Chemistry of Thiobenzoates: Syntheses, Structures, and NMR Spectra of Salts of $[M(SOCPh)_3]^-$ (M = Zn, Cd, Hg)

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The salts $(Ph_4E)[M(SOCPh)_3]$ (M = Zn, Cd, or Hg; E = P or As) are produced by the reaction of $Zn(NO_3)_2{\cdot}6H_2O$, $Cd(NO_3)_2{\cdot}4H_2O$ or $HgCl_2$ with $Et_3NH^+PhCOS^-$ and $(Ph_4E)X$ (E = P, X = Br; E = As, X = Cl) in aqueous MeOH in the ratios M(II):$PhCOS^-$:Ph_4E^+ = 1:≥3:≥1. The crystal structures of $(Ph_4P)[Zn(SOCPh)_3]$ (**1**), $(Ph_4As)[Cd(SOCPh)_3]$ (**2**) and $(Ph_4P)[Hg(SOCPh)_3]$ (**3**) have been determined by single-crystal X-ray diffraction experiments. Crystal data for **1**: triclinic; space group $P\bar{1}$; $Z = 2$; $a = 10.819(2)$ Å, $b = 13.219(3)$ Å, $c = 15.951(3)$ Å; $\alpha = 101.75(2)°$, $\beta = 97.92(1)°$, $\gamma = 109.18(2)°$. Crystal data for **2**: triclinic; space group $P\bar{1}$; $Z = 2$; $a = 10.741(2)$ Å, $b = 13.168(2)$ Å, $c = 15.809(2)$ Å; $\alpha = 101.00(1)°$, $\beta = 97.65(1)°$, $\gamma = 109.88(1)°$. Crystal data for **3**: monoclinic; space group $P2_1/n$; $Z = 4$; $a = 13.302(2)$ Å, $b = 14.276(2)$ Å, $c = 21.108(2)$ Å; $\beta = 90.92(1)°$. The compounds **1** and **2** are isomorphous and isostructural. In the anions $[M(SOCPh)_3]^-$ the metal atoms have trigonal planar coordination by three sulfur atoms. The metal atoms are further more weakly coordinated intramolecularly to one (M = Hg) or two (M = Zn, Cd) thiobenzoate oxygen atom(s). Using the Bond Valence approach it is found that the contribution of M···O bonding to the total bonding is in the order Cd > Zn > Hg. The metal (^{113}Cd, ^{199}Hg) NMR signals of $[M(SOCPh)_3]^-$ (M = Cd, Hg) are more shielded than those found for MS_3 kernels in thiolate complexes, a difference attributed to the M···O bonding in the thiobenzoate complexes. The ^{113}Cd resonance of $[Cd(SOCPh)_3]^-$ in dilute solution is in the region anticipated from dilution data for $[Na(Cd\{SOCPh\}_3)_2]^-$.

Introduction

The ligand behavior of monothiocarboxylates has not been very extensively studied.[1−3] However, the ligands $RCOS^-$ are interesting because they contain both a soft sulfur donor site and a hard oxygen donor site, and the presence of these disparate sites can lead to aggregation of soft and hard metal centers. An example is provided by the structure of $(Me_4N)[Na\{Cd(SCOPh)_3\}_2]$, which we reported recently.[3] In the $[Na\{Cd(SCOPh)_3\}_2]^-$ anion, the relatively soft Cd(II) is bound preferentially to the sulfur atoms, giving nearly trigonal planar coordination, while the relatively hard Na(I) is attached to six oxygen atoms. Planar CdS_3 kernels are uncommon. In thiolato-species, $[Cd(SR)_3]^-$ or $RSCd(\mu\text{-}SR)_2CdSR$, they are known only for particularly bulky R groups.[4−6] Since the formation of a CdS_3 kernel in $[Na\{Cd(SCOPh)_3\}_2]^-$ might be influenced by the interaction of the $SCOPh^-$ ligands with the Na^+ ion, we felt it important to investigate the geometry about the Cd(II) in $[Cd(SCOPh)_3]^-$ itself. Accordingly, we report here the syntheses and characterization of salts of $[Cd(SOCPh)_3]^-$. For additional comparison, we have extended our studies to include salts of $[M(SCOPh)_3]^-$ (M = Zn, Hg). In thiolates, the kernels MS_3 (M = Zn, Hg) are also formed only (M = Zn[7,8]) or mainly (M = Hg[4,5,9]) with bulky thiolates.

Experimental Section

General Procedure. All the preparations were carried under Ar, with solvents that had been sparged with Ar. As solids, the new compounds are stable in air at room temperature for days at least. For longer period of time they were normally stored under Ar at 5 °C. Solutions of these materials under Ar were stable for days at room temperature.

$(Ph_4P)[Zn(SOCPh)_3]$ (1). Et_3NH^+ $SCOPh^-$ was prepared *in situ* by mixing Et_3N (1.72 g, 17.0 mmol) in 20 mL of MeOH with thiobenzoic acid (2.35 g, 17.0 mmol). To this stirred solution was added $Zn(NO_3)_2{\cdot}6H_2O$ (1.69 g, 5.68 mmol) in 15 mL of H_2O. The resultant yellow solution with some viscous orange oil at the bottom was treated with Ph_4PBr (2.38 g, 5.66 mmol) in 20 mL of MeOH, and the mixture was heated to boiling, giving a clear yellow solution. The solution was filtered while hot and left in the refrigerator at 5°C for crystallization. The dark yellow crystals were separated by filtration, washed with MeOH and Et_2O, and then dried in a flow of Ar (yield 2.51 g). The washings were combined with the filtrate and allowed to evaporate at room temperature to get a second crop of crystals (yield 1.44 g). Total isolated yield 3.95 g (85%). Anal. (crop II) Calcd for $C_{45}H_{35}O_3P_1S_3Zn_1$ (mol wt 816.33): C, 66.21; H, 4.32. Found: C, 65.63, 65.71; H, 4.19, 4.24. ^{13}C NMR of anion[10] (CH_2Cl_2): δ 206.8 (PhC(O)S), 140.7 (C_1), 131.8 (C_4), 128.9 ($C_{2/6}$ or $C_{3/5}$), 127.9 ($C_{3/5}$ or $C_{2/6}$).

$(Ph_4As)[Zn(SOCPh)_3]$. This preparation was essentially the same as that of **1**. However, the amounts of the starting materials were as follows: $Zn(NO_3)_2{\cdot}6H_2O$, 0.63 g, 2.1 mmol; $Ph_4AsCl{\cdot}H_2O$, 1.79 g, 4.10 mmol; PhCOSH, 2.36 g, 17.1 mmol; Et_3N, 1.72 g, 17.0 mmol. The yield of orange needles was 1.56 g, 86%. Anal. Calcd for $C_{45}H_{35}O_3As_1S_3Zn_1$ (mol wt 860.28): C, 62.83; H, 4.10. Found: C,

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[⊗] Abstract published in *Advance ACS Abstracts,* April 15, 1996.

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(10) Carbon-13 NMR spectrum of PPh_4^+ (CH_2Cl_2): 136.0 (C_4, ^4J(P−C) = 3 Hz), 134.7 ($C_{2,6}$, ^2J(P−C) = 10 Hz), 130.9 ($C_{3,5}$, ^3J(P−C) = 13 Hz), 117.7(C_1, ^1J(P−C) = 90 Hz).

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62.56; H, 4.10. ^{13}C NMR of anion[11] (CH_2Cl_2): δ 206.7 (Ph*C*(O)S), 140.9 (C_1), 131.7 (C_4), 128.8 ($C_{2/6}$ or $C_{3/5}$), 127.9 ($C_{3/5}$ or $C_{2/6}$).

(Ph$_4$P)[Cd(SOCPh)$_3$]. Solid PhCOSH (2.35 g, 17.0 mmol) was added to Et_3N (1.72 g, 17.0 mmol) in 20 mL of MeOH. To the mixture was added a solution of $Cd(NO_3)_2{\cdot}4H_2O$ (1.75 g, 5.67 mmol) in 15 mL of H_2O, producing a pale yellow solution with some yellow oil at the bottom. A light yellowish white precipitate was obtained on addition of Ph_4Br (2.38 g, 5.67 mmol) in 20 mL of MeOH. Addition of MeCN (20 mL) plus 5 mL of CH_2Cl_2 produced a clear yellow solution, which was left at 5 °C overnight. The bright yellow crystals so produced were isolated by decantation, then washed and dried (yield 3.27 g), and a second crop obtained, as for **1** (yield 0.82 g). Total yield 4.09 g (84%). Anal. (crop I) Calcd for $C_{45}H_{35}Cd_1O_3P_1S_3$ (mol wt 863.35): C, 62.60; H,4.09. Found: C, 62.42; H, 3.91. ^{13}C NMR of anion[10] (CH_2Cl_2): δ 207.7 (Ph*C*(O)S), 140.7 (C_1), 131.7 (C_4), 129.2 ($C_{2/6}$ or $C_{3/5}$), 127.8 ($C_{3/5}$ or $C_{2/6}$).

(Ph$_4$As)[Cd(SOCPh)$_3$] (2). The synthesis was similar to that of the Ph_4P^+ salt except that $Ph_4AsCl{\cdot}HCl{\cdot}xH_2O$ was used instead of Ph_4PBr. Total yield: 3.86 g (~75%). Anal. Calcd for $C_{45}H_{35}As_1Cd_1O_3S_3$ (mol wt 907.30): C, 59.57; H, 3.89. Found: C, 59.76; H, 3.75. ^{13}C NMR of anion[11] (CH_2Cl_2): δ 207.7 (Ph*C*(O)S), 140.7 (C_1), 131.7 (C_4), 129.2 ($C_{2/6}$ or $C_{3/5}$), 127.8 ($C_{3/5}$ or $C_{2/6}$).

The same product (characterized by ^{13}C and ^{113}Cd NMR) was obtained in 87% yield using the same conditions but the following amounts of reagents: $Cd(NO_3)_2{\cdot}4H_2O$, 0.63 g, 2.0 mmol; $Ph_4AsCl{\cdot}H_2O$, 1.72 g, 3.94 mmol; PhCOSH, 2.25 g, 16.3 mmol; Et_3N, 1.65 g, 16.3 mmol.

(Ph$_4$P)[Hg(SOCPh)$_3$] (3). A 2.1 g portion of liquid PhCOSH (15 mmol) was added to Et_3N (1.44 g, 14.2 mmol) in 15 mL of MeOH. To the stirred mixture was added a solution of $HgCl_2$ (1.29 g, 4.75 mmol) in 10 mL of MeOH by syringe very close to the surface, to produce a clear yellow solution. (Addition of the $HgCl_2$ in this way is necessary to avoid any formation of black particles.) Upon addtion of Ph_4PBr (1.99 g, 4.75 mmol) in 10 mL of MeOH, a bright lemon yellow precipitate was formed, which on continued stirring slowly underwent partial dissolution. After addition of MeCN (10 mL) and CH_2Cl_2 (10 mL), the mixture was heated to ca. 50 °C for ca. 10 min, giving a clear yellow solution. This was allowed to cool to room temperature (ca. 20 min), then refrigerated at 5 °C overnight, producing long yellow needles. The crystalline product was isolated as for the Cd analogue. Yield: 3.69 g. The washings were combined with the decantate and kept at room temperature. On partial evaporation of the solvent, many light pink blocklike crystals were formed, contaminated with a small amount of black powder. These crystals were separated, washed with MeOH and Et_2O and dried in Ar. Yield: 0.39 g. Total yield isolated: 90%. Anal. (crop I) Calcd for $C_{45}H_{35}Hg_1O_3P_1S_3$ (mol wt 951.53): C, 56.80; H, 3.71. Found: C, 57.10: H, 3.58. ^{13}C NMR of anion[10] (CH_2Cl_2): δ 199.7 (Ph*C*(O)S), 141.4 (C_1), 131.8 (C_4), 128.8 ($C_{2/6}$ or $C_{3/5}$), 128.0 ($C_{3/5}$ or $C_{2/6}$).

The blocklike pink crystals were used for the single-crystal X-ray diffraction studies. A preliminary determination of cell data of the yellow crystals obtained in the first crop confirmed that it is isomorphous to the pink form. Cell data (25 °C): monoclinic, Laue symmetry $2/m$, $a = 13.227(1)$ Å, $b = 14.297(2)$ Å, $c = 21.142(2)$ Å, $\beta = 90.82(1)°$, $V = 3997.5(9)$ Å^3.

(Ph$_4$As)[Hg(SOCPh)$_3$]. The synthetic procedure was similar to that used for **3**. However, the reagents $HgCl_2$ (0.65 g, 2.4 mmol, in 10 mL of MeOH), PhCOSH (1.47 g, 10.6 mmol), Et_3N (0.97 g, 9.6 mmol, in 15 mL of MeOH) and $Ph_4AsCl{\cdot}H_2O$ (2.08 g, 4.76 mmol, in 10 mL of MeOH) were used in the ratio 1:4.4:4.2:2.1, and MeCN (10 mL), followed by CH_2Cl_2 (20 mL), was added to get a clear solution. Very light creamy, needle-like crystals were obtained in the first crop. Yield: 1.75 g. The crystals of the second crop were again light red and block-shaped. Yield: 0.38 g. A third crop of crystals was even darker red. Yield: 0.083 g. Total yield: 93%. Anal. (crop I) Calcd for $C_{45}H_{35}As_1Hg_1O_3S_3$ (mol wt 995.48): C, 54.30; H, 3.54. Found: C, 54.00; H, 3.45. ^{13}C NMR of anion[11] (CH_2Cl_2): δ 200.0 (Ph*C*(O)S), 141.7 (C_1), 131.7 (C_4), 128.8 ($C_{2/6}$ or $C_{3/5}$), 128.0 ($C_{3/5}$ or $C_{2/6}$).

Preliminary X-ray data of the crystals obtained in crop I and crop II indicated that they are isomorphous with the Ph_4P^+ salts. Cell data: yellow form, crop I, monoclinic, $a = 13.252(7)$ Å, $b = 14.302(6)$ Å, $c = 21.164(11)$ Å, $\beta = 91.42(4)°$, $V = 4010(3)$ Å^3; Red form, crop II, monoclinic, $a = 13.277(9)$ Å, $b = 14.323(7)$ Å, $c = 21.144(6)$ Å, $\beta = 91.37(4)°$, $V = 4020(4)$ Å^3.

NMR Spectra. Samples for both ^{13}C and metal NMR spectroscopy were prepared in Ar-flushed 10 mm o.d. NMR tubes, using solvents that had been sparged with Ar. The concentration in all cases was 0.1 mol of solute/L of solvent.

Proton-decoupled ^{13}C NMR spectra were obtained at 50.30 MHz and 296 ± 1 K using a Varian Gemini-200 spectrometer system. After preshimming of the field, no ^{2}D lock was used. Field drift was negligible. Chemical shifts were measured relative to a solvent signal as primary reference ($\delta_C(CH_2Cl_2) = 54.25$; $\delta_C(H_3CCN) = 1.82$).

Cadmium-113 and ^{199}Hg NMR spectra were measured using a Varian XL-300 spectrometer system operating at 66.53 and 53.72 MHz, respectively, again with no ^{2}D lock. Typically, ^{113}Cd spectra were obtained using a spectral window of 2.5 kHz, pulse width of 13.7 μs (ca. 73°), acquisition time of 1 s (2.5 W decoupling), and a 4 s delay (decoupler off). Typical conditions for measurement of ^{199}Hg NMR spectra were as follows: continuous 2.5 W decoupling, spectral window 5 kHz, pulse width 18 μs (ca. 90°), and acquisition time and cycle time 1 s.

External referencing of the metal NMR spectra was achieved by sample interchange, using 0.1 M $Cd(ClO)_4$(aq) at 296 K and pure $HgMe_2$ at 297 K for ^{113}Cd and ^{199}Hg, respectively. Chemical shifts were found to be reproducible to better than ±1 ppm and ca. ±2 ppm for ^{113}Cd and ^{199}Hg, respectively.

X-ray Structure Determination. The single crystals were obtained during the syntheses, as described. All the crystals are stable in air and were mounted at the end of a glass fiber using epoxy glue for diffraction experiments. The density measurements were made by the neutral buoyancy method. The diffraction experiments were carried out on a Siemens P4 diffractometer with the XSCANS software package[12] using graphite-monochromated Mo Kα radiation at 23(2) °C. The cell constants were obtained by centering 25 high angle reflections. The data were collected in $\theta - 2\theta$ scan mode at variable scan speeds (2−10 deg/min). Background measurements were made at the ends of the scan range. Three or four standard reflections were monitored at the end of every 297 reflections. The Laue symmetries were determined by merging equivalent reflections, and the space groups were determined from the systematic absences. *SHELXTL*[13] programs were used for data processing, solution, and the least-squares refinements (on F^2). All the non-hydrogen atoms in the anions and the P and As atoms were refined anisotropically. Isotropic thermal parameters were refined for the carbon atoms of the phenyl rings in the cation. Two-fold symmetry constraints were applied to the phenyl rings of the cations Ph_4E^+ (E = P or As). All the hydrogen atoms were placed in calculated ideal positions for the purpose of structure factor calculations only. There is no shift in the final cycles. A summary of the crystallographic data is given in Table 1, and selected positional parameters are given in Table 2. Complete crystallographic data, positional and thermal parameters, complete bond distances and angles, anisotropic thermal parameters, hydrogen atom coordinates, selected torsion angles, selected weighted least-squares planes, selected dihedral angles, and close contacts have been included in the Supporting Information.

Results and Discussion

Synthesis. The thiobenzoate complexes $[M(SOCPh)_3]^-$ (M = Zn, Cd, Hg) were synthesized straightforwardly according to eq 1. The $SOCPh^-$ anion was produced *in situ* by reaction

$$3SOCPh^- + M^{2+} \rightarrow [M(SOCPh)_3]^- \qquad (1)$$

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(11) Carbon-13 NMR spectrum of $AsPh_4^+$ (CH_2Cl_2): 135.2 (C_4), 133.2 ($C_{2,6}$), 131.6 ($C_{3,5}$), 120.6 (C_1).

(12) XSCANS. Siemens Analytical X-Ray Instruments Inc., Madison, WI, 1990.

(13) *SHELXTL Version 5 Reference Manual*; Siemens Analytical X-Ray Instruments Inc.: Madison, WI, 1994.

Table 1. Crystallographic Data for $(Ph_4P)[Zn(SCOPh)_3]$ (**1**), $(Ph_4As)[Cd(SCOPh)_3]$ (**2**), and $(Ph_4P)[Hg(SCOPh)_3]$ (**3**)

	1	**2**	**3**
empirical formula	$C_{45}H_{35}P_1O_3S_3Zn_1$	$C_{45}H_{35}As_1Cd_1O_3S_3$	$C_{45}H_{35}Hg_1P_1O_3S_3$
fw	816.25	907.23	951.47
temp, °C		23	
radiation; wavelength, Å		Mo Kα, 71073	
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
unit cell dimens			
a, Å	10.819(2)	10.741(2)	13.202(2)
b, Å	13.219(3)	13.168(2)	14.276(2)
c, Å	15.951(3)	15.809(2)	21.108(2)
α, deg	101.75(2)	101.00(1)	90
β, deg	97.92(1)	97.65(1)	90.92(1)
γ, deg	109.18(2)	109.88(1)	90
volume, $Å^3$	2057.1(7)	2005.7(4)	3978.0(9)
Z	2	2	4
ρobsd, g cm^{-3}; ρcalcd, g cm^{-3}	1.37(5); 1.318	1.51(5); 1.502	...; 1.589
abs coeff, mm^{-1}	0.83	1.559	4.107
final *R* indices			
$[I > 2\sigma(I)]$			
R1[a]	0.0551	0.0391	0.0435
wR2[a]	0.1186	0.0820	0.0913

[a] $R1 = \sum(||F_o| - |F_c||)/|\sum F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

Table 2. Selected Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$)

atom	*x*	*y*	*z*	*U*(eq)[a]
		1, $(Ph_4P)[Zn(SCOPh)_3]$		
Zn(1)	4407.1(6)	1981.1(5)	2584.9(4)	64.0(2)
S(1)	4434(1)	1341(1)	1134(1)	69.2(4)
S(2)	2645(2)	2015(1)	3308(1)	77.5(4)
S(3)	6578(2)	2568(1)	3499(1)	77.4(5)
O(1)	1992(4)	1366(5)	980(3)	114(2)
O(2)	4135(4)	3684(3)	2812(2)	69(1)
O(3)	4897(4)	551(3)	3244(2)	73(1)
C(1)	2827(5)	1207(4)	590(4)	65(1)
C(2)	3187(6)	3361(5)	3194(3)	65(1)
C(3)	6043(5)	1233(4)	3636(3)	55(1)
		2, $(Ph_4As)[Cd(SCOPh)_3]$		
Cd(1)	4390.0(4)	1939.2(3)	2527.0(3)	58.0(2)
S(1)	4533(2)	1337(1)	979(1)	68.1(4)
S(2)	2567(2)	2100(1)	3329(1)	72.1(4)
S(3)	6735(2)	2554(1)	3515(1)	76.2(5)
O(1)	2104(4)	1309(5)	941(3)	103(2)
O(2)	4103(4)	3770(3)	2833(2)	65(1)
O(3)	4981(3)	566(3)	3275(2)	64(1)
C(1)	2907(5)	1184(4)	498(4)	59(1)
C(2)	3168(5)	3448(4)	3215(3)	55(1)
C(3)	6125(5)	1234(4)	3660(3)	48(1)
		3, $(Ph_4P)[Hg(SCOPh)_3]$		
Hg(1)	378.4(2)	1962.0(2)	1120.0(2)	60.6(1)
S(1)	−784(2)	2369(2)	1983(1)	58.7(6)
S(2)	1583(2)	712(2)	1016(1)	73.2(7)
S(3)	90(2)	3309(2)	357(1)	84.2(8)
O(1)	120(4)	950(4)	2547(2)	63(2)
O(2)	2653(5)	2233(4)	860(3)	79(2)
O(3)	−1130(5)	1923(4)	134(3)	85(2)
C(1)	−491(5)	1582(5)	2601(3)	47(2)
C(2)	2657(6)	1386(6)	889(4)	57(2)
C(3)	−931(6)	2742(7)	23(3)	60(2)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

of PhCOSH with Et_3N rather than Na, to avoid the incorporation of Na^+ into the product that was found earlier[3] for M = Cd. A peculiarity of the reaction with M = Hg (as $HgCl_2$) is that the solution of $SOCPh^-$ must be added close to the surface of the Hg(II)-containing solution to avoid formation of a black substance, presumed to be β-HgS. An analogous situation was observed[14] in the synthesis of thiobenzoates of Pb(II) and Bi(III). The complex anions were isolated analytically pure as tetraphenyl-phosphonium and -arsonium salts ($[EPh_4][M(SOCPh)_3]$ (M = Zn, Cd, or Hg; E = P or As).

Table 3. Metal NMR Data for $[M(SOCPh)_3]^-$ (M = Cd or Hg)

compound	solvent[a]	T/K[b]	δ_{Cd}[c] ($\Delta\upsilon_{1/2}$ (approx)/Hz)	δ_{Hg}[d] ($\Delta\upsilon_{1/2}$ (approx)/Hz)
$(Ph_4P)[Cd(SOCPh)_3]$	CH_2Cl_2	294	287 (8)	
$(Ph_4As)[Cd(SOCPh)_3]$	CH_2Cl_2	295	287 (7)	
$(Ph_4As)[Cd(SOCPh)_3]$	MeCN[e]	294	291 (∼20)	
$(Ph_4P)[Hg(SOCPh)_3]$	CH_2Cl_2	298		−749 (200)
$(Ph_4As)[Hg(SOCPh)_3]$	CH_2Cl_2	296		−757 (190)

[a] Concentration = 0.1 mol/L of solvent, except as noted. [b] ±1 K. [c] ^{113}Cd, measured relative to external 0.1 M $Cd(ClO_4)_2$(aq). [d] ^{199}Hg, measured relative to external neat $HgMe_2$. [e] Concentration 0.002 mol/L of MeCN.

Under the synthetic conditions used, we were not able to isolate salts of $[M(SOCPh)_4]^{2-}$ when $PhCOS^-:M^{2+} \geq 4$. Such mixtures yielded only $[M(SOCPh)_3]^-$.

NMR Spectra. Metal NMR chemical shifts and line widths are given in Table 3. The ^{113}Cd NMR chemical shift of 291 ppm obtained for a dilute solution of $[Cd(SOCPh)_3]^-$ in MeCN is in the region (≤292 ppm) anticipated[3] from dilution data for the anion $(Na[Cd\{SOCPh)_3]_2)^-$. This is consistent with the suggestion[3] that $(Na[Cd\{SOCPh)_3]_2)^-$ undergoes dissociation in solution, releasing $[Cd(SOCPh)_3]^-$.

The metal resonances of $[M(SOCPh)_3]^-$ (M = Cd or Hg) are significantly more shielded than those obtained for $[M(SR)_3]^-$ (Table 4), even though the thiobenzoates and thiolates all have planar MS_3 skeletons. Almost certainly this can be attributed to the effect of weak interactions with the oxygen atoms in $[M(SOCPh)_3]^-$ (see below), as we have argued previously,[3,14] but further study is desirable.

A noteworthy feature of the ^{13}C NMR spectra of $[M(SOCPh)_3]^-$ is the irregular variation of the δ_C(PhCOS) (and hence the corresponding $\Delta\delta_C = \delta_C(\text{complexed}) - \delta_C(\text{free})$[17]) with M: the values are 207.7 (−5.1), 206.8 (−6.0) and 199.7

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(17) C-13 NMR spectrum of $PhCOS^-$ (in a solution in CH_2Cl_2 where NMe_3: PhCOSH = 2:1): 212.8 (Ph*C*OS) 144.2 (C_1), 130.3 (C_4), 128.5 ($C_{2/6\text{ or }3/5}$), 127.5 ($C_{3/5\text{ or }2/6}$).

Table 4. Metal NMR Data for $[M(SR)_3]^-$ (M = Cd or Hg)[a]

compound	δ_{Cd}[b]	δ_{Hg}[c]	ref
$(Ph_4P)[Cd(S\text{-}2,4,6\text{-}Pr^i{}_3C_6H_2)_3]$	577 (in $CDCl_3$ or DMF);[d] 668[e] (solid state)		4, 5
$(Me_4N)[Hg(SPr^i)_3]$		−79 (solid state)	15
$(Et_4N)[Hg(SBu^t)_3]$		−157 (in DMSO); −158 (solid state)	16
$(Bu^n{}_4N)[Hg(SPh)_3]$		−354 (in DMSO); −341[e] (solid state)	5, 16
$(Ph_4P)[Hg(S\text{-}2,3,4,5\text{-}Me_4C_6H)_3]$		−247 (solid state, form 1); −276 (solid state, form 2)	5

[a] At ambient probe temperature. [b] ^{113}Cd relative to external 0.1 M $Cd(ClO_4)_2(aq)$. [c] ^{199}Hg relative to external $HgMe_2$. [d] Reference 4. [e] Reference 5.

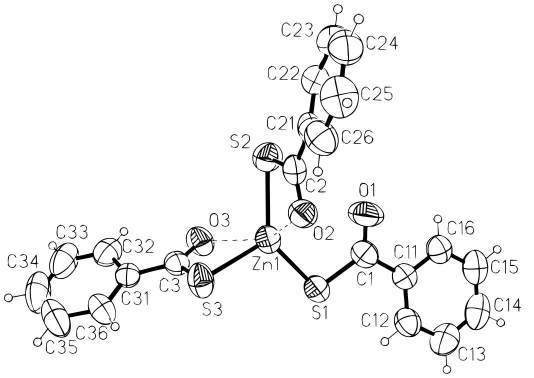

Figure 1. View of the $[Zn(SOCPh)_3]^-$ anion in **1**, showing the numbering scheme and 50% probability thermal ellipsoids. The same numbering scheme is used for the isostructural anion in **2**.

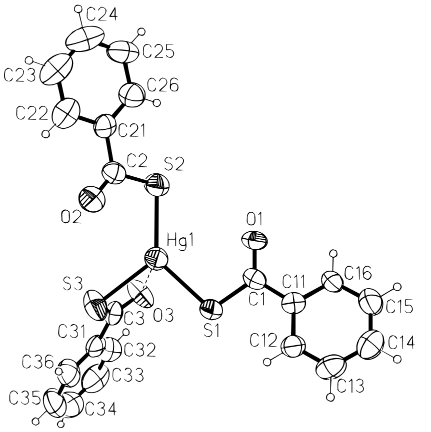

Figure 2. View of the $[Hg(SOCPh)_3]^-$ anion in **3**, showing the numbering scheme and 50% probability thermal ellipsoids.

ppm (−13.1 ppm for M = Cd, Zn, and Hg as the PPh_4^+ salts. It may be significant Zn appears to be intermediate between Cd and Hg in the percentage of the total bonding interaction that is provided by sulfur also (see below). Irregular variations have been observed for other nuclei attached directly and indirectly to the group 12 elements, e.g. ^{77}Se for both Se_α and Se_β in $[M(Se_4)_2]^{2-}$;[18,19] ^{125}Te for both Te_α and Te_β in $[M(Te_4)_2]^{2-}$.[20]

Structures of $[M(SOCPh)_3]^-$ (M = Zn−Hg). The crystal structures of **1**−**3** each consist of discrete cations and anions. The compounds **1** and **2** are isomorphous and isostructural. The structures of the cations in **1**−**3** are unexceptional and will not be discussed further. The structures of the anions in **1** and **3** are shown in Figures 1 and 2, while selected distances, angles and deviations of M from the S_3 and O_3 planes are given in Table 5.

Table 5. Selected Bond Distances (Å), Angles (deg), and Deviations (Å) from the S_3 and O_3 Planes in the Anions of **1**, **2**, and **3**

	1	**2**	**3**
Bond Distances			
M(1)−S(1)	2.304(2)	2.453(2)	2.470(2)
M(1)−S(2)	2.368(2)	2.514(2)	2.402(2)
M(1)−S(3)	2.376(2)	2.545(2)	2.533(2)
M(1)−O(1)	3.156(4)	3.019(4)	3.364(5)
M(1)−O(2)	2.328(4)	2.490(4)	3.086(6)
M(1)−O(3)	2.505(4)	2.557(3)	2.858(6)
S(1)−C(1)	1.769(5)	1.736(6)	1.761(7)
S(2)−C(2)	1.738(6)	1.728(5)	1.737(8)
S(3)−C(3)	1.737(5)	1.712(5)	1.714(9)
O(1)−C(1)	1.215(6)	1.214(6)	1.216(8)
O(2)−C(2)	1.263(6)	1.237(6)	1.211(9)
O(3)−C(3)	1.251(6)	1.224(5)	1.222(9)
C(1)−C(11)	1.525(7)	1.495(7)	1.497(10)
C(2)−C(21)	1.510(7)	1.483(7)	1.513(10)
C(3)−C(31)	1.508(6)	1.506(7)	1.523(11)
Bond Angles			
S(1)−M(1)−S(2)	132.50(6)	136.31(5)	131.48(7)
S(1)−M(1)−S(3)	110.96(6)	108.50(6)	101.59(8)
S(2)−M(1)−S(3)	116.32(6)	115.18(6)	126.79(9)
S(1)−M(1)−O(1)	55.00(9)	55.33(9)	50.76(10)
S(2)−M(1)−O(1)	78.60(9)	81.15(9)	80.78(11)
S(3)−M(1)−O(1)	164.10(9)	162.86(9)	151.52(11)
S(1)−M(1)−O(2)	109.92(10)	110.68(9)	136.04(13)
S(2)−M(1)−O(2)	67.58(10)	62.65(9)	55.20(13)
S(3)−M(1)−O(2)	98.97(10)	99.19(10)	85.91(13)
S(1)−M(1)−O(3)	101.95(10)	105.12(9)	96.2(2)
S(2)−M(1)−O(3)	94.33(9)	96.71(9)	111.94(14)
S(3)−M(1)−O(3)	64.27(9)	60.38(8)	57.02(13)
O(2)−M(1)−O(1)	81.17(13)	83.39(14)	109.05(14)
O(3)−M(1)−O(1)	122.68(13)	125.61(13)	124.4(2)
O(3)−M(1)−O(2)	147.79(12)	143.15(12)	122.8(2)
C(1)−S(1)−M(1)	101.9(2)	96.9(2)	105.3(3)
C(2)−S(2)−M(1)	80.2(2)	82.1(2)	98.4(3)
C(3)−S(3)−M(1)	84.9(2)	84.2(2)	90.7(3)
C(1)−O(1)−M(1)	80.2(3)	85.8(3)	80.9(4)
C(2)−O(2)−M(1)	92.0(3)	93.5(3)	82.4(5)
C(3)−O(3)−M(1)	90.8(3)	94.5(3)	88.4(5)
O(1)−C(1)−C(11)	120.2(5)	120.6(5)	120.9(7)
O(1)−C(1)−S(1)	122.8(4)	121.8(4)	122.8(6)
C(11)−C(1)−S(1)	117.0(4)	117.6(4)	116.2(5)
O(2)−C(2)−C(21)	120.0(5)	119.5(5)	121.0(8)
O(2)−C(2)−S(2)	120.2(4)	121.8(4)	123.9(7)
C(21)−C(2)−S(2)	119.8(4)	118.7(4)	115.0(6)
O(3)−C(3)−C(31)	120.7(5)	119.0(4)	118.8(8)
O(3)−C(3)−S(3)	120.0(4)	121.0(4)	122.9(7)
C(31)−C(3)−S(3)	119.2(4)	120.1(4)	118.3(7)
Deviations of M from S_3 Planes			
	−0.0641	−0.0063	−0.0527
Deviations of M from O_3 Planes			
	0.3785	0.3917	0.3466

In each anion, the metal atom is bonded to three $PhCOS^-$ ligands. Within each, the metal atom lies in the plane of the three sulfur atoms. Each metal atom is further bonded weakly to oxygen atoms. In the $PhCOS^-$ ligands, COS planes are twisted from the planes of the associated phenyl rings. The dihedral angles range from 7.0 to 19.6°.

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The Zn−S distances in **1** are range from 2.304 to 2.376 Å and thus are longer than the 2.278 Å reported[21] for [Zn-$(SCOPh)_2(H_2O)_2$], the 2.217−2.243 Å observed[7] in trigonal planar [Zn(S-2,3,5,6-$Me_4C_6H)_3]^-$ and the 2.184 and 2.203Å found[8] for the terminal Zn−S bonds of the trigonal planar ZnS_3 kernels in dimeric [Zn(S-2,4,6-$Bu^t{}_3C_6H_2)_2]_2$. The three Zn−O distances, 3.156, 2.328, and 2.505 Å in **1** are significantly different from each other and all shorter than that of 3.293 Å found[21] for the analogous interactions in [$Zn(SCOPh)_2(H_2O)_2$]. The Zn(1)−O(2) and Zn(1)−O(3) distances are less than the sum of the van der Waals radii for Zn and O (2.9 Å[22]). Including these two Zn−O interactions in the coordination sphere, the geometry of zinc may be described as a trigonal bipyramid. The C(1) and O(1) atoms are approximately in the ZnS_3 plane, between S(1) and S(2). The location of O(1) is reflected in the relatively large value of the angle S(1)−Zn-(1)−S(2) (132.5°) and the relatively small value of the angle O(1)−Zn(1)−S(2) (78.6°). The Zn atom is only 0.38 Å out of the O_3 plane, the sum of the O−Zn−O angles being 351.6°. The dihedral angle between the S_3 and O_3 planes is 75.2°.

The structure of **2** is very similar to that of **1** as noted earlier. The Cd−S distances (2.453−2.545 Å; mean 2.504 Å) observed in **2** are comparable to those found[3] in (Me_4N)[Na(M-{SCOPh}$_3)_2$] (2.485−2.521 Å; mean 2.50 Å) but longer than the Cd−S distances measured for the trigonal planar kernels of [Cd(S-*i*-$Pr_3C_6H_2$-2,4,6)$_3]^-$ (2.419−2.428 Å[4]) and [Cd(S-2,4,6-$Bu^t{}_3C_6H_2)_2]_2$ (2.377 Å for the terminal bonds[6]). Paralleling **1**, C(1) and O(1) are approximately in the CdS_3 plane between S(1) and S(2). Thus the angle O(1)−Cd(1)−S(2) (81.2°) is relatively small, while the angle S(1)−Cd(1)−S(2) is opened up (136.3°). The sum of the O−Cd−O angles is 352.1°, with the Cd displaced from the O_3 plane by 0.39 Å. The dihedral angles between the S_3 and O_3 planes is 71.9°.

The Hg-S distances of 2.402, 2.470, and 2.533 Å oberved in **3** are marginally larger on average than those reported[4,5,9] for various [$Hg(SAr)_3]^-$. The Hg···O distances are in the range 2.858−3.364 Å. The Hg(1)−O(3) distance, 2.858 Å is smaller than the sum of the van der Waals radii of Hg and O (3.0 Å[22,23]) indicating a weak interaction between Hg and this O atom. If O(3) is included in the coordination sphere of Hg, [$Hg(SOCPh)_3]^-$ has a trigonal pyramidal HgS_3O kernel.

The structural difference between the anion in **3** and those in **1** or **2** stems from the orientation of S(2), S(3), O(2), and O(3). The carbonyl group C(2)−O(2) in **3** occupies the space between S(2) and S(3), closer to the S_3 plane than in **1** or **2**. This leads to a comparatively large S(2)−Hg(1)−S(3) angle (126.8°). Also noteworthy is the unexpected trend observed for the M−S distances, Zn < Hg < Cd. We believe that this reflects different extents of interaction with oxygen (see below).

In the compounds **1**, **2**, and **3**, trigonal planar geometry of the MS_3 kernel is maintained regardless of the orientation of the COPh groups. Probably the steric bulk of the $PhCOS^-$ ligands promotes a planarity that is unaffected by the relatively weak M···O interaction(s). The contributions of the carbonyl oxygen atoms to the total bonding in [$M(SCOPh)_3]^-$ may be estimated using the bond-valence approach.[24] The results are shown in Table 6. They suggest that the interaction with oxygen contributes most in the case of **2** and that this contribution is reduced by competition with Na^+ in [Na(Cd{SOCPh}$_3)_2]^-$, as expected. Also noteworthy is the relatively small contribution that oxygen makes in **3**. This suggests that [$Hg(SOCPh)_3]^-$ should be an even better oxygen-donor metalloligand than [$Cd(SOCPh)_3]^-$.

Table 6. Bond Valences[a] of Zn−Hg in Some Thiobenzoate Complexes[b]

compound	tot. bond valence, V_i, of M	% of M−S	% of M−O
1	1.838	82.6	17.4
2	2.182	80.5	19.5
3	2.129	92.3	7.7
(Me_4N)[Na(Cd{SOCPh}$_3)_2$]	2.080	85.1	14.9

[a] See ref 23. [b] Based on bond distances given in this paper and ref 3.

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Supporting Information Available: Tables of crystallographic data for **1**, **2**, and **3**, positional and thermal parameters, complete bond distances and angles, anisotropic thermal parameters, calculated hydrogen atom coordinates, selected torsion angles, selected weighted least-squares planes, selected dihedral angles, and close contacts in **1**, **2** and **3**, and a figure showing a view of the [$Cd(SOCPh)_3]^-$ anion in **2** (37 pages). Ordering information is given on any current masthead page.

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