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Synthesis, Structure, and Nuclear Magnetic Resonance Spectra (^{111}Cd, ^{23}Na) of Tetramethylammonium Hexakis(thiobenzoato)(dicadmiumsodium)ate. A Trinuclear Anion with Cadmium in Nearly Trigonal Planar Coordination and Sodium in Octahedral Coordination

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Reaction of $Cd(NO_3)_2{\cdot}4H_2O$, NaSOCPh, and Me_4NCl in aqueous MeOH in ratios from 1:2.7:0.67 to 1:4:2 produces the salt $(Me_4N)(Na[Cd\{SOCPh\}_3]_2)$ (**1**). The structure of **1** has been determined by single-crystal X-ray diffractometry techniques. Crystal data: triclinic, space group $P\bar{1}$; $Z = 1$; $a = 11.026(1)$, $b = 11.886(2)$, $c = 10.906(1)$ Å; $\alpha = 94.32(1)$, $\beta = 113.25(1)$, $\gamma = 71.53(1)°$; $V = 1243.5(5)$ Å^3. The structure was refined to $R = 5.59\%$, $R_w = 6.58\%$, for 4001 ($I \geq 3\sigma(I)$) observations and 271 variables using full-matrix least-squares techniques on F. The unusual trinuclear anion in **1** contains a distorted octahedral NaO_6 kernel, with Na–O distances from 2.303(4) to 2.470(5) Å. Around each Cd, there is near planar coordination of three sulfur atoms with Cd–S distances in the range 2.485(2)–2.521(2) Å. In addition, the cadmium centers interact weakly with three oxygen atoms at distances of 2.659(5)–2.828(5) Å. Cadmium-111 NMR data for solutions of **1** in Me_2CO or MeCN are consistent with the retention of bonding between Cd and both S and O. The concentration-dependent ^{23}Na NMR of these solutions, compared with that of analogous solutions of $NaBPh_4$, shows that dissociation to Na^+ occurs. As well, the effect of added $NaBPh_4$ on δ_{Cd} of **1** in Me_2CO and MeCN is reported.

Introduction

For several years we have been interested in adamantane-like chalcogenate-bridged tetranuclear complexes of the elements of the zinc group.[1] Now we have started a study aimed at extension of the types of bridging groups that can be included in the $M_4(\mu\text{-}L)_6$ core of such species. An attempt to synthesize $(Me_4N)_2[Cd_4(SOCPh)_{10}]$, using a method that has been successful for salts of the anions $[M_4(EPh)_{10}]^{2-}$ (M = Zn, Cd; E = S, Se),[2] led instead to $(Me_4N)(Na[Cd\{SOCPh\}_3]_2)$ (**1**). The synthesis, X-ray analysis and some properties of this unusual salt are described in this paper.

Experimental Section

Materials and General Procedures. All reagents were from commercial sources. Sodium tetraphenylborate was recrystallized from Me_2CO but all other reagents were used as received. Solvents were stored over 3A molecular sieves. Solvents for use in synthesis and the preparation of NMR samples were deoxygenated by sparging with Ar.

Synthesis of $(Me_4N)(Na[Cd\{SOCPh\}_3]_2$ (1). A solution of NaSOCPh was prepared by dissolution of Na (0.356 g, 15.5 mmol) then PhCOSH (2 mL, ca. 2.34 g, 17.0 mmol) in 25 mL of MeOH. This solution was added with stirring to a solution of $Cd(NO_3)_2{\cdot}4H_2O$ (1.18 g, 3.83 mmol) in 10 mL of water, followed by a solution of Me_4NCl (0.844 g, 7.70 mmol) in 25 mL of MeOH. The yellow slurry was heated to 60 °C and MeCN was added until most of the solid had dissolved. The remaining solids were removed by filtration. The clear yellow filtrate was refrigerated to 5 °C overnight for crystallization to occur. The orange-yellow transparent crystals were separated by decantation, washed with MeOH and dried in vacuo. Yield: 1.37 g (62.4%). Anal. Calcd for $C_{46}H_{42}Cd_2NNaO_6S_6$: C, 48.25; H, 3.70; N, 1.22. Found: C, 48.26, 48.23; H, 3.52, 3.56; N, 1.16, 1.32. ^{1}H NMR ($(CD_3)_2CO$, 294 K): 3.39 ($N(CH_4)_4^+$, $^2J(^{14}N\text{–}C\text{–}^1H) = 0.6$ Hz), 7.31–8.18 ($SOCC_6H_5$); intensity ratio Ph/Me = 1.5. ^{13}C NMR ($(CD_3)_2CO$, 294 K): 60.7 ($N(CH_3)_4^+$, $^1J(^{14}N\text{–}^{13}C) = 4.0$ Hz), 128.4 ($C_{3(\text{or }2)}$) 129.5 ($C_{2(\text{or }3)}$), 132.4 (C_4), 141.3 (C_1), 208.1 (PhCOS).

When an essentially identical procedure was followed using $Cd(NO_3)_2$:NaSOCPh:Me_4NCl = 1:3:1, **1** was isolated in 70% yield. Anal. Found: C, 47.95; H, 3.84; N, 1.27. The ^{1}H and ^{13}C NMR spectra were identical to those described above. Similarly, use of $Cd(NO_3)_2$:NaSOCPh:Me_4NCl = 1.5:4.1:1 gave a 44% yield of **1** that was pure by ^{1}H and ^{13}C NMR.

X-ray Structure Determination. Single crystals were produced during the synthesis of **1** using $Cd(NO_3)_2$:NaSOCPh:Me_4NCl = 1:4:2. A crystal of suitable quality was mounted in air on a glass fibre with epoxy cement. The crystal density was measured by the neutral buoyancy method using a mixture of carbon tetrachloride and hexane. The data collection was carried out on an Enraf-Nonius CAD4F diffractometer using Cu Kα radiation[3] with nickel filter at 23 °C. Photo and automatic indexing routines, followed by least squares fits of 21 accurately centered reflections ($50.2 \leq 2\theta \leq 69.1°$), gave cell constants and an orientation matrix. Intensity data were recorded in ω–2θ mode, at variable scan speeds (0.824–4.12° min^{-1}) and a scan width of $0.70 \pm 0.15 \tan\theta$, with a maximum time per datum of 60 s. Static background measurements were made at the end points of the width $0.8 \pm 0.15 \tan\theta$. Three standard reflections $\bar{1}00$, $00\bar{2}$ and $0\bar{1}0$ were monitored every 120 min of X-ray exposure time and showed 3.6% random decay over the total period of 46.1 h. In all, 5056 reflections in the 2θ range $0 \rightarrow 140°$ ($-13 \leq h \leq 1$, $-14 \leq k \leq 14$, $-13 \leq l \leq 13$) and 39 repetitions of the standards were recorded. Corrections were made for Lorentz, monochromator and crystal polarization, and background radiation effects, but not for decay, using the Structure Determination Package[4] running on a PDP11/23+ computer. As the crystal faces could not be indexed due to etching, a numerical absorption correction could not be applied. Hence an empirical absorption correction was applied to the data[5] based on ψ scans ($\psi = 0 \rightarrow 360°$ every 10°) for χ values near 90°. Eight sets of reflections with θ ranging from 8.8 to 35.1° gave an absorption profile with maximum and minimum transmission values 99.75 and 77.29. A p value of 0.06 was applied to the data.[6] Equivalent reflections were averaged ($R = 0.0468$) giving 4724 unique data. In the triclinic system, for $Z = 1$, the space group $P\bar{1}$ was assumed. This imposes a crystallographic center of inversion in the molecule. The structure was solved by a combination of SHELXS-86[7] and difference Fourier techniques. Refinement was by full-matrix least-

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Table I. Summary of the X-ray Structure Determination

compound, fw	$C_{46}H_{42}Cd_2N_1Na_1O_6S_6$, 1145.025
crystal system, space group	triclinic, $P\bar{1}$
cell dimens (Å; deg)	$a = 11.026(1)$, $b = 11.886(2)$, $c = 10.906(1)$; $\alpha = 94.32(1)$, $\beta = 113.25(1)$, $\gamma = 71.53(1)$
cell volume (Å^{-3}), Z	1243.5(5), 1
density, g·cm^{-3}: obsd, calcd	1.528(5), 1.529
$F(000)$	576
diffractometer, filter	Enraf Nonius CAD4F; nickel
radiation, wavelength (Å)	Cu Kα, 1.541 84
abs coeff (cm^{-1})	93.6
no. of observ, variables	4001 ($I \geq 3\sigma(I)$), 271
final model:[a] R, R_w	0.0559, 0.0658

[a] Where $R = \sum||F_o| - |F_c||$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

squares techniques on F, using the SHELX-76 software[8] running on a SUN 3/80 workstation. Scattering factors for neutral, non-hydrogen atoms and the Na^+ ion were taken from ref 9a. Anisotropic thermal parameters were assigned for all the non-hydrogen atoms in the anion and the N atom in the cation and were refined. The hydrogen atoms of the phenyl rings were placed in their ideal positions (with C–H = 0.95 Å) and included in the least-squares for the structure factors calculations only. A common temperature factor was assigned for these hydrogen atoms and was refined in the least-squares. By virtue of the space group $P\bar{1}$[9b] with $Z = 1$, the carbon atoms present in the $(CH_3)_4N^+$ cation were disordered with the nitrogen atom sitting at the centre of inversion. The tetramethylammonium ion was treated as an ideal tetrahedron with N-C distances, 1.485 Å. No hydrogen atom of the disordered cation was included in the structure factors calculations. In the final least-squares cycles refinement, with the use of 4001 ($I \geq 3\sigma(I)$) observations and 271 variables, the model converged at agreement factors $R = 0.0559$, $R_w = 0.0658$ using a weighting scheme of the form $w = k/\sigma^2(F_o) + gF^2$ where $k = 1.00$ and $g = 0.003\,148$. The top six peaks in the final difference Fourier synthesis have electron density in the range 1.32–0.78 e·Å^3; of these the top five were associated with the disordered cation and the sixth peak was near Cd atom at 0.68 Å. The secondary extinction coefficient was refined to 0.024(1) and the maximum $\Delta/\sigma = 0.23$.

The space group $P1$ was also considered as the intensity statistics computed using NZTEST[10] suggested this acentric space group. The structure was readily solved and refined. The model converged at $R = 0.0559$, $R_w = 0.0637$ for 4288 ($I \geq 3\sigma(I)$) observations and 244 variables. For the inverted model, $R = 0.0556$ and $R_w = 0.0631$ with the same number of observations and variables. Between centrosymmetric and noncentrosymmetric space group, the centrosymmetric description is recommended by Marsh.[11] On this basis, and also on the basis of geometry and ESDs, the original choice of the space group $P\bar{1}$ was retained.

The crystal data and the experimental details and the positional and U(equiv) thermal parameters are given in Tables I and II, respectively.

NMR Spectra. Proton and ^{13}C NMR spectra were obtained at ambient probe temperature using Varian XL-200 and XL-300 spectrometer systems, respectively, with solutions in standard 5 mm o.d. NMR tubes. The ^2D resonance of the solvent, $(CD_3)_2CO$, was used as a field/frequency lock. Signals from the solvent were used as internal references (δ_H(CD_2H) = 2.04; δ_C(CD_3) = 29.8).

Cadmium NMR spectra were measured using the ^{111}Cd nuclide,[12] since on both XL spectrometer systems artifacts are present in the region of the ^{113}Cd NMR spectrum where signals from the CdS_n kernel are expected to occur. No primary isotope effect is expected, i.e. chemical shifts should be the same for both ^{111}Cd and ^{113}Cd. The external reference was 0.1 M $Cd(ClO_4)_2$(aq) at ambient probe temperature and the operating frequencies at the reference were 42.41 and 63.59 MHz for the XL-200 and -300 spectrometer, respectively. Sodium-23 NMR spectra were measured using the XL-300 NMR spectrometer operating at 79.34 MHz. The external reference was 0.1 M $NaBPh_4$ in Me_2CO at ambient probe temperature. For ^{111}Cd and ^{23}Na NMR spectra, samples were prepared in 10 mm od NMR tubes with concentrations measured on the basis of mass of solute/volume of solvent. Data were collected without a ^2D field/frequency lock. On the XL-200 spectrometer, which was used for most of the measurements, the field drift is <0.03 ppm/day. To allow the use of more dilute solutions, data for **1**:$NaBPh_4$ mixtures were collected using the XL-300 spectrometer. In this case, chemical shifts were corrected for the measured drift (ca. 0.5 ppm/day), which was assumed to be linear. Between sessions, δ_{Cd} was found to be reproducible to ±1 ppm or better. In a single session, reproducibility is thought to be ±0.1 ppm or better. Probe temperatures were measured using a thermocouple probe in a stationary sample of the appropriate solvent.

Table II. Atomic Positional (×10^4) and Thermal (×10^3) Parameters[a]

atom	x	y	z	U_{eq} (Å^2)
Na	5000	5000	5000	44(1)
Cd	5166.4(4)	5788.5(4)	2001.5(4)	48.4(2)
S(1)	7443(2)	6170(2)	2961(2)	67(1)
S(2)	3099(2)	7610(2)	1253(2)	66(1)
S(3)	4731(3)	3941(2)	874(2)	73(1)
O(1)	6309(6)	6216(5)	4674(6)	72(2)
O(2)	3195(5)	6392(4)	3186(5)	61(2)
O(3)	5656(6)	3858(4)	3429(4)	60(2)
C(1)	10592(7)	5799(6)	−405(8)	45(0)
C(2)	8518(6)	5240(5)	−913(6)	45(0)
C(3)	10102(6)	5218(5)	1391(6)	45(0)
C(11)	8268(7)	6911(6)	5555(7)	53(2)
C(12)	9632(8)	6648(7)	5688(8)	66(3)
C(13)	10550(10)	7125(10)	6703(10)	85(4)
C(14)	10056(14)	7908(10)	7510(10)	98(5)
C(15)	8652(14)	8238(10)	7348(10)	96(5)
C(16)	7764(9)	7687(7)	6381(7)	67(3)
C(21)	1148(6)	8030(6)	2354(7)	48(2)
C(22)	194(7)	8815(6)	1249(8)	58(2)
C(23)	−1070(9)	9488(8)	1227(11)	80(4)
C(24)	−1414(10)	9414(10)	2271(13)	102(5)
C(25)	−485(11)	8638(10)	3347(12)	101(5)
C(26)	785(10)	7965(8)	3397(9)	77(4)
C(31)	5305(6)	2058(5)	2582(6)	45(2)
C(32)	4708(7)	1432(6)	1528(8)	59(3)
C(33)	4740(9)	274(7)	1766(11)	81(4)
C(34)	5374(10)	−229(7)	3027(12)	91(5)
C(35)	5946(10)	378(7)	4082(11)	81(4)
C(36)	5917(8)	1522(7)	3873(8)	63(3)
N	10000	5000	0	37(4)
C(10)	10592	5799	−405	45(5)
C(20)	8518	5240	−913	45(5)
C(30)	10102	5218	1391	45(5)
C(40)	10788	3744	−72	45(5)

[a] All atoms except C(10) to C(40) were assigned anisotropic thermal parameters given as the isotropic equivalent displacement parameter defined as $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}\cdot a^*_i\cdot a^*_j\cdot a_i\cdot a_j$.

Elemental Microanalyses. All C, H, and N microanalyses were performed by Guelph Chemical laboratories Ltd.

Results and Discussion

Synthesis. The salt **1** is formed in aqueous methanol from mixtures of $Cd^{2+}/NaSOCPh/Me_4NCl$ in ratios from 1:2.7:0.67 to 1:4:2. Crystallization of **1** may be achieved by addition of MeCN to the reaction mixture. Orange-yellow **1** is soluble in THF, Me_2CO, MeCN, DMSO, and DMF but insoluble in Et_2O, MeOH, EtOH, $CHCl_3$, and CH_2Cl_2.

Structure of $(Me_4N)(Na[Cd\{SOCPh\}_3]_2)$ (1). The structure of **1** consists of discrete and well separated anions and cations. A perspective view of the anion $(Na[Cd\{SOCPh\}]_2)^-$ is shown in Figure 1 along with the numbering scheme. The closest nonbonded distance of 2.644 Å is H(23)···H(33) ($-x$, $1-y$, $-z$). The closest interanionic Cd···S(3) distance of 3.226(2) Å ($1-x$, $1-y$, $-z$) shows that interanionic bridging of cadmiums through sulfur is minimal. The shortest intramolecular interaction is H(26)···H(36) ($1-x$, $1-y$, $1-z$), 2.612 Å. Selected interatomic dimensions are given in Table III.

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(12) Cadmium-111 and -113 are both spin $^1/_2$ nuclei. They have similar receptivities; e.g. the receptivities relative to ^{13}C, D^C, are 6.97 and 7.67, respectively.[13]

(13) Harris, R. K. *Nuclear Magnetic Resonance Spectroscopy*; Pitman: London, 1983; p 230.

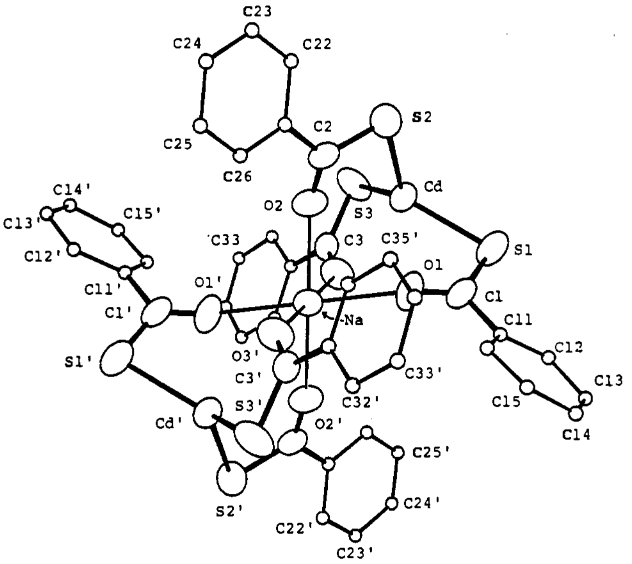

Figure 1. View of the $(Na[Cd\{SOCPh\}_3]_2)^-$ anion in **1**, showing the atom-numbering scheme.

The anion contains six thiobenzoate ligands, two Cd(II) centers and a Na(I) center. It has a crystallographically imposed centre of symmetry, with the Na^+ sitting at the inversion center. The Cd···Na distance is 3.557(1) Å. The Na^+ is bonded to each of the $C_6H_5C(=O)S^-$ ligands through an oxygen atom. Thus the sodium ion is six-coordinate and has a distorted octahedral coordination geometry. The Na–O distances (2.470(5), 2.431(4), and 2.303(4) Å) are significantly different from each other. However, all fall in the range 2.304(4)–2.512(4) Å that has been established[14] for simple sodium carboxylates. The Na–O distances may be further compared with the Na–(bridging)O distance of 2.46(2) Å found[15] in $NaI{\cdot}3Me_2CO$ and the Na–(thiobenzilato)O distances of 2.376(14)–2.557(14) Å reported very recently[16] for $[NBu^n_4]Na\{Mo(O_2CC(S)Ph_2\}_3]{\cdot}H_2O{\cdot}MeOH$. Around the sodium ion, the O–Na–O angles range from 78.7 to 101.3°.

Each Cd atom is S-bonded to three thiobenzoate ions. Of the three Cd–S distances observed (2.485(2), 2.493(2), and 2.521(2) Å), the Cd–S(3) distance, 2.521 Å, is significantly longer than the other two. The sulfur atom S(3) is associated with the thiocarboxylate group having the *shortest* Na–O distance. Overall, the Cd–S distances are similar to those found in polymeric $Cd(SOCPh)_2{\cdot}EtOH$ (2.51(1)–2.58(1) Å[17]) and monomeric $Cd(SOCPh)_2{\cdot}2py$ (2.49 and 2.56 Å, with a maximum esd of 0.005 Å[18]), and in $(Et_4N)[Cd\{S_2COEt\}_3]$ for the η^1-S_2COEt^- ligand (2.508(4)).[19] The Cd–S distances for $(Na[Cd\{SOCPh\}_3]_2)^-$ are larger than those found for three-coordination in $[Cd\{S\text{-}2,4,6\text{-}C_6H_2Pr^i{}_3\}_3]^-$ (2.419(3)–2.455(4) Å[20]) but fall into the range 2.460(4)–2.554(3) Å that has been observed[21] for four-coordinate cadmium with simple terminal thiolates. It is unclear whether the increase in the Cd–S distance of the CdS_3 kernel that occurs from $[Cd\{S\text{-}2,4,6\text{-}C_6H_2Pr^i{}_3\}_3]^-$ to $(Na[Cd\{SOCPh\}_3]_2)^-$ is a result of the difference in the S-donor ligands or of the weak Cd–O bonding that occurs in the second anion (see below), or both. In any case, it is evident that the Cd interacts strongly with the S atoms of the thiobenzoates. The S–Cd–S angles are in the range 114.4–125.8°, with a sum of 355.0°, indicating that the CdS_3 skeleton is close to planarity.

Table III. Selected Interatomic Distances (Å) and Angles (deg)[a]

Cd–S(1)	2.485(2)	Cd–S(2)	2.493(2)
Cd–S(3)	2.521(2)	Cd–O(1)	2.761(5)
Cd–O(2)	2.828(5)	Cd–O(3)	2.659(5)
Na–O(1)	2.470(5)	Na–O(2)	2.431(4)
Na–O(3)	2.303(4)	S(1)–C(1)	1.737(8)
S(2)–C(2)	1.725(7)	S(3)–C(3)	1.727(6)
C(1)–O(1)	1.237(8)	C(2)–O(2)	1.233(7)
C(3)–O(3)	1.226(7)	C(1)–C(11)	1.503(9)
C(2)–C(21)	1.486(9)	C(3)–C(31)	1.471(8)
C(11)–C(12)	1.384(10)	C(12)–C(13)	1.399(10)
C(13)–C(14)	1.367(16)	C(14)–C(15)	1.411(17)
C(15)–C(16)	1.409(12)	C(11)–C(16)	1.384(11)
C(21)–C(22)	1.407(9)	C(22)–C(23)	1.362(11)
C(23)–C(24)	1.350(15)	C(24)–C(25)	1.377(15)
C(25)–C(26)	1.357(12)	C(21)–C(26)	1.361(10)
C(31)–C(32)	1.376(9)	C(32)–C(33)	1.407(11)
C(33)–C(34)	1.355(14)	C(34)–C(35)	1.354(14)
C(35)–C(36)	1.385(10)	C(31)–C(36)	1.398(9)
S(2)–Cd–S(1)	114.73(8)	S(3)–Cd–S(2)	114.37(8)
S(3)–Cd–S(1)	125.85(8)	S(1)–Cd–O(1)	59.5(2)
S(1)–Cd–O(2)	124.7(1)	S(1)–Cd–O(3)	102.7(1)
S(2)–Cd–O(1)	98.9(1)	S(2)–Cd–O(2)	58.0(1)
S(2)–Cd–O(3)	130.0(2)	S(3)–Cd–O(1)	131.0(1)
S(3)–Cd–O(2)	100.1(1)	S(3)–Cd–O(3)	59.1(1)
O(1)–Cd–O(2)	67.6(2)	O(1)–Cd–O(3)	72.0(2)
O(2)–Cd–O(3)	73.9(2)	C(1)–S(1)–Cd	88.9(2)
C(2)–S(2)–Cd	91.3(2)	C(3)–S(3)–Cd	87.8(2)
O(1)–Na–O(2)	78.7(2)	O(1)–Na–O(2)′	101.3(2)
O(1)–Na–O(3)	83.6(2)	O(1)–Na–O(3)′	96.4(2)
O(2)–Na–O(3)	88.3(2)	O(2)–Na–O(3)′	91.7(2)
C(3)–O(3)–Na	145.6(5)	O(1)–C(1)–S(1)	122.3(6)
C(11)–C(1)–S(1)	117.7(5)	C(11)–C(1)–O(1)	119.9(7)
O(2)–C(2)–S(2)	121.6(5)	C(21)–C(2)–S(2)	118.0(4)
C(21)–C(2)–O(2)	120.2(6)	O(3)–C(3)--S(3)	119.1(4)
C(31)–C(3)–S(3)	119.9(4)	C(31)–C(3)–O(3)	121.0(5)
C(12)–C(11)–C(1)	121.4(7)	C(16)–C(11)–C(1)	117.4(7)
C(16)–C(11)–C(12)	121.1(7)	C(13)–C(12)–C(11)	120.4(9)
C(14)–C(13)–C(12)	118.8(9)	C(15)–C(14)–C(13)	121.7(9)
C(16)–C(15)–C(14)	118.7(10)	C(15)–C(16)–C(11)	119.0(9)
C(22)–C(21)–C(2)	121.3(6)	C(26)–C(21)–C(2)	120.0(6)
C(26)–C(21)–C(22)	118.7(7)	C(23)–C(22)–C(21)	120.2(7)
C(24)–C(23)–C(22)	120.4(8)	C(25)–C(24)–C(23)	119.4(9)
C(26)–C(25)–C(24)	121.3(9)	C(25)–C(26)–C(21)	119.9(8)
C(32)–C(31)–C(3)	124.0(6)	C(36)–C(31)–C(3)	117.5(6)
C(36)–C(31)–C(32)	118.5(6)	C(33)–C(32)–C(31)	119.8(8)
C(34)–C(33)–C(32)	120.1(8)	C(35)–C(34)–C(33)	121.2(7)
C(36)–C(35)–C(34)	119.7(9)		

[a] Primed atoms are related to their unprimed counterparts by the symmetry operator (1 – *x*, 1 – *y*, 1 – *z*).

Kernels of the type CdS_3 are unusual and previously have been observed only in $Cd(SR)_3^-$ in which R is a bulky substitutent.[20] In the case of $(Na[Cd\{SOCPh\}_3]_2)^-$, the weighted least-squares plane calculation shows that the Cd is moved towards Na by 0.326 Å from the S_3 plane. This may be attributed to intramolecular interactions with the oxygen atoms of the PhC(=O)S group. The structural chemistry of simple cadmium carboxylates is extremely complicated, with a variety of bonding modes observed

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for the carboxylate moieties.[22] The range of Cd–O distances that has been observed in such compounds is 2.199(5)–2.843(5) Å, with the large majority of values falling in the lower half of the range.[22] The Cd–O distances observed for $(\mathrm{Na[Cd\{SOCPh\}_3]_2})^-$ are 2.761(5), 2.828(5), and 2.659(5) Å. It is clear that in the trinuclear complex the Cd–O interactions are weak. There is an evident preference for Cd–S bonding rather than Cd-O bonding to the $\mathrm{SOCPh^-}$ ligand, as has been noted earlier for $\mathrm{Cd(SOCPh)_2{\cdot}2py}$.[18]

If the Cd–O interactions are considered important, then the geometry of the $\mathrm{CdS_3O_3}$ skeleton is that of a highly distorted trigonal prism. The cadmium atom is grossly off-center, much closer to the $\mathrm{S_3}$ plane than to the $\mathrm{O_3}$ plane. (The distance of the Cd from the weighted least squares $\mathrm{O_3}$ plane is 2.030 Å.) The twist angle, ϕ, is 22(3)°.

In the $\mathrm{PhCOS^-}$ ligands, the COS planes are twisted from the phenyl rings. The dihedral angles are 34.1(6), 16.3(14), and 9.2(20)°. The C-S distances range from 1.725(7) to 1.737(8) Å and the C-O distances are in the range 1.226(7)–1.237(8) Å. These distances are normal and compare with those observed in $\mathrm{(PhCOS)_2}$[23] and $\mathrm{(PhCOSLi{\cdot}TMEDA)_2}$.[24] The mean C–C distance in the benzene rings is 1.38(2) Å.

In effect, $(\mathrm{Na[Cd\{SOCPh\}_3]_2})^-$ contains two $[\mathrm{Cd\{SOCPh\}_3}]^-$ anions acting as uninegative tridentate O-donor ligands toward $\mathrm{Na^+}$. We are at present examining the ligand behavior of $[\mathrm{Cd\{SOCPh\}_3}]^-$ in more detail, as well as exploring the coordination chemistry of a wider range of ligands of the general type $[\mathrm{M\{SOCR\}_3}]^-$.

Metal NMR. At a concentration of 0.025 mol/L of solvent, δ_{Cd} = 292 and 301 for solutions of **1** in $\mathrm{Me_2CO}$ and MeCN, respectively, at 296 K (Table IV). These signals are significantly more shielded than those observed for $\mathrm{Cd(SR)_3^-}$ (δ_{Cd} = 577–668[20]). However, for the $\mathrm{CdS_3O_3}$ kernels found in $\mathrm{Cd_{10}(SCH_2CH_2OH)_{16}^{4+}}$ δ_{Cd} = 388–409,[25] while for those found in $\mathrm{Cd_{10}(SCH_2CH_2OH)_{16}Cl_n^{(4-n)+}}$ δ_{Cd} = 382–392.[26] Thus addition of O-donors to $\mathrm{Cd(SR)_3^-}$ leads to shielding. Accordingly, δ_{Cd} for solutions of **1** suggests the persistence of the bonding of Cd to both O and S from the solid state into solution.

Table IV. Metal NMR Data for Solutions of **1** and **1**/$\mathrm{NaBPh_4}$ Mixtures at 296 ± 1 K

solvent	concn of **1**[a]	$\mathrm{NaBPh_4}$:**1**	δ_{Cd}[b]	δ_{Na}[c]	$\Delta\delta_{\mathrm{Na}}$[d]
$\mathrm{Me_2CO}$	0.001		≈286	0.02	0.00
	0.005		288.9	–0.16	–0.19
	0.025		292.3	–0.26	–0.33
		1.0	297.2	–0.22	*e*
		4.0	302.2	–0.14	*e*
		10.0	304.7	–0.09	*e*
		19.8	306.6	–0.07	*e*
MeCN	0.001		≈292	0.53	–0.08
	0.005		296.0	0.45	–0.16
	0.025		300.7	0.36	–0.23
		1.0	306.4	0.41	*e*
		5.0[f]	313.5	0.53	*e*
		10.0[f]	315.6	0.60	*e*
		20.0[f]	317.7	0.70	*e*

[a] mol of **1**/L of solvent. [b] $^{111}\mathrm{Cd}$ NMR chemical shift measured relative to external 0.1 M $\mathrm{Cd(ClO_4)_2(aq)}$. [c] $^{23}\mathrm{Na}$ NMR chemical shift measured relative to external 0.1 M $\mathrm{NaBPh_4}$ in $\mathrm{Me_2CO}$. [d] $\Delta\delta_{\mathrm{Na}} = \delta_{\mathrm{Na}}(\mathrm{sample}) - \delta_{\mathrm{Na}}(\mathrm{NaBPh_4})$ in same solvent at the same concentration. [e] Not measured. [f] Precipitation of $\mathrm{(Me_4N)(BPh_4)}$ occurs.

With decreasing concentration, $^{23}\mathrm{Na}$ NMR chemical shifts for solutions of **1** approach those of equimolar solutions of $\mathrm{NaBPh_4}$, as shown by $\Delta\delta_{\mathrm{Na}}$ in Table IV. Evidently there is dissociation of $(\mathrm{Na[Cd\{SOCPh\}]_2})^-$ in solution with release of $\mathrm{Na^+}$ (eqs 1 and 2) and, at 296 K, rapid exchange of $^{23}\mathrm{Na}$ between the species

$$(\mathrm{Na[Cd\{SOCPh\}_3]_2})^- \rightleftharpoons (\mathrm{Na[Cd\{SOCPh\}_3]}) + [\mathrm{Cd\{SOCPh\}_3}]^- \quad (1)$$

$$(\mathrm{Na[Cd\{SOCPh\}_3]}) \rightleftharpoons \mathrm{Na^+} + [\mathrm{Cd\{SOCPh\}_3}]^- \quad (2)$$

involved in the equilibria. Values of δ_{Cd} for solutions of **1** (Table IV) show that decreasing concentration (increasing dissociation) leads to increasing shielding of the cadmium resonance. Again exchange is rapid on the NMR time scale. From Table 4 it is evident that at 296 K δ_{Cd} for sodium-free $[\mathrm{Cd\{SOCPh\}_3}]^-$ is ≤286 in $\mathrm{Me_2CO}$ and ≤292 in MeCN. As expected, addition of $\mathrm{NaBPh_4}$ to solutions of **1** (0.025 mol/L of solvent) causes an increase in δ_{Cd} (Table IV). The absence of a saturation effect on the monotonic increase shows that even a 20-fold excess of $\mathrm{Na^+}$ is insufficient to completely form $(\mathrm{Na[Cd\{SOCPh\}_3]})$. However, δ_{Cd} for $(\mathrm{Na[Cd\{SOCPh\}_3]})$ must be ≥307 in $\mathrm{Me_2CO}$ and ≥318 in MeCN at 296 K. Based on the discussion given above, the decrease in Cd shielding on coordination of $\mathrm{Na^+}$ is consistent with a weakening of the Cd–O bonding of the $\mathrm{CdS_3O_3}$ kernel when the oxygens act as bridges.

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Supplementary Material Available: Tables of anisotropic thermal parameters, calculated hydrogen positional parameters, weighted least-squares planes and dihedral angles, and torsion angles (3 pages). Ordering information is given on any current masthead page.

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