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Thioacetate complexes of Group 12 metals. Structures of $[Ph_4P][Zn(SC\{O\}Me)_3(H_2O)]$ and $[Ph_4P][Cd(SC\{O\}Me)_3]$ †

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The compounds $[Ph_4P][Zn(SC\{O\}Me)_3(H_2O)]$ **1** and $[Ph_4P][M(SC\{O\}Me)_3]$ (M = Cd **2** or Hg **3**) were synthesized by treating the appropriate metal salt with $Et_3NH^+MeC\{O\}S^-$ and Ph_4PCl in the ratio 1 : 3 : 1 in water. The structures of **1** and **2** were determined by single crystal X-ray diffraction methods. In **1** the Zn is bonded to sulfur atoms of three thioacetate ligands and an oxygen atom of the H_2O molecule to have an idealised tetrahedral geometry. The hydrogen atoms of the co-ordinated H_2O molecule are involved in intramolecular O–H · · · O hydrogen bonding with two carbonyl oxygen atoms. Approximate mirror symmetry is present in the anion. In the $[Cd(SC\{O\}Me)_3]^-$ anion in **2** a propeller-like arrangement of the three co-ordinated $MeC\{O\}S^-$ is found. The three sulfur atoms are strongly bound to Cd giving a pyramidal CdS_3 kernel. The anion is best described as having *fac* octahedral geometry with an approximate C_3 symmetry. Metal NMR data have been measured for **2** and **3**. The reduced temperature cadmium-113 NMR spectrum of a $[Cd(SC\{O\}Me)_3]^-$–$[Cd(SC\{O\}Ph)_3]^-$ mixture provides evidence for $[Cd(SC\{O\}Me)_x(SC\{O\}Ph)_{3-x}]^-$ (x = 3–0), confirming the integrity of the two parent complexes in solution. Cadmium-113 NMR spectra of **2** : L mixtures (L = H_2O, DMF or DMSO) show that $[Cd(SC\{O\}Me)_3]^-$ is a weak acceptor. Mercury-199 NMR spectra of analogous **3** : L mixtures show that $[Hg(SC\{O\}Me)_3]^-$ has, at best, a weaker acceptor ability towards H_2O, DMF and DMSO than its cadmium analogue. The syntheses and metal NMR data show that the acceptor ability of $[M(SC\{O\}Me)_3]^-$ (M = Zn to Hg) towards H_2O varies with M in the order $Zn^{II} > Cd^{II} > Hg^{II}$.

Introduction

For the past several years we have been interested in the chemistry of thiobenzoates.[1–10] The presence of both hard and soft donor sites makes thiocarboxylates, $RC\{O\}S^-$ in general, interesting ligands. Recently, we have reported[1] homoleptic anionic complexes $[M(SC\{O\}Ph)_3]^-$ (M = Mn, Co or Ni) in which both oxygen and sulfur atoms of the thiobenzoate ligands are bonded to the central metal atom in a bidentate fashion. In contrast, the cadmium atoms in $[Na\{Cd(SC\{O\}Ph)_3\}_2]^-$ have trigonal planar geometry with respect to the sulfur atoms.[2] In this trinuclear anion the planarity of the CdS_3 kernel was attributed to the presence of the Na^+, which binds to the oxygen atoms of the carbonyl groups, precluding (or at least reducing) their bonding to cadmium. However, a similar trigonal planar MS_3 geometry, supported by one or more intramolecular M · · · O interactions, was observed[3–5] in $[M(SC\{O\}Ph)_3]^-$ (M = Zn, Cd or Hg) even when the alkali metal cation was absent. For M = Zn to Hg, trigonal planar MS_3 kernels are generally found only within complexes with hindered thiolate ligands.[11–16] Rhombohedral $[Ph_4P][Cd(SC\{O\}Ph)_3]$ has a unique structure containing both planar and pyramidal CdS_3 kernels.[9] Unlike those of $[M(SC\{O\}Ph)_3]^-$ (M = Mn, Co or Ni), the pyramidal MS_3 kernels in the rhombohedral salt exhibit only weak M · · · O interactions.

The structural studies of $[M(SC\{O\}Ph)_3]^-$ (M = Zn to Hg) raise several interesting questions. Is $[Cd(SC\{O\}Ph)_3]^-$ unique in exhibiting polytopal isomerism? What are the structures (and stabilities) of $[M(SC\{O\}R)_3]^-$ in solution? Does the commonly found MS_3 planar geometry occur only in complexes with the $Ph\{O\}CS^-$ ligand or in complexes of the Group 12 metals with other thiocarboxylate ligands $R\{O\}CS^-$ also? As a contribution to answering some of these questions, we have carried out a study of the thioacetate complexes of the zinc-group elements. Here we report the synthesis of anionic thioacetato-complexes of Zn, Cd and Hg and the structures of those of Zn and Cd. The ^{113}Cd and ^{199}Hg NMR chemical shifts have been measured for the complexes of Cd and Hg in solution, for comparison with those of the thiobenzoato-complexes.[3] In addition, metal NMR data have been obtained for $[M(SC\{O\}Me)_3]^-$–$[M(SC\{O\}Ph)_3]^-$ mixtures and for mixtures of $[M(SC\{O\}Me)_3]^-$ and the potential ligands H_2O, DMF and DMSO.

Thioacetate complexes of the Group 12 metals are potential candidates as single-source precursors to make metal sulfide materials. Hampden-Smith and co-workers have successfully used the adducts of $M(SC\{O\}Me)_2$ (M = Zn or Cd) with tmen[17] and lutidine (2,6-dimethylpyridine) (Lut)[18] to deposit the corresponding metal sulfides.

Experimental

General procedure

All materials were obtained commercially and used as received. The compounds *monoclinic*-$[Ph_4P][Cd(SC\{O\}Ph)_3]$ and $[Ph_4P][Hg(SC\{O\}Ph)_3]$ were prepared as described in the literature.[3] All reactions were performed under an atmosphere of N_2(g). All non-aqueous solvents were dried over 3 Å molecular sieves. They and water were degassed with N_2(g) or Ar(g)

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† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/4419/

Also available: ^{113}Cd NMR titration data. For direct electronic access see http://www.rsc.org/suppdata/dt/1999/4419/, otherwise available from BLDSC (No. SUP 57673, 3 pp.) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (http://4419.rsc.org/dalton).

before the reactions or preparation of NMR samples. The yields are reported with respect to the metal salts. The prepared complexes were stored under a N_2 atmosphere and at 5 °C as they deteriorate on prolonged standing in the air at room temperature. The Microanalytical Laboratory at National University of Singapore performed microanalyses.

Preparations

$[Ph_4P][Zn(SC\{O\}Me)_3(H_2O)]$ 1. Thioacetic acid (2.0 mL, 28 mmol) was added dropwise to a stirred aqueous solution of Et_3N (3.9 mL, 28 mmol) to obtain a solution of Et_3NH^+ $Me\{O\}CS^-$. To this was added $ZnCl_2\cdot 1.5H_2O$ (1.226 g, 9 mmol) in water (5 mL). The resulting solution was stirred for 10 min. When a solution of Ph_4PCl (3.369 g, 9 mmol) in water was added a cream-coloured precipitate was formed. The mixture was stirred for 1 h, after which CH_2Cl_2 (8 mL) was added. The precipitate in the aqueous layer was extracted into the CH_2Cl_2 layer, which became yellow. The CH_2Cl_2 layer was separated and washed with 30 mL portions of deionised water 3 or 4 times to remove the side product, Et_3NHCl. Then Et_2O was added to the CH_2Cl_2 solution until turbidity was noticed, when the mixture was set aside in a refrigerator overnight, to obtain yellow crystals. The crystals were decanted, washed with Et_2O and dried in vacuum. Yield: 3.66 g (62.7%). Suitable single crystals were selected and used for X-ray diffraction experiments. Calc. for $C_{30}H_{31}O_4PS_3Zn$: C, 55.60; H, 4.82; P, 4.78; S, 14.84; Zn, 10.09. Found: C, 55.62; H, 4.75; P, 4.68; S, 15.04; Zn, 10.15%. ^1H NMR: δ 2.34 (s, $CH_3\{O\}CS$, 9 H), 4.75 (H_2O) and 7.6–7.8 (m, C_6H_5, 20 H). ^{13}C NMR: δ 36.8 ($CH_3\{O\}CS$), 117.9 (Ph C^1, ^1J(P–C) = 89.7), 131.3 (Ph $C^{3,5}$, ^3J(P–C) = 24.2), 134.8 (Ph $C^{2,6}$, ^2J(P–C) = 9.8), 136.3 (Ph C^4, ^4J(P–C) = 2.3 Hz) and 212.2 ($CH_3\{O\}CS$).

$[Ph_4P][Cd(SC\{O\}Me)_3]$ 2. The preparation was as for complex **1**, except that the cadmium was added as a solution of $CdCl_2\cdot H_2O$ (1.812 g, 9 mmol) in water (5 mL). Yield of yellow crystals: 3.2 g (53%). The crystals were suitable for single crystal X-ray studies. Calc. for $C_{30}H_{29}CdO_3PS_3$: C, 53.21; H, 4.32; Cd, 16.60; P, 4.57; S,14.21. Found: C, 53.07; H, 3.93; Cd, 15.46; P, 4.11; S, 14.44%. ^1H NMR: δ 2.29 (s, $CH_3\{O\}CS$, 9 H) and 7.6–7.8 (m, C_6H_5, 20H). ^{13}C NMR: δ 35.4 ($CH_3\{O\}CS$), 118.0 (Ph C^1, ^1J(P–C) = 89.6), 131.3 (Ph $C^{3,5}$, ^3J(P–C) = 12.9), 135.0 (Ph $C^{2,6}$, ^2J(P–C) = 10.4), 136.4 (Ph C^4, ^4J(P–C) = 2.0 Hz) and 213.2 ($CH_3\{O\}CS$).

$[Ph_4P][Hg(SC\{O\}Me)_3]$ 3. This complex was synthesized in the same way as **1**, but on half the scale and using $HgCl_2$ (1.222 g, 4.5 mmol) in 11 mL of MeOH–water (1 : 10 v/v) as the source of mercury. Yield of yellow crystals: 4.56 g (66.3%). Calc. for $C_{30}H_{29}HgO_3PS_3$: C, 47.08; H, 3.82; Hg, 26.21; P, 4.05; S, 12.57. Found: C, 46.78; H, 3.55; Hg, 25.51; P, 3.62; S, 12.47. ^1H NMR: δ 2.30 (s, $CH_3\{O\}CS$, 9 H), 7.6–7.8 (m, C_6H_5, 20H). ^{13}C NMR: δ 36.1 ($CH_3\{O\}CS$), 117.9 (Ph C^1, ^1J(P–C) = 89.1), 131.3 (Ph $C^{3,5}$, ^3J(P–C) = 12.8), 134.9 (Ph $C^{2,6}$, ^2J(P–C) = 9.8), 136.3 (Ph C^4, ^4J(P–C) = 3 Hz) and 205.9 ($CH_3\{O\}CS$).

NMR Spectra

Proton and ^{13}C-$\{^1H\}$ NMR spectra were recorded at 298 K on a Bruker ACF 300 MHz spectrometer. Samples were made up in 5 mm od NMR tubes with CD_2Cl_2 or $CDCl_3$ as solvent and TMS as internal reference. Metal NMR spectra were obtained using a Varian XL-300 spectrometer system, operating at 66.53 and 53.72 MHz for ^{113}Cd and ^{199}Hg, respectively. Proton decoupling was continuous for ^{199}Hg but inverse-gated for ^{113}Cd, which has a negative Overhauser effect. Spectra were obtained with the field pre-shimmed, but without a field-frequency lock (field drift is negligible). Temperatures were measured using a calibrated thermocouple in a stationary dummy sample. External referencing was carried out by sample interchange using 0.1 M $Cd(ClO_4)_2$ (aq) at 294 ± 1 K and neat $HgMe_2$ at 296 ± 1 K for ^{113}Cd and ^{199}Hg, respectively. Samples were prepared in 10 mm od NMR tubes under an atmosphere of argon, with solvents which had been degassed with Ar(g), and used directly. (In initial experiments, samples were prepared using ice-cold solvent. However, it was found that, except for samples containing **3** with added water, the metal NMR spectra at ambient probe temperature do not change over a period of hours, indicating that the precaution of cooling the solvent is unwarranted.) Concentrations are expressed as mass of solute per volume of solvent. For the chemical shift titrations, additions of DMSO, DMF or water to solutions in CH_2Cl_2 were made under a flow of Ar(g) using a 10 µL syringe.

The stability constants for eqn. (4) were found by successive approximation based on the fit of the fractional populations calculated from them to eqn. (1)[19] ($\Delta\delta_{Cd}$ ($=\delta_{Cd}([Cd(SC\{O\}Me)_3]^- + L) - \delta_{Cd}([Cd(SC\{O\}Me)_3]^-)$; complex = $[Cd(SC\{O\}Me)_3(L)]^-$). This method puts all of the error into the value of $\Delta\delta_{Cd}$(complex). The approach was validated by the values of r^2 and the reasonableness of the values found for $\Delta\delta_{Cd}$(complex). Regression analyses of the metal chemical shift titration data *vs.* P(complex) were carried out using QuattroPro 8.0 (Corel Corporation, Ottawa, Canada, 1997). For the purposes of these calculations, concentrations in mol per L of solvent were taken to approximate molarities. Also, because such small amounts of the prospective ligands L were used, the approximation was made that these additions caused no general solvent effects on the chemical shifts.

$$\Delta\delta_{Cd} = P(\text{complex})\cdot\Delta\delta_{Cd}(\text{complex}) \qquad (1)$$

Thermogravimetric analysis

Thermogravimetric analysis of complex **1** was carried out using a SDT 2980 TGA Thermal Analyser with a heating rate of 20 °C min^{-1} in a N_2 atmosphere using a sample size about 5–10 mg per run.

X-Ray crystallography

The diffraction experiments were carried out on a Bruker SMART CCD diffractometer. The softwares used were: SMART,[20] for collecting frames of data, indexing reflections and determination of lattice parameters; SAINT,[20] for integration of intensity of reflections and scaling; SADABS,[21] for absorption correction; and SHELXTL,[22] for space group and structure determination, least-squares refinements on F^2, graphics and structure reporting. The hydrogen atoms attached to the oxygen of the H_2O molecule in complex **1** were successfully located. The positional and common isotropic thermal parameters were refined in the least-squares cycles. The absolute structure (Flack) parameter was refined to −0.03(2) for **2**. A brief summary of the crystallographic data is given in Table 1.

CCDC reference number 186/1705.

See http://www.rsc.org/suppdata/dt/1999/4419/ for crystallographic files in .cif format.

Results and discussion

All three complexes were prepared by a general route from the metal salts and deprotonated $Me\{O\}CS^-$ in the ratio of 1 : 3, eqn. (2), and isolated as the Ph_4P^+ salts. Only the zinc(II) compound picked up a molecule of H_2O, eqn. (3).

$$M^{2+} + 3\,Me\{O\}CS^- \xrightarrow{H_2O} [M(SC\{O\}Me)_3]^- \qquad (2)$$

$$[Zn(SC\{O\}Me)_3]^- + H_2O \longrightarrow [Zn(SC\{O\}Me)_3(H_2O)]^- \qquad (3)$$

Table 1 Crystallographic data for $[Ph_4P][Zn(SC\{O\}Me)_3(H_2O)]$ **1** and $[Ph_4P][Cd(SC\{O\}Me)_3]$ **2**

	1	2
Chemical formula	$C_{30}H_{31}O_4PS_3Zn$	$C_{30}H_{29}CdO_3PS_3$
Formula weight	648.07	677.08
T/K	296	296
Radiation, wavelength/Å	Mo-Kα, 0.71073	Mo-Kα, 0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1$
a/Å	11.6160(3)	10.7195(1)
b/Å	19.2122(3)	13.0561(2)
c/Å	14.3978(3)	11.2199(2)
β/°	93.281(1)	100.701(1)
V/Å^3	3207.9(1)	1542.97(4)
Z	4	2
μ/mm^{-1}	1.042	0.991
Reflections measured	14196	9847
Independent reflections	6666 ($R_{int} = 0.0292$)	6857 ($R_{int} = 0.0128$)
Final R indices $[I > 2\sigma(I)]$		
$R1$	0.0556	0.0271
$wR2$	0.1015	0.0656

Table 2 Metal NMR data for thioacetato- and thiobenzoato-complexes of cadmium and mercury[a]

Complex	T/K	$\delta_{Cd}(\Delta\delta_{\frac{1}{2}}$(approx.)/Hz)[b]	$\delta_{Hg}(\Delta\delta_{\frac{1}{2}}$(approx.)/Hz)[c]
$[Cd(SC\{O\}Me)_3]^-$ [d]	295	309(45)	
	178	303(90)	
$[Cd(SC\{O\}Ph)_3]^-$ [e]	295[f]	287(7)	
	178	280(15)	
$[Hg(SC\{O\}Me)_3]^-$ [d]	294		−689(170)
	178		−636(210)
$[Hg(SC\{O\}Ph)_3]^-$ [e]	296[f]		−757(190)
	178		−624(≈500)

[a] This work unless otherwise specified. [b] Relative to external 0.1 M $Cd(ClO_4)_2$(aq.). [c] Relative to external $HgMe_2$. [d] Ph_4P^+ salt. [e] Ph_4As^+ salt. [f] Ref. 3.

The ^1H and ^{13}C NMR spectra in solution of these compounds are consistent with the proposed formula. The presence of the water molecule in **1** was indicated in the initial weight loss observed in TG in the temperature range 70–100 °C (observed 3.0%, calculated 2.8%).

Metal NMR studies

The metal chemical shifts are given in Table 2, with data for the corresponding thiobenzoato-complexes for comparison. At ambient probe temperature the metal resonances of the thioacetato-complexes are deshielded relative to the thiobenzoato complexes for both ^{113}Cd and ^{199}Hg. The temperature sensitivities of the chemical shifts, $d\delta/dT$, are small and positive for both cadmium complexes, but larger in magnitude and negative for both mercury complexes. For $[Hg(SC\{O\}Ph)_3]^-$ both the sign[23] and the magnitude of $d\delta/dT$, -1.1 ppm K^{-1}, are noteworthy. Possibly conformational changes occur in this anion as the temperature is changed.

The integrity of both $[Cd(SC\{O\}Me)_3]^-$ and $[Cd(SC\{O\}Ph)_3]^-$ in solution is shown by a mixing experiment. At 294 K a 1 : 1 solution of these two ions (each 0.1 mol per L of solvent) shows a single broad resonance, $\delta_{Cd} = 298$, $\Delta\nu_{\frac{1}{2}} \approx 180$ Hz. At reduced temperature fine structure becomes evident, and at 178 K four resonances are observed, with approximately binomial intensities and δ(approx $\Delta\nu_{\frac{1}{2}}$) of ≈304 (300), 297.6 (150), 289.2 (90) and 279.5 (50 Hz). These four signals can be assigned to $[Cd(SC\{O\}Me)_x(SC\{O\}Ph)_{3-x}]^-$, with $x = 3, 2, 1$, or 0, respectively. Evidently the complexes remain triligated in solution. Furthermore, the similarity of the chemical shifts for $[Cd(SC\{O\}R)_3]^-$ (R = Me or Ph or mixtures of these) points to the same MS_3 skeletal geometry in solution, although it cannot be determined whether this is planar or pyramidal. The relative linewidths indicate that the limiting no-exchange spectrum has not been reached at 178 K. A similar mixing experiment for $[Hg(SC\{O\}Me)_3]^-$ and $[Hg(SC\{O\}Ph)_3]^-$ was not definitive. A single resonance was observed at 296 K, $\delta_{Hg}(\Delta\nu_{\frac{1}{2}}) = -721$ (≈130 Hz), but at 178 and at ≈168 K (for a partially frozen solution) only two broad signals were observed with $\delta_{Hg} \approx -646$ and -629, with the former being the more intense. It seems that even at the freezing point the slow exchange region is barely attained. The rate of exchange of S-donor ligands bound to Hg is typically faster than the rate of ligand exchange in the corresponding cadmium complexes.[24,25]

Table 3 Some formation constants, K, and ^{113}Cd NMR complexation shifts, $\Delta\delta_{Cd}([Cd(SC\{O\}Me)_3(L)]^-)$ for L : **2** mixtures in CH_2Cl_2 [a]

L	T/K	K/mol L^{-1}	$\Delta\delta_{Cd}([Cd(SC\{O\}Me)_3(L)]^-)$
H_2O	294[b]	1.0	173 ± 2[c]
DMSO	178[d]	5.0	119 ± 3[e]
DMF	178[f]	1.0	94 ± 5[g]

[a] See text. Cadmium concentration is 0.1 mol per L of solvent. [b] Water is insoluble in the solution when H_2O : **2** = *ca.* 2 : 1; it is insufficiently soluble at 178 K to collect sufficient data for evaluation of K and $\Delta\delta_{Cd}([Cd(SC\{O\}Me)_3(L)]^-)$. [c] $r^2 = 0.9997$. [d] Values of $\Delta\delta_{Cd}$ are too small at 294 K for evaluation of K and $\Delta\delta_{Cd}([Cd(SC\{O\}Me)_3(DMSO)]^-)$; *e.g.* 7 ppm when DMSO : **2** = 5.0 : 1. [e] $r^2 = 0.998$. [f] Values of $\Delta\delta_{Cd}$ are too small at 294 K for evaluation of K and $\Delta\delta_{Cd}([Cd(SC\{O\}Me)_3(DMF)]^-)$; *e.g.* 5 ppm when DMSO : **2** = 5.0 : 1. [g] $r^2 = 0.995$.

Acceptor behaviour of $[Zn(SC\{O\}Me)_3]^-$ is shown by the isolation of complex **1**. The complexation shifts, $\Delta\delta_{Cd}$ (= $\delta_{Cd}([Cd(SC\{O\}Me)_3]^- + L) - \delta_{Cd}([Cd(SC\{O\}Me)_3]^-)$), that are found when the ligands H_2O, DMSO or DMF are added incrementally to solutions of **2** in CH_2Cl_2 (SUP 57673), indicate that $[Cd(SC\{O\}Me)_3]^-$ behaves as a weak acceptor towards these ligands. The data can be analysed (Experimental section) in terms of eqn. (4) to give the formation constants, and

$$[Cd(SC\{O\}Me)_3]^- + L \rightleftharpoons [Cd(SC\{O\}Me)_3(L)]^- \quad (4)$$

the complexation ^{113}Cd NMR chemical shifts, $\Delta\delta_{Cd}$ ($[Cd(SC\{O\}Me)_3L]^-$), of $[Cd(SC\{O\}Me)_3L]^-$. Table 2 presents a summary of the results. We regard the values in Table 2 to be approximate, because of the approximations that were made in their derivations (Experimental section). However, the fits to the formation of a 1 : 1 complex from an unassociated $[Cd(SC\{O\}Me)_3]^-$ are good enough to rule out appreciable formation of any 2 : 1 (L : **2**) complex or appreciable aggregation of the precursor $[Cd(SC\{O\}Me)_3]^-$. The chemical shift and complexation shift, $\Delta\delta_{Cd}$, of **2** in pure DMSO at 294 K are ≈387 and ≈78. Those of **2** in pure DMF are 337 (28) at 294 K and ≈376 (≈71) at 213 K, with an extrapolated value for $\Delta\delta_{Cd}$ of ≈90 at 178 K. The remarkable agreement between the last value and that calculated for $[Cd(SC\{O\}Me)_3(DMF)]^-$ in CH_2Cl_2 from complexation shifts (Table 3) is probably fortuitous.

Mercury-199 NMR shows that $[Hg(SC\{O\}Me)_3]^-$ (as **3**) is an insignificant acceptor of DMSO and DMF. Even at 178 K values of $\Delta\delta_{Hg}$ are so small that they could be due to changes in the composition of the solvent when the potential donor is added. For example, with L : Hg = 10.0 : 1, $\Delta\delta_{Hg} = 3$ for both L = DMSO and DMF. Clearly negligible complexation is occurring. It is reasonable to expect that $\Delta\delta_{Hg}([Hg(SC\{O\}Me)_3(L)]^-)$ will be larger than $\Delta\delta_{Cd}([Cd(SC\{O\}Me)_3(L)]^-)$.[26] Addition of water to a solution of complex **3**, 0.1 mol per L of CH_2Cl_2, at 294 K produces *shielding*. The value of $\Delta\delta_{Hg} \approx -11$ when $[H_2O]/[\mathbf{3}] = 2.0$. Unfortunately, δ_{Hg} for **3**–water mixtures changes slowly with time, so that values of K and $\Delta\delta_{Hg}$(complex) could not be obtained. Even so it seems evident that $[Hg(SC\{O\}Me)_3(OH_2)]^-$ is less stable than its cadmium counterpart.

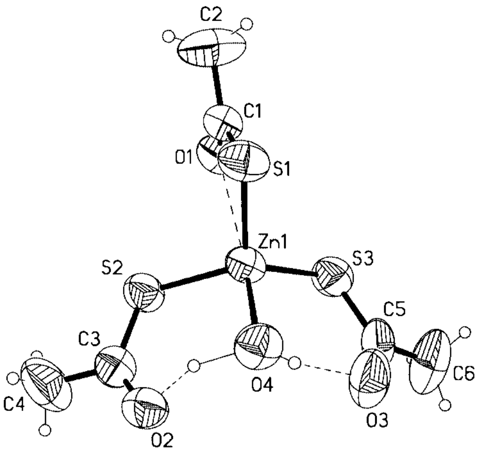

Fig. 1 A perspective view of the $[Zn(SC\{O\}Me)_3(H_2O)]^-$ anion. Hydrogen bonding distances (Å) and angles (°): O2 ··· O4 2.663(5); O3 ··· O4 2.614(5); O4–H1 1.29(4) and O4–H2 0.84(4); O4–H1 ··· O2 150(3) and O4–H2 ··· O3 166(4).

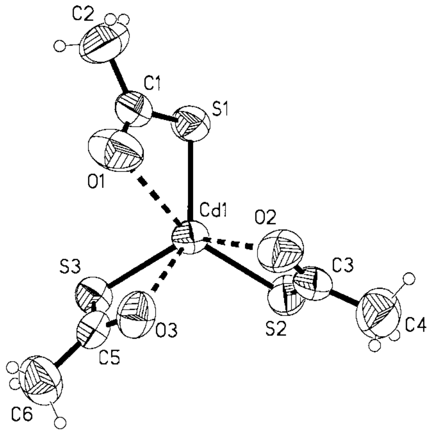

Fig. 2 An ORTEP[28] diagram of the anion $[Cd(SC\{O\}Me)_3]^-$ with 50% probability thermal ellipsoids and the numbering scheme. The hydrogen atoms are omitted for clarity.

The evidence from the syntheses, together with the metal NMR measurements, shows that acceptor ability for $[M(SC\{O\}Me)_3]^-$ (M = Zn, Cd or Hg), with the oxygen donors studied here, is in the order Zn > Cd > Hg. Evidently the order of "hardness" of the metal centres, $Zn^{II} > Cd^{II} > Hg^{II}$ is unaffected by co-ordination of the "soft" thiobenzoate sulfur atoms.

Structures of the complexes 1 and 2

The crystal structures of compounds **1** and **2** reveal that they consist of discrete mononuclear anions and cations. The structures of the anions in **1** and **2** are given in Figs. 1 and 2. Selected bond angles and lengths are given in Tables 4 and 5. The cations are unexceptional and warrant no further discussion.

In the $[Zn(SC\{O\}Me)_3(H_2O)]^-$ anion of **1** the Zn^{II} is bonded to three thioacetate ligands through sulfur atoms, and to the oxygen atom of an H_2O molecule giving a distorted tetrahedral geometry at the metal center. The hydrogen atom of the water molecule is involved in intramolecular O–H ··· O hydrogen bonding to the oxygen atoms, O(2) and O(3), of two carbonyl groups. Each hydrogen bond completes a stable six-membered ring.

Table 4 Selected bond distances (Å) and angles (°) for the anion in complex **1**

Zn(1)–S(1)	2.310(1)	C(3)–O(2)	1.233(4)
Zn(1)–S(2)	2.345(1)	C(5)–S(3)	1.733(5)
Zn(1)–S(3)	2.333(1)	C(5)–O(3)	1.226(5)
Zn(1)–O(4)	2.084(3)	C(1)–C(2)	1.506(6)
C(1)–S(1)	1.732(5)	C(3)–C(4)	1.504(6)
C(1)–O(1)	1.224(4)	C(5)–C(6)	1.508(6)
C(3)–S(2)	1.699(4)		
S(1)–Zn(1)–S(2)	113.01(4)	Zn(1)–S(3)–C(5)	105.9(2)
S(2)–Zn(1)–S(3)	116.27(4)	S(1)–C(1)–O(1)	122.7(3)
S(3)–Zn(1)–S(1)	115.28(4)	S(2)–C(3)–O(2)	126.6(3)
O(4)–Zn(1)–S(1)	105.69(9)	S(3)–C(5)–O(3)	125.2(4)
O(4)–Zn(1)–S(2)	100.32(9)	S(1)–C(1)–C(2)	117.4(4)
O(4)–Zn(1)–S(3)	103.92(9)	S(2)–C(3)–C(4)	114.6(3)
Zn(1)–S(1)–C(1)	89.5(1)	S(3)–C(5)–C(6)	115.6(4)
Zn(1)–S(2)–C(3)	109.0(2)		

Table 5 Selected bond distances (Å) and angles (°) for the anion in complex **2**

Cd(1)–S(1)	2.5334(9)	C(5)–S(3)	1.721(3)
Cd(1)–S(2)	2.5510(8)	C(1)–O(1)	1.217(5)
Cd(1)–S(3)	2.5687(8)	C(3)–O(2)	1.228(4)
Cd(1)–O(1)	2.689(3)	C(5)–O(3)	1.263(4)
Cd(1)–O(2)	2.555(3)	C(1)–C(2)	1.502(6)
Cd(1)–O(3)	2.562(3)	C(3)–C(4)	1.514(5)
C(1)–S(1)	1.694(4)	C(5)–C(6)	1.505(5)
C(3)–S(2)	1.713(4)		
S(1)–Cd(1)–S(2)	115.40(4)	S(1)–C(1)–O(1)	121.4(3)
S(2)–Cd(1)–S(3)	112.52(3)	S(2)–C(3)–O(2)	121.6(3)
S(3)–Cd(1)–S(1)	115.36(3)	S(3)–C(5)–O(3)	121.5(3)
O(1)–Cd(1)–O(2)	97.9(1)	Cd(1)–S(1)–C(1)	87.7(1)
O(2)–Cd(1)–O(3)	77.10(8)	Cd(1)–O(1)–C(1)	92.0(2)
O(3)–Cd(1)–O(1)	79.7(1)	Cd(1)–S(2)–C(3)	83.6(1)
O(1)–Cd(1)–S(1)	58.35(8)	Cd(1)–O(2)–C(3)	94.0(2)
O(2)–Cd(1)–S(2)	60.66(6)	Cd(1)–S(3)–C(5)	83.6(1)
O(3)–Cd(1)–S(3)	61.24(5)	Cd(1)–O(3)–C(5)	93.7(2)

The three Zn–S bond distances in complex **1**, 2.310(1), 2.333(1) and 2.345(1) Å, are not equal. The S(1) atom of the thioacetate group which is not involved in hydrogen bonding is involved in a shorter bond to Zn^{II} than the other two. The Zn–S distances observed are somewhat higher than the range, 2.294–2.312 Å, observed in the neutral adducts $[Zn(SC\{O\}Me)_2(tmen)]$[17] and $[Zn(SC\{O\}Me)_2(Lut)_2]$[18] by Hampden-Smith and co-workers. However, the bond distances observed in **1** fall into the range of 2.304–2.376 Å found[3] for $[Zn(SC\{O\}Ph)_3]^-$. The Zn–O distance, 2.084(3) Å, is longer than the corresponding distance, 2.031(6) Å, found in $[Zn(SC\{O\}Ph)_2(OH_2)_2]$.[27] The S–Zn–S angles, 113.01(4)–116.27(4)°, are higher than the ideal tetrahedral angle while the S–Zn–O angles, 100.32(9)–105.69(9)°, are lower than the ideal value, 109°28′. The C=O distances are equal, and unaffected by involvement in hydrogen bonding, or lack of it. There is a weak interaction between Zn(1) and the carbonyl oxygen atom, O(1), which is not involved in hydrogen bonding. The distance Zn(1) ··· O(1), at 2.698(3) Å, is less than the sum of the van der Waals radii, 2.90 Å.[29] This existence of the weak interaction is supported by the occurrence of a relatively small C–S–Zn angle, C(1)–S(1)–Zn(1) 89.5(1)°, for the ligand concerned (the corresponding angles in the other two ligands are 109.0(2) and 105.9(2)°). If this Zn ··· O interaction is taken into account the co-ordination geometry of Zn^{II} is high distorted trigonal bipyramidal. The interplanar angle between the Zn(1)S(2)C(3)C(4)O(2)O(4) plane (plane 2 with deviation, 0.094 Å) and the Zn(1)S(3)C(5)C(6)O(3)O(4) plane (plane 3 with deviation, 0.041 Å) at the Zn(1)–O(4) fold is 60.2(1)°. The plane containing atoms Zn(1)S(1)O(1)C(1)C(2)O(4) (plane 1, deviation, 0.053 Å) bisects planes 2 and 3 at the angles 61.2(1) and 60.2(1)° respectively. In other words, there is an approximate non-crystallographic mirror symmetry present in the anion along plane 1.

In the anion in complex **2** the CdS_3 kernel is not planar or near-planar, as it is in the majority of $[M(SC\{O\}R)_3]^-$ anions of the Group 12 elements (Table 6). The central Cd^{II} is bonded strongly to the sulfur atoms of the three $CH_3C\{O\}S^-$ ligands

Table 6 Deviations of M from the S_3 plane for various compounds

Compound	Deviation in Å	ΣS–M–S/°	Ref.
$[Ph_4P][Zn(SC\{O\}Ph)_3]$	−0.06	359.8	3
$[Ph_4As][Cd(SC\{O\}Ph)_3]$	−0.01	360.0	3
$[Ph_4P][Hg(SC\{O\}Ph)_3]$	−0.05	359.9	3
$[Me_4N][Na(Cd\{SC\{O\}Ph\}_3)_2]$	0.33	361.0	2
$[Ph_4P][Cd(SC\{O\}Ph)_3]$, m form	0.36	354.2	9
r form	0.11[a]	359.5[a]	9
	0.77[b]	333.3[b]	9
	0.65[c]	341.3[c]	9
$[Me_4N][Hg(SC\{O\}Ph)_3]$	0.10	359.5	4
$[Et_3NH][Cd(SC\{O\}Ph)_3]$[d]	0.18	358.5	5
	0.30	355.8	5
$[Ph_4P][Zn(SC\{O\}Me)_3(H_2O)]$	0.54	344.6	This work
$[Ph_4P][Cd(SC\{O\}Me)_3]$	0.61	343.3	This work

[a] Data for the Type B anion. [b] Data for the Type A anion. [c] Data for Type C anion. [d] Data for two independent 'ion pairs'.

and weakly to the oxygen atoms of the carbonyl groups in such a way as to have, roughly, a *fac* octahedral geometry. The disposition of the three carbonyl groups on the opposite side of the Cd to the S_3 plane results in the anion having a propeller-like geometry with an approximate C_3 point group symmetry, as found also for thiobenzoate complexes of Co, Ni and Mn,[1] and the type A and C anions of rhombohedral $[Ph_4P][Cd(SC\{O\}Ph)_3]$.[9] Overall, the geometry is most reminiscent of that of the type C anions in rhombohedral $[Ph_4P][Cd(SC\{O\}Ph)_3]$.[9] It is interesting that the compound **2** has crystallised in a polar space group ($P2_1$) as observed for the thiobenzoate complexes having (some) anions with *fac* geometry.[1,9] The Cd–S distances in **2**, 2.5334(9), 2.5510(8) and 2.5687(8) Å, are in the order Cd(1)–S(1) > Cd(1)–S(2) > Cd(1)–S(3). They fall into the range established for $[Cd(SC\{O\}Ph)_3]^-$,[2,3,5,9] as do the Cd–O distances, 2.689(3), 2.555(3) and 2.562(3) Å. However, the Cd–S distances are longer than those observed in $[Cd(SC\{O\}Me)_2(tmen)]$[17] and $[Cd(SC\{O\}Me)_2(Lut)_2]$.[18] The Cd $\cdots$ O distances of $[Cd(SC\{O\}Me)_3]^-$ are less than the sum of the van der Waals radii, 3.10 Å.[29] The C–S and C–O distances are in the same order as the Cd–S distances. In the present work the shortest C–S distance noted is 1.694 Å for **2** and 1.699 Å for **1**. The changes in the bond parameters may be attributed to the methyl group substitution.

(Near) trigonal planar is the geometry most commonly observed for the MS_3 skeletons of the tris(thiobenzoato) anions of the Group 12 metals (Table 6). The central metal atom Cd(1) in complex **2** does not have trigonal planar geometry with respect to the sulfur atoms; it is 0.612 Å away from the S_3 plane. Also, the sum of the S–Cd–S angles, 343.28°, is far below the expected angle of 360° (Table 6). Interestingly, the only other two discrete thiocarboxylato-complexes of Zn to Hg which have pyramidal MS_3 kernels also have Cd as the central atom.[9] Nonetheless, **2** is unique among salts of thiocarboxylato-complexes of Zn or Cd in containing *only* anions with a pyramidal MS_3 skeleton, suggesting a definite role for the R group of $R\{O\}CS^-$. It is also interesting that the ^{113}Cd NMR results point to a uniformity of MS_3 skeleton for $[Cd(SC\{O\}R)_3]^-$ (R = Me or Ph, or mixtures of these) in solution, in contrast to the results for the solid state.

It would be interesting to have a structural analysis of complex **3**. If its anion had a pyramidal HgS_3 skeleton, pyramidalisation could be correlated more definitely with the change of R from Ph to Me, since $[Hg(SC\{O\}Ph)_3]^-$ is known with a (near-)planar HgS_3 skeleton *only*.[3,4] Unfortunately, we have not yet been able to obtain crystals of the relatively unstable compound **3** that are suitable for single crystal X-ray analysis. In this case too, the metal NMR results point to a common geometry for the skeletons of the $[Hg(SC\{O\}R)_3]^-$ anions in solution.

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