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MONONUCLEAR, THREE-COORDINATE METAL THIOLATES: PREPARATION AND CRYSTAL STRUCTURES OF $[NBu^n_4][Hg(SPh)_3]$ AND $[NPr^n_4][Pb(SPh)_3]$

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Abstract—Dissolution of HgO or PbO in methanolic solutions of NaSPh yields homogeneous solutions from which highly crystalline $[NBu^n_4][Hg(SPh)_3]$ (**1**) or $[NPr^n_4][Pb(SPh)_3]$ (**2**) can be isolated on addition of appropriate quaternary ammonium salts. **1** crystallizes in monoclinic space group $P2_1/a$ with $a = 20.663(7)$, $b = 16.812(6)$, $c = 9.757(3)$ Å, $\beta = 95.52(2)°$ and $Z = 4$. The anion consists of a rare example of trigonal planar coordinated Hg; there are no weaker, intermolecular Hg ... S axial interactions. **2** crystallizes in triclinic space group $P\bar{1}$ with $a = 12.689(7)$, $b = 11.255(6)$, $c = 12.046(7)$ Å, $\alpha = 107.93(3)$, $\beta = 109.64(3)$, $\gamma = 86.01(3)°$, and $Z = 2$. The anion consists of a trigonal pyramidal coordinated PbS_3 unit. The structures were solved using data collected at approx. $-160°C$ and refined to conventional R values of 5.7 and 4.6%, respectively for **1** and **2**.

The biological chemistry of mercury has attracted considerable interest due to its high toxicity to living systems.[1] In particular, it is thought that this metal strongly interacts with the thiolate function of the cysteine amino acid residue, a belief supported by the high stability constant of the mercury–thiolate bond.[1,11] Some recent interest has focused on the metallothioneins[2] which are low molecular weight proteins believed to be involved in the control of zinc and copper metabolism and the detoxification of metals such as cadmium and mercury. In their native form they contain a total of seven Zn and/or Cd atoms bound in two polynuclear aggregates[3] by 20 cysteinyl thiolate groups;[4] the metal-free apoprotein can, however, bind other metals such as Cu, Ag, Co and Hg. Indeed, mercury-containing metallothionein has been isolated from mammals to which mercury has been administered.[5] Similar metal-thiolate interactions *in vivo* may also obtain for lead, another highly toxic metal to living systems.

Despite this, very few anionic complexes of Hg(II) and Pb(II) with small organic thiolates are known and in even fewer cases is structural information available. The isolation of the homoleptic species $[Hg(SR)_4]^{2-}$ (R = Ph,[6a] C_6H_4-*p*-Cl,[6b] C_6F_5[6c] and C_6Cl_5[6d]) have been reported and the R = C_6H_4-*p*-Cl species has been crystallographically shown to be a tetrahedrally-coordinated monomer.[6b] In contrast, $[Hg(SPh)_3]^-$, $[Hg(SBu^t)_3]^-$ and $[Pb(SC_6F_5)_3]^-$ have not been structurally characterized and are reported to be trigonal pyramids based on vibrational evidence or comparison with the corresponding halides;[7,8a] the reaction of $Pb(SPh)_2$ and excess PhS^- has been reported to yield $[Pb(SPh)_3]^-$ based on ^{207}Pb NMR studies and comparison with the corresponding Sn(II) reactions which are better characterized.[8b] Among Hg(II)- and Pb(II)-thiolate chemistry, the only complex with a ligand : metal ratio of 3 : 1 to be structurally characterized is $[Hg(SMe)_3]^-$ and this has been shown[6b] to be dimeric with four-

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coordinate Hg(II) *viz.* $[(\mathrm{MeS})_2\mathrm{Hg}(\mu\text{-SMe})_2\mathrm{Hg}(\mathrm{SMe})_2]^{2-}$.

During our investigations into the reactions of HgO and PbO with four equivalents of NaSPh, we obtained in high yields crystalline materials of empirical formulation $[\mathrm{NR}_4][\mathrm{M}(\mathrm{SPh})_3]$ (M = Hg, Pb). To unambiguously determine their nuclearity and coordination geometry, we have obtained the crystal structures of $[\mathrm{NBu}^n{}_4][\mathrm{Hg}(\mathrm{SPh})_3]$ (**1**) and $[\mathrm{NPr}^n{}_4][\mathrm{Pb}(\mathrm{SPh})_3]$ (**2**) which both proved to be monomeric, and herein report the result of this work.

EXPERIMENTAL

Synthesis

All manipulations were performed under a nitrogen atmosphere employing standard inert-atmosphere techniques.

$[\mathrm{NBu}^n{}_4][\mathrm{Hg}(\mathrm{SPh})_3]$ (**1**). Sodium metal (1.84 g, 80 mmol) was dissolved in MeOH (100 cm^3) and benzenethiol (8.21 cm^3, 80 mmol) added, followed by solid HgO (4.33 g, 20 mmol). The solid slowly dissolved with stirring and slight warming to produce a pale yellow solution. After 0.5 hr, $\mathrm{NBu}^n{}_4\mathrm{Br}$ (12.9 g, 40 mmol) in EtOH (80 cm^3) was added to

Table 1. Summary of crystal data, intensity collection and structure refinement for $(\mathrm{NR}_4)[\mathrm{M}(\mathrm{SPh})_3]$ (M = Hg, R = Bu^n; M = Pb, R = Pr^n)

Quantity	M = Hg(II)	M = Pb(II)
formula	$\mathrm{C}_{34}\mathrm{H}_{51}\mathrm{NS}_3\mathrm{Hg}$	$\mathrm{C}_{30}\mathrm{H}_{43}\mathrm{NS}_3\mathrm{Pb}$
molecular weight	770.56	721.05
cryst. system	monoclinic	triclinic
space group	$P2_1/a$	$P\bar{1}$
temperature, °C	approx. -160	approx. -160
a, Å	20.663(7)	12.689(7)
b, Å	16.812(6)	11.255(6)
c, Å	9.757(3)	12.046(7)
α, deg	------	107.93(3)
β, deg	95.52(2)	109.64(3)
γ, deg	------	86.01(3)
V, Å^3	3373.50	1540.43
Z	4	2
cryst. dimens., mm	0.15x0.15x0.15	0.16x0.08x0.16
radiation ($\mathrm{MoK}_{\bar{\alpha}}$)	0.71069 Å	0.71069 Å
abs. coeff., cm^{-1}	47.613	57.327
scan speed, deg. mm^{-1}	5(θ/2θ)	3(θ/2θ)
scan range, deg	1.8 + dispersion	2.0 + dispersion
data collected	$6° \leq 2\theta \leq 45°$	$6° \leq 2\theta \leq 45°$
Unique data	4406	4022
data with F > 2.33σ(F)	3437	3487
goodness of fit	1.267	1.709
R, %	5.7	4.6
R_w, %	5.3	4.5

yield a copious precipitate of small plate-like crystals. The flask was left at 0°C overnight and the solid collected by filtration, washed copiously with EtOH and dried *in vacuo*. The crude material was dissolved in warm MeCN (45 cm^3, ~ 50°C), filtered and EtOH (45 cm^3) added at this temperature. Slow cooling to ambient temperature and then 0°C overnight produced large pale yellow prisms which were collected by filtration, washed copiously with EtOH and dried *in vacuo*. Yield: 11.8 g (77%). Found: C, 53.52; H, 6.80; N, 1.82; S, 11.40; Hg, 25.90. Calc. for $C_{34}H_{51}NS_3Hg$: C, 53.00; H, 6.67; N, 1.82; S, 12.48; Hg, 26.02%.

$[NPr^n_4][Pb(SPh)_3]$ (**2**). This material was prepared in an analogous manner employing PbO (4.46 g, 20 mmol) and recrystallized as yellow prisms from MeCN/EtOH. Yield: 9.1 g (64%). Found: C, 50.14; H, 5.97; N, 1.95; S, 12.30; Pb, 28.70. Calc. for $C_{30}H_{43}NS_3Pb$: C, 49.97; H, 6.01; N, 1.94; S, 13.34; Pb, 28.73%.

X-Ray studies

Suitable crystals were mounted on the goniostat of a Picker four-circle diffractometer and cooled to approx. − 160°C. The diffractometer system, low temperature apparatus and general techniques for collection and reduction of data have been described previously.[9] Unit cell dimensions were obtained from 30 and 41 centred reflections for **1** and **2**, respectively. The crystal and machine parameters employed in the subsequent data collection and structure solution are collected in Table 1.

$[NBu^n_4][Hg(SPh)_3]$ (**1**). The position of the Hg atom was located by a Patterson function and standard Fourier techniques located the remaining non-hydrogen atoms. After initial refinement cycles, a difference Fourier showed the positions of all the hydrogen atoms, which were included in the final refinement with isotropic thermal parameters; all other atoms were refined anisotropically. No absorption correction was performed. Final refinement parameters are included in Table 1.

$[NPr^n_4][Pb(SPh)_3]$ (**2**). The structure was solved and refined in a manner analogous to (**1**) except that hydrogen atoms were included in the final refinement cycles in calculated positions.

RESULTS AND DISCUSSION

HgO and PbO readily dissolve in methanolic solutions of NaSPh to yield pale yellow solutions (eqn 1) from which the $[M(SPh)_3]^-$ (M = Hg, Pb) anions can be precipitated in high yield by the addition of bulky quaternary ammonium salts. We have employed the metal oxides rather than the halides as reagents to avoid the presence of potentially ligating halide ions. The use of MO (M = Zn or Pb) to prepare neutral $M(SC_6Cl_5)_2$ has been described elsewhere.[6d]

$$MO + 4NaSPh \xrightarrow[N_2]{MeOH} Na[M(SPh)_3] + NaSPh + [Na_2O] \qquad (1)$$

Previously it had been shown[6c] that $Hg(NO_3)_2$ will react with four equivalents of $NaSC_6H_4\text{-}p\text{-}Cl$ to yield $[NMe_4]_2[Hg(SC_6H_4\text{-}p\text{-}Cl)_4]$ (**3**) in the presence of NMe_4^+ cations. Our isolation of a three-coordinate complex from a similar system suggests an equilibrium in solution between the mono- and di-anions (eqn 2). Such equilibria are

$$[Hg(SPh)_4]^{2-} \rightleftarrows [Hg(SPh)_3]^- + PhS^- \qquad (2)$$

well established[10] for Hg(II) with monodentate ligands such as CN^- and Cl^- and, in addition, it has been shown[7] that $[Hg(SPh)_4]^{2-}$ can be obtained from solutions containing preformed $[Hg(SPh)_3]^-$ and added NaSPh. The stoichiometry of the precipitated anion (**1**) or (**3**) would thus seem to be a function of solubility dependent upon the cation employed. In contrast, only one species $[Pb(SPh)_3]^-$ is detected by ^{207}Pb NMR of $Pb(SPh)_2/PhS^-$ reaction mixtures, even in the presence of two equivalents of PhS^-.[8b]

Description of structures

(**1**) and (**2**) crystallize in monoclinic and triclinic space groups, respectively, and contain discrete cations and anions. The structure and metric parameters of the former and the phenyl groups of the latter are unexceptional and will not be discussed further.

The structure of the anion of (**1**) is depicted in Fig. 1. Relevant bond lengths and angles are listed in Table 2. Three PhS^- groups are terminally ligated to a trigonal planar mercury atom which lies only 0.018 Å above the S(2, 3, 4) least squares plane. In $[Hg(TePh)_3]^-$, which also possesses trigonal planar coordination,[11] and Hg atom is 0.09 Å above the Te_3 plane. The central HgS_3 core is significantly distorted from local D_{3h} symmetry, however, for two reasons no doubt due to lattice effects: (i) rotation about Hg in the HgS_3 plane of the Hg–S(4) vector by 17.1° towards Hg–S(2), yielding the S–Hg–S angles in Table 2; and (ii) significant variation in the Hg–S bond distances, 2.407(3)–2.507(3) Å (mean 2.448 Å). **3** possesses longer Hg–S distances,[6c] in accord with its greater

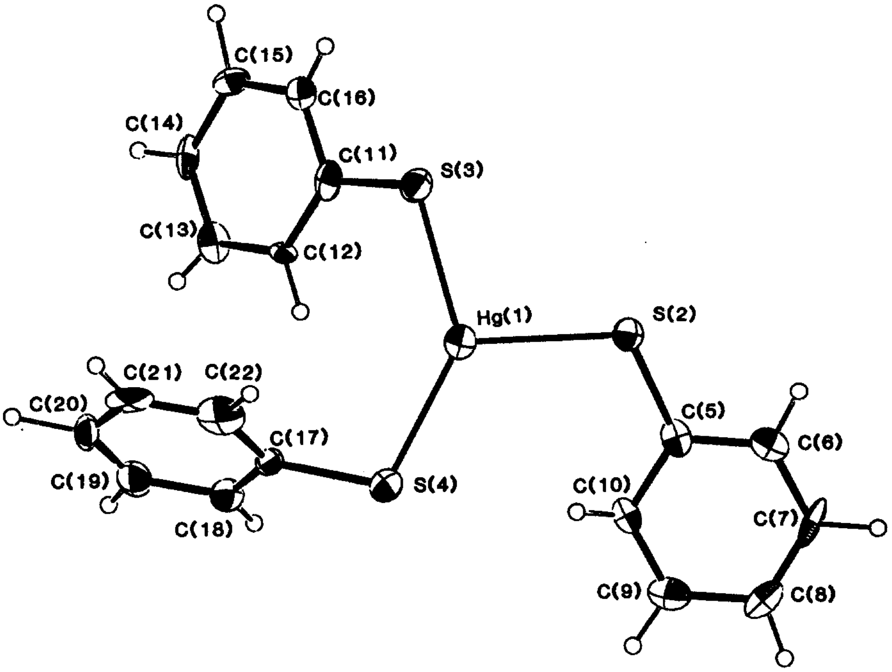

Fig. 1. The structure of the anion of 1 showing the atom labelling scheme. Non-hydrogen atoms are depicted as 50% probability ellipsoids.

coordination number, and in a much narrower range 2.537(1)–2.552(1) Å (mean 2.545 Å).

Mercury(II) usually forms complexes which are either linear two- or tetrahedral four-coordinate, but many species of empirical formulation Hg(ligand)$_3$ have been isolated. In many cases, however, crystallographic studies have shown these to be *bis*-(μ-bridged) dimers retaining four-coordination around each metal, e.g. $[Cl_2Hg(\mu\text{-}Cl)_2HgCl_2]^{2-}$,[12] $[(MeS)_2Hg(\mu\text{-}SMe)_2Hg(SMe)_2]^{2-}$,[6c] $[Cl_2Hg(\mu\text{-}urea)_2HgCl_2]$[13] and $[X(PR_3)Hg(\mu\text{-}X)_2HgX(PR_3)]$ (X = Cl, Br, I).[14,15] Even for mononuclear species such as $[CH_3S][HgI_3]$,[16] $[NMe_4][HgX_3]$ (X = Cl, Br, I)[17] and $HgCl_2$(9-methyl-hypox anthine),[18] weaker intermolecular Hg···X interactions have been detected such that the coordination of the Hg

Table 2. Selected bond lengths (Å) and angles (°) in $[M(SPh)_3]^-$ (M = Hg(II), Pb(II)) anions

Quantity	M = Hg(II)	M = Pb(II)
M-S(2)	2.507(3)	2.696(3)
M-S(3)	2.407(3)	2.665(3)
M-S(4)	2.431(3)	2.633(3)
Mean	2.448(43)	2.675(15)
S(2)-C(5)	1.760(11)	1.779(10)
S(3)-C(11)	1.779(11)	1.768(10)
S(4)-C(17)	1.782(11)	1.775(10)
S(2)-M-S(3)	120.0(1)	102.7(1)
S(2)-M-S(4)	102.9(1)	93.7(1)
S(3)-M-S(4)	137.1(1)	89.7(1)
Mean	120.0	95.4
M-S(2)-C(5)	110.7(4)	98.1(3)
M-S(3)-C(11)	105.8(4)	94.9(3)
M-S(4)-C(17)	104.8(4)	93.7(3)

Table 3. Comparison of selected distances and angles in monomeric three-coordinate species

Compound	M-L (Å)	L-M-L (°)	M-L_3 (Å)[a]	References
$[Hg(SPh)_3]^-$ (1)	2.407-2.507 mean 2.448	102.9-137.1 mean 120.0	0.018	b
$[Hg(TePh)_3]^-$	2.682-2.717 mean 2.697	110.7-125.2 mean 119.9	0.09	11
$[HgI_3]^-$	2.683-2.688 mean 2.686	114.7-122.7 mean 120.0	0[c]	12
$[Cu(SPh)_3]^{2-}$	2.274-2.335 mean 2.295	111.7-135.4 mean 120.0	0.05	19

[a] M-L_3 denotes the displacement of the metal atom from the L_3 least squares plane.

[b] This work.

[c] The Hg atom lies on a C_2 axis through one Hg-I vector.

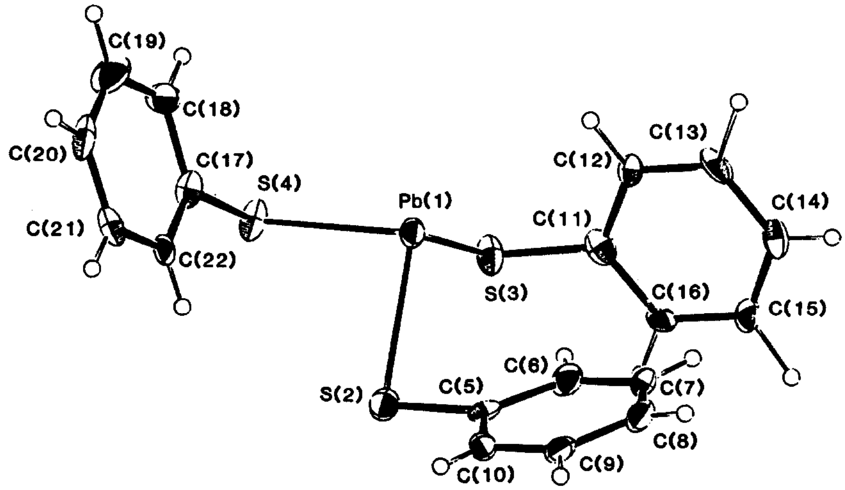

Fig. 2. The structure of the anion of **2** showing the atom labelling scheme. Non-hydrogen atoms are depicted as 50% probability ellipsoids.

atoms is best described as trigonal bipyramidal. **1** possesses no intermolecular Hg···S interactions within 5 Å and is thus a rare example of a true trigonal planar Hg(II) complex; [Ph$_4$As][Hg(TePh)$_3$][12] and [NBu$^n_4$][HgI$_3$][13] are two further examples, and pertinent structural data for these three compounds are compared in Table 3. Also included is the corresponding data for [Cu(SPh)$_3$]$^{2-}$,[19] the only established trigonal planar metal thiolate in the first transition series. In all cases, metal atom displacements (M–L$_3$) from the ligand least-squares plane are small ($\leq$ 0.09 Å) yielding mean L–M–L angles of ~120°, as expected for trigonal planar geometry. Metal–ligand distances are smaller in the Cu(I) complex reflecting the smaller radius of Cu(I)(3d^{10}) vs Hg(II)(5d^{10}), and, similarly, the size of the ligand atom is reflected in variation of Hg–L distances amongst the Hg(II) complexes. Otherwise the four complexes are very similar.

The structure of the anion of **2** is depicted in Fig. 2 and relevant bond lengths and angles are listed in Table 2. The coordination geometry of the lead(II) atom can be described as either trigonal pyramidal or pseudo-tetrahedral (with a stereochemically active lone pair occupying one site). The Pb atom lies 1.382 Å above the S(2, 3, 4) least squares plane of three terminally bound benzenethiolate groups. The PbS$_3$ core possesses essential C$_{3v}$ symmetry but, as in **1**, significant deviations from this symmetry are apparent. Thus, (i) the Pb–S distances range between 2.633(3)–2.696(3) Å (mean 2.675 Å) and (ii) S–Pb–S angles range between 89.7(1)–102.7(1)°. These angles are significantly less than the tetrahedral angle (109.5°) in accord with the steric requirements of a lone pair.

To our knowledge, **2** is the first structurally characterized example of an anionic lead(II) thiolate and supports the assignment of similar trigonal pyramidal coordination to [Ph$_4$As][Pb(SC$_6$F$_5$)$_3$], which was based on the structures of [MCl$_3$]$^-$ (M = Pb, Sn) anions,[8] and [Pb(SPh)$_3$]$^-$ generated in solution.[8b]

Complexes **1** and **2** represent rare examples of mononuclear three-coordinate metal thiolates and may prove useful starting materials for the preparation of higher nuclearity metal-thiolate systems. Based on ^{113}Cd NMR studies of metallothionein,[3] the metals in this protein appear to be in two polynuclear aggregates of 3 and 4 metal atoms of postulated formulation Cd$_4$(SPh)$_{11}^{3-}$ and Cd$_3$(SPh)$_9^{3-}$. If mercury metallothionein binds the metal atoms similarly, the corresponding mercury species should be present; such units are unknown at the present time in mercury thiolate chemistry. It has been shown that trigonal planar [Cu(SPh)$_3$]$^{2-}$ can be converted to adamantane-like [Cu$_4$(SPh)$_6$]$^{2-}$ on treatment with equimolar Cu(I) salts.[19] We have, therefore, explored a similar reaction of **1** with HgCl$_2$ in an attempt to prepare [Hg$_4$(SPh)$_6$]$^{2+}$ or [Hg$_4$(SPh)$_6$Cl$_4$]$^{2-}$. Preliminary experimentation, however, has yielded only Hg(SPh)$_2$ as an isolable product but further investigation is obviously warranted.

Supplementary material. A listing of F$_o$/F$_c$, atomic coordinates, temperature factors, and bond lengths and angles have been deposited with the Editor from whom copies are available on request. Atomic coordinates have also been deposited with the Cambridge Crystallographic Data Base.

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