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Synthesis, structure and solution NMR properties of $(Ph_4P)[M(SeC\{O\}Tol)_3]$, M = Zn, Cd and Hg

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Metal selenocarboxylate salts $(PPh_4)[M(SeC\{O\}Tol)_3]$ (M = Zn (**1**), Cd (**2**) and Hg (**3**); Tol = C_6H_4-*p*-CH_3) have been synthesized by reacting $Zn(NO_3)_2{\cdot}6H_2O$, $Cd(NO_3)_2{\cdot}4H_2O$ or $HgCl_2$ with $Na^+TolC\{O\}Se^-$ and PPh_4Cl in the ratio of 1 : 4 : 1. The structures of these compounds were determined by single-crystal X-ray diffraction methods. The crystal structures contain discrete cations and anions. In the each anion, the metal center is bound to three TolC{O}Se ligands, primarily through Se, though some long M···O interactions also occur. NMR spectra (^{113}Cd, ^{199}Hg and ^{77}Se, as appropriate) are reported for solutions of $[M(SeC\{O\}Tol)_3]^-$, and of $[M(SeC\{O\}Tol)_3]^-$–$[M(SC\{O\}Ph)_3]^-$ mixtures (M = Zn–Hg), in CH_2Cl_2 at reduced temperatures. In addition, ESI-MS data have been obtained for $[M(SeC\{O\}Tol)_3]^-$–$[M(SC\{O\}Ph)_3]^-$ mixtures (M = Zn–Hg) in acetone and in CH_2Cl_2. The NMR and ESI-MS studies show that the complexes $[M(SeC\{O\}Tol)_n(SC\{O\}Ph)_{3-n}]^-$ (n = 3–0) persist in solution.

Introduction

In the recent years, there has been significant interest in the development of the chemistry of metal–thiocarboxylate complexes, stemming not only from their interesting structural chemistry[1–4] but also from the fact that many of them can be used as molecular single precursors for the low-temperature synthesis of bulk metal sulfides, thin films and nanoparticles.[5–8] Monothiocarboxylates ($RC\{O\}S^-$) represent an interesting class of organic ligands equipped with both hard and soft donor sites.[1] These donor sites enable the incorporation of a combination of hard and soft metal centers into a coordination compound, as illustrated by the claw-like $[M(SC\{O\}Ph)_3]^-$ metalloligands of the complexes $(Me_4N)[A\{M(SC\{O\}Ph)_3\}_2]$ (A = Na, K; M = Cd, Hg).[2] In these metalloligands, the metal centers have a trigonal planar MS_3 kernel, a situation attributed to the presence of the hard alkali metals, which bind to the oxygen atoms of the carbonyl groups. Similar trigonal planar MS_3 geometry, but with the support of weak intermolecular M···O interactions, was observed for the anions in alkali-metal-free salts of $[M(SC\{O\}Ph)_3]^-$ (M = Zn, Cd or Hg).[3] The structures of the latter anions contrast with those of the homoleptic transition metal complexes $[M(SC\{O\}Ph)_3]^-$ (M = Co, Mn or Ni) which were found to contain discrete octahedral anions with MO_3S_3 kernels as a result of O,S-chelation.[4]

In contrast, little is known about the chemistry of metal-selenocarboxylate complexes to date. A major impediment to the development of this chemistry has been the difficulty of synthesizing the metal selenocarboxylate starting materials. Thus, for example, monoselenocarboxylate anions, $RC\{O\}Se^-$, are highly air and moisture-sensitive. Several years ago, Kato *et al.* reported a general synthesis of alkali metal selenocarboxylates,[9,10] including *p*-tolylmonoselenocarboxylate ($TolC\{O\}Se^-$). This provided an opportunity to study the chemistry of certain copper selenocarboxylate complexes.[11] The study revealed that the chemistry of monoselenobenzoates is distinct from that of the monothiocarboxylates. This raises a question about selenocarboxylate complexes of the Group 12 elements: will planar MSe_3 geometry also occur in $[M(SeC\{O\}R)_3]^-$ (M = Zn, Cd, Hg), as it does in the corresponding $[M(SC\{O\}Ph)_3^-$ anions? To date, only two examples of MSe_3 planar geometry have been reported, neither involving selenocarboxylate ligands.[12,13] To answer the question, as well as to extend the chemistry of selenobenzoates generally, we have carried out a synthetic and structural study of the monoselenocarboxylate complexes $[M(SeC\{O\}Tol)_3]^-$ (M = Zn–Hg). In addition, ^{77}Se, ^{113}Cd and ^{199}Hg NMR have been utilized to characterize the new complexes in solution. Further, ligand exchange between $[M(SeC\{O\}Tol)_3]^-$ and $[M(SC\{O\}Ph)_3]^-$ in solution has been monitored by both ESI-MS and metal NMR studies.

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Experimental

All materials were obtained commercially and were used as received except for *p*-toluoyl chloride, which was purified by distillation under N_2. Acetonitrile was distilled from calcium hydride under N_2. Na_2Se was prepared according to the literature method.[14] All reactions were performed under an atmosphere of argon using Schlenk techniques.

Synthesis of $(PPh_4)[Zn(SeC\{O\}Tol)_3]$, 1

To the solution of $Na^{+-}SeC\{O\}Tol$ (4.0 mmol) in MeCN, prepared as described above, $Zn(NO_3)_2{\cdot}6H_2O$ (0.30 g, 1.01 mmol) and PPh_4Cl (0.38 g, 1.01 mmol) were added. This solution was stirred for 1.5 h, then the insoluble $NaNO_3$ was separated by filtration. The solvent from the filtrate was removed using vacuum, then the yellow–orange sticky product was dissolved in 5 mL of CH_2Cl_2. The CH_2Cl_2 solution was layered with *ca.* 20 mL of hexane and left at 278 K overnight to obtain a yellow sticky product. Yellow rod like crystals of **1** were obtained by layering Et_2O onto a solution of the product in an MeCN–acetone (1 : 1 v/v) solution. Yield 0.63 g (63%). Anal. Calc. for $C_{48}H_{41}ZnPO_3Se_3$ (mol. wt 999.10): C, 57.70; H, 4.14. Found: C, 57.48; H, 3.99%. δ_H ($CDCl_3$): 2.27 (9H, S, CH_3–$C_6H_4C\{O\}Se$), 6.99–7.01 (6H, d, J = 6 Hz, *meta*-H), 7.89–7.91 (6H, d, J = 6 Hz, *ortho*-H), 7.52–7.83 (20 H, PPh_4). δ_C ($CDCl_3$):[15] 207.2 (Tol*C*{O}Se), 141.5 (C_4), 140.7 (C_1), 128.5 ($C_{2/6}$ or $C_{3/5}$), 127.9 ($C_{3/5}$ or $C_{2/6}$), 21.3 (CH_3–$C_6H_4C\{O\}Se$). ESI-MS (acetone): *m*/*z* 660.9 ($[M(SeC\{O\}Tol)_3]^-$, 100%), 199.5 ($TolC\{O\}Se^-$, 15%), 339.0 (PPh_4^+, 100%).

Synthesis of $(PPh_4)[Cd(SeC\{O\}Tol)_3]$, 2

The initial sticky crude product was obtained from $Na^{+-}SeC\{O\}Tol$ (4.0 mmol), $Cd(NO_3)_2{\cdot}4H_2O$ (0.31 g, 1.01 mmol) and

PPh_4Cl (0.38 g, 1.01 mmol), as described for **1**. The crude product was dissolved in 20 mL of MeCN–acetone (1 : 1 v/v), and the resulting yellow solution was then layered with *ca.* 50 mL of Et_2O. Following refrigeration at 278 K overnight, yellow rod like crystals of **2** were obtained. These crystals were separated by filtration and washed with MeOH and Et_2O. Yield 0.57 g (54%). Anal. Calc. for $C_{48}H_{41}CdPO_3Se_3$ (mol. wt 1046.12): C, 55.11; H, 3.95. Found: C, 55.10; H, 3.80%. δ_H ($CDCl_3$): 2.29 (9H, s, C*H*$_3$–C_6H_4C{O}Se), 7.01–7.03 (6H, d, *J* = 6 Hz, *meta*-H), 7.89–7.91 (6H, d, *J* = 6 Hz, *ortho*-H), 7.57–7.83 (20 H, m, PPh_4). δ_C ($CDCl_3$):[15] 207.3 (Tol*C*{O}Se), 141.5 (C_4), 140.8 (C_1), 128.9 ($C_{2/6}$ or $C_{3/5}$), 127.9 ($C_{3/5}$ or $C_{2/6}$), 21.3 (*C*H$_3$–C_6H_4C{O}Se). ESI-MS (acetone): *m*/*z* 708.9 ([M(SeC{O}Tol)$_3$]$^-$, 100%), 199.5 (TolC{O}Se$^-$, 10%), 339.0 (PPh_4^+, 100%).

Synthesis of (PPh_4)[Hg(SeC{O}Tol)$_3$], 3

To the solution of Na^{+-}SeC{O}Tol (4.0 mmol), an ice-cold solution of $HgCl_2$ (0.28 g, 1.01 mmol) and PPh_4Cl (0.38 g, 1.01 mmol) in 5 mL MeCN was added by syringe very close to the surface (to prevent the formation of black precipitate, HgSe[3]), to produce a yellow solution. This solution was stirred for 1.5 h and the insoluble NaCl was filtered off. This solution was concentrated by 50% and then refrigerated at 278 K overnight. The crystals of **3** were collected by filtration, washed with ice-cold MeOH and Et_2O, and dried in vacuum. Yield 0.35 g (31%). Anal. Calc. for $C_{48}H_{41}HgPO_3Se_3$ (mol. wt 1134.30): C, 50.83; H, 3.64. Found: C, 50.85; H, 3.55%. δ_H ($CDCl_3$): 2.31 (9H, s, C*H*$_3$–C_6H_4C{O}Se), 7.05–7.07 (6H, *J* = 6 Hz, d, *meta*-H), 7.96–7.98 (6H, d, *J* = 6 Hz, *ortho*-H), 7.48–7.79 (20 H, m, PPh_4). δ_C ($CDCl_3$):[15] 199.7 (Tol*C*{O}Se), 141.7 (C_4), 140.8 (C_1), 128.7 ($C_{2/6}$ or $C_{3/5}$), 128.2 ($C_{3/5}$ or $C_{2/6}$), 21.4 (*C*H$_3$–C_6H_4C{O}Se). ESI-MS (acetone): *m*/*z* 795.0 ([M(SeC{O}Tol)$_3$]$^-$, 80%), 199.5 (TolC{O}Se$^-$, 100%), 339.4 (PPh_4^+, 100%).

Compounds **1**–**3** were stored at 278 K under N_2. However, they are air stable as solids under ambient laboratory conditions, except for **3**, which is only stable under these conditions for about 2 h.

X-Ray crystallography

Single crystals were obtained during the synthesis. The diffraction experiments were carried out at 223 K on a Bruker SMART CCD diffractometer with a Mo-Kα sealed tube. The program SMART[16] was used for collecting frames of data, indexing reflection and determination of lattice parameters, SAINT[16] for integration of the intensity of reflections and scaling. SADABS[17] was used for absorption correction and SHELXTL[18] for space group and structure determination and least squares refinements on F^2. A brief summary of the crystallographic data is given in Table 1.

CCDC reference numbers 242797–242799.

See http://www.rsc.org/suppdata/dt/b4/b409621e/ for crystallographic data in CIF or other electronic format.

NMR studies

Samples for ^{77}Se, ^{113}Cd or ^{199}Hg NMR spectroscopy were prepared in 10 mm od NMR tubes under an atmosphere of Ar(g), using CH_2Cl_2 that had been dried by standing over 3 Å molecular sieves then, just before use, sparged with Ar(g). Because of the thermal instability of the solutions, the NMR tube containing the prospective solute(s) was chilled in ice prior to addition of sufficient solvent to give a concentration of 0.1 mol of solute(s)/litre of CH_2Cl_2 at ambient laboratory temperature. Each sample was transferred to the pre-cooled NMR probe directly after it had been prepared.

NMR spectra were measured using a Varian INOVA 400 Spectrometer System, at 76.240, 88.663 and 71.60 MHz for ^{77}Se, ^{113}Cd and ^{199}Hg, respectively, without a field-frequency lock; negligible field drift was measured. External referencing was carried out by sample interchange using neat Me_2Se, 0.1 M $Cd(ClO_4)_2$ (aq), and neat $HgMe_2$ at 299 K for ^{77}Se, ^{113}Cd and ^{199}Hg, respectively. Temperatures were calibrated using the ^{1}H NMR spectrum of MeOH[19] when no decoupling was used, and the heating effect of decoupling was measured using 50 : 50 v/v CCl_4–Me_2CO.[20] To measure the spectra of the selenocarboxylate samples, proton-decoupling was continuous for ^{77}Se and ^{199}Hg but inverse-gated for ^{113}Cd, which has a negative Overhauser effect. Typically, the pulse-widths used for ^{77}Se and ^{199}Hg were 5.0 µs (39°) and 12.7 µs (52.7°), and the in both cases the acquisition time and re-cycle time was 1 s. For ^{113}Cd, the pulse width used was 9.5 µs (68°), the acquisition time was 1 s and the re-cycle time was 4 s. After each temperature change, 30 min was allowed to reach a steady state before the spectrum was measured; this was particularly important for the ^{199}Hg NMR spectra, since the chemical shifts show a large temperature dependence.

Table 1 Crystal data and experimental details

	1	**2**	**3**
Formula	$C_{48}H_{41}O_3PSe_3Zn$	$C_{48}H_{41}O_3PSe_3Cd$	$C_{48}H_{41}O_3PSe_3Hg$
M	999.03	1046.06	1134.25
λ/Å	0.71073	0.71073	0.71073
Space group	*P*2$_1$/*c*	*P*2$_1$/*c*	*P*2$_1$/*c*
a/Å	18.6651(7)	18.6691(6)	18.4603(6)
b/Å	12.3597(5)	12.5193(4)	12.7772(4)
c/Å	20.0688(8)	19.9006(7)	19.6026(6)
β/°	110.862(2)	110.581(1)	109.362(1)
V/Å^3	4326.2(3)	4354.4(2)	4362.2(2)
Z	4	4	4
D_c/g cm^{-3}	1.534	1.596	1.727
µ/mm^{-1}	3.169	3.086	6.108
*R*1^a	0.0521	0.0476	0.0450
*wR*2^a	0.0960	0.0846	0.0869

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

ESI-MS studies

Positive- and negative-ion ESI-MS spectra were measured using a Finnigan/Mat LCQ spectrometer. Equimolar amounts of [M(SeC{O}Tol)$_3$$^-$] and [M(SC{O}Ph)$_3$$^-$] (M = Zn–Hg) were mixed in acetone or CH_2Cl_2 under ambient conditions. Immediately after mixing, a small portion of the solution was injected into the mass spectrometer, with the temperature of the ionization chamber preset at 323 K. Individual species were detected in the mass spectra and confirmed from their simulated isotopic envelopes. The *m*/*z* values listed in this paper are those of the principal ions. The positive-ion spectra gave only the signal from PPh_4^+; therefore these are not discussed further in this paper.

Results and discussion

Sodium *p*-tolylmonoselenocarboxylate was allowed to react with PPh_4Cl and appropriate metal salt in the ratio 4 : 1 : 1 in MeCN to obtain analytically pure salts of homoleptic selenocarboxylato anions containing Group 12 metal ions, (PPh_4)[M(SeC{O}Tol)$_3$].

NMR spectra

Metal (^{113}Cd or ^{199}Hg, as appropriate) and ^{77}Se NMR spectra have been measured for solutions of [M(SeC{O}Tol)$_3$]$^-$ and [M(SeC{O}Tol)$_3$]$^-$–[M(SC{O}Ph)$_3$]$^-$ mixtures (M = Zn–Hg) in CH_2Cl_2, at reduced temperatures; solutions of [M(SeC{O}Tol)$_3$]$^-$ decompose on standing at ambient probe temperature. The results of these measurements are summarized in Table 2.

Compared with the metal NMR signals of the complexes [M(SC{O}Ph)$_3$]$^-$ (M = Cd or Hg), with the primary kernel MS_3, those of [M(SeC{O}Tol)$_3$]$^-$, with the primary kernel MSe_3 (see below) are more shielded. This is expected, as both ^{113}Cd and ^{199}Hg are known[21–23] to exhibit an "inverse chalcogen

Table 2 Metal and ^{77}Se NMR spectral parameters of $[M(SeC\{O\}Tol)_n(SC\{O\}Ph)_{3-n}]^-$ in CH_2Cl_2[a]

M	n	T/K	δ_M ($\Delta\nu$½, approx./Hz)	δ_{Se}[b] ($\Delta\nu$½, approx./Hz))	^1J(M–Se)/Hz
Zn	3	223		342.4 (70),[c] 340.3 (200)	
	2	223		320.4 (80)	
	1	223		305.9 (70)	
Cd[d]	3	193	250.1 (140),[c] 250.0 (200)	363.6 (60),[c] 361.7 (130)	—[e]
	2	193	264.9 (100)	354.1 (75)	—[e]
	1	193	275.3 (70)	346.1 (90)	—[e]
	0	193	283.0 (50)[f]		
Hg[g]	3	193	−729.6 (70),[c,h] −729.8 (100)	427.3 (10),[b] 427.0 (20)	1060 ± 10[i,j]
	2	193	—[k]	424.2 (25)	945 ± 15[i]
	1	193	—[k]	421.0 (20)	825 ± 15[i]
	0	193	−672.8 (70),[c,l] −671.9 (80)		

[a] In mixtures containing $[M(SeC\{O\}Tol)_3]^-$–$[M(SC\{O\}Ph)_3]^-$ = 1 : 1, except as noted. [b] Measured relative to neat Me_2Se at 299 K. [c] In a solution containing $[M(SeC\{O\}Tol)_3]^-$ or $[M(SC\{O\}Ph)_3]^-$ alone (as appropriate). [d] M = ^{113}Cd, measured relative to 0.1 M $Cd(ClO_4)_2$(aq) at 299 K. [e] Not observed in either ^{77}Se or ^{113}Cd NMR spectrum. [f] δ_{Cd} ($\Delta\nu$½, approx.) = 287 (7 Hz) at 295 K.[7] [g] M = ^{199}Hg, measured relative to neat $HgMe_2$ at 299 K; the ^{199}Hg chemical shifts show a large temperature dependence (see text). [h] δ_{Hg} ($\Delta\nu$½, approx.) = −799 (250 Hz) at 253 K. [i] In the ^{77}Se NMR spectrum. [j] Also observed in the ^{199}Hg NMR spectrum of the parent $[Hg(SeC\{O\}Tol)_3]^-$ alone. [k] See text. [l] δ_{Hg} ($\Delta\nu$½, approx.) = −749 (200 Hz) at 298 K.[7]

dependence" (shielding depending on the attached atom in the order Te > Se > S), analogous to the better-known[24] inverse halogen dependence (shielding order with attached atom I > Br > Cl). Determination of the size of this effect is complicated for ^{199}Hg by the very large temperature dependences that we observe for the shielding of both $[Hg(SeC\{O\}Tol)_3]^-$ and $[Hg(SC\{O\}Ph)_3]^-$, +1.2 ppm K^{-1} (193–253 K) and +0.72 ppm K^{-1} (193–298 K), respectively (see Table 2). However, at 193 K, $\delta_M([M(SC\{O\}Ph)_3]^-) - \delta_M([M(SeC\{O\}Tol)_3]^-)$ = 58 and 33, for M = ^{199}Hg and ^{113}Cd, respectively, in concert with the larger chemical shift range known for ^{199}Hg than for ^{113}Cd.[25] At temperatures below approximately 233 K, ^{77}Se satellites are observed in the ^{199}Hg NMR spectrum of $[Hg(SeC\{O\}Tol)_3]^-$. However, the value of $^1J(^{77}Se–^{199}Hg)$ can be measured more accurately in the corresponding ^{77}Se NMR spectrum, where the signals are sharper (see Table 2 and below).

The ^{77}Se NMR chemical shifts of $[M(SeC\{O\}Tol)_3]^-$ vary with M in the order Zn < Cd < Hg. This contrasts with the irregular order Cd < Hg < Zn observed for both directly and indirectly bound ^{77}Se nuclei in $[M(Se_4)_2]^{2-}$.[26] The ^{77}Se NMR chemical shifts of $[M(SeC\{O\}Tol)_3]^-$ show only slight temperature dependence for M = Cd and Hg; $\Delta\delta_{Se}$ = +1.1 and −0.6 ppm, respectively, as the temperature is changed from 193 to 233 K. The complex $[Zn(SeC\{O\}Tol)_3]^-$ shows a change in $\Delta\delta_{Se}$ of −1.8 ppm over the same temperature range: the values of δ_{Se} ($\Delta\nu_{½}$, approx./Hz) are 344.6 (100), 344.3 (340), 342.2 (180), 342.4 (70) and 342.8 (30) at 193, 203, 213, 223 and 233 K, respectively. These changes are reversible. A plausible explanation is that a change in conformation is occurring around 203–213 K, with both conformers present, and exchanging, in the region where the line width is greatest.

At 253 K, no sharp ^{199}Hg satellites are observed in the ^{77}Se NMR spectrum of $[Hg(SeC\{O\}Tol)_3]^-$, but the satellites are evident below 233 K. The size of $^1J(^{77}Se–^{199}Hg)$, 1060 Hz, is of the same order of magnitude as other such couplings in the literature, *e.g.* 1270 Hz in $[Hg(SePPh_3)_3]^{2+}$.[22] We were unable to observe any ^{113}Cd–^{77}Se coupling in the ^{77}Se (or ^{113}Cd) NMR spectrum of $[Cd(SeC\{O\}Tol)_3]^-$, or corresponding mixed-ligand complexes; since clear slow-exchange ^{77}Se and ^{113}Cd NMR spectra are observed for $[Cd(SeC\{O\}Tol)_n(SC\{O\}Ph)_{3-n}]^-$ (see following), we attribute the lack of an observable one-bond coupling to the relative broadness of the signals in both ^{77}Se and ^{113}Cd NMR spectra, which could easily obscure a one-bond coupling that is expected to be of order 50–200 Hz.[21,27]

When the reduced-temperature ^{77}Se NMR spectra of mixtures of $[M(SC\{O\}Ph)_3]^-$ and $[M(SeC\{O\}Tol)_3]^-$ are examined for M = Zn, Cd or Hg, a total of three signals is observed (see Table 2). One is that of the parent $[M(SeC\{O\}Tol)_3]^-$ and for the intensities to be consistent with the known compositions of the solutions, the other two must be assigned to complexes with mixed ligands, as shown in the Table 2. The redistribution of the ligands is evidently close to statistical. At 253 K, the ^{77}Se NMR spectra of the mixtures containing Cd or Hg have collapsed to a single very broad line, but three very broad signals are observed in the Zn-containing mixtures; it is clear that inter-complex exchange of $[SeC\{O\}Tol]^-$ is occurring for all complexes at this temperature, the exchange rates being Cd, Hg > Zn.

Consistent with the reduced-temperature ^{77}Se NMR spectra of mixtures of $[Cd(SC\{O\}Ph)_3]^-$ and $[Cd(SeC\{O\}Tol)_3]^-$, the reduced temperature ^{113}Cd NMR spectra of these mixtures show a total of four signals, corresponding to the four possible anions $[M(SeC\{O\}Tol)_n(SC\{O\}Ph)_{3-n}]^-$ (n = 3–0). Once again the signal intensities confirm a close to statistical distribution of ligands. The signals attributed to the complexes with n = 3, 2, 1 and 0 have relative intensities that are approximately 1, 3, 3 and 1 in a mixture where $[Cd(SC\{O\}Ph)_3]^-$:$[Cd(SeC\{O\}Tol)_3]^-$ = 1 : 1.

Strangely, the ^{199}Hg NMR spectra of mixtures of $[Hg(SC\{O\}Ph)_3]^-$ and $[Hg(SeC\{O\}Tol)_3]^-$ show a total of only three signals, at −672, −721, and −730 ppm ($\Delta\nu_{1/2}$ values approximately 110, 170 and 170 Hz), with intensities approximately 1 : 3.5 : 3.5 for a 1 : 1 mixture at 213 K. The ^{77}Se NMR spectrum of the same mixture shows that $[Hg(SeC\{O\}Tol)_n(SC\{O\}Ph)_{3-n}]^-$ (n = 1–3) are present in an approximately statistical ratio. To be consistent with the intensity data in the ^{77}Se NMR spectrum, $[Hg(SC\{O\}Ph)_3]^-$ must also be present, which is also in agreement with the ESI MS data (see below). Therefore four ^{199}Hg NMR signals should be observed for the 1 : 1 mixture; some signal overlap must be occurring. The small relative intensity of the signal at −672 ppm, together with its position means that it can be assigned to $[Hg(SC\{O\}Ph)_3]^-$. The signal at −730 ppm is in the correct position to be assigned to $[Hg(SeC\{O\}Ph)_3]^-$, but its relative intensity is too high for the known binomial concentration distribution. Tentatively, we suggest that the resonance at −721 ppm is that of $[Hg(SeC\{O\}Tol)(SC\{O\}Ph)_2]^-$, and that the resonance at −730 ppm is a superimposition of those of $[Hg(SeC\{O\}Tol)_n(SC\{O\}Ph)_{3-n}]^-$, n = 3 and 2.

Overall, the metal and ^{77}Se NMR spectra confirm that the complexes $[M(SeC\{O\}Tol)_n(SC\{O\}Ph)_{3-n}]^-$ (M = Zn–Hg, n = 3–0) persist in solution, and that ligand exchange is slow (relative to the appropriate chemical shift differences) at or below approximately 253 K for M = Zn, and at or below approximately 233 K for M = Cd or Hg.

ESI-MS studies

Negative-ion ESI-MS data have been obtained for acetone solutions containing equimolar amounts of $[M(SeC\{O\}Tol)_3]^-$ and $[M(SC\{O\}Ph)_3]^-$ (M = Zn–Hg) at 323 K. In each case, signals from the four distinct species $[M(SeC\{O\}Tol)_n(SC\{O\}Ph)_{3-n}]^-$ (n = 0, 1, 2 and 3; M = Zn–Hg) occur in the spectrum.

Table 3 Table showing the *m*/*z* of the products of ligand exchange, $[\mathrm{M(SeC\{O\}Tol)}_n(\mathrm{SC\{O\}Ph})_{3-n}]^-$, in ESI-MS spectra of mixtures of $[\mathrm{M(SC\{O\}Ph)_3}]^-$ and $[\mathrm{M(SeC\{O\}Tol)_3}]^-$ (M = Zn–Hg) in acetone

M	Principal ions (*m*/*z*, %)
Zn	*n* = 0 (475, 38), *n* = 1 (537, 100), *n* = 2 (599, 46), *n* = 3 (661, 8)
Cd	*n* = 0 (525, 56), *n* = 1 (585, 100), *n* = 2 (647, 70), *n* = 3 (707, 12)
Hg	*n* = 0 (613, 52), *n* = 1 (673, 100), *n* = 2 (735, 62), *n* = 3 (795, 12)

The *m*/*z* values of the principal ions for these species are given in Table 3. Surprisingly, the relative intensities of the four species are not consistent with the approximately binomial concentration distribution suggested by the ^{77}Se NMR spectra (see above). In each case, more selenium-rich species are under-represented. Tentatively, we suggest that the parent $[\mathrm{M(SeC\{O\}Tol)_3}]^-$ anions undergo decomposition under the conditions used in the ESI-MS experiments. When the solvent was changed from acetone to $\mathrm{CH_2Cl_2}$, signals from three extra species appeared in the ESI-MS spectra of Zn mixtures: those of $[\mathrm{Zn(SeC\{O\}Ph)}_n(\mathrm{SC\{O\}Ph})_{2-n}\mathrm{Cl}]^-$ (*n* = 0, 1 and 2) (*m*/*z* values: 375.4, 435.5 and 480.4). Analogous species are not observed for Cd- or Hg-containing mixtures, perhaps because Cl^- is a relatively hard donor, and Cd(II) and Hg(II) are softer acceptors than Zn(II).

Structures of $[\mathrm{M(SeC\{O\}Tol)_3}]^-$ (M = Zn–Hg)

The crystal structure of each compound consists of discrete anions and cations. These compounds are isomorphous. 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 Figs. 1 and 2, while selected distances, angles and deviations of M from $\mathrm{Se_3}$ and $\mathrm{O_3}$ planes are given in Table 4.

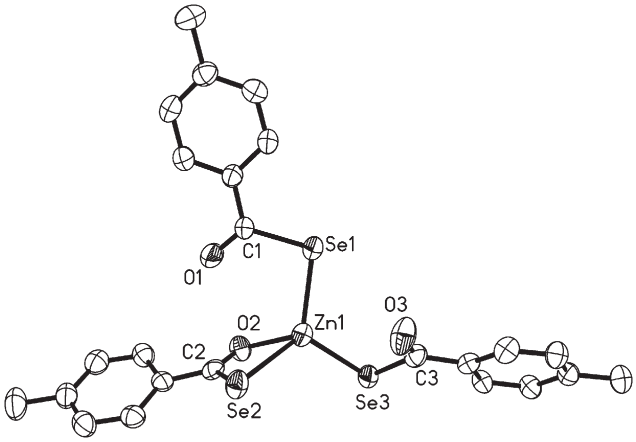

Fig. 1 Diagram showing the numbering scheme and 50% probability thermal ellipsoids of the $[\mathrm{Zn(SeC\{O\}Tol)_3}]^-$ anion in **1**. Hydrogen atoms are omitted for clarity.

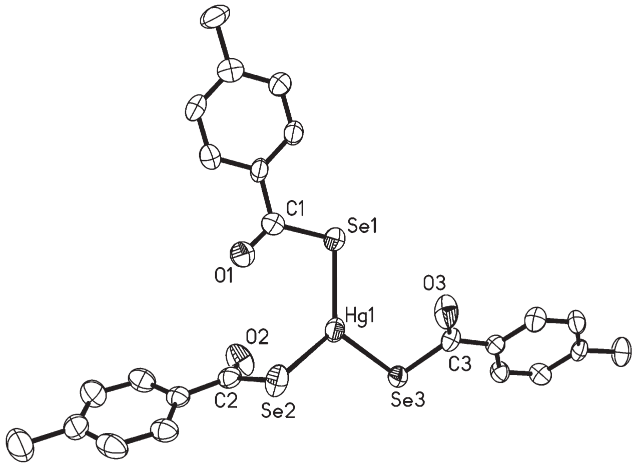

Fig. 2 Diagram showing the numbering scheme and 50% probability thermal ellipsoids of the $[\mathrm{Hg(SeC\{O\}Tol)_3}]^-$ anion in **3**. The same numbering scheme is used as for anions of **1**. Hydrogen atoms are omitted for clarity.

Table 4 Selected bond distances (Å), angles (°) and deviations (Å) from the $\mathrm{Se_3}$ and $\mathrm{O_3}$ planes in the anions of **1**–**3**

	1 (M = Zn)	**2** (M = Cd)	**3** (M = Hg)
M(1)–Se(1)	2.3973(6)	2.5686(4)	2.5433(5)
M(1)–Se(2)	2.4738(5)	2.6178(4)	2.5728(5)
M(1)–Se(3)	2.4114(5)	2.6036(4)	2.5867(5)
M(1)–O(1)	3.263(2)	3.280(3)	3.317(6)
M(1)–O(2)	2.217(2)	2.535(2)	2.927(4)
M(1)–O(3)	2.973(2)	2.836(3)	3.106(4)
Se(1)–C(1)	1.920(3)	1.914(3)	1.898(5)
Se(2)–C(2)	1.885(3)	1.887(3)	1.897(5)
Se(3)–C(3)	1.921(4)	1.913(3)	1.926(4)
O(1)–C(1)	1.217(4)	1.200(4)	1.204(6)
O(2)–C(2)	1.244(4)	1.230(3)	1.206(5)
O(3)–C(3)	1.213(4)	1.219(4)	1.210(5)
C(1)–C(11)	1.485(5)	1.508(4)	1.516(6)
C(2)–C(21)	1.486(5)	1.493(4)	1.499(6)
C(3)–C(31)	1.490(4)	1.485(4)	1.468(6)
Se(1)–M(1)–Se(2)	118.87(2)	123.34(2)	126.04(2)
Se(1)–M(1)–Se(3)	117.80(2)	117.91(1)	116.55(2)
Se(2)–M(1)–Se(3)	119.32(2)	117.81(1)	117.34(2)
Se(1)–M(1)–O(1)	55.86(5)	54.50(5)	54.09(7)
Se(2)–M(1)–O(2)	70.50(6)	63.79(5)	59.21(6)
Se(3)–M(1)–O(3)	60.30(5)	60.17(5)	56.78(6)
C(1)–Se(1)–M(1)	99.6(1)	97.1(1)	98.3(2)
C(2)–Se(2)–M(1)	73.9(1)	79.4(1)	88.7(1)
C(3)–Se(3)–M(1)	91.9(1)	86.4(1)	93.1(1)
C(1)–O(1)–M(1)	81.7(2)	84.7(2)	82.9(4)
C(2)–O(2)–M(1)	96.4(2)	96.1(2)	89.8(3)
C(3)–O(3)–M(1)	85.9(2)	92.3(2)	88.7(3)
O(1)–C(1)–C(11)	120.3(3)	120.1(3)	118.5(5)
O(1)–C(1)–Se(1)	121.6(3)	122.4(3)	123.5(4)
C(11)–C(1)–Se(1)	118.1(2)	117.4(2)	117.8(3)
O(2)–C(2)–C(21)	120.8(3)	120.5(3)	121.0(4)
O(2)–C(2)–Se(2)	119.0(2)	120.3(2)	121.9(4)
C(21)–C(2)–Se(2)	120.1(2)	119.1(2)	117.1(3)
O(3)–C(3)–C(31)	121.4(3)	121.6(3)	122.0(4)
O(3)–C(3)–Se(3)	120.8(3)	120.0(2)	120.4(3)
C(31)–C(3)–Se(3)	117.8(2)	118.5(2)	117.6(3)
Deviations of M from $\mathrm{Se_3}$ plane	0.2826	−0.1451	−0.0372
Deviations of M from $\mathrm{O_3}$ plane	0.2826	−0.1451	−0.0372

In each of the anions, the three $\mathrm{TolC\{O\}Se^-}$ ligands are bonded to the metal atom primarily through selenium, each metal atom being located roughly in the plane of the three selenium atoms. In addition, weak metal···oxygen interactions occur in these anions, as is also observed for the corresponding benzenemonothiocarboxylate complexes.[7] In the $\mathrm{TolC\{O\}Se^-}$ ligands, the COSe planes are twisted from the aromatic rings; dihedral angles of these two planes vary from 10.4 to 24.1°.

In compound **1**, the Zn–Se distances range from 2.397 to 2.474 Å, which are longer than the 2.377 and 2.378 Å observed in $[\mathrm{Zn(SeC_6H_2Me_3\text{-}2,4,6)_2(C_5H_5N)_2}]$.[28] The three Zn–O bond distances (2.217, 2.973 and 3.263 Å) in **1** are quite different from each other. Only one of the Zn–O distances (Zn(1)–O(2)) is found to be less than the sum of van der Waals radii for Zn and O (2.9 Å).[29] Thus a Zn···O interaction is present in **1**, so that the geometry of the Zn(II) center can be considered as distorted tetrahedral. The Zn atom is only 0.057 Å out of the $\mathrm{O_3}$ plane; the sum of the O–Zn–O angles is 359.7°.[30] The dihedral angle between the $\mathrm{O_3}$ and $\mathrm{Se_3}$ planes in **1** is 62.2°.

The Cd–Se bond distances in **2** (2.569–2.618 Å; mean 2.597 Å) appear to be slightly longer than those found in $[\mathrm{Cd(Se\text{-}2,4,6\text{-}{}^iPr_3C_6H_2)_2(bpy)}]$[31] (2.549–2.557 Å; mean 2.553 Å) but shorter than those presence in $[\mathrm{Cd\{N(PPh_2Se)_2\text{-}}\mathit{Se,Se'}\}_2]$[32] (2.617–2.642 Å; mean 2.634 Å) and $\mathrm{(Me_4N)_2[(\mu\text{-}SePh)_6(CdBr)_4]}$[33] (2.627–2.654 Å; mean 2.638 Å) Two of the Cd–O bond distances in **2** (Cd(1)–O(2) and Cd(1)–O(3)) are found to be less than the sum of van der Waals radii for Cd and O (3.10 Å). When these two Cd…O interactions are included in the coordination kernel, the geometry of Cd may be described as distorted trigonal

Table 5 Bond valences parameters of Zn–Hg in **1**–**3**

Compound	Total bond valence, V_i of M	% of M–Se	% of M–O
1	2.048	85.5	14.5
2	2.129	86.0	13.4
3	2.351	93.7	6.3

bipyramidal ($\tau = 0.76$).[34] The O(1) atom in **2** is located much closer to the Se_3 plane compared to **1**, and this interaction leads to the large Se(1)–Cd(1)–Se(2) angle (123.34°). The sum of the O–Cd–O angles is 359.8° with the Cd atom displaced from the O_3 plane by 0.049 Å, and the dihedral angle between the O_3 and Se_3 planes is 59.4°.[30]

The Hg–Se distances in **3** (2.543–2.587 Å) are comparable with those presence in the reported compound, $(Bu_4N)[Hg(SePh)_3]$[12] (2.536–2.600 Å). The large Se(1)–Hg(1)–Se(2) angle (126.04°) is consistent with the location of the C(1)–O(1) carbonyl group between Se(1) and Se(2). The sum of the van der Waals radii of Hg and O (4.02 Å) indicates that there are interactions between the Hg atom and all three carbonyl oxygen atoms. Nevertheless, a bond valence calculation (see below) suggests that this interaction contributes only weakly to the overall metal–ligand bonding in the anion. The sum of the Se–Hg–Se angles, 359.93° supports trigonal planar geometry at the metal centre. Further, the Hg atom in **3** is located much further from the O_3 plane (0.164 Å; the sum of the O–Hg–O angles is 308.2°)[30] than is found for Zn and Cd, in **1** and **2**.

The relatively longer M–Se(2) distances as compared to M–Se(1) and M–Se(3), and shorter C–Se bonds found for ligand 2 in **1** and **2** suggest larger C–Se double bond character. This is reflected in relatively longer C(2)–O(2) distances, indicating the possibility of electron delocalization in this selenocarboxylate ligand (Table 4). As a result the carbonyl oxygen atom O(2) binds most strongly to M. The extent of electron delocalization is in the order **1** > **2** > **3**. In addition, the M···O(2) bonding in **1** and **2** is further confirmed from the fact that M–Se(2)–C(2) angles are smaller than the other two and M–O(2)–C(2) angles are larger than the other two.

MS_3 trigonal planar geometry is well known for thiolate species having bulky ligands.[35,36] Thus, a plausible explanation to the MSe_3 trigonal planar geometry in compounds **1**–**3** is the presence of relatively 'inactive' carboxylate groups. Interestingly, the mean M–Se bond distances in these compounds (Table 4) follow the unexpected trend, Zn < Hg < Cd. The analogous trend was found for the corresponding $[M(SC\{O\}Ph)_3]^-$, and is known in other instances for Zn–Hg.[37]

The bond valence approach[38] was used to estimate the contribution of metal···oxygen interaction toward the overall bonding in the anions of **1**–**3**. The results of the bond valence calculation are shown in Table 5 and suggest that compound **3** could be a better oxygen donor metalloligand (oxygen atoms more available for "outside" coordination) than **1** or **2**. Overall, the monoselenocarboxylatometallate anions in **1**–**3** contain structural features very similar to those found in their sulfur analogues, $[M(SC\{O\}Ph)_3]^-$; these appear to be due to geometrical restraints imposed by the presence of the carbonyl groups once the three Se or S are bound to the metal.

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