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Dedicated to professor Gh. Marcu at his 80th anniversary

NEW ORGANOTIN(IV) AND – LEAD(IV) *N*,*N*-DIMETHYLDITHIOCARBAMATES: SYNTHESIS, SOLUTION NMR CHARACTERIZATION AND SINGLE-CRYSTAL X- RAY STRUCTURE OF $Ph_2MCl(S_2CNMe_2)$ (M = Sn, Pb) AND $Ph_2Sn(S_2CNMe_2)_2$

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ABSTRACT. New *N*,*N*-dimethyldithiocarbamato derivatives of organotin(IV) and – lead(IV), $R_2MCl(S_2CNMe_2)$ (R = Bu, M = Sn; R = Ph, M = Sn, Pb), $R_2M(S_2CNMe_2)_2$ (R = Bu, Ph, M = Sn) and $R_3M(S_2CNMe_2)$ (R = Ph, M = Sn, Pb; R = Me, M = Pb), were prepared and characterized by multinuclear (^1H, ^{13}C, 2D) NMR spectroscopy in solution. The molecular structures of $Ph_2SnCl(S_2CNMe_2)$ (**3**), $Ph_2Sn(S_2CNMe_2)_2$ (**4**) and $Ph_2PbCl(S_2CNMe_2)$ (**6**) were established by single-crystal X-ray diffraction. In all cases the dithio ligand acts as an asymmetric monometallic biconnective moiety. The mixed chloro-dithiocarbamato derivatives **3** and **6** exhibit distorted trigonal bipyramidal C_2MClS_2 cores, with a sulfur and chlorine atoms in axial positions. For $Ph_2Sn(S_2CNMe_2)_2$ (**4**) a distorted octahedral environment is achieved, with *cis* organic groups attached to tin atom.

Key-words: organotin, organolead, dithiocarbamato ligands, solution NMR studies, X-ray diffraction

INTRODUCTION

Main group dithiocarbamato complexes find various applications in materials and separation science, and have potential use as chemotherapeutics, pesticides, and fungicides. In addition, the dithiocarbamato moiety is a highly versatile ligand towards main group metals, they can stabilize a variety of oxidation states and coordination geometries and small modifications to the ligand can often lead to significant changes in the structure of the complexes formed. The literature on the structural aspects of tin and lead dithiocarbamates was recently reviewed [1], and a search of the Cambridge Structure Database revealed many gaps concerning the structure investigations of organotin(IV) dimethyldithiocarbamates, while no structure of an organolead(IV) analog was so far established by single-crystal X-ray diffractometry.

We report here on the synthesis and solution behavior of several diorgano- and triorganometal(IV) (M = Sn, Pb) dimethyldithiocarbamates, the molecular structures of $Ph_2SnCl_x(S_2CNMe_2)_{2-x}$ (x = 0, 1) as well as the first molecular structure of a diorganolead(IV) dithiocarbamate, *i.e.* $Ph_2PbCl(S_2CNMe_2)$.

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EXPERIMENTAL

The starting materials, *i.e.* organotin(IV)- and organolead(IV)- chlorides and $Me_2NCS_2Na\cdot 2H_2O$, were commercially available (Aldrich) and were used without further purification. Room-temperature ^1H and ^{13}C NMR spectra, including 2D experiments, were recorded in dried $CDCl_3$ on a BRUKER AVANCE DRX 400 instrument operating at 400.16 and 100.62 MHz, respectively. The chemical shifts are reported in ppm relative to the residual peak of solvent (ref. $CDCl_3$: ^1H 7.26 ppm, ^{13}C 77.0 ppm).

Preparation of $Bu_2SnCl(S_2CNMe_2)$ (***1***)

$Me_2NCS_2Na\cdot 2H_2O$ (0.460 g, 2.567 mmol) was added to a solution of Bu_2SnCl_2 (0.782 g, 2.574 mmol) in CH_2Cl_2. A white precipitate of NaCl formed in short time. After removing the NaCl, the solvent was evaporated and the title compound was isolated as viscous yellowish oil. ^1H NMR: δ 0.93t [6H, $\mathrm{C}\mathit{H}_3$-$(CH_2)_3$-Sn, $^3J_{HH}$ 5.8 Hz], 1.41m,br [4H, CH_3-$\mathrm{C}\mathit{H}_2$-$(CH_2)_2$-Sn], 1.83m,br [8H, CH_3-CH_2-$(\mathrm{C}\mathit{H}_2)_2$-Sn], 3.40s (6H, $\mathrm{C}\mathit{H}_3$-N). ^{13}C NMR: δ 13.58s (C_δ), 26.21s (C_γ, $^3J_{SnC}$ 98 Hz), 27.75s (C_β, $^2J_{SnC}$ 34 Hz), 29.08s (C_α, $^1J_{SnC}$ 501 / 522 Hz), 45.10s ($\mathit{C}\mathrm{H}_3$-N), 198.04 (N-$\mathit{C}\mathrm{S}_2$).

Preparation of $Bu_2Sn(S_2CNMe_2)_2$ (***2***)

$Me_2NCS_2Na\cdot 2H_2O$ (0.922 g, 5.146 mmol) was added to a solution of Bu_2SnCl_2 (0.782 g, 2.574 mmol) in CH_2Cl_2. A white precipitate of NaCl formed in short time. After removing the NaCl, the solvent was evaporated and the title compound was isolated as yellowish solid. Yield: 0.95 g (78%), m.p. 137-140°C. ^1H NMR: δ 0.91t [6H, $\mathrm{C}\mathit{H}_3$-$(CH_2)_3$-Sn, $^3J_{HH}$ 7.3 Hz], 1.41tq [4H, CH_3-$\mathrm{C}\mathit{H}_2$-$(CH_2)_2$-Sn, $^3J_{H\text{-}H}$ 7.2 Hz], 1.88m [4H, CH_3-CH_2-$\mathrm{C}\mathit{H}_2$-CH_2-Sn], 2.01m [4H, CH_3-$(CH_2)_2$-$\mathrm{C}\mathit{H}_2$-Sn], 3.42s (12H, $\mathrm{C}\mathit{H}_3$-N). ^{13}C NMR: δ 13.70s (C_δ), 26.36s (C_γ, $^3J_{SnC}$ 124 Hz), 28.46s (C_β), 34.18s (C_α, $^1J_{SnC}$ 576 / 598 Hz), 44.58s ($\mathit{C}\mathrm{H}_3$-N), 200.93 (N-$\mathit{C}\mathrm{S}_2$).

The following compounds were prepared similarly:

$Ph_2SnCl(S_2CNMe_2)$ (***3***), from Ph_2SnCl_2 (1.605 g, 4.668 mmol) and $Me_2NCS_2Na\cdot 2H_2O$ (0.837 g, 4.668 mmol) in CH_2Cl_2. Yield: 1.30 g (65%), m.p. 240-241°C. ^1H NMR: δ 3.40s (6H, $\mathrm{C}\mathit{H}_3$-N), 7.47m (6H, $\mathrm{C}_6\mathit{H}_5$-*meta+para*), 8.07d (4H, $\mathrm{C}_6\mathit{H}_5$-*ortho*, $^3J_{HH}$ 7.8, $^3J_{SnH}$ 88 Hz). ^{13}C NMR: δ 45.83s ($\mathit{C}\mathrm{H}_3$-N), 128.77s (C_m, $^3J_{SnC}$ 88 Hz), 130.16s (C_p, $^4J_{Sn\text{-}C}$ 18 Hz), 135.66s (C_o, $^2J_{SnC}$ 64 Hz), 141.85s (C_i), 196.81 (N-$\mathit{C}\mathrm{S}_2$).

$Ph_2Sn(S_2CNMe_2)_2$ (***4***), from Ph_2SnCl_2 (1.605 g, 4.668 mmol) and $Me_2NCS_2Na\cdot 2H_2O$ (1.673 g, 9.336 mmol) in CH_2Cl_2. Yield: 1.68 g (70%), m.p. 160-165°C. ^1H NMR: δ 3.30s (12H, $\mathrm{C}\mathit{H}_3$-N), 7.42m (6H, $\mathrm{C}_6\mathit{H}_5$-*meta+para*), 8.06m (4H, $\mathrm{C}_6\mathit{H}_5$-*ortho*, $^3J_{SnH}$ 88 Hz). ^{13}C NMR: δ 45.80s ($\mathit{C}\mathrm{H}_3$-N), 128.75s (C_m, $^3J_{SnC}$ 88 Hz), 130.15s (C_p), 135.64s (C_o, $^2J_{SnC}$ 63 Hz), 141.83s (C_i), 196.75 (N-$\mathit{C}\mathrm{S}_2$).

$Ph_3Sn(S_2CNMe_2)$ (***5***), from Ph_3SnCl (0.82 g, 2.127 mmol) and $Me_2NCS_2Na\cdot 2H_2O$ (0.38 g, 2.120 mmol) in CH_2Cl_2. Yield: 0.31 g (31%), m.p. 275-280°C. ^1H NMR: δ 3.46s (6H, $\mathrm{C}\mathit{H}_3$-N), 7.42m (9H, $\mathrm{C}_6\mathit{H}_5$-*meta+para*), 7.76m (6H, $\mathrm{C}_6\mathit{H}_5$-*ortho*, $^3J_{SnH}$ 61 Hz). ^{13}C NMR: δ 45.95s ($\mathit{C}\mathrm{H}_3$-N), 128.47s (C_m, $^3J_{SnC}$ 61 Hz), 129.08s (C_p, $^4J_{Sn\text{-}C}$ 13 Hz), 136.67s (C_o, $^2J_{SnC}$ 46 Hz), 142.16s (C_i, $^1J_{SnC}$ 579 / 606 Hz), 196.76 (N-$\mathit{C}\mathrm{S}_2$).

$Ph_2PbCl(S_2CNMe_2)$ (***6***), from Ph_2PbCl_2 (1.561 g, 3.61 mmol) and $Me_2NCS_2Na\cdot 2H_2O$ (0.647 g, 3.61 mmol) in CH_2Cl_2. Yield: 1.57 g (84%), m.p. 190-192°C. ^1H NMR: δ 3.35s (6H, $\mathrm{C}\mathit{H}_3$-N), 7.41t (2H, $\mathrm{C}_6\mathit{H}_5$-*para*, $^3J_{HH}$ 7.4 Hz), 7.56dd (4H, $\mathrm{C}_6\mathit{H}_5$-*meta*, $^3J_{HH}$ 7.6 Hz), 8.26d (4H, $\mathrm{C}_6\mathit{H}_5$-*ortho*, $^3J_{HH}$ 7.9, $^3J_{PbH}$ 175 Hz). ^{13}C NMR: δ 45.29s ($\mathit{C}\mathrm{H}_3$-N), 129.93s (C_p), 130.28s (C_m, $^3J_{PbC}$ 43 Hz), 134.83s (C_o, $^2J_{PbC}$ 115 Hz), 137.92s (C_i), 200.87 (N-$\mathit{C}\mathrm{S}_2$).

$Ph_3Pb(S_2CNMe_2)$ (***7***), from Ph_3PbCl (0.793 g, 1.674 mmol) and $Me_2NCS_2Na{\cdot}2H_2O$ (0.30 g, 1.674 mmol) in CH_2Cl_2. Yield: 0.53 g (57%), m.p. 199-200^oC. ^1H NMR: δ 3.48s (6H, CH_3-N), 7.38t (3H, C_6H_5-*para*, $^3J_{HH}$ 7.4 Hz), 7.50dd (6H, C_6H_5-*meta*, $^3J_{HH}$ 7.4 Hz), 7.86d (4H, C_6H_5-*ortho*, $^3J_{HH}$ 6.8, $^3J_{PbH}$ 105 Hz). ^{13}C NMR: δ 46.21s (CH_3-N), 128.96s (C_p, $^4J_{PbC}$ 22 Hz), 129.79s (C_m, $^3J_{PbC}$ 100 Hz), 136.89s (C_o, $^2J_{PbC}$ 83 Hz), 158.18s (C_i, $^1J_{PbC}$ 563 Hz), 199.14 (N-CS_2).

$Me_3Pb(S_2CNMe_2)$ (***8***), from Me_3PbCl (0.70 g, 2.433 mmol) and $Me_2NCS_2Na{\cdot}2H_2O$ (0.438 g, 2.444 mmol) in CH_2Cl_2. Yield: 0.54 g (60%), m.p. 235-237^oC. ^1H NMR: δ 1.44s (9H, CH_3-Pb, $^2J_{PbH}$ 64 Hz), 3.47s (6H, CH_3-N). ^{13}C NMR: δ 13.30s (CH_3-Pb, $^1J_{PbC}$ 282 Hz), 45.30s (CH_3-N), 201.24 (N-CS_2).

X-ray Crystallographic Study

Data were collected with a SMART APEX diffractometer (*National Center for X-Ray Diffractometry*, “Babes-Boyai” University, Cluj-Napoca, Romania) at 297 K. In all cases a graphite monochromator was used to produce a wavelength (Mo-$K\alpha$) of 0.71073 Å. The crystal structure measurement and refinement data for compounds **3, 4** and **6** are given in Table 1. Absorption corrections were applied using the multi-scan (Bruker SAINT) method [2]. The structures were solved by direct methods (full-matrix least-squares on F^2). All non hydrogen atoms were refined with anisotropic thermal parameters. For structure solving and refinement a software package SHELX-97 was used [3]. The drawings were created using the Diamond program by Crystal Impact GbR [4].

CCDC-601481 (**3**), CCDC-601483 (**4**) and CCDC-601482 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1.

Crystallographic data for compounds **3**, **4** and **6**.

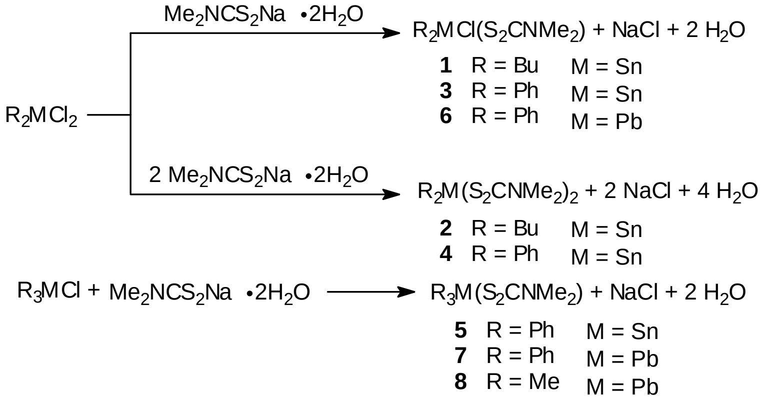
	3	**4**	**6**
Empirical formula	$C_{15}H_{16}ClNS_2Sn$	$C_{18}H_{22}N_2S_4Sn$	$C_{15}H_{16}ClNPbS_2$
Formula mass	428.55	513.31	517.05
Crystal system	Triclinic	Tetragonal	Triclinic
Space group	*P-1*	I4(1)/a	*P-1*
a [Å]	9.1505(13)	16.532(2)	6.68(3)
b [Å]	9.7273(14)	16.532(2)	9.36(4)
c [Å]	11.8051(17)	15.533(4)	14.97(6)
α [^{o}]	79.367(2)	90	79.06(6)
β [^{o}]	67.558(2)	90	81.35(7)
γ [^{o}]	62.500(2)	90	69.98(6)
V [$Å^3$]	861.4(2)	4245.1(13)	859(6)
Z	2	8	2
$D_{calcd.}$ [g/cm^3]	1.652	1.606	1.999
F(000)	424	2064	488
Crystal size [mm]	0.22x0.16x0.16	0.26x0.13x0.10	0.23x0.20x0.15
μ(Mo-Kα) [mm^{-1}]	1.870	1.601	10.209
θ range [^{o}]	1.87-26.37	1.80-26.36	2.34-25.35
No. of reflections collected	9227	16801	8144
No. of independent reflections	3507 (R_{int} = 0.0265)	2171 (R_{int} = 0.0565)	3107 (R_{int} = 0.0376)

No. of parameters	183	116	183
R_1 [$I > 2\sigma(I)$]	0.0334	0.0560	0.0287
wR_2	0.0723	0.0635	0.0675
GOF on F^2	1.144	1.271	1.150
Largest difference electron density [e/Å^3]	0.714/-0.784	0.803/--0.946	1.006/-1.244

RESULTS AND DISCUSSION

Synthesis

The new compounds were obtained by reacting R_2MCl_2 and R_3MCl with sodium dimethyldithiocarbamate in 1:1 and 1:2 molar ratios, in CH_2Cl_2, at room temperature, according to the following equations:



Most of the organotin(IV)- and organolead(IV) dithiocarbamates were isolated in good yield as yellowish solids. Compound **1** was obtained as viscous yellowish oil. They are air-stable compounds, soluble in common organic solvents. All compounds were investigated by NMR spectroscopy (^{1}H, ^{13}C, 2D) in $CDCl_3$ solutions and for compounds **3, 4** and **6** the molecular structures were established using single-crystal X-ray diffraction.

NMR Spectroscopy

For both the organoSn(IV) and -Pb(IV) complexes the spectra contain characteristic resonance signals for equivalent organic groups bonded to the metal centre as well as for the dimethyldithiocarbamato ligand, thus providing evidences for the identity of the obtained compounds. The ^{1}H resonances assigned to the *ortho* protons in the phenyl groups attached to the metal and to the methyl protons in the trimethyllead(IV) derivative, as well as most of the ^{13}C resonances for the organic groups bound to tin or lead, show satellites due to metal-proton or metal-carbon couplings.

The coordination geometry of organotin(IV) derivatives is reflected in the NMR parameters [5]. Thus, based on the reported dependence on the $^1J(^{119}Sn^{13}C)$ coupling constants in butyltin(IV) derivatives [$|^1J(^{119}Sn^{13}C)| = 9.99\theta-746$] [6], the estimated values for the C-Sn-C angle (θ) are 126.9^o [$^1J(^{119}Sn^{13}C$ 522 Hz] in **1** and 134.5^o [$^1J(^{119}Sn^{13}C$ 598 Hz] in **2**. This suggests a distorted trigonal bipyramidal structure for the chloro(dithiocarbamato)tin(IV) derivative **1** and a skew-trapezoidal bipyramid (or highly distorted octahedron) for the bis(dithiocarbamato)tin(IV) derivative **2**. Similar coordination geometries were previously reported for several related organotin(IV) derivatives [1].

The magnitude of the lead-proton and lead-carbon coupling constants is consistent with the presence of diphenyllead(IV) moiety in compound **6** [$^3J(^{207}Pb^1H)$ 175 Hz, $^2J(^{207}Pb^{13}C)$ 115 Hz] and triorganolead(IV) fragments in compounds **7** [R = Ph, $^3J(^{207}Pb^1H)$ 105 Hz, $^2J(^{207}Pb^{13}C)$ 183 Hz, $^1J(^{207}Pb^{13}C)$ 563 Hz] and **8** [R = Me, $^3J(^{207}Pb^1H)$ 64 Hz, $^1J(^{207}Pb^{13}C)$ 282 Hz], respectively [7,8].

The ^1H and ^{13}C NMR spectra of compounds **1** – **8** are very similar with respect to the dimethyldithiocarbamato moiety. The presence of sharp singlets for the methyl protons in the ^1H NMR spectra and for the methyl carbons in the ^{13}C NMR spectra, respectively, indicates the equivalence of the methyl groups on nitrogen. Taking into account the restricted rotation about the $(S_2)C$-N partial double bond of the dithiocarbamato group, this behavior is consistent with a fast fluxional behavior on the NMR chemical shift time scale which alternatively brings the two sulfur atoms in the same position of the primary coordination sphere of the metal centre.

Single-crystal X-ray diffraction studies

Single-crystals suitable for X-ray diffraction studies were obtained by slow diffusion from a mixture of chloroform and hexane (1/4, v/v) for compounds $Ph_2SnCl(S_2CNMe_2)$ (**3**) and $Ph_2PbCl(S_2CNMe_2)$ (**6**). The crystal of **3** consists of discrete monomers separated by normal van der Waals distances, while in the crystal of **6** dimeric associations might be considered (see subsequent discussion). The ORTEP diagrams of the molecular structures of compounds **3** and **6**, with the atom numbering scheme, are shown in Figures 1 and 2. Selected interatomic distances and angles are listed in Table 2.

The molecular structure of compounds **3** and **6** exhibits some common structural features. The dimethyldithiocarbamato moiety behaves as *asymmetric monometallic biconnective units*, with short [Sn(1)-S(1) 2.4718(10) Å in **3**, and Pb(1)-S(1) 2.607(8) Å in **6**] and long [Sn(1)-S(2) 2.6834(10) Å in **3**, and Pb(1)-S(2) 2.821(8) Å in **6**] metal-sulfur distances.

The length of the Sn(1)-S(1) primary bond in **3** is typical for a covalent bond, while the secondary Sn(1)-S(2) bond is stronger than that observed in the related $Me_2SnCl(S_2CNMe_2)$ [Sn-S 2.48(1) Å, Sn···S 2.79(1) Å] [9] or $(PhCH_2)_2SnCl(S_2CNMe_2)$ [Sn-S 2.464(2) Å, Sn···S 2.707(2) Å] [10].

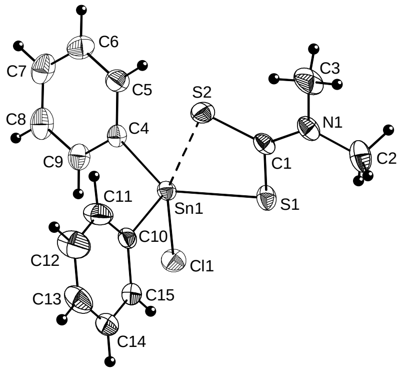


Figure 1. ORTEP representation at 30% probability and atom numbering scheme for $Ph_2SnCl(S_2CNMe_2)$ (**3**).

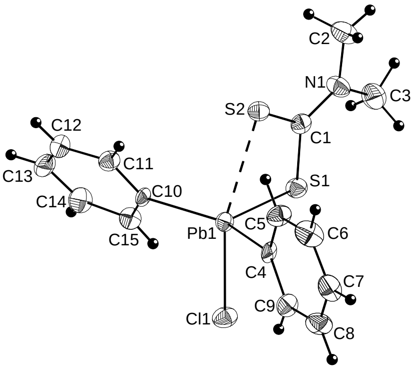


Figure 2. ORTEP representation at 30% probability and atom numbering scheme for $Ph_2PbCl(S_2CNMe_2)$ (**6**).

Table 2.

Interatomic bond distances (Å) and angles (^{o}) for compounds **3** and **6**.

3		**6**	
Sn(1)-C(4)	2.137(3)	Pb(1)-C(4)	2.195(8)
Sn(1)-C(10)	2.140(3)	Pb(1)-C(10)	2.232(10)
Sn(1)-Cl(1)	2.4486(9)	Pb(1)-Cl(1)	2.617(10)
Sn(1)-S(1)	2.4718(10)	Pb(1)-S(1)	2.607(8)
Sn(1)-S(2)	2.6834(10)	Pb(1)-S(2)	2.821(8)
C(1)-S(1)	1.739(4)	C(1)-S(1)	1.754(9)
C(1)-S(2)	1.713(4)	C(1)-S(2)	1.704(8)
C(1)-N(1)	1.317(4)	C(1)-N(1)	1.339(10)
C(2)-N(1)	1.457(5)	C(2)-N(1)	1.466(11)
C(3)-N(1)	1.460(5)	C(3)-N(1)	1.467(11)
C(4)-Sn(1)-C(10)	116.93(13)	C(4)-Pb(1)-C(10)	146.5(3)
S(1)-Sn(1)-C(4)	132.35(10)	S(1)-Pb(1)-C(4)	109.0(3)
S(1)-Sn(1)-C(10)	109.10(9)	S(1)-Pb(1)-C(10)	103.8(3)
Cl(1)-Sn(1)-C(4)	96.77(10)	Cl(1)-Pb(1)-C(4)	95.0(3)
Cl(1)-Sn(1)-C(10)	98.25(10)	Cl(1)-Pb(1)-C(10)	93.09(18)
Cl(1)-Sn(1)-S(1)	87.99(4)	Cl(1)-Pb(1)-S(1)	87.4(2)
S(2)-Sn(1)-C(4)	92.91(10)	S(2)-Pb(1)-C(4)	93.7(3)
S(2)-Sn(1)-C(10)	96.47(10)	S(2)-Pb(1)-C(10)	93.2(2)
S(2)-Sn(1)-S(1)	69.70(3)	S(2)-Pb(1)-S(1)	66.4(3)
Cl(1)-Sn(1)-S(2)	156.36(4)	Cl(1)-Pb(1)-S(2)	153.84(9)
Sn(1)-S(1)-C(1)	89.42(12)	Pb(1)-S(1)-C(1)	90.2(3)
Sn(1)-S(2)-C(1)	83.21(12)	Pb(1)-S(2)-C(1)	84.3(4)

Table 2.

(continued).

N(1)-C(1)-S(1)	120.4(3)	N(1)-C(1)-S(1)	119.1(5)
N(1)-C(1)-S(2)	122.1(3)	N(1)-C(1)-S(2)	122.1(6)
S(1)-C(1)-S(2)	117.5(2)	S(1)-C(1)-S(2)	118.8(5)
C(1)-N(1)-C(2)	122.8(3)	C(1)-N(1)-C(2)	121.3(7)
C(1)-N(1)-C(3)	121.5(4)	C(1)-N(1)-C(3)	122.4(7)
C(2)-N(1)-C(3)	115.7(3)	C(2)-N(1)-C(3)	116.2(7)

The Pb(1)-S(1) primary bond [2.607(8) Å] in **6** is considerably stronger, while the secondary Pb(1)-S(2) bond [2.821(8) Å] is similar with respect to those found for lead(II) dithiocarbamates *e.g.* $Pb(S_2CNMe_2)_2$ [Pb-S 2.779(5) Å; Pb···S 2.873(6) Å] [11], $Pb(S_2CNEt_2)_2$ [Pb-S 2.744(9), 2.786(9) Å; Pb···S 2.885(11), 2.940(10) Å] [12], or $Pb(S_2CNPr^i{}_2)_2$ [Pb-S 2.673(4), 2.681(4) Å; Pb···S 2.843(5), 2.859(5) Å] [13].

The tin-chlorine distance in **3** [Sn(1)-Cl(1) 2.4486(9) Å] compares well with those observed in $Me_2SnCl(S_2CNMe_2)$ [Sn-Cl 2.465(9) Å] [9] or $(PhCH_2)_2SnCl(S_2CNMe_2)$ [Sn-Cl 2.482(2) Å] [10]. The lead-chlorine bond in **6** [Pb(1)-Cl(1) 2.617(10) Å] is shorter than that observed in the polymeric Ph_2PbCl_2 starting material [Pb-Cl 2.795(1) Å in the Pb-Cl-Pb bridges] [14], but of the same magnitude as found in the related $Ph_2PbCl[S(S)CPPh_2(O)]$ [Pb-Cl 2.62(1) Å] [15], respectively.

The resulting coordination geometry at the metal centre is best described as highly distorted trigonal bipyramidal, with the dithiocarbamato ligand spanning axial–equatorial positions. The long metal-S(2) bond is axial, in *trans* to the chlorine atom [Cl(1)-Sn(1)-S(2) $156.36(4)^o$ in **3**, and Cl(1)-Pb(1)-S(2) $153.84(9)^o$ in **6**]. The equatorial plane is described by the C(4), C(10) and S(1) atoms, with the metal atom displaced from this plane towards the chlorine atom with 0.163 and 0.104 Å in **3** and **6**, respectively. The S(1)Sn(1)S(2) plane is almost perpendicular to the C(4)C(10)S(1) basal plane (dihedral angle 84.1^o and 89.3^o in **3** and **6**, respectively). The distortion is mainly due to the small bite of the ligand [S(1)···S(2) 2.951(2) and 2.98(1) Å in **3** and **6**, respectively].

The main difference between these two molecular structures is the opened equatorial C(4)-Pb(1)-C(10) angle [$146.5(3)^o$] in **6** compared to the corresponding C(4)-Sn(1)-C(10) angle [$116.93(13)^o$] in **3**. A closer check of the crystal structure of the lead derivative revealed the presence of a weak intermolecular π-Pb–phenyl interaction [$Pb(1)\cdots C_{6,7,8}$ 3.77(1)-4.23(2) Å] which involves one of the aromatic rings attached to the metal centre. The vector of this π-Pb–phenyl interaction bisects the C(4)-Pb(1)-C(10) angle, in *trans* to the S(1) atom, and might be the cause of enlargement of this equatorial angle. Based on these interactions dimer associations might be considered to be formed, in which the coordination geometry around the lead can be described as distorted octahedral (Figure 3). Similar intra- or intermolecular π-Pb–phenyl interactions were previously described in the monomeric $Pb[(SPPh_2)_2N]_2$ [$Pb(1)\cdots C_{1,2,6}$ 3.31(1)-3.70(2) Å] [16] and the dimeric $[Pb\{(OPPh_2)(SPPh_2)N\}_2]_2$ [$Pb(1)\cdots C_{1,2,6}$ 3.424-3.579 Å] [17].

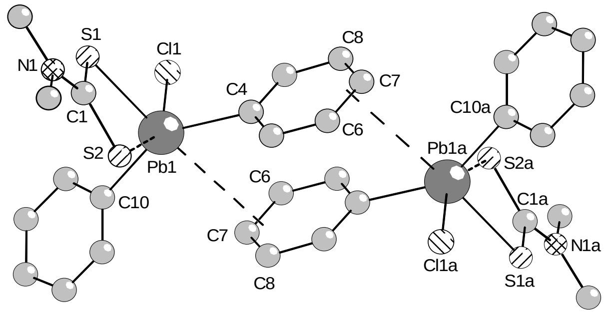


Figure 3. Dimeric association in the crystal of $Ph_2PbCl(S_2CNMe_2)$ (**6**).

The molecular structure of $Ph_2Sn(S_2CNMe_2)_2$ (**4**) was also established by single-crystals X-ray diffraction studies [the crystals were obtained from a chloroform and hexane (1/4, v/v) mixture]. The crystal of **4** consists of discrete monomers separated by normal van der Waals distances. The ORTEP diagram of the molecular structure of compound **4**, with the atom numbering scheme, is shown in Figure 4. Selected interatomic distances and angles are listed in Table 3.

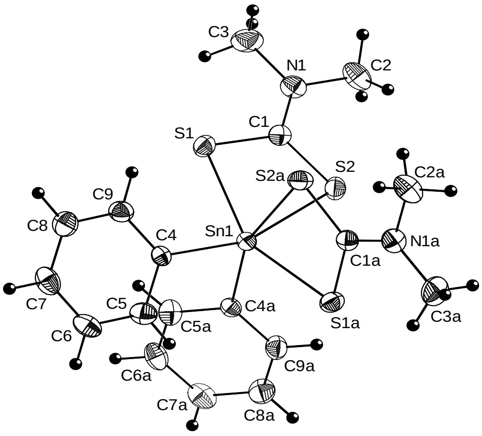


Figure 4. ORTEP representation at 30% probability and atom numbering scheme for $Ph_2Sn(S_2CNMe_2)_2$ (**4**).

Table 3.

Interatomic bond distances (Å) and angles $(^{o})$ for compound **4**.

Sn(1)-C(4)	2.165(5)	C(4)-Sn(1)-C(4a)	98.2(3)
Sn(1)-S(1)	2.5860(14)	S(1)-Sn(1)-S(2)	68.34(5)
Sn(1)-S(2)	2.6632(15)	S(1)-Sn(1)-S(1a)	152.83(7)
		S(1)-Sn(1)-S(2a)	90.90(5)
C(1)-S(1)	1.728(5)	S(2)-Sn(1)-S(1a)	90.90(5)
C(1)-S(2)	1.702(5)	S(2)-Sn(1)-S(2a)	82.45(7)
C(1)-N(1)	1.329(7)	S(1a)-Sn(1)-S(2a)	68.34(5)
C(2)-N(1)	1.467(7)		

C(3)-N(1)	1.450(8)	C(4)-Sn(1)-S(1)	93.81(14)
		C(4)-Sn(1)-S(2)	161.15(14)
N(1)-C(1)-S(1)	120.2(4)	C(4)-Sn(1)-S(1a)	103.94(14)
N(1)-C(1)-S(2)	121.3(4)	C(4)-Sn(1)-S(2a)	92.18(14)
S(1)-C(1)-S(2)	118.6(3)		
		C(4a)-Sn(1)-S(1)	103.94(14)
C(1)-N(1)-C(2)	121.4(5)	C(4a)-Sn(1)-S(2)	92.18(14)
C(1)-N(1)-C(3)	122.1(5)	C(4a)-Sn(1)-S(1a)	93.81(14)
C(2)-N(1)-C(3)	116.5(5)	C(4a)-Sn(1)-S(2a)	161.15(14)
		Sn(1)-S(1)-C(1)	87.39(18)
		Sn(1)-S(2)-C(1)	85.44(18)

As in compound **3**, both dimethyldithiocarbamato moieties in a molecular unit of **4** act as *asymmetric monometallic biconnective units*, with short [Sn(1)-S(1) 2.5860(14) Å] and long [Sn(1)-S(2) 2.6632(15) Å] tin-sulfur distances. However, the Sn(1)-S(1) primary bonds are much longer than in **3** [2.4718(10) Å] and thus the extent of asymmetry is considerably reduced (Δ = [Sn(1)-S(2)] - [Sn(1)-S(1)] is 0.077 Å in **4** *vs.* 0.212 Å in **3**).

The resulting coordination geometry around the tin atom is highly distorted octahedral, with *cis* phenyl groups [C(4)-Sn(1)-C(4a) 98.2(3)°] and axial shorter tin-sulfur bonds [S(1)-Sn(1)-S(1a) 152.83(7)°]. The distortion is mainly due to the small bite of the ligand [S(1)···S(2) 2.949(2)] and is reflected by the dihedral angles: C(4)Sn(1)C(4a) / S(1)Sn(1)S(1a) 83.2°; S(1)Sn(1)S(2) / S(1a)Sn(1)S(2a) 72.5°. Similar coordination geometries were reported for other related diphenyltin(IV) derivatives, *i.e.* $Ph_2Sn(S_2CNEt_2)_2$ (regardless the monoclinic [18,19] or tetragonal [20] forms) or $Ph_2Sn(S_2CNCy_2)_2$ [21]. By contrast, for the $Me_2Sn(S_2CNMe_2)_2$ the geometry at tin was found to be a highly distorted skew-trapezoidal bipyramid, with angular C-Sn-C angle [136.45(1)°] and a planar equatorial SnS_4 system [22].

With respect to the dimethyldithiocarbamato ligand in compounds **3**, **4** and **6** some common features should be noted. The MS_2CNC_2 skeleton is basically planar. Although, consistent with the *asymmetric monometallic biconnective* pattern, short and long metal-sulfur distances are established, in the dithio ligand unit the sulfur-carbon distances are almost equivalent on the basis of the 3σ criteria [C(1)-S(1) 1.739(4) Å in **3**, 1.754(9) Å in **6** and 1.728(5) Å in **4** *versus* C(1)-S(2) 1.713(4) Å in **3**, 1.704(8) Å in **6** and 1.702(5) Å in **4**, respectively]. The carbon-nitrogen bond distance and the planarity of the NC_3 fragment reflect the double bond character and the sp^2 hybridization of the nitrogen atom, respectively.

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