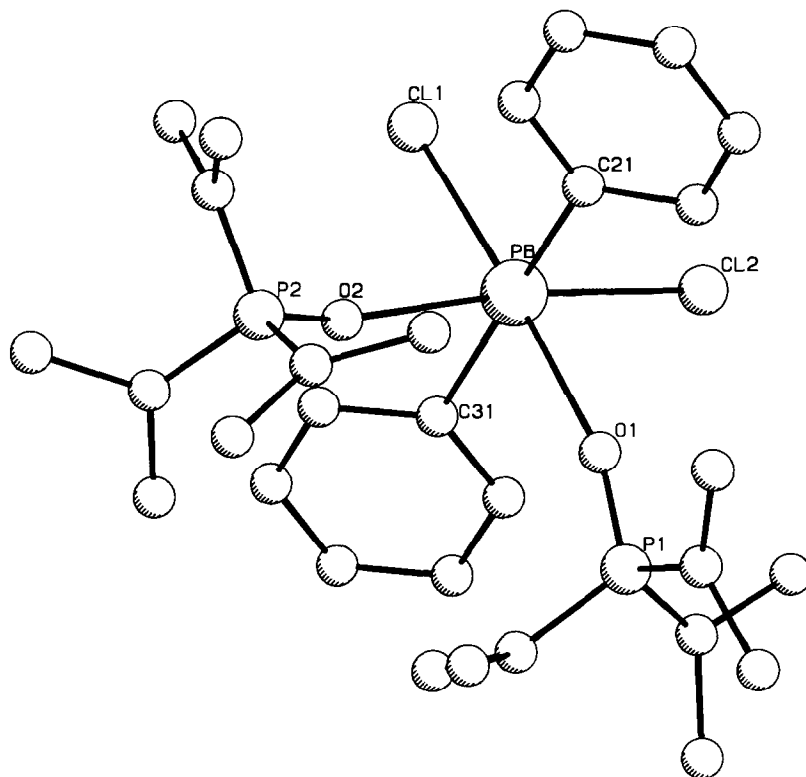


Fig. 2. A perspective view of **II** showing the atom labelling scheme.

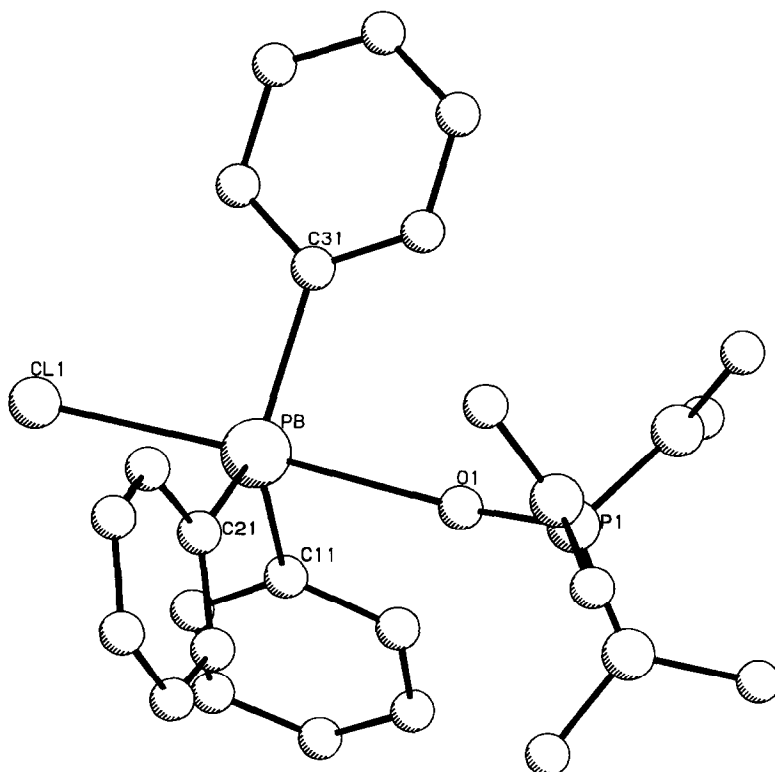


Fig. 3. A perspective view of **III** showing the atom labelling scheme.

bond lengths and angles are presented in Table 2. Contrary to  $\text{Ph}_2\text{Pb}(\text{NCS})_2(\text{HMPT})_2$ <sup>8</sup> and to  $\text{Ph}_2\text{PbCl}_2(\text{imidazole})_2$ ,<sup>1</sup> with an all-*trans* arrangement of ligands around the lead atom, in structures **I** and **II** the donor molecules DMSO and HMPT and chlorine atoms are placed *cis* to each other, with *trans*-positioned phenyl groups (the terms *cis* and *trans* will be used below with respect to the  $\text{MD}_2\text{Hal}_2$  plane). The difference in energies of *cis*- and *trans*-isomers seems to be insignificant, which is in accordance with the simultaneous presence of both isomers in the structure of  $\text{Et}_2\text{SnCl}_2(\text{TPPO})_2$  (TPPO = triphenylphosphine oxide).<sup>9</sup> However, the bond lengths in polyhedra with *cis* and *trans* coordination are markedly different. Taking into consideration the fact that the donor properties of the chloride ion are close to those of isothiocyanate, we propose that in *trans*- $\text{Ph}_2\text{PbCl}_2(\text{HMPT})_2$  the Pb—O bond lengths should be approximately the same as in  $\text{Ph}_2\text{Pb}(\text{NCS})_2(\text{HMPT})_2$ , i.e. 2.35–2.36 Å, and the Pb—Cl bond lengths should be 2.69–2.70 Å as in *trans*- $\text{Ph}_2\text{PbCl}_2(\text{imidazole})_2$ . In the *cis*-structures **I** and **II** we have 2.60 Å for Pb—Cl (0.09 Å shorter) and 2.52 Å for Pb—O (0.16 Å longer)

bonds. This redistribution of bond lengths in linear Cl—Pb—O moieties is caused by the higher electron-donating capacity of the chloride anion in comparison with HMPT, DMSO and other analogous donor molecules, and by the hypervalent character of these bonds, which are formed by participation of only one lead *p*-orbital per three-atom group, whereas *s*-electrons do not play a significant role.<sup>10</sup>

In structure **III**, Pb—C bonds are formed in accordance with the model mentioned above by *sp*<sup>2</sup>-hybridized orbitals, and bonds in the linear fragment are also hypervalent, so the Pb—Cl and Pb—O bond lengths in **II** and **III** are almost the same. In real structures the geometry of Cl—Pb—O fragments differs from linearity by 2–15°. In **I** and **II** this is due to the distortion of the equatorial plane (increasing Cl—Pb—Cl angle and decreasing O—Pb—O angle), which is usual for similar structures, and in **III** it is due to different orientation of the phenyl rings. Two of them are perpendicular to the  $\text{PbC}_3$  plane, the third is almost parallel to it, and the Pb—Cl and Pb—O bonds are slightly bent to this ring.

Table 2. Selected bond lengths (Å) and angles (°) for structures **I–III**

<b><math>\text{Ph}_2\text{PbCl}_2(\text{DMSO})_2</math></b>					
Pb—Cl(1)	2.637(2)	Pb—O(2)	2.543(6)	S(1)—O(1)	1.509(6)
Pb—Cl(2)	2.580(2)	Pb—C(11)	2.165(8)	S(2)—O(2)	1.518(7)
Pb—O(1)	2.482(6)	Pb—C(21)	2.164(8)		
Cl(1)—Pb—Cl(2)	95.39(7)	Cl(2)—Pb—O(2)	164.5(2)	O(2)—Pb—C(11)	84.7(3)
Cl(1)—Pb—O(1)	175.3(2)	Cl(2)—Pb—C(11)	97.4(2)	O(2)—Pb—C(21)	81.6(2)
Cl(1)—Pb—O(2)	99.9(2)	Cl(2)—Pb—C(21)	94.7(2)	C(11)—Pb—C(21)	165.5(3)
Cl(1)—Pb—C(11)	92.8(2)	O(1)—Pb—O(2)	82.1(2)	Pb—O(1)—S(1)	124.8(3)
Cl(1)—Pb—C(21)	94.0(2)	O(1)—Pb—C(11)	83.1(3)	Pb—O(2)—S(2)	142.3(4)
Cl(2)—Pb—O(1)	82.9(1)	O(1)—Pb—C(21)	90.5(2)		
<b><math>\text{Ph}_2\text{PbCl}_2(\text{HMPT})_2</math></b>					
Pb—Cl(1)	2.605(3)	Pb—O(2)	2.506(7)	P(1)—O(1)	1.479(6)
Pb—Cl(2)	2.603(2)	Pb—C(21)	2.178(13)	P(2)—O(2)	1.473(7)
Pb—O(1)	2.536(6)	Pb—C(31)	2.135(16)		
Cl(1)—Pb—Cl(2)	97.85(9)	Cl(2)—Pb—O(2)	172.3(2)	O(2)—Pb—C(21)	87.1(3)
Cl(1)—Pb—O(1)	174.4(2)	Cl(2)—Pb—C(21)	93.4(3)	O(2)—Pb—C(31)	85.4(6)
Cl(1)—Pb—O(2)	89.8(2)	Cl(2)—Pb—C(31)	93.2(6)	C(21)—Pb—C(31)	170.1(6)
Cl(1)—Pb—C(21)	93.0(4)	O(1)—Pb—O(2)	85.1(2)	Pb—O(1)—P(1)	159.0(4)
Cl(1)—Pb—C(31)	93.4(5)	O(1)—Pb—C(21)	84.7(4)	Pb—O(2)—P(2)	164.3(4)
Cl(2)—Pb—O(1)	87.4(2)	O(1)—Pb—C(31)	88.2(5)		
<b><math>\text{Ph}_3\text{PbCl}(\text{HMPT})</math></b>					
Pb—Cl	2.614(3)	Pb—C(11)	2.189(10)	Pb—C(31)	2.194(9)
Pb—O(1)	2.500(7)	Pb—C(21)	2.175(9)	O(1)—P(1)	1.476(8)
Cl—Pb—O(1)	174.5(2)	O(1)—Pb—C(11)	87.5(3)	C(11)—Pb—C(31)	122.6(4)
Cl—Pb—C(11)	95.4(3)	O(1)—Pb—C(21)	82.8(3)	C(21)—Pb—C(31)	120.9(4)
Cl—Pb—C(21)	91.8(2)	O(1)—Pb—C(31)	89.2(3)	Pb—O(1)—P(1)	167.6(5)
Cl—Pb—C(31)	93.1(3)	C(11)—Pb—C(21)	115.4(3)		

Table 3. Bond lengths (Å) and angles (°) in comparable lead and tin complexes (averaged; Δ is the difference between values for lead and tin)

Compound	Parameter	Pb	Sn	Δ
Ph <sub>2</sub> MCl <sub>2</sub> (DMSO) <sub>2</sub> <sup>a</sup>	M—Cl	2.609 <sup>j</sup>	2.494 <sup>11</sup>	0.12
	M—O	2.513	2.318	0.20
	M—C	2.165	2.117	0.05
	Cl—M—Cl	95.4	95.2	0.2
	C—M—C	165.2	167.2	−2.0
Ph <sub>2</sub> MCl <sub>2</sub> Dipy <sup>a</sup>	M—Cl	2.632 <sup>2</sup>	2.510 <sup>19</sup>	0.12
	M—N	2.521	2.360	0.16
	M—C	2.167	2.152	0.02
	Cl—M—Cl	111.5	103.5	8.0
	C—M—C	177.3	173.5	3.8
Ph <sub>2</sub> M(NCS) <sub>2</sub> (HMPT) <sub>2</sub> <sup>b</sup>	M—N	2.418 <sup>8</sup>	2.236 <sup>8</sup>	0.18
	M—O	2.345	2.184	0.16
	M—C	2.155	2.138	0.02
[R <sub>2</sub> MN <sub>2</sub> Cl <sub>2</sub> ] <sup>c</sup> [Ph <sub>2</sub> PbCl <sub>2</sub> (imidazole) <sub>2</sub> and ( <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> SnCl <sub>2</sub> (4,4'-Me <sub>2</sub> Dipy)]	M—Cl	2.700 <sup>1</sup>	2.484 <sup>20</sup>	0.22
	M—N	2.45	2.314	0.14
	M—C	2.18	2.163	0.02
	Cl—M—Cl	160.9	163.2	−2.3
Ph <sub>2</sub> M(2,6-pyridinedicarboxylate) monohydrate <sup>d</sup>	C—M—C	129.1	106.3	22.8
	M—N	2.452 <sup>21</sup>	2.338 <sup>22</sup>	0.11
	M—O(carboxyl)	2.468	2.347	0.12
	M—O(H <sub>2</sub> O)	2.472	2.271	0.20
	M—C	2.143	2.124	0.02
Ph <sub>3</sub> MCl(OPR <sub>3</sub> ) <sup>e</sup> [Ph <sub>3</sub> PbCl(HMPT) and Ph <sub>3</sub> SnCl{bis (diphenylphosphonyl)ethylene}]	C—M—C	172.8	172.4	0.4
	M—Cl	2.614 <sup>f</sup>	2.489 <sup>23</sup>	0.13
	M—O	2.499	2.346	0.15
	M—C	2.186	2.142	0.04
Ph <sub>3</sub> M(OH) <sup>f</sup>	Cl—M—Cl	93.4	95.1	−1.7
	M—O	2.37 <sup>24</sup>	2.197 <sup>24</sup>	0.17
	M—O'	2.44	2.255	0.18
	M—C	2.18	2.137	0.04
Ph <sub>3</sub> M(NCS) <sup>f</sup>	M—N	2.45 <sup>2</sup>	2.22 <sup>25</sup>	0.23
	M—S	2.91	2.92	−0.01
Ph <sub>3</sub> M(NCO) <sup>f</sup>	M—N	2.38 <sup>17</sup>	2.122 <sup>26</sup>	0.26
	M—O	2.65	2.807	−0.16
	M—O'	2.326 <sup>27</sup>	2.205 <sup>28</sup>	0.12
Me <sub>3</sub> M(acetate) <sup>f</sup>	M—O	2.554	2.390	0.16
	M—O'	2.181	2.128	0.05
	M—C	2.181	2.128	0.05
Cs <sub>2</sub> MCl <sub>6</sub> <sup>g</sup>	M—Cl	2.510 <sup>29</sup>	2.423 <sup>30</sup>	0.09
	M—C	2.19 <sup>18</sup>	2.163 <sup>18</sup>	0.03
Cat <sub>2</sub> [PhMCl <sub>3</sub> ] <sup>g</sup> (Cat = Cs for Pb, NMe <sub>4</sub> for Sn)	M—Cl <sub>cis</sub>	2.626	2.489	0.14
	M—Cl <sub>trans</sub>	2.461	2.427	0.03
	M—C	2.209 <sup>2</sup>	2.139 <sup>31</sup>	0.07
	M—S	2.194 <sup>14</sup>	2.429 <sup>33</sup>	0.08
Ph <sub>3</sub> M(2-(NMe <sub>2</sub> )C <sub>6</sub> H <sub>4</sub> S) <sup>h</sup>	M—C	2.510 <sup>32</sup>	2.429 <sup>33</sup>	0.08
	M—S	2.213	2.146	0.07
Ph <sub>2</sub> M(S <sub>2</sub> C <sub>4</sub> O) <sup>h</sup>	M—S	2.495 <sup>34</sup>	2.402 <sup>35</sup>	0.09
	M—C	2.195	2.137	0.06
K <sub>4</sub> MO <sub>4</sub> <sup>h</sup>	M—O	2.073 <sup>36</sup>	1.956 <sup>37</sup>	0.12
Li <sub>8</sub> MO <sub>6</sub> <sup>g</sup>	M—O	2.182 <sup>38</sup>	2.092 <sup>39</sup>	0.09
Li <sub>2</sub> MO <sub>3</sub> <sup>g</sup>	M—O	2.162 <sup>40</sup>	2.069 <sup>41</sup>	0.09
MO <sub>2</sub> <sup>g</sup>	M—O	2.163 <sup>42</sup>	2.054 <sup>43</sup>	0.11
[MO <sub>8</sub> ] <sup>i</sup> [Cu <sub>6</sub> Pb <sub>1</sub> (Cl, Br) <sub>1</sub> O <sub>7.5</sub> and Sn(NO <sub>3</sub> ) <sub>4</sub> ]	M—O	2.28 <sup>44</sup>	2.16 <sup>45</sup>	0.12

Types of environments of metal atoms are as follows: <sup>a</sup>octahedral with *trans* Ph and *cis* X and D; <sup>b</sup>all-*trans* octahedral; <sup>c</sup>octahedral with *cis* Ph and D and *trans* X; <sup>d</sup>pentagonal-bipyramidal; <sup>e</sup>trigonal-bipyramidal; <sup>f</sup>polymeric trigonal-bipyramidal; <sup>g</sup>octahedral; <sup>h</sup>tetrahedral; <sup>i</sup>eight-coordinated.

<sup>j</sup>This work.

Contrary to the fairly symmetrical coordination polyhedron of **II**, complex **I** has additional features of distortion of the equatorial plane: due to the different orientation of DMSO molecules, the S(1) atom has an intramolecular contact with Cl(2) [torsion angle of S(1)—O(1)—Pb—Cl(2) is 37.0°] and S(2) is receded from Cl(1) [angle of S(2)—O(2)—Pb—Cl(1) is 122.5°]. The S(1)···Cl(2) distance of 3.49 Å is 0.2 Å shorter than the sum of van der Waals radii and the attraction between these atoms leads to the decrease of the Cl(2)—Pb—O(1) angle, which is 17° smaller than the opposite Cl(1)—Pb—O(2). This interaction also causes the difference in Pb—O—S angles. The Pb—Cl and Pb—O bonds in **I** differ by 0.057 and 0.061 Å, respectively, shorter distances being associated with the ligands involved in S···Cl interaction. The analogous tin complex Ph<sub>2</sub>SnCl<sub>2</sub>(DMSO)<sub>2</sub> can be prepared in two crystal forms, one of which is isomorphous with **I**.<sup>11</sup> In this structure the S···Cl contact also exists on one side of the equatorial plane (S···Cl distance of 3.44 Å), but on the other side similar interaction is absent. The geometry of the equatorial plane is distorted here in a way similar to that observed in **I**: O—Sn—Cl angles differ by 11.5° and the Sn—Cl and Sn—O distances by 0.038 and 0.076 Å, respectively. In the other crystal form, S···Cl contacts are absent and chemically equivalent bond lengths and angles in the tin environment are almost identical.<sup>12</sup>

#### Comparison of lead and tin complexes

As one can see in Table 3, the differences between Pb—L and Sn—L bond lengths in mixed-ligand complexes are not equal: the replacement of tin by lead leads to the lengthening of M—Cl, M—O and M—N bonds by 0.11–0.20 Å and M—C bonds by 0.02–0.05 Å. The fact that hypervalent bonds are lengthened more in comparison with covalent bonds is not substantial evidence of their weakening, since according to Pauling's equation:<sup>13</sup>

$$d(n) = d(1) - C \log(n) \quad (\text{where } n \text{ is the bond order}).$$

We can derive the difference of bond lengths assuming that  $n = n'$ :

$$\Delta = d - d' = d(1) - d(1)' - (C - C') \cdot \log(n).$$

In the case when constants  $C$  and  $C'$  are different, the difference  $\Delta$  will depend on the value of  $n$ . However, in compounds containing equal ligands around a metal atom with different coordination numbers, the  $D$  values are fairly close: 0.07–0.12 Å with e.s.d.s of bond lengths 0.003–0.008 Å. One can see in the example of coordination polyhedra

[MO<sub>*m*</sub>] ( $m = 4, 6, 8$ ) that the value of  $\Delta$  does not tend to grow with the decrease of  $n(\text{M—O})$  from 1 to 2/3 and 1/2, and remains in the limits 0.09–0.12 Å. In this case, the above-mentioned essential lengthening of Pb—Cl, Pb—N and Pb—O bonds with insignificant (less than in tetraphenyl derivatives) lengthening of Pb—C gives unambiguous evidence of their relative weakening in lead complexes. We point out that Pb—C bond distances in octahedral complexes Ph<sub>2</sub>PbX<sub>2</sub>D<sub>2</sub> are 0.035–0.055 Å shorter than in Ph<sub>4</sub>Pb,<sup>14</sup> whereas in tin complexes such a shortening is not observed.

It may be concluded that the rehybridization of valent orbitals in lead complexes is more effective; namely, the above-mentioned concentration of  $s$ -electrons on Pb—C bonds is realized in larger extent and/or the gap between  $s$ - and  $p$ -levels of the lead atom is larger in comparison with tin. The high oxidation capacity of Pb<sup>4+</sup> and the high stability of Pb<sup>2+</sup> favour the last assertion. The result of more effective rehybridization is the decrease of electron-withdrawing capacity of the Ph<sub>2</sub>Pb<sup>2+</sup> and Ph<sub>3</sub>Pb<sup>+</sup> groups, i.e. the increase of Pb—X bond ionicity in phenyl halides and pseudohalides (leading to the formation of polymeric structures in Ph<sub>2</sub>PbCl<sub>2</sub>,<sup>2,15</sup> Ph<sub>3</sub>PbCl,<sup>16</sup> Ph<sub>3</sub>PbBr,<sup>16</sup> Ph<sub>3</sub>PbNCS,<sup>2</sup> and Ph<sub>3</sub>PbNCO<sup>17</sup>) and greater redistribution of electron density in hypervalent fragments. In *cis*-complexes of Ph<sub>2</sub>PbCl<sub>2</sub> with DMSO and Dipy, Pb—D bonds are lengthened more than Pb—Cl, whereas in all-*trans* Ph<sub>2</sub>Pb(NCS)<sub>2</sub>(HMPT)<sub>2</sub>  $\Delta(\text{M—O})$  and  $\Delta(\text{M—N})$  are fairly close. The relative weakening of Pb—D bonds is not accompanied by an increase of tetrahedralization of the residual moiety (C—Pb—C and C—Sn—C angles are almost equal) as found in similar cases, since the concentration of  $s$ -electrons on Pb—C bonds occurs simultaneously.

As a result of structural investigation in RMCl<sub>2</sub><sup>2-</sup>-containing salts (M = Sn, Pb),<sup>18</sup> we conclude that effects of the mutual influence of ligands (*cis*-weakening and *trans*-strengthening) in lead complexes manifest themselves more distinctly than in tin complexes. This fact can also be explained in terms of the more effective rehybridization.

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