Synthesis, Structure, and Multi-NMR Studies of $(Me_4N)[A\{M(SC\{O\}Ph)_3\}_2]$ (A = Na, M = Hg; A = K, M = Cd or Hg)

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The compounds $(Me_4N)[A\{M(SC\{O\}Ph)_3\}_2]$ (A = K, M = Cd (**2**); A = Na, M = Hg (**3**); and A = K, M = Hg (**4**)) were synthesized by reacting the appropriate metal chloride with $A^+PhC\{O\}S^-$ and Me_4NCl in the ratios 1:3:1 and 2:6:1. The structures of these compounds were determined by single-crystal X-ray diffraction methods. All the compounds are isomorphous, isostructural, and crystallized in the space group $P\bar{1}$ with $Z = 1$. Single-crystal data for **2**: $a = 10.6670(2)$ Å, $b = 11.1522(2)$ Å, $c = 11.9294(2)$ Å, $\alpha = 71.782(1)°$, $\beta = 85.208(1)°$, $\gamma = 69.418(1)°$, $V = 1261.40(4)$ Å^3, $D_{calc} = 1.528$ g cm^{-3}. Single-crystal data for **3**: $a = 10.840(2)$ Å, $b = 10.946(4)$ Å, $c = 12.006(3)$ Å, $\alpha = 72.18(2)°$, $\beta = 86.75(2)°$, $\gamma = 67.43(2)°$, $V = 1249.3(6)$ Å^3, $D_{calc} = 1.756$ g cm^{-3}. Single-crystal data for **4**: $a = 10.4780(1)$ Å, $b = 11.2563(2)$ Å, $c = 11.9827(2)$ Å, $\alpha = 71.574(1)°$, $\beta = 85.084(1)°$, $\gamma = 70.705(1)°$, $V = 1265.23(3)$ Å^3, $D_{calc} = 1.755$ g cm^{-3}. In the $[A\{M(SC\{O\}Ph)_3\}_2]^-$ anions, each M(II) atom is bonded to three thiobenzoate ligands through sulfur atoms, giving a trigonal planar MS_3 geometry. The carbonyl oxygen atoms from the two $[M(SC\{O\}Ph)_3]^-$ anions are bonded to the alkali metal atom, providing an octahedral environment. Solution metal NMR studies showed the concentration-dependent dissociation of the alkali metal ions in the trinuclear anions.

Introduction

A number of macrocycles have been designed to complex the alkali metal ions.[1−6] However, only a few clawlike metalloligands have been found to form complexes with alkali metals.[7−13] A sodium ion bound to a clawlike metalloligand is found in the $[Na\{Cd(SC\{O\}Ph)_3\}_2]^-$ anion.[14] In this anion, the soft sulfur atoms of the $PhC\{O\}S^-$ ligands are bonded to Cd(II) ions to provide a planar CdS_3 coordination geometry around each Cd(II) center and the oxygen atoms are attached to Na(I) ions to give an octahedral coordination geometry. Bond valence calculations suggested that $[Hg(SC\{O\}Ph)_3]^-$ should be a better oxygen-donor metalloligand than $[Cd(SC\{O\}Ph)_3]^-$.[15] However, to date, our attempts to prepare the trinuclear anions based on $[Hg(SC\{O\}Ph)_3]^-$ have resulted in alkali metal free $(Me_4N)[Hg(SC\{O\}Ph)_3]$ [16] or a salt of $[Hg_2Cl_4(S\{O\}CPh)_2]^{2-}$ [17] as the only crystalline products. We remain interested in finding out whether similar trinuclear groups 1−12 anions exist for combinations of metal ions other than $NaCd_2$. A wider group of anions would allow an investigation of the way in which the structural parameters and geometry of M(II) are influenced by the presence of alkali metal ions more generally. Therefore, in continuation of our investigations on the chemistry of metal thiocarboxylate compounds,[18−24] we describe here the syntheses and structures of trinuclear groups 1−12 anions of type KCd_2, $NaHg_2$, and KHg_2 with thiobenzoate ligands. We have also investigated the stability of these anionic species in solution by metal NMR spectroscopy.

Experimental Section

General Methods. All materials were obtained commercially and were used as received except for $Na[BPh_4]$, which was recrystallized from Me_2CO. All reactions were performed under an atmosphere of

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Table 1. Crystal Data and Experimental Details

	2	**3**	**4**
empirical formula	$C_{46}H_{42}Cd_2KNO_6S_6$	$C_{46}H_{42}Hg_2NaNO_6S_6$	$C_{46}H_{42}Hg_2KNO_6S_6$
fw	1161.07	1321.34	1337.45
temp, °C	23	23	23
radiation wavelength, Å	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	10.6670(2)	10.840(2)	10.4780(1)
b, Å	11.1522(2)	10.946(4)	11.2563(2)
c, Å	11.9294(2)	12.006(3)	11.9827(2)
α, deg	71.782(1)	72.18(2)	71.574(1)
β, deg	85.208(1)	86.75(2)	85.084(1)
γ, deg	69.418(1)	67.43(2)	70.705(1)
vol, Å^3	1261.40(4)	1249.3(6)	1265.23(3)
Z	1	1	1
ρ observed, g/cm^3	1.528	1.756	1.755
abs coeff, mm^{-1}	1.219	6.442	6.435
final *R* indices [$I > 2\sigma(I)$]			
R1^a	0.0599	0.0346	0.0323
wR2^a	0.1304	0.0797	0.0864

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

N_2(g). The literature method[14] was used to prepare $(Me_4N)[Na\{Cd(SC\{O\}Ph)_3\}_2]$, **1**. All nonaqueous solvents were dried over 3 Å molecular sieves. They were degassed with N_2(g) or Ar(g) before the reactions or preparation of NMR samples. The yields are reported with respect to the metal salts. The Microanalytical Laboratory at NUS performed microanalyses.

$(Me_4N)[K\{Cd(SC\{O\}Ph)_3\}_2]$, 2. A solution of $CdCl_2$ (1.227 g, 6.09 mmol) in 10 mL of water was added to $C_6H_5C\{O\}S^-K^+$ prepared in situ by reacting KOH (1.026 g, 18.29 mmol) in 15 mL of water with $C_6H_5C\{O\}SH$ (2.14 mL, 18.29 mmol) in 10 mL of methanol, followed by the addition of Me_4NCl (0.668 g, 6.09 mmol), which resulted in a creamy white precipitate. To this mixture MeCN (12.5 mL) was added, and the solution was warmed to get a near-clear solution. The solution was filtered hot and left at 5 °C for crystallization. Creamy yellow crystals were separated by filtration, washed with MeOH and Et_2O, and dried in vacuo. Yield: 2.10 g (59.3%). Anal. Calcd for $C_{46}H_{42}Cd_2KNO_6S_6$ (mol wt 1161.07): C, 47.58; H, 3.65; S, 16.57; N, 1.21; K, 3.37; Cd, 19.36. Found: C, 47.88; H, 3.23; S, 15.16; N, 1.47; K, 2.93; Cd, 18.13. ^{1}H NMR (CD_3CN): δ, ppm, 3.29 (12H, $(CH_3)_4N$), 7.38−8.16 (30H, $C_6H_5C\{O\}S$). ^{13}C NMR (CD_3CN): δ, ppm, 56.53 ($N(CH_3)_4$), 128.72 ($C_{3/2}$), 129.33($C_{2/3}$), 132.75 (C_4), 140.98(C_1), 208.27(Ph*C*OS).

$(Me_4N)[Na\{Hg(SC\{O\}Ph)_3\}_2]$, 3. The synthesis followed that of **2** closely but employed NaOH and $HgCl_2$ (dissolved in 5 mL of MeOH) in place of KOH and $CdCl_2$, respectively. Yield: 66%. Anal. Calcd for $C_{46}H_{42}Hg_2NaNO_6S_6$ (mol wt 1321.34): C, 41.81; H, 3.20; N, 1.06; Na, 1.74. Found: C, 41.69; H, 3.17; N, 1.19; Na, 1.85. ^{1}H NMR (CD_3CN): δ, ppm, 3.06 (12H, $N(CH_3)_4$), 7.38−8.11 (30H, $C_6H_5C\{O\}S$). ^{13}C NMR (CD_3CN): δ, ppm, 56.04 ($N(CH_3)_4$), 128.79 ($C_{3/2}$), 129.00($C_{2/3}$), 132.70 (C_4), 141.87(C_1), 201.55 (Ph*C*OS).

$(Me_4N)[K\{Hg(SC\{O\}Ph)_3\}_2]$, 4. Compound **4** was obtained as creamy yellow crystals when the synthesis was carried out as for **3** but using KOH in place of NaOH. Yield: 71.3%. Anal. Calcd for $C_{46}H_{42}Hg_2KNO_6S_6$ (mol wt 1337.45): C, 41.31; H, 3.17; N, 1.05; K, 2.92. Found: C, 41.03; H, 3.18; N, 1.27; K, 3.12. ^{1}H NMR (CD_3CN): δ, ppm, 3.07 (12H, $(CH_3)_4N$), 7.38−8.10 (30H, $C_6H_5C\{O\}S$). ^{13}C NMR (CD_3CN): δ, ppm, 56.01 ($N(CH_3)_4$), 128.80 ($C_{3/2}$), 128.99 ($C_{2/3}$), 132.70 (C_4), 141.84 (C_1), 201.16 (Ph*C*OS).

Compounds **2**−**4** were also obtained when the starting materials Me_4NCl, metal salt, and alkali thiobenzoate were in the ratio 1:2:6. Under similar experimental conditions, the zinc chloride yielded only $(Me_4N)[Zn(SC\{O\}Ph)_3]$.

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 o.d. NMR tubes with CD_3CN as solvent and TMS as internal reference. Metal NMR spectra were obtained using a Varian XL-300 spectrometer system operating at 97.34, 66.53, and 53.72 MHz for ^{23}Na, ^{113}Cd, and ^{199}Hg, respectively. No proton-decoupling was used for ^{23}Na. 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 preshimmed 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 $Na[BPh_4]$ in Me_2CO at 294 ± 1 K, 0.1 M $Cd(ClO_4)_2$ (aq) at 294 ± 1 K and neat $HgMe_2$ (as a sealed sample. *CAUTION! HIGHLY TOXIC!*) at 296 ± 1 K for ^{23}Na, ^{113}Cd, and ^{199}Hg, respectively. Samples were prepared in 10 mm o.d. NMR tubes, with concentrations expressed as mass of solute/volume of solvent.

X-ray Crystallography. Single crystals were obtained during the synthesis. The diffraction experiments were carried out on a Bruker SMART CCD diffractometer with a Mo Kα sealed tube at 23 °C. The collected frames were integrated using the preliminary cell-orientation matrix. The softwares used were the following: SMART[25] for collecting frames of data, indexing reflection, and determining lattice parameters; SAINT[25] for integrating intensity of reflections and scaling; SADABS[26] for correcting for absorption; and SHELXTL[27] for determining space group and structure, least-squares-refining on F^2, and reporting graphics and structure. The space groups were determined from the systematic absences. Anisotropic thermal parameters were refined for all the non-hydrogen atoms. All the C−H hydrogen atoms were placed in their calculated positions and included in the structure factor calculations. The carbon atoms of the Me_4N^+ cations were disordered. Two different orientations with occupancies 0.5/0.5 were included. Common isotropic thermal parameters were included for each model. A brief summary of the crystallographic data is given in Table 1.

Results and Discusison

Synthesis. The compounds **2**−**4** were isolated from M(II) salts, Me_4NCl, and AS{O}CPh in the ratios 1:1:3 and 2:1:6 from a concentrated solution of water/MeOH/MeCN. Salts of groups 1−12 anions did not crystallize from dilute solutions. Instead $(Me_4N)[M(SC\{O\}Ph)_3]$ was isolated. The same alkali metal free salts resulted when attempts were made to recrystallize **2**−**4** by diffusion methods. Evidently the trinuclear anions dissociate on dilution. (This is confirmed by NMR studies; see below.) Further, under experimental conditions similar to those used to prepare **1**−**4**, only the alkali metal free salt was isolated for M = Zn. The compounds **2**−**4** are soluble in MeCN and

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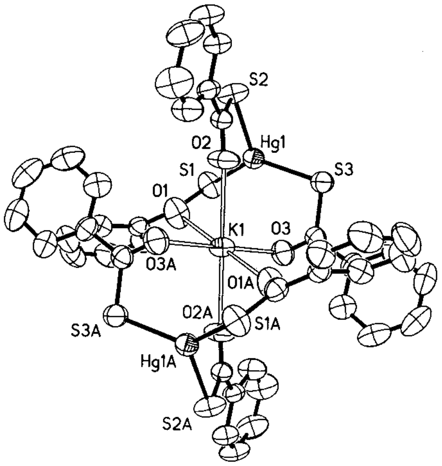

Figure 1. ORTEP diagram (with 50% probability thermal ellipsoids) of the $[K\{Hg(SC\{O\}Ph)_3\}_2]^-$ anion. The hydrogen atoms are omitted for clarity.

acetone and insoluble in CH_2Cl_2 and $CHCl_3$, whereas the corresponding alkali metal free Ph_4P^+ and Ph_4As^+ salts are freely soluble in CH_2Cl_2 and $CHCl_3$. The Me_4N^+ cation appears to be important for the isolation of salts of the trinuclear anions.

Structural Description of Compounds 2−4. The common features in compounds **2**−**4** are summarized below. All the three compounds and **1** are isomorphous and isostructural and consist of discrete anions and cations in the crystal lattice. The Me_4N^+ cations in all the compounds were found to be disordered. The $[A\{M(SC\{O\}Ph)_3\}_2]^-$ anion (A = Na, K for M = Hg; A = K for M = Cd) is trinuclear, with an alkali metal ion sandwiched between two $[M(SC\{O\}Ph)_3]^-$ anions by coordinating to all six carbonyl oxygens of the $PhC\{O\}S^-$ ligands. The M(II) ion in each $[M(SC\{O\}Ph)_3]^-$ anion is S-bonded by three thiobenzoate anions to have a near-trigonal-planar geometry. The alkali metal atom is located at the center of inversion in the molecule and has a distorted octahedral geometry. A representative structure of the anions, that of $[K\{Hg(S\{O\}CPh)_3\}_2]$, is shown in Figure 1, and selected bond distances, angles, and other relevant parameters are displayed in Table 2. The three M−S distances for each compound were unequal. The average Cd−S bond distance in **2** is very slightly less than that of the corresponding Hg−S distances in **3** and **4**, a trend that has been observed for the metalloligands themselves.[16−18] The sums of the S−M−S angles are close to 360°, and the distances of M(II) from the S_3 planes are very small (Table 2), indicating a trigonal planar MS_3 geometry in each anion. In **2**, the Cd is closer to the S_3 plane (Table 2) than in **1** where the Cd is moved away from S_3 plane, toward Na, by 0.326 Å. The Cd···O distances in **2** (2.811−3.003 Å) are longer than those found in **1** (2.659−2.828 Å), and bond valence calculations[28] show that there is a reduction in M−O contribution from 15.0% in **1** to 10.5% in **2**.

Table 2. Selected Distances [Å] and Angles [deg] for **2**−**4**[a]

parameters	**2**	**3**	**4**
A−M	3.8376(5)	3.7108(7)	3.8274(2)
A−O(1)	2.688(4)	2.447(4)	2.680(4)
A−O(2)	2.685(4)	2.443(3)	2.718(3)
A−O(3)	2.676(5)	2.331(4)	2.736(4)
M−S(1)	2.482(2)	2.443(2)	2.441(1)
M−S(2)	2.492(2)	2.485(2)	2.496(1)
M−S(3)	2.532(2)	2.468(2)	2.501(1)
M−O(1)	2.811(3)	3.059(3)	3.062(2)
M−O(2)	2.892(3)	3.036(3)	3.055(2)
M−O(3)	3.003(3)	2.978(3)	3.208(2)
S(1)−C(1)	1.725(6)	1.743(6)	1.739(5)
S(2)−C(2)	1.738(6)	1.743(5)	1.733(5)
S(3)−C(3)	1.740(6)	1.740(5)	1.770(5)
O(1)−C(1)	1.217(6)	1.217(6)	1.219(6)
O(2)−C(2)	1.226(6)	1.214(5)	1.230(6)
O(3)−C(3)	1.216(7)	1.216(5)	1.214(6)
C(1)−C(11)	1.507(7)	1.493(7)	1.495(6)
C(2)−C(21)	1.489(7)	1.489(7)	1.517(6)
C(3)−C(31)	1.498(7)	1.490(6)	1.502(7)
O(3)−A−O(2)	92.8(2)	95.0(1)	101.2(1)
O(3)−A−O(2A)	87.2(2)	85.0(1)	78.8(1)
O(3)−A−O(1A)	101.7(1)	90.8(1)	95.7(1)
O(2)−A−O(1A)	107.9(1)	97.0(1)	103.6(1)
O(3)−A−O(1)	78.3(1)	89.2(1)	84.3(1)
O(2)−A−O(1)	72.2(1)	83.0(1)	76.4(1)
S(1)−M−S(2)	120.21(6)	115.31(6)	120.97(5)
S(1)−M−S(3)	130.85(6)	130.08(6)	133.52(5)
S(2)−M−S(3)	108.43(6)	114.39(6)	105.45(5)
C(1)−S(1)−M	90.7(2)	96.6(2)	97.4(2)
C(2)−S(2)−M	92.5(2)	95.8(2)	96.2(2)
C(3)−S(3)−M	96.6(2)	96.3(2)	101.3(2)
C(1)−O(1)−A	148.0(4)	153.8(4)	145.1(4)
C(2)−O(2)−A	166.6(4)	160.5(3)	164.8(4)
C(3)−O(3)−A	116.4(4)	140.0(4)	109.4(3)
O(1)−C(1)−S(1)	122.2(4)	123.9(4)	123.1(4)
C(11)−C(1)S(1)	117.4(4)	115.5(4)	116.7(3)
O(2)−C(2)−S(2)	122.1(4)	123.3(4)	119.0(5)
C(21)−C(2)−S(2)	117.5(4)	116.1(3)	117.3(3)
O(3)−C(3)−S(3)	119.4(5)	120.4(4)	120.7(4)
C(31)−C(3)−S(3)	118.5(4)	118.5(3)	117.0(3)
distance of M from S_3 plane	−0.102	−0.066	0.034
dihedral angle between MSOC planes	68.7(1)	73.0(1)	66.0(1)
	87.6(1)	76.7(1)	83.3(1)
	70.3(1)	60.0(1)	70.4(1)
dihedral angle between SOCC plane and Ph ring	33.1(2)	37.8(2)	35.1(2)
	18.9(3)	17.8(3)	18.2(2)
	10.5(3)	5.9(3)	15.3(3)

[a] Symmetry operator for the atoms with the extension A: $1 - x$, $1 - y$, $1 - z$.

A complete set of data for a meaningful comparison is available for NMe_4^+ salts of Hg. While average Hg−S distances are not affected by alkali metal complexation, the average Hg−O distances are in the order $(Me_4N)[Hg(SC\{O\}Ph)_3]$ < **3** < **4**. The sum of the S−Hg−S angles is close to 360° for all three compounds, and the deviation from planarity is also less than 0.07 Å. In other words, the complexation with alkali metal ions does not affect the MS_3 planarity and only the orientations of the carbonyl groups are affected. The main structural difference between compounds **1**−**4** and the alkali free $[M(SC\{O\}Ph)_3]^-$ anions is the orientation of carbonyl groups. In compounds **1**−**4** they are oriented on one side of the MS_3 plane, while they are random in the alkali metal free metalloligands, with the exception of the type A anions in rhombohedral $(Ph_4P)[Cd(S\{O\}CPh)_3]$.[19] The Na···O distances found in **3** are normal and comparable to the range 2.130−2.978 Å reported for six-coordinated Na−O distances.[29] Similarly, the K···O distances observed in **2** and **4** fall within the range 2.811(3)−3.208(2) Å, which is normal for six-coordinated K−O distances.[30] The MS_3 kernels observed in the thiobenzoate complexes of group 12 metals have the unusual trigonal planar geometry (this work and refs 14−16, 18). Normally, this geometry is observed for group 12 metals only in the presence of thiolate[31] or phenolate[32] ligands having bulky substituents.

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Metal NMR Studies in Solution. The ^{113}Cd NMR chemical shifts of **2** in Me$_2$CO and MeCN (Supporting Information) are similar to those of **1** in the same solvents. For example, δ_{Cd}(**1**) = 292.3 and 300.7 ppm in Me$_2$CO and MeCN, respectively, at 296 K when the concentration is 0.025 mol/L of solvent,[14] while the corresponding values for **2** are 287.9 and 294.8 ppm. Thus, it is clear that the Cd(S{O}CPh)$_3$ moiety is intact in **2**. Evidently, the change in Cd···O distances from **1** to **2** (see above) causes little difference in the (exchange-averaged) ^{113}Cd NMR chemical shifts. This suggests that the chemical shifts may be a reflection of the electronic properties of the ligand as an S donor rather than a manifestation of the weak M···O interaction, as we have previously assumed.[14]

As is the case with **1**,[14] the values of δ_{Cd} for **2** decrease with increasing dilution, reaching the value for [Cd(S{O}CPh)$_3$]$^-$ itself, 291 ppm for a solution containing 0.002 mol of (Ph$_4$As)[Cd(S{O}CPh)$_3$]/L of MeCN at 294 K.[15] It is clear that the trinuclear anion in **2** is extensively dissociated according to

$$[\mathrm{A}\{\mathrm{M}(\mathrm{S}\{\mathrm{O}\}\mathrm{CPh})_3\}_2]^- \overset{K_1}{\rightleftharpoons} [\mathrm{A}\{\mathrm{M}(\mathrm{S}\{\mathrm{O}\}\mathrm{CPh})_3\}] + [\mathrm{M}(\mathrm{S}\{\mathrm{O}\}\mathrm{CPh})_3]^- \tag{1}$$

and

$$[\mathrm{A}\{\mathrm{M}(\mathrm{S}\{\mathrm{O}\}\mathrm{CPh})_3\}] \overset{K_2}{\rightleftharpoons} [\mathrm{M}(\mathrm{S}\{\mathrm{O}\}\mathrm{CPh})_3]^- + \mathrm{A}^+ \tag{2}$$

where A = K, M = Cd, at the lowest concentration used. Furthermore, the exchange among [Cd(S{O}CPh)$_3$]$^-$, [KCd(S{O}CPh)$_3$], and [K{Cd(S{O}CPh)$_3$}$_2$]$^-$ is evidently fast at ambient probe temperature.

The ^{199}Hg NMR spectra of **3** and **4** at 298 K (Supporting Information) show signals in the region expected for the Hg(S{O}CPh)$_3$ moiety.[15] With dilution, δ_{Hg} for samples in Me$_2$CO tend toward that of [Hg(S{O}CPh)$_3$]$^-$ (−781 ppm (approximately $\Delta\nu_{1/2}$ = 120 Hz) for a saturated solution of (PPh$_4$)[Hg(S{O}CPh)$_3$] in Me$_2$CO; the PPh$_4^+$ salt is insufficiently soluble in MeCN to make ^{199}Hg NMR spectroscopy of its MeCN solutions worthwhile). Dissociation according to eqs 1 and 2 is again indicated, with exchange between the components of the equilibrium mixture being fast on the time scale of $\Delta\delta_{\mathrm{Hg}}$. The values of $\Delta\delta_{\mathrm{Na}}$ for solutions of **3** (Supporting Information) confirm that for this salt dissociation of the trinuclear anion to Na$^+$ and [Hg(S{O}CPh)$_3$]$^-$ is not complete even at the lowest concentration studied (0.001 mol of **3**/L of solvent).

The metal NMR spectra of 1:1 mixtures (0.025 mol/L of Me$_2$CO for each component) of **1**/**3** and **2**/**4** at 178 K consisted of just one ^{113}Cd NMR signal and one ^{199}Hg NMR signal; δ_{Cd} (approximate $\Delta\nu_{1/2}$) and δ_{Hg} (approximate $\Delta\nu_{1/2}$) were 291 (175 Hz) and −810 (200 Hz) for the **1**/**3** mixture and 283.8 (20 Hz) and −801 (375 Hz) for the **2**/**4** mixture. Thus, there was no evidence for the trinuclear anions with mixed metalloligands, [{(PhC{O}S)$_3$M}A{M′(S{O}CPh)$_3$}]$^-$, under these conditions and, by extension, no evidence that the various anions [A{M(S{O}CPh)$_3$}$_2$]$^-$ remain intact under these conditions. Although the result for the **1**/**3** mixture is rendered ambiguous by the relatively broad lines that are observed for both nuclei, that for the **2**/**4** mixture is less so because the ^{113}Cd resonance at least is quite sharp. Evidently, either rapid exchange of metalloligands persists at reduced temperature in the **2**/**4** mixture or the ^{113}Cd resonances of [{(PhC{O}S)$_3$Cd}K{Hg(S{O}CPh)$_3$}]$^-$ and [K{Cd(S{O}CPh)$_3$}$_2$]$^-$ are accidentally degenerate.

Addition of Na[BPh$_4$] to a solution of **3** causes the exchange-averaged ^{199}Hg resonance to become increasingly shielded (Supporting Information). The signal must approach the chemical shift of [Na{Hg(S{O}CPh)$_3$}], which must therefore be less than −853 ppm in Me$_2$CO and less than −855 ppm in MeCN. On the assumption that the dissociation of eq 1, A = Na and M = Hg, is complete while that of eq 2 is not, the $\Delta\delta_{\mathrm{Hg}}$ data for the **3**/Na[BPh$_4$] mixtures together with those obtainable from δ_{Hg} for solutions of **3** alone (Table 3) should fit the equation[33]

$$\Delta\delta_{\mathrm{Hg}} = P([\mathrm{Na}\{\mathrm{Hg}(\mathrm{S}\{\mathrm{O}\}\mathrm{CPh})_3\}])\,\Delta\delta_{\mathrm{Hg}}([\mathrm{Na}\{\mathrm{Hg}(\mathrm{S}\{\mathrm{O}\}\mathrm{CPh})_3\}]) \tag{3}$$

$$(\text{where } P([\mathrm{Na}\{\mathrm{Hg}(\mathrm{S}\{\mathrm{O}\}\mathrm{CPh})_3\}]) = \text{fractional population of Hg as } [\mathrm{Na}\{\mathrm{Hg}(\mathrm{S}\{\mathrm{O}\}\mathrm{CPh})_3\}])$$

for some value of K_2. However, no value of K_2 could be found that gave a completely satisfactory fit in terms of a sensible slope, sensible intercept, and reasonable scatter pattern. We conclude therefore that the first dissociation is not complete and that in general these solutions contain all three compounds [Na{Hg(S{O}CPh)$_3$}$_2$]$^-$, [Na{Hg(S{O}CPh)$_3$}], and [Hg(S{O}CPh)$_3$]$^-$. Unfortunately, there are insufficient data to obtain the two values of K and $\Delta\delta_{\mathrm{Hg}}$ for the two coupled equilibria.

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Supporting Information Available: Metal NMR data for **2**−**4** and for **3**/Na[BPh$_4$] mixtures at 298 K and X-ray crystallographic files in CIF format for the structure determinations of complexes **2**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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