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Methyllead(IV) Derivatives Stabilized by $DAPTSC^{2-}$: Synthesis and Structures of New Diorganolead(IV) Complexes

José S. Casas,*[a] Eduardo E. Castellano,[b] Javier Ellena,[b] María S. García-Tasende,[a] Facundo Namor,[a] Agustín Sánchez,[a] José Sordo,[a] and María J. Vidarte[a]

Dedicated to Professor Joachim Strähle on the occasion of his 70th birthday

Keywords: Lead / Diorganolead(IV) complexes / Metallation

The reaction of the bis(thiosemicarbazone) of dimethyl pyridine-2,6-diyl diketone, $H_2DAPTSC$, with $PbMe_2(OAc)_2$, $PbMePh(OAc)_2$ or $PbPh_2(OAc)_2$ in MeOH afforded the complexes $[PbMe_2(DAPTSC)]$, $[PbMePh(DAPTSC)]$ or $[PbPh_2(DAPTSC)]$ (in the first two cases together with $[Pb(DAPTSC)]$). X-ray crystallography of the Pb(IV) complexes showed that the metal has a pentagonal bipyramidal coordination sphere. The N_3,S_2-bound $DAPTSC^{2-}$ anion occupied the equatorial plane and the organic groups were in the apical positions. These compounds retain the same coordination mode in DMSO solution. $DAPTSC^{2-}$ is also N_3,S_2-bound in $[Pb(DAPTSC)]$, a complex with a stereochemically active Pb^{II} lone pair. The reaction of $PbPh_2Cl_2$ with $H_2DAPTSC$, also in methanol at room temperature, afforded $[PbPh_2(H_2DAPTSC)]_2[PbPh_2Cl_4]Cl_2{\cdot}6CH_3OH$. X-ray crystallography of this centrosymmetric complex showed it to consist of two $[PbPh_2(H_2DAPTSC)]^{2+}$ cations of similar structure to the neutral $[PbR_2(DAPTSC)]$ complexes, together with a *trans*-octahedral $[PbPh_2Cl_4]^{2-}$ anion and two Cl^- anions. This compound decomposes in DMSO solution, probably evolving to $H_2DAPTSC$ and $PbPh_2Cl_2(DMSO)_n$. In order to evaluate the changes undergone by $H_2DAPTSC$ under metallation, the X-ray structure of the free molecule was also determined.

Introduction

Structural information on methyllead(IV) coordination compounds is rather scarce. Apart from a small number of compounds with lead–metal bonds or with relatively simple anions (tetramethyllead,[1] trimethyllead chloride,[2] trimethyllead iodide,[3] trimethyllead acetate,[4] trimethyllead 2-furate,[5] trimethyllead diphenylphosphinate[6] or trimethyllead methylthiolato[7]), the only such structure in the CSD[8] is that of the complex bis(tetraphenylimidodiphosphanato)dimethyllead(IV), which was obtained in the recrystallization of the corresponding trimethyllead compound.[6] This paucity of information is probably related to the intrinsic instability of methyllead(IV) compounds, which are more unstable than the corresponding phenyl derivatives.

According to the classic papers of Huber et al.,[9] the decomposition of dimethyllead(IV) compounds occurs through redistribution of the methyl groups as shown in Equation (1).

$$2\ PbMe_2X_2 \rightarrow PbMe_3X + PbMeX_3 \quad (1)$$

This is followed by a reduction-elimination step carried out by the monomethyl derivative, see Equation (2).

$$PbMeX_3 \rightarrow MeX + PbX_2 \quad (2)$$

This evolution seems to be stimulated by the presence of Lewis bases such as DMSO, possibly because these bases stabilize the decomposition products.

As the redistribution process probably involves short distance between the lead centres,[10] we speculated that the starting organolead compound might be more stable, the bulkier the ligand X. We have investigated this idea using the potentially pentadentate bis(thiosemicarbazone) ligand ($H_2DAPTSC$, Figure 1) as X_2. This Schiff base coordinates well, in both neutral and deprotonated forms, to a variety of metal and organometal ions.[11] Coordination usually occurs through N(3), N(4), N(5), S(1) and S(2), and results in the occupation of a significant part of the volume around the metal centre.

Herein we describe the synthesis and structures of new complexes obtained using this strategy, including the first methylphenyllead(IV) and only the second dimethyllead(IV) coordination compounds to have been studied by X-ray diffractometry.

[a] Departamento de Química Inorgánica, Facultad de Farmacia, Universidad de Santiago de Compostela, 15782 Santiago de Compostela, Spain
E-mail: qiscasas@usc.es
[b] Instituto de Física de São Carlos, Universidade de São Paulo, CEP 13560 São Carlos, Brazil

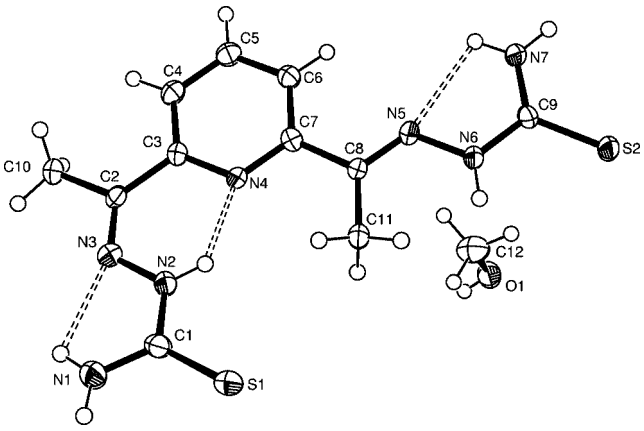


Figure 1. Molecular structure of H_2DAPTSC·MeOH. Ellipsoids are drawn at the 50% probability level.

Results and Discussion

Synthesis

H_2DAPTSC was combined in methanol with $PbMe_2(OAc)_2$, $PbMePh(OAc)_2$, $PbPh_2(OAc)_2$, $PbPh_3(OAc)$ and $PbPh_2Cl_2$. The reaction of the diacetates evolved as expected: the bis(thiosemicarbazone) replaced the acetate anions, the basicity of which favoured the observed deprotonation of the incoming ligand.

$$PbR_2(OAc)_2 + H_2DAPTSC \rightarrow [PbR_2(DAPTSC)] + 2\ HOAc$$

However, the additional isolation of [Pb(DAPTSC)] when the organometallic moiety had methyl groups showed that hindrance of the redistribution reaction, Equation (1), was not complete. $[PbPh_2(DAPTSC)]$ was also the product of the reaction between H_2DAPTSC and $PbPh_3(OAc)$, probably through a protodephenylation (acidic decomposition) reaction. Reaction of H_2DAPTSC with $PbPh_2Cl_2$ gave a product, the stoichiometry of which suggested that the bis(thiosemicarbazone) ligand was neutral and only replaced the chloride ligands of two-thirds of the $PbPh_2Cl_2$ molecules, the remaining third accepting half of the displaced Cl^- anions, see Equation (3).

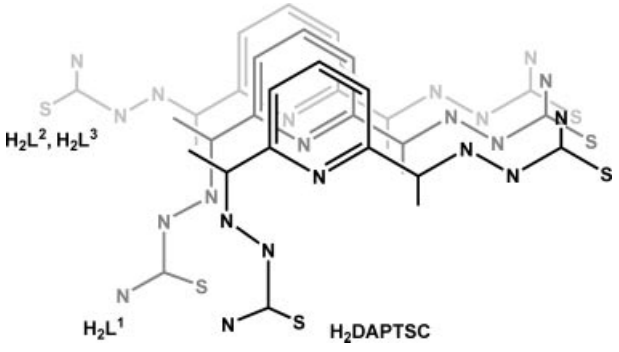
$$3\ PbPh_2Cl_2 + 2\ H_2DAPTSC \rightarrow 2\ [PbPh_2(H_2DAPTSC)]^{2+} + [PbPh_2Cl_4]^{2-} + 2\ Cl^- \quad (3)$$

This explains why unreacted H_2DAPTSC was recovered in spite of the reaction having being carried out in a 1:1 mol ratio. A somewhat related process has been observed[12] when $PbPh_2Cl_2$ was combined with certain monothiosemicarbazones (HTSCs), although in these cases only one chloride ligand was displaced from the coordination sphere of the metal, giving $[PbPh_2Cl(HTSC)]^+$.

Solid-State Structures

Figure 1 shows the molecular structure of H_2DAPTSC·MeOH, which, unlike those of certain similar compounds (see paragraph below),[13] has not hitherto been determined by X-ray crystallography. Although the diffraction data were not of high quality, the conformations and relative orientations of the thiosemicarbazide chains are unquestionable, and this information is relevant to the analysis of the changes that occur upon deprotonation and coordination. The bond lengths and angles in these chains (Table 1) are unexceptional.[14] The chain bearing S(1) is roughly parallel to the line through C5 and N4 (named the "closed-arm" orientation in this article), and places the methyl group $C(10)H_3$ *trans* to N(4). By contrast, the chain bearing S(2) is roughly orthogonal to the line C5–N4 (the "open-arm" orientation), and places the methyl group $C(11)H_3$ *cis* to N(4). These orientations, together with the (*Z*) configuration about C(2)=N(3) in the closed arm, the (*E*) configuration about C(8)=N(5) in the open arm, and the mutually *trans* orientations of the N–N and C=S bonds in both chains, allow the stabilization of the molecule by three intramolecular hydrogen bonds (Figure 1 and Table 2). That the same structure has been observed in the dimethylthallium(III) complex $[TlMe_2(HDAPTSC)]$[15] suggests that it holds in methanol solutions of H_2DAPTSC as well as in the solid state.

Interestingly, the above structure differs from the structures of the three N1- or N2-substituted bis(thiosemicarbazones) derived from dimethyl pyridine-2,6-diyl diketone that were studied previously by X-ray diffractometry, namely the bis(3-hexamethyleneiminylthiosemicarbazone) (H_2L^1·H_2O),[13a] the bis(1-ethylthiosemicarbazone) (H_2L^2)[13b] and the bis(1-methylthiosemicarbazone) (H_2L^3),[13c] although these compounds differ compositionally only concerning the substituents at N(1) and N(7) (H_2L^1 and H_2L^1) or N(2) and N(5) (H_2L^3). Note that the lattices of H_2L^2 and H_2L^3 contain only the bis(thiosemicarbazone) molecules, whereas those of H_2L^1·H_2O and H_2DAPTSC·MeOH also feature molecules of solvent. Although there is a thiosemicarbazide chain with open-arm orientation in all four molecules, the other arm is open in H_2L^2 and H_2L^3, closed in H_2DAPTSC·MeOH and "semi-closed" in H_2L^1·H_2O (Scheme 1). Such variety is not unexpected given the flexibility of thiosemicarbazide chains, which readily adapt their conformations to minimize weak intra- and intermolecular forces. Together with the differences in composition and in the number and nature of intermolecular hydrogen bonds, it leads to these compounds



Scheme 1.

Table 1. Selected bond lengths [Å] and angles [°] in the ligand and complexes.

Parameter	H_2DAPTSC·MeOH	[$PbMe_2$(DAPTSC)][a]	[PbPhMe(DAPTSC)]·0.45H_2O
Pb–C		2.205(12)	2.170(12) (Me)
		2.207(11)	2.212(13) (Ph)
Pb–N(3)		2.533(6)	2.540(9)
Pb–N(4)		2.509(9)	2.473(10)
Pb–N(5)			2.561(9)
Pb–S(1)		2.769(2)	2.734(3)
Pb–S(2)			2.736(3)
S(1)–C(1)	1.674(4)	1.725(7)	1.763(13)
S(2)–C(9)	1.694(4)		1.726(12)
N(1)–C(1)	1.336(5)	1.346(9)	1.358(14)
N(2)–C(1)	1.367(4)	1.317(10)	1.285(18)
N(3)–C(2)	1.296(5)	1.293(10)	1.256(16)
N(3)–N(2)	1.367(5)	1.378(9)	1.395(13)
N(4)–C(7)	1.341(4)		1.351(13)
N(4)–C(3)	1.353(5)	1.351(8)	1.367(14)
N(5)–C(8)	1.288(4)		1.266(16)
N(5)–N(6)	1.383(4)		1.403(13)
N(6)–C(9)	1.361(4)		1.280(16)
C(2)–C(3)	1.494(5)	1.496(9)	1.515(16)
C(7)–C(8)	1.489(5)		1.378(14)
C–Pb–C		172.9(5)	168.7(5)
S(1)–Pb–N(3)		69.58(15)	70.0(3)
N(3)–Pb–N(4)		64.14(15)	65.0(3)
N(4)–Pb–N(5)			64.9(3)
N(5)–Pb–S(2)			69.9(3)
S(1)–Pb–S(2)			90.36(10)
	[$PbPh_2$(DAPTSC)]·MeOH	[$PbPh_2(H_2$DAPTSC)]$_2$[$PbPh_2Cl_4$]Cl_2·6CH_3OH[b]	[Pb(DAPTSC)][c]
Pb–C	2.215(3)	2.189(4), 2.191(4) (Pb1)	
	2.218(4)	2.201(4), 2.8023(10) (Pb2)	
Pb–N(3)	2.530(3)	2.546(3)	2.612(18)
Pb–N(4)	2.474(3)	2.531(3)	2.48(2)
Pb–N(5)	2.543(3)	2.580(3)	2.67(2)
Pb–S(1)	2.6598(9)	2.7684(10)	2.848(7)
Pb–S(2)	2.6954(9)	2.7973(11)	2.825(8)
S(1)–C(1)	1.733(4)	1.703(4)	1.73(4)
S(2)–C(9)	1.737(4)	1.699(4)	1.76(3)
N(1)–C(1)	1.351(4)	1.307(6)	1.31(3)
N(2)–C(1)	1.337(5)	1.361(5)	1.36(5)
N(3)–C(2)	1.296(4)	1.281(5)	1.32(4)
N(3)–N(2)	1.386(4)	1.368(5)	1.40(3)
N(4)–C(7)	1.351(4)	1.347(5)	1.38(3)
N(4)–C(3)	1.349(4)	1.347(5)	1.39(3)
N(5)–C(8)	1.303(5)	1.297(6)	1.31(3)
N(5)–N(6)	1.387(4)	1.373(5)	1.38(3)
N(6)–C(9)	1.326(5)	1.364(6)	1.25(4)
C(2)–C(3)	1.493(5)	1.485(6)	1.43(3)
C(7)–C(8)	1.483(5)	1.489(6)	1.51(4)
C–Pb–C	169.57(12)	174.67(15)	
S(1)–Pb–N(3)	70.78(7)	70.70(8)	65.1(4)
N(3)–Pb–N(4)	65.56(9)	63.75(11)	62.5(6)
N(4)–Pb–N(5)	65.56(9)	63.73(11)	60.7(6)
N(5)–Pb–S(2)	70.86(7)	69.62(8)	65.2(4)
S(1)–Pb–S(2)	88.29(3)	93.33(3)	72.6(2)

[a] S(1)–Pb–S(1)^i 93.25(11) (i = $-x$, y, z). [b] Pb(2)–Cl(2) 2.7005(10); Pb(2)–Cl(1) 2.8023(10); C–Pb(2)–C^i 180.0, Cl(1)–Pb(2)–Cl(1)^i 180.0, Cl(2)–Pb(2)–Cl(2)^i 180.0 (i = $-x$ + 2, $-y$, $-z$). [c] Pb–S(1)^i = 3.312(8), Pb–S(2)^i 3.385(8), (i = 1 + x, y, z).

having very different supramolecular structures: dimers in H_2L^1·H_2O and H_2L^3, chains in H_2L^2 and two-dimensional sheets in H_2DAPTSC·MeOH.

The molecular structure of [$PbMe_2$(DAPTSC)] is shown, together with its numbering scheme, in Figure 2. The dideprotonated ligand coordinates to the dimethyllead(IV) unit through S1, S(1)^i, N(3), N(3)^i and N(4) (i = $-x$, y, z). The two chains bind the lead atom symmetrically, and together with the nitrogen atom of the pyridine ring occupy the equatorial plane of a pentagonal bipyramidal coordination polyhedron in which the two methyl groups of the almost linear $PbMe_2^{2+}$ unit [C–Pb–C 172.9(5)°] are apical. The resulting [$PbC_2N_3S_2$] kernel has not hitherto been observed. The strongest Pb–N interaction is with the pyridine nitro-

Table 2. Intra- and intermolecular hydrogen bonds in the ligand and complexes [Å, °].

	D–H	H···A	D···A	D–H···A
H_2DAPTSC·MeOHA[a]				
N(1)–H(1A)···N(3)	0.86	2.26	2.623(4)	105.6
N(1)–H(1B)···S(2)^{i}	0.86	2.53	3.385(3)	172.8
N(2)–H(2)···N(4)	0.86	1.96	2.639(4)	134.6
N(6)–H(6A)···S(2)^{ii}	0.86	2.65	3.499(3)	170.9
N(7)–H(7A)···N(5)	0.86	2.30	2.650(4)	104.3
N(7)–H(7A)···O(1)^{iii}	0.86	2.29	3.032(4)	144.6
N(7)–H(7B)···S(1)^{iv}	0.86	2.57	3.431(3)	177.9
O(1)–H(11)···S(1)^{v}	0.69(5)	2.56(5)	3.236(4)	167(5)
[$PbMe_2$(DAPTSC)][b]				
N(1)–H(1A)···S(1)^{ii}	0.8600	2.8374	3.5630(7)	143.13
N(1)–H(1B)···N(2)^{iii}	0.8600	2.1109	2.9546(9)	166.76
[PbPhMe(DAPTSC)]·0.45H_2O[c]				
N(1)–H(1A)···N(6)^{i}	0.8800	2.1635	3.0368(13)	171.63
N(7)–H(7A)···N(2)^{ii}	0.8800	202461	3.1194(12)	171.63
[$PbPh_2$(DAPTSC)]·MeOH[d]				
N(1)–H(1A)···O(1S)	0.8800	2.2570	2.9220(4)	132.23
N(1)–H(1B)···N(6)^{i}	0.8800	2.2558	3.1229(4)	168.46
O(1S)–H(1S)···N(7)	0.8400	2.3681	3.1760(4)	161.51
N(7)–H(7A)···O(1S)^{ii}	0.8800	2.1632	2.9283(4)	145.06
N(7)–H(7B)···N(2)^{ii}	0.8800	2.2244	3.0997(4)	172.95
[$PbPh_2$(H_2DAPTSC)]$_2$[$PbPh_2Cl_4$]Cl_2·6CH_3OH[e]				
N(1)–H(1A)···Cl(3)^{ii}	0.8800	2.4405	3.2540(4)	153.92
N(1)–H(1B)···O(31)^{iii}	0.8800	1.9695	2.8222(5)	162.80
N(2)–H(2)···Cl(3)^{ii}	0.8800	2.4104	3.2116(4)	151.55
N(6)–H(6)···Cl(1)	0.8800	2.5243	3.3107(4)	149.16
N(7)–H(7A)···Cl(1)	0.8800	2.4429	3.2686(4)	156.45
N(7)–H(7B)···Cl(3)^{iv}	0.8800	2.4029	3.2438(4)	160.07
O(31)–H(31)···Cl(3)^{iii}	0.8400	2.4629	3.2598(3)	158.69
O(41)–H(41)···O(51)^{iii}	0.8400	1.9029	2.7405(6)	174.81
O(51)–H(51)···Cl(3)	0.8400	2.3474	3.1822(4)	172.57
[Pb(DAPTSC)][f]				
N(1)–H(1A)···N(6)^{ii}	0.880	2.3178	3.0966(3)	147.55
N(7)–H(7A)···N(1)^{iii}	0.880	2.5993	3.1230(3)	119.07
N(7)–H(7B)···N(2)^{iv}	0.880	2.3379	3.1254(3)	149.03

Symmetry operations: [a] i = $x-1$, $-y+0.5$, $z-0.5$; ii = $-x+2$, $-y+1$, $-z$; iii = $-x+2$, $-y+0.5$, $-z+0.5$; iv = $x+1$, $-y+0.5$, $z+0.5$; v = x, $-y+0.5$, $z+0.5$. [b] ii = $0.5-x$, $-1-y$, $-0.5+z$; iii = $0.2-x$, $-1-y$, $0.5+z$. [c] i = $x-0.5$, $-y+0.5$, $z+0.5$; ii = $x+0.5$, $-y+0.5$, $z-0.5$. [d] i = $0.5+x$, $0.5-y$, $-0.5+z$; ii = $0.5-x$, $0.5+y$, $0.5-z$. [e] ii = $0.5+x$, $0.5-y$, $-0.5+z$; iii = $0.5-x$, $0.5+y$, $0.5-z$; iv = $0.5-x$, $0.5+y$, $0.5-z$. [f] ii = $-1+x$, y, $-1+z$; iii = $1+x$, y, $1+z$; iv = x, y, $1+z$.

gen [Pb–N(4) 2.509(9)], although this bond is longer than the sum of the covalent radii, 2.35 Å.[16] The identical thiosemicarbazone chains adopt *E* conformation around C(2)–N(3) and *Z* around C(1)–N(2). The conformational changes with respect to free H_2DAPTSC are summarized in Scheme 2. The C–S bond is longer in the complex [1.725(7) Å] than in H_2DAPTSC [1.674(4) and 1.694(4) Å], showing the expected thione-to-thiol evolution upon metallation. Two hydrogen bonds involving the N(1)H_2 groups and the S and N(2) atoms of neighbouring molecules (see Table 2) give rise to a 2D network in the *xz* plane.

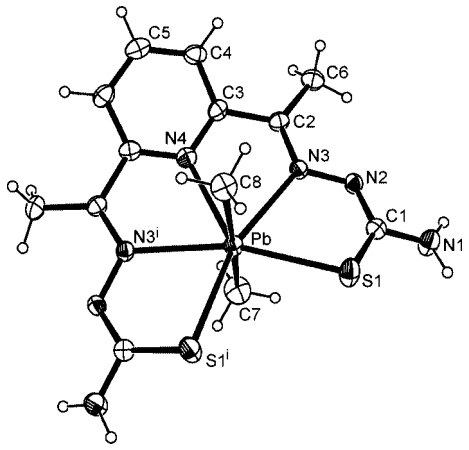
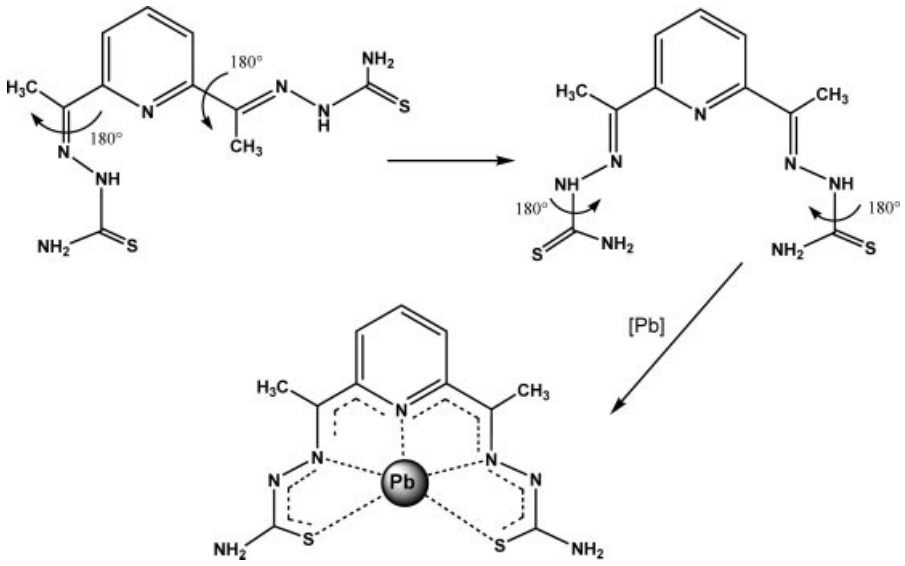


Figure 2. Molecular structure of [$PbMe_2$(DAPTSC)]. Ellipsoids are drawn at the 50% probability level.

That DAPTSC^{2-}, as expected, embraces the organometallic moiety, and must hamper intermolecular approach, but the observed formation of [Pb(DAPTSC)] shows that it is still possible to approach the Pb centre from above or below the equatorial coordination plane. We are currently investigating whether more enveloping ligands provide better stabilization of their methyllead(IV) complexes, so reducing the formation of lead(II) derivatives.

The structures of [PbPhMe(DAPTSC)]·0.45H_2O (Figure 3) and [$PbPh_2$(DAPTSC)]·MeOH (see Figure S1 in the electronic supplementary information) are similar to that of [$PbMe_2$(DAPTSC)], showing only minor differences in certain bond lengths and angles and the expected packing differences deriving from their solvent molecules. Analysis of these small structural differences is difficult, because the esd values are not always similar and because the intermolecular forces can influence the intramolecular ones. For example, the Pb–S bonds of [$PbMe_2$(DAPTSC)] are slightly longer than those of [$PbPh_2$(DAPTSC)]·MeOH (see Table 1), but this could be due either to an intrinsically smaller acceptor capacity of the Me_2Pb^{2+} moiety or to the lessening of the donor ability of the sulfur as a consequence of its intermolecular N(1)–H(1)···S bond. Also, in the diphenyllead(IV) complex the two arms of the ligand are no longer equivalent, showing small differences in the Pb–N and Pb–S bond lengths.

Figure 4 shows the molecular structure and numbering scheme of [$PbPh_2$(H_2DAPTSC)]$_2$[$PbPh_2Cl_4$]Cl_2·6CH_3OH. This complex is centrosymmetric, consisting of two [$PbPh_2$(H_2DAPTSC)]$^{2+}$ cations, a [$PbPh_2Cl_4$]$^{2-}$ anion and the two chloride anions. As in the [PbR_2(DAPTSC)] complexes (see also ref.[11c,17–20]), in the cation [$PbPh_2$(H_2DAPTSC)]$^{2+}$ the thiosemicarbazone ligand binds to the diphenyllead(IV) fragment through its two sulfur and three nitrogen atoms. However, there are two major differences with respect to [$PbPh_2$(DAPTSC)]·MeOH: i) all the metal–ligand bonds are longer, and ii) both the C–S bond lengths suggest scant evolution of the ligand to the thiol form. Both these differences reflect weaker interaction with the organometallic cation.



Scheme 2.

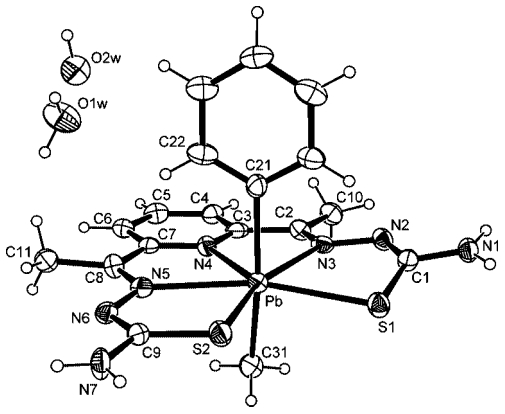


Figure 3. Molecular structure of [PbPhMe(DAPTSC)]·0.45H_2O. Ellipsoids are drawn at the 50% probability level.

In the anion $[PbPh_2Cl_4]^{2-}$, the Pb(2) atom is octahedrally coordinated. This fragment was previously found in $[\{PbPh_2(BPyTSC)\}_2(PbPh_2Cl_4)]$·2MeOH,[12] although in that case it interacted with the $[PbPh_2(BPyTSC)]$ moiety through chloro bridges, while in the present case it is only linked to the $[PbPh_2(H_2DAPTSC)]^{2+}$ cation by the hydrogen bonds N(6)–H(6)···Cl(1) and N(7)–H(7A)···Cl(1) (see Table 2). In keeping with this, the Pb(2)–Cl(2) bond in the present compound is shorter than any of the Pb–Cl bonds in the BPyTSC complex, in which both Cl atoms are bridges and one takes part in a hydrogen bond. By contrast, the Pb(2)–Cl(1) bond is longer than any of the Pb–Cl bonds in $[\{PbPh_2(BPyTSC)\}_2(PbPh_2Cl_4)]$·2MeOH, probably because of the two hydrogen bonds of Cl(1). These interactions, together with others involving the isolated chloride ion Cl(3) and the solvent molecules (Table 2), give rise to a complicated two-dimensional network.

Figure 5 shows the molecular structure of [Pb(DAPTSC)]. In this case, the five donor atoms of the ligand define the base of a pentagonal pyramid, and the Pb^{II} cation is 1.1 Å from this plane. The location of all the metal–ligand interactions on the same side of the metal centre suggests the presence of a stereochemically active lone-

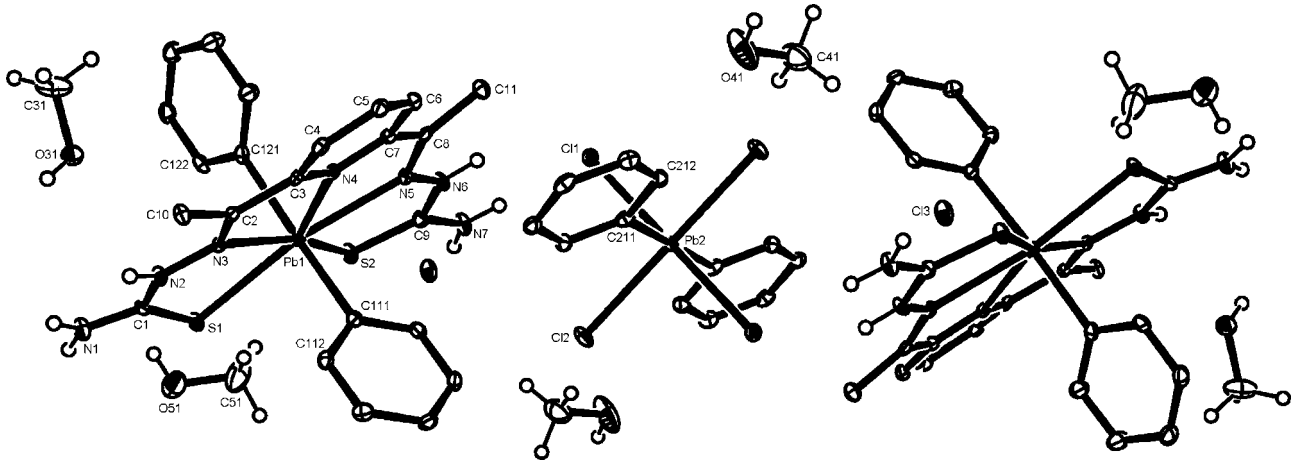


Figure 4. Crystal structure of $[PbPh_2(H_2DAPTSC)]_2[PbPh_2Cl_4]Cl_2$·6$CH_3OH$. All hydrogen atoms, except those on MeOH, and N atoms have been omitted for clarity. Ellipsoids are drawn at the 30% probability level.

pair on the other side. Except for minor differences in bond lengths, this is the same molecular structure as when the ligand is N(1),N(7)-dimethylated,[21] but the crystal packing is different. In the lattice of [Pb(DAPTSC)] the molecules stack along the *x* axis, each Pb centre increasing its coordination number to 7 by means of two weak Pb···S^{i} interactions with the neighbouring molecule on the side opposite its own ligand (i = 1 + *x*, *y*, *z*) and giving rise to a polymeric chain (Figure 6). These polymeric chains interact by N–H···N hydrogen bonds (see Table 2) to form two-dimensional networks in the *xz* plane. In the N(1),N(7)-dimethylated complex[21] no secondary interactions are observed, and each monomer links to another two through π–π interactions between their pyridine rings and the resulting polymeric chains are linked in 2D networks by NH···S hydrogen bonds.

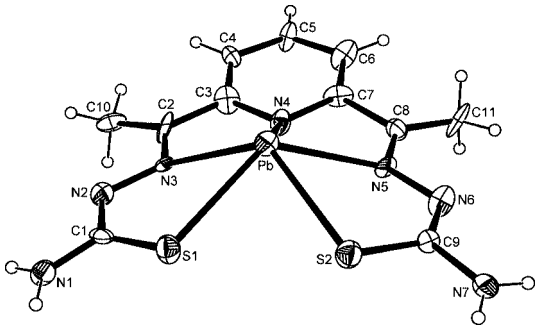


Figure 5. Molecular structure of [Pb(DAPTSC)]. Ellipsoids are drawn at the 50% probability level.

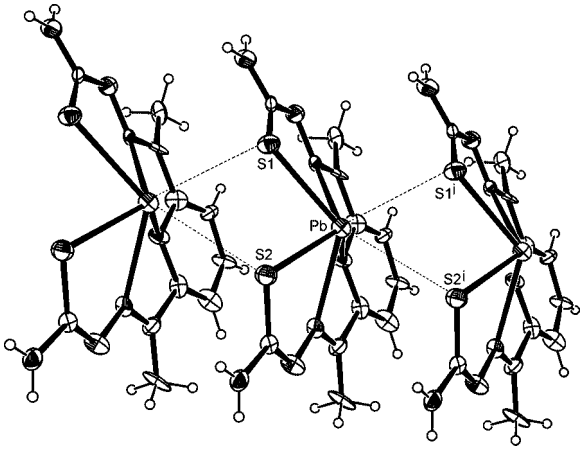


Figure 6. Intermolecular Pb···S interactions in [Pb(DAPTSC)].

Solution Studies

The ^{1}H, ^{13}C and ^{207}Pb NMR spectroscopic data for the complexes are included in the Experimental Section. Only ^{1}H spectra could be obtained for [$PbMe_2$(DAPTSC)] (because of the small amount of solid isolated) and [Pb(DAPTSC)] (because of its poor solubility). The ^{207}Pb NMR signal was only located for [$PbPh_2$(H_2DAPTSC)]$_2$[$PbPh_2Cl_4$]Cl_2·6CH_3OH and [$PbPh_2$(DAPTSC)]. ^{1}H and ^{13}C NMR spectra were interpreted by comparison with those of the ligand.[11a]

The ^{1}H and ^{13}C NMR spectra of [$PbPh_2$(H_2DAPTSC)]$_2$[$PbPh_2Cl_4$]Cl_2·6CH_3OH show signals in positions similar to those found in the spectra of the free ligand and $PbPh_2Cl_2$ in [D_6]DMSO. This suggests that Equation (3) has been shifted to the left, possibly because $PbPh_2Cl_2$ forms adducts with the solvent DMSO.[22] The ^{207}Pb chemical shift and ^{3}J(^{13}C-^{207}Pb) coupling constant support this conclusion, their values being the same as those obtained for $PbPh_2Cl_2$ in DMSO solution.[12] The value of the molar conductivity in DMSO, 8.0 S·cm^2·mol^{-1} (10^{-3} M), rules out any ionic behaviour,[23] and is likewise in accordance with the proposed evolution.

The ^{1}H spectra of [$PbMe_2$(DAPTSC)], [$PbPh_2$-(DAPTSC)], [PbMePh(DAPTSC)] and [Pb(DAPTSC)] are all similar. With respect to the spectrum of the free ligand, the signals corresponding to the N(2,6)H protons disappear because of the formation of DAPTSC^{2-} in the complexes; the signals of the N(1,7)H_2 groups shift to higher fields and merge to form just one signal; the C(5)H protons become slightly deshielded and C(4,6)H is shielded. The ^{13}C NMR spectra of [$PbPh_2$(DAPTSC)] and [PbPhMe(DAPTSC)] are also similar: in both complexes, C(1,9), C(2,8) and C(3,7) are all more shielded than in the free ligand, while C(4,6), C(5) and C(10,11) become deshielded. The shielding of C(1,9) by about 3 ppm is in accordance with evolution of the C=S group to the thiol form when S coordinates to the metal. The shielding of C(2,8) and deshielding of C(10,11) testify to the persistence of Pb–N(3) and Pb–N(5) interactions when the complexes are dissolved in DMSO, while the deshielding of the pyridine ring carbons C(4,6) and C(5) suggests that the Pb–N(4) interaction also perdures. This behaviour is similar to that of the analogous dimethyl and diphenyltin(IV) complexes, [SnR_2(DAPTSC)],[11a] which in the solid state show the same coordination scheme as in the lead complexes.

The above conclusions are also supported by the available NMR spectroscopic data for the diorganolead(IV) moieties. For [$PbPh_2$(DAPTSC)], a coordination of at least seven is suggested by the fact that the ^{3}J and ^{4}J(^{1}H-^{207}Pb) coupling constants are larger than in compounds with a coordination number of six;[24] and although the chemical shift of ^{207}Pb for this compound, –608.9 ppm, is very close to those found in the spectra of certain diaryllead(IV) acetates, for which a coordination number of six has been postulated,[25] this chemical shift is probably not at odds with heptacoordination to C, N and S atoms, as N and S atoms exert a smaller shielding effect than O atoms.

Similarly, the ^{2}J(^{1}H-^{207}Pb) value for [$PbMe_2$(DAPTSC)], 190.0 Hz, is close to those found for other dimethyllead(IV) complexes[26] with a coordination number of seven in DMSO solution, and the ^{2}J value for [PbPhMe(DAPTSC)], 209.2 Hz, is even larger. To the best of our knowledge, the only previously reported ^{2}J value for a methylphenyllead(IV) complex is that of $PbPhMeCl_2$, 105.4 Hz, for which a coordination number of five was assumed.[27]

Conclusions

The reactions of the diorganolead(IV) derivatives $PbMe_2(OAc)_2$ and $PbPhMe(OAc)_2$ with $H_2DAPTSC$ each afford two products: the corresponding dimethyllead(IV) or methylphenyllead(IV) complex, and the lead(II) compound [Pb(DAPTSC)]. Isolation of the former confirms that this bis(thiosemicarbazone) ligand can impede, albeit only partially, the decomposition of methyllead(IV) compounds to "inorganic" lead(II) derivatives. The reaction of $H_2DAPTSC$ with $PbPh_2(OAc)_2$ proceeds without any appreciable decomposition of the organometallic moiety to form $[PbPh_2(DAPTSC)]_2$, which can also be prepared by reacting $H_2DAPTSC$ with $PbPh_3(OAc)$ (probably through a protodephenylation process).

The deprotonation of the incoming ligand in the above processes is attributable to the basicity of the outgoing acetate groups. When $H_2DAPTSC$ reacts with $PbPh_2Cl_2$ it remains neutral and is only able to displace chloride from part of the substrate molecules, competing unsuccessfully with the displaced Cl^- ions for the remainder. The resulting ionic compound, $[PbPh_2(H_2DAPTSC)]_2[PbPh_2Cl_4]Cl_2$, comprises $[PbPh_2(H_2DAPTSC)]^{2+}$ cations and $[PbPh_2Cl_4]^{2-}$ and Cl^- anions.

The above complexes were studied by X-ray diffraction in the solid state, and by ^1H, ^{13}C and ^{207}Pb NMR spectroscopy in DMSO solution. In the solid state, both neutral $H_2DAPTSC$ and dianionic $DAPTSC^{2-}$ behave as pentadentate ligands, although the former establishes longer, weaker bonds with the metal. The weaker donor capacity of $H_2DAPTSC$ is corroborated by its displacement by the solvent when $[PbPh_2(H_2DAPTSC)]_2[PbPh_2Cl_4]Cl_2$ is dissolved in dimethyl sulfoxide.

Experimental Section

Chemicals: 2,6-Diacetylpyridine (Aldrich), thiosemicarbazide (Merck), dichlorodiphenyllead (Panreac), chlorotriphenyllead (Aldrich), lead iodide (Aldrich), methyl iodide (Aldrich) and methyllithium (Aldrich), all of reagent grade, were used without further purification.

Physical Measurements: Elemental analyses for C, H, N and S were performed with a Fisons 1108 microanalyzer. Melting points were determined with a Gallenkamp electrically heated apparatus. NMR spectra were recorded in DMSO using a Bruker AMX 300 spectrometer for ^1H spectra (at 300.14 MHz) and ^{13}C spectra (75.4 MHz) (these are referred to TMS through the solvent signals: ^1H, 2.50 ppm; ^{13}C, 39.50 ppm), and a Bruker AMX 500 at 104.58 MHz for ^{205}Pb spectra [using a saturated solution of $PbPh_4$ in $CDCl_3$ (δ = 178.0 ppm) ppm as external reference]. Conductance measurements ($S{\cdot}cm^2{\cdot}mol^{-1}$) were performed at room temperature using a Crison MicroMC 2202 conductivity meter and 10^{-3} M samples prepared in dry DMSO (Aldrich) under N_2 in a glovebox. Elemental analyses and spectroscopic measurements were carried out in the RIAIDT services of the University of Santiago de Compostela. X-ray data were collected at the RIAIDT services of the University of Santiago de Compostela and at the São Carlos Institute of Physics of the University of São Paulo.

Synthesis of the Ligands and the Starting Organolead(IV) Compounds: $H_2DAPTSC$ was prepared as described previously[28] from 2,6-diacetylpyridine and thiosemicarbazide. Crystals appropriate for X-ray study were obtained by recrystallization from MeOH. $PbMe_2Br_2$ was prepared using a published method,[29] by reaction of PbI_2 with IMe and LiMe in ether, and subsequent reaction of the tetramethyllead formed with Br_2. $C_2H_6Br_2Pb$ (397.1): calcd. C 6.05, H 1.52; found C 5.3, H 1.5. $PbPhMeCl_2$ was prepared[27] by reacting MeMgI and MeI with $PbPh_3Cl$. The $PbPh_3Me$ thus formed was dissolved in chloroform and this solution was treated with a stream of HCl(g) until a solid formed. $C_7H_8Cl_2Pb$ (370.25): calcd. C 22.71, H 2.18; found C 21.8, H 2.1. $PbR_2(OAc)_2$ (R = Me, Ph), $PbPhMe(OAc)_2$ and $PbPh_3(OAc)$ were prepared by reaction of the corresponding dihalides or monohalide with AgOAc in 1:2 or 1:1 mol ratio in methanol. The AgX formed was filtered out and the solution containing the organolead(IV) acetate was used immediately in the preparation of the complexes.

Synthesis of the Complexes: The complexes were prepared by reacting $H_2DAPTSC$ with $PbMe_2(OAc)_2$, $PbPhMe(OAc)_2$ $PbPh_2Cl_2$, $PbPh_2(OAc)_2$ or $PbPh_3(OAc)$ in methanol.

Caution! Lead is a highly toxic cumulative poison. Lead compounds should be handled carefully.[30]

[$PbMe_2$(DAPTSC)]: A freshly prepared solution of $PbMe_2(OAc)_2$ (0.22 g, 0.62 mmol) in MeOH (20 mL) was slowly stirred into a yellow suspension of $H_2DAPTSC$ (0.156 g, 0.503 mmol) in the same solvent (20 mL). The orange suspension obtained was stirred for 1 h at room temperature, and the yellow-orange solid formed was filtered out. The ^1H NMR spectrum of this solid suggests a mixture consisting of the complex [Pb(DAPTSC)] [also formed when the ligand reacts with $PbMePh(OAc)_2$, vide infra] together with a small amount of the free ligand. A few monocrystals of [$PbMe_2$(DAPTSC)] that were suitable for X-ray study were obtained from the mother liquor after slow evaporation of the solvent. M.p. 227 °C. ^1H NMR ([D_6]DMSO): δ = 6.9 [br. s, 2 H, N(1,7)H_2], 7.8 [d, 2 H, C(4,6)H], 8.14 [t, 1 H, C(5)H], 2.50 [s, C(10,11)H_3, overlaps with solvent signal], 1.65 [s, $^2J(^1H\text{-}^{207}Pb)$ = 190.2 Hz, 6 H, CH_3–Pb] ppm.

[PbPhMe(DAPTSC)]·0.45H_2O and [Pb(DAPTSC)]: A solution of freshly prepared $PbPhMe(OAc)_2$ (0.10 g, 0.24 mmol) was slowly added to a suspension of $H_2DAPTSC$ (0.07 g, 0.24 mmol) in the same solvent (10 mL). The orange suspension obtained was stirred for 12 h at room temperature. The orange solid formed was filtered out and vacuum-dried. The ^1H NMR spectrum of this solid indicated a mixture of [Pb(DAPTSC)] and [PbPhMe(DAPTSC)]. Evaporation of the mother liquor gave crystals of these two complexes that were suitable for X-ray diffractometry. [PbPhMe(DAPTSC)]·0.45H_2O. $C_{18}H_{21.9}N_7O_{0.45}PbS_2$ (614.8): calcd. C 35.13, H 3.59, N 15.95, S 10.43; found C 34.90, H 3.51, N 16.25, S 10.57. ^1H NMR ([D_6]DMSO): δ = 7.02 [br. s, 4 H, N(1,7)H_2], 7.78 [d, 2 H, C(4,6)*H*], 8.06 [t, 1 H, C(5)*H*], 2.50 [s, C(10,11)H_3, overlaps with the solvent signal], 7.51 [d, 2 H, H_o(Ph-Pb)], 7.20 [t, 3 H, $H_{m,p}$(Ph-Pb)], 1.79 [s, $^2J(^1H\text{-}^{207}Pb)$ = 209.2 Hz, 3 H, CH_3-Pb] ppm. ^{13}C NMR ([D_6]DMSO): δ = 176.8 [C(1,9)], 150.7 [C(3,7)], 146.9 [C(2,8)], 122.1 [C(4,6)], 140.3[C(5)], 14.2 [C(10,11)], 130.7 [C_o(Ph-Pb)], 129.1 [C_m(Ph-Pb)], 127.8 [C_p(Ph-Pb)] ppm. The signal for Me-Pb has not been located. [Pb(DAPTSC)]. M.p. 270 °C. $C_{11}H_{14}N_7PbS_2$ (515.60): calcd. C 25.62, H 2.74, N 19.02, S 12.44; found C 26.20, H 2.63, N 18.76, S 12.33. ^1H NMR ([D_6]DMSO): δ = 7.02 [br. s, 4 H, N(1,7)H_2], 7.83 [d, 2 H, C(4,6)*H*], 8.18 [t, 1 H, C(5)*H*], 2.50 [s, C(10,11)H_3, overlaps with solvent signal] ppm.

[$PbPh_2$(DAPTSC)]: A freshly prepared solution of $PbPh_2(OAc)_2$ (0.36 g, 0.758 mmol) in MeOH (20 mL) was slowly stirred into a suspension of $H_2DAPTSC$ (0.18 g, 0.578 mmol) in the same solvent (20 mL). The mixture was stirred for 1 h at room temperature and

the orange solid formed was filtered out. M.p. 230 °C. $C_{23}H_{23}N_7PbS_2$ (668.8): calcd. C 41.31, H 3.47, N 14.66, S 9.59; found C 40.48, H 3.90, N 14.02, S 9.74. ^{1}H NMR ([D$_6$]DMSO): δ = 7.14 [br. s, 4 H, N(1,7)H_2], 7.72 [d, 2 H, C(4,6)H], 7.98 [t, 1 H, C(5)H], 2.51 [s, C(10,11)H_3], 7.56 [d, ^3J(^{1}H-^{207}Pb) = 228.2 Hz, 4 H, H_o(Ph-Pb)], 7.20 [t, ^4J(^{1}H-^{207}Pb) = 83.0 Hz, 4 H, H_m(Ph-Pb)], 7.13 [t, 2 H, H_p(Ph-Pb)] ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 176.8 [C(1,9)], 150.3 [C(3,7)], 147.2 [C(2,8)], 122.3 [C(4,6)], 40.3 [C(5)], 14.4 [C(10,11)], 173.0 [C_{ipso}(Ph-Pb)], 130.7 [^2J(^{13}C-^{207}Pb) = 117.7 Hz, C_o(Ph-Pb)], 129.1 [^3J(^{13}C-^{207}Pb) = 217.0 Hz, C_m(Ph-Pb)], 127.8 [^4J(^{13}C-^{207}Pb) = 36.3 Hz, C_p(Ph-Pb)] ppm. ^{207}Pb NMR ([D$_6$]-DMSO): δ = –608.7 ppm.

[PbPh$_2$(DAPTSC)] was also obtained by reaction of H$_2$DAPTSC with PbPh$_3$(OAc), as follows: a solution of PbPh$_3$(OAc) (0.2 g, 0.42 mmol) in MeOH (20 mL) was added to a yellow suspension of H$_2$DAPTSC (0.13 g, 0.42 mmol) in the same solvent (20 mL). The orange solution obtained was stirred overnight at room temperature and filtered to remove a small amount of H$_2$DAPTSC in suspension. Slow concentration of the filtrate afforded orange crystals of [PbPh$_2$(DAPTSC)]·MeOH that were suitable for X-ray study.

[PbPh$_2$(H$_2$DAPTSC)]$_2$[PbPh$_2$Cl$_4$]Cl$_2$·6CH$_3$OH: A suspension of PbPh$_2$Cl$_2$ (0.1 g, 0.23 mmol) in MeOH (10 mL) was stirred into a yellow suspension of H$_2$DAPTSC (0.071 g, 0.23 mmol) in the same solvent (10 mL). The deep yellow suspension obtained was stirred for 4 h at room temperature, after which the yellow solid in suspension was filtered out and discarded (its ^{1}H NMR spectrum and elemental analysis corresponded to H$_2$DAPTSC). Slow concentration of the mother liquor afforded a yellow-green crystalline solid that was suitable for X-ray study. M.p. 197 °C. $C_{64}H_{84}Cl_6N_{14}O_6Pb_3S_4$ (2108.02): calcd. C 36.47, H 4.02, N 9.30, S 6.08; found C 35.80, H 3.90, N 10.03, S 6.94. Λ_m (DMSO, 10^{-3} M) = 8.0 S·cm^2·mol^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 8.40 s, 8.13 [s, 4H N(1,7)H_2], 10.30 [s, 2 H, N(2,6)H], 8.41 [d, 2 H, C(4,6)H], 7.76 [t, 1 H, C(5)H], 2.43 [s, C(10,11)H_3], 8.12 [d, 8 H, H_o(Ph-Pb)], 7.60 [t, 8 H, H_m(Ph-Pb)], 7.43 [t, 4 H, H_p(Ph-Pb)] ppm. ^{13}C NMR ([D$_6$]-DMSO): δ = 179.0 [C(1,9)], 153.4 [C(3,7)], 148.0 [C(2,8)], 120.4 [C(4,6)], 136.6 [C(5)], 12.0 [C(10,11)], 170.5 [C_{ipso}(Ph-Pb)], 133.5 [C_o(Ph-Pb)], 129.6 [^3J(^{13}C-^{207}Pb) ≈ 200, C_m(Ph-Pb)], 129.5 [C_p(Ph-Pb)] ppm. ^{207}Pb NMR ([D$_6$]DMSO): δ = –507.3 ppm.

X-ray Crystallography: Crystal data were collected at room temperature ([PbMe$_2$(DAPTSC)]) or low temperature (all others) on

Table 3. Selected crystallographic data for the ligand and complexes.

	H$_2$DAPTSC·MeOH	[PbMe$_2$(DAPTSC)]	[PbPhMe(DAPTSC)]·0.45H$_2$O
Empirical formula	$C_{12}H_{19}N_7OS_2$	$C_{13}H_{19}N_7PbS_2$	$C_{18}H_{21.90}N_7O_{0.45}PbS_2$
Formula mass	341.46	544.66	614.84
T/K	120.00(10)	293(2)	120(2)
λ/Å	1.54180	1.54184	0.71073
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/c$	$Pmn21$ (No. 31)	$P2_1/n$
a/Å	10.493(5)	15.880(2)	10.026(2)
b/Å	10.590(5)	7.9249(10)	11.996(2)
c/Å	14.745(5)	7.5304(8)	17.560(3)
α/°	90.000(5)	90	
β/°	98.420(5)	90	98.924(9)
γ/°	90.000(5)	90	
V/Å^3	1620.8(12)	947.7(2)	2086.4(6)
Z	4	2	4
μ/mm^{-1}	3.096	19.443	8.308
Reflections collected	10955	985	9672
Independent reflections	2734 [R(int) = 0.0636]	965 [R(int) = 0.0208]	3556 [R(int) = 0.0963]
Final R_1, wR_2 [$I > 2\sigma(I)$]	0.0748, 0.1928	0.0241, 0.0651	0.0564, 0.1111
Gof	1.07	1.071	1.015
	[PbPh$_2$(DAPTSC)]·MeOH	[PbPh$_2$(H$_2$DAPTSC)]$_2$[PbPh$_2$Cl$_4$]Cl$_2$·6MeOH	[Pb(DAPTSC)]
Empirical formula	$C_{24}H_{27}N_7OPbS_2$	$C_{64}H_{84}Cl_6N_{14}O_6Pb_3S_4$	$C_{11}H_{13}N_7PbS_2$
Formula mass	700.84	2107.96	514.59
T/K	120(2)	110(2)	120(2)
λ/Å	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	$\bar{P}$	$P2_1$
a/Å	10.1550(1)	9.4450(1)	4.9586(7)
b/Å	15.9560(2)	11.1110(2)	14.015(2)
c/Å	15.9780(2)	18.7520(3)	10.5900(10)
α/°	90	83.462(1)	
β/°	91.632(1)	77.782(1)	102.923(9)
γ/°	90	77.714(1)	
V/Å^3	2587.92(5)	1874.39(5)	717.31(16)
Z	4	1	2
μ/mm^{-1}	6.712	7.104	12.055
Reflections collected	42027	52099	3746
Independent reflections	4559 [R(int) = 0.0486]	6603 [R(int) = 0.1091]	2177 [R(int) = 0.1079]
Final R_1, wR_2 [$I > 2\sigma(I)$]	0.0259, 0.0684	0.0253, 0.0629	0.0719, 0.1495
Gof	1.092	1.103	1.052

a CCD-2000 Bruker-Nonius (RIAIDT, University of Santiago de Compostela) or on an Enraf-Nonius CAD4 or Enraf-Nonius Kappa CCD (São Carlos Institute of Physics, University of São Paulo). The data were corrected for absorption by numerical[31] [$PbMe_2$(DAPTSC)], empirical[32] (H_2DAPTSC) or semi-empirical[33] (all others) methods. Structures were solved by direct methods for the ligand and the Patterson method for the complexes, followed by normal difference Fourier techniques. Hydrogen atoms were included in idealized positions and refined with isotropic displacement parameters, except that the H bound to the oxygen atom in H_2DAPTSC·MeOH was located on the density map and refined isotropically. The program used was SHELX97.[34]

Although the data for the ligand and the Pb^{II} complex were not of very good quality, successive refinements allowed the full resolution of both structures. In [PbPhMe(DAPTSC)]·0.45H_2O the water molecules are disordered, their O atoms occupying two positions, O1W and O2W, with occupancy factors 3.5 and 0.1, respectively. O2W was not refined anisotropically.

Molecular graphics were obtained with ORTEP[35] and PLATON.[36] Crystal data, experimental details and refinement parameters are listed in Table 3.

CCDC-634589 (for H_2DAPTSC·MeOH), -634590 (for [$PbMe_2$(DAPTSC)]), -634591 (for [PbPhMe(DAPTSC)]·0.45H_2O), -634592 (for [$PbPh_2$(DAPTSC)]·MeOH), -634593 (for [$PbPh_2$(H_2DAPTSC)]$_2$[$PbPh_2Cl_4$]Cl_2·6MeOH) and -634594 (for [Pb(DAPTSC)]) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Figure S1 shows the molecular structure of [$PbPh_2$(DAPTSC)]·MeOH.

Acknowledgments

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