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Reactions of $Cd(SR)_2$ (R = *n*-Butyl, Phenyl) and the Molecular Structure of the 2,2′-Bipyridine Adduct of Bis(*n*-butyl thioxanthato)cadmium(II)

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$Cd(SC_6H_5)_2$ forms a series of 1:1, 1:2, and 2:1 adducts with neutral bidentate nitrogen donors, via reaction in *N*,*N*-dimethylformamide solution, but $Cd(SC_4H_9\text{-}n)_2$ does not react under these or other conditions. On the other hand, $Cd(SC_4H_9\text{-}n)_2$ readily reacts with CS_2 to give the corresponding bis(thioxanthate), which forms stable adducts; in contrast, $Cd(SC_6H_5)_2$ reacts only slowly to give $Cd(SC_6H_5)_2CS_2$, which can also be prepared by direct electrochemical oxidation. The mechanism of these reactions is discussed. The crystal structure of $Cd(S_2CSC_4H_9\text{-}n)_2\cdot$2,2′-bipyridine, $Cd(S_3C_5H_9)_2\cdot C_{10}H_8N_2$, is monoclinic, with $a = 22.184$ (3) Å, $b = 9.001$ (2) Å, $c = 12.687$ (6) Å, $\beta = 99.90$ (3)°, $V = 2{,}550.8$ Å^3, $Z = 4$, and space group $C2/c$; $R = 0.025$, and $T = 20$ °C. The molecule has a distorted CdS_4N_2 kernel, with bond distances of 2.664 (1) and 2.704 (1) Å (Cd–S) and 2.363 (3) Å (Cd–N); the thioxanthate ligand is bidentate. $Cd(SR)_2$ reacts with R′COCl to give the corresponding R′COSR thio esters in good yield.

Introduction

A number of recent papers from this laboratory have described direct one-step syntheses of thiolato complexes of zinc,[1–3] cadmium,[1–3] mercury,[1] tin, and lead[4] by the anodic oxidation of a sacrificial anode in a nonaqueous solution of RSH or R_2S_2. The results are explicable in terms of attack on the metal by RS^- anions generated by reduction of the solute.

In the case of zinc, cadmium, and mercury, the $M(SR)_2$ products, which form in high yield, are insoluble and apparently polymeric substances. We have now investigated the properties of $Cd(SR)_2$ (R = $n\text{-}C_4H_9$, C_6H_5) both in terms of the formation of adducts with bidentate donors and of the insertion of carbon disulfide into the M–S bond. It has also been shown that $Cd(SR)_2$ is a useful reagent for the synthesis of thio esters from the corresponding acid chloride. The structure of the CS_2 insertion product has been confirmed by an X-ray crystallographic study of the 2,2′-bipyridine adduct of bis(*n*-butyl thioxanthato)cadmium(II).

Experimental Section

General Data. Solvents were distilled and dried over molecular sieves. All other reagents were used as supplied. Cadmium metal (Alfa Inorganics; m3N5) was in the mossy granulated form.

Metal analysis was carried out by atomic absorption spectrophotometry. Microanalysis was performed by Guelph Chemical Laboratories Ltd. Compounds were characterized by analysis and by NMR and mass spectroscopy (Table I), using techniques described earlier.[1–4]

Electrochemical Procedures. The electrochemical synthesis of $Cd(SR)_2$ followed the procedure described earlier,[1] in that a cadmium metal anode was electrochemically oxidized in an acetonitrile solution of either C_6H_5SH or $n\text{-}C_4H_9SH$ to give the corresponding air-stable $Cd(SR)_2$ products, which are insoluble in CH_3CN and most common organic solvents (see below).

Electrochemical Synthesis of $Cd(SC_6H_5)(S_2CSC_6H_5)$. The electrochemical oxidation of a cadmium anode in a solution phase of 40 mL of acetonitrile, 5 mL of C_6H_5SH (48.6 mmol), 20 mL of CS_2 (0.43 mol), and 20 mg of tetraethylammonium perchlorate for 5 h at 20 V and a current of 20 mA led to the dissolution of 220 mg of cadmium. In a separate experiment, the electrochemical efficiency E_F (moles of metal dissolved per faraday of electricity) was found to be 0.52 mol faraday^{-1}. The reaction mixture was filtered to remove any precipitated particles of metal, and the filtrate was slowly evaporated; the yellow crystals, which deposited on cooling, were washed several times with acetonitrile and then petroleum ether and dried in vacuo. This material was identified as $Cd(SC_6H_5)(S_2CSC_6H_5)$, and was identical with the material prepared from the reaction of $Cd(SC_6H_5)_2$ with CS_2 (see below).

Electrochemical Synthesis of Adducts of $Cd(SC_6H_5)_2$. In addition to the preparation of adducts of $Cd(SC_6H_5)_2$ by conventional techniques (see below), we have shown that such compounds can be obtained by the electrochemical route. Electrolysis of cadmium into a solution of 1 mL of C_6H_5SH (9.7 mmol), 0.8 g of 1,10-phenanthroline (phen) (4.4 mmol) and 40 mg of tetraethylammonium perchlorate in 50 mL of acetonitrile for 2 h at 15 V and 40 mA led to the dissolution of 0.182 g (1.62 mmol) of Cd (E_F = 0.54 mol faraday^{-1}). The yellow crystals, which formed in the cell during the experiment, were collected and washed successively with acetonitrile and *n*-pentane; during the latter procedure, the crystals disintegrated to a yellow powder, identified as $Cd(SC_6H_5)_2(phen)_2$. This substance is insoluble in common organic solvents.

A similar experiment in which 2,2′-bipyridine (bpy) replaced phen (1 mL of C_6H_5SH (9.7 mmol), 0.9 g of bpy (5.8 mmol), 50 mL of CH_3CN; 15 V, 40 mA, 3 h; 0.273 g of Cd (2.4 mmol) dissolved; E_F = 0.54 mol faraday^{-1}) yielded a solution from which an oil precipitated on slow evaporation of the solvent in vacuo. This oil was triturated with ethanol, whereupon a yellow powder, $[Cd(S_6H_5)_2]\cdot$bpy, was formed. Insolubility precluded NMR studies, but infrared spectroscopy confirmed the presence of both ligands, as was also the case for the phen compound above.

Adduct Formation with $Cd(SC_6H_5)_2$. As reported earlier,[1] the thiolate derivatives of zinc, cadmium, and mercury are insoluble in most common organic solvents, but $Cd(SC_6H_5)_2$ dissolves readily in *N*,*N*-dimethylformamide (dmf) and dimethyl sulfoxide. Solutions in the former provide a convenient medium for the preparation of adducts. Addition of acetone to a solution of $Cd(SC_6H_5)_2$ in dmf precipitated the starting material, so that the presumed solvated species in solution do not give rise to stable adducts in the solid phase.

A solution of 0.107 g of $Cd(SC_6H_5)_2$ (0.32 mmol) and 0.48 g of 2,2′-bipyridine (3.1 mmol) in 10 mL of dmf was stirred at room temperature overnight, during which time the colorless mixture turned pink. The resultant solution was cooled to 0 °C and methanol added, producing a pink oil, which was collected and triturated with cold methanol and then mixtures of methanol and diethyl ether at room temperature to yield $Cd(SC_6H_5)_2\cdot$bpy as a pink solid.

A similar reaction between $Cd(SC_6H_5)_2$ and 1,10-phenanthroline (equimolar quantities) in dmf led to the precipitation of an orange oil, which yielded $Cd(SC_6H_5)_2\cdot$phen as an orange solid. The supernatant liquid from this reaction was treated with diethyl ether, which caused the precipitation of the yellow solid $[Cd(SC_6H_5)_2]_2\cdot$phen. With $Cd(SC_6H_5)_2$ and excess *N*,*N*,*N′*,*N′*-tetramethylethanediamine (tmen), the green oil that was formed proved impossible to crystallize, but addition of diethyl ether to the supernatant yielded $[Cd(SC_5H_5)_2]_2\cdot$tmen as a colorless solid.

The reaction of $Cd(SC_6H_5)_2$ (0.303 g, 0.90 mmol) and triphenylphosphine (0.488 g, 1.86 mmol) in dmf (10 mL) at room temperature gave a clear solution. Addition of methanol gave a white precipitate, which was collected and dried in vacuo. The composition corresponds to $[Cd(SC_6H_5)_2]_4\cdot P(C_6H_5)_3$ (see Table I).

Bis(*n*-butyl thiolato)cadmium(II) is insoluble in dmf, as it is in solutions of other organic solvents, in solutions of bpy or phen in dmf, and in solutions of bpy in benzene or acetonitrile. We were therefore unable to prepare adducts of this compound.

Reactions with Carbon Disulfide. (i) $Cd(SC_4H_9\text{-}n)_2$ is readily soluble in carbon disulfide at room temperature, and a clear yellow solution resulted when 0.3 g (1.03 mmol) of the solid was stirred with 30 mL of CS_2 at room temperature. Slow removal of the solvent yielded $(n\text{-}C_4H_9S)_2Cd\cdot CS_2$ as a yellow solid. The corresponding $Cd(SC_6H_5)_2$ is

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Table I. Analytical and ^{1}H NMR Results for Adducts and Derivatives of $Cd(SR)_2$ ($R = C_6H_5$, n-C_4H_9)

		% Cd		^{1}H NMR (Me$_2$SO-d_6),[g] ppm from Me$_4$Si	
compound	color	found	calcd	SR	ligand
$Cd(SC_6H_5)_2$	white	33.6	34.0	7.51–6.81 m	
$[Cd(SC_6H_5)_2]_2 \cdot$tmen	white	28.7	28.9	7.32–6.72 m	2.40 s, 2.20 s
$Cd(SC_6H_5)_2 \cdot$bpy	pink	23.7	23.1	7.25–6.71 m	
$[Cd(SC_6H_5)_2]_2 \cdot$bpy	yellow	27.7	27.5	insoluble	
$Cd(SC_6H_5)_2 \cdot$phen	orange	21.1	22.0	7.2–6.5 m	9.08–7.8 m
$[Cd(SC_6H_5)_2]_2 \cdot$phen	yellow	26.5	26.7	insoluble	
$Cd(SC_6H_5)_2$(phen)$_2$	yellow	16.7	16.3[a]	insoluble	
$[Cd(SC_6H_5)_2]_4P(C_6H_5)_3$	white	28.1	28.4[b]	7.0–6.5 m	7.9–7.0 m
$Cd(SC_6H_5)_2 \cdot CS_2$	yellow	27.6	27.7[c]	insoluble	
$Cd(SC_4H_9)_2$	white	38.2	38.7	insoluble	
$Cd(S_2CSC_4H_9)_2 \cdot$tmen	yellow	19.8	20.1	3.20 q, 1.50 m, 0.80 t	2.62 s, 2.40 s
$Cd(S_2CSC_4H_9)_2 \cdot$bpy	yellow	17.9	18.8[d]	3.05 q, 1.45 m, 0.85 t	8.85–7.60 m
$Cd(S_2CSC_4H_9)_2 \cdot$phen	yellow	17.2	18.1[e]	3.07 q, 1.46 m, 0.86 t	9.35–7.96 m
$Cd(SC_4H_9)_2 \cdot CS_2 \cdot$phen	yellow	20.9	20.6[f]	3.06 q, 1.52 m, 0.83 t	9.25–8.01
$Cd(SC_4H_9)_2 \cdot CS_2$	yellow	30.8	30.6	3.05 q, 1.55 m, 0.90 t	

[a] Found: C, 62.3; H, 4.06; N, 7.32. Calcd: C, 62.6; H, 3.79; N, 8.11. [b] Found: C, 50.4; H, 3.73. Calcd: C, 50.0; H, 3.47. [c] Found: C, 38.2; H, 2.81. Calcd: C, 38.4; H, 2.46. [d] Found: C, 39.9; H, 4.55; N, 4.50. Calcd: C, 40.1; H, 4.37; N, 4.67. [e] Found: C, 42.9; H, 4.68; N, 4.68. Calcd: C, 42.4; H, 4.18; N, 4.50. [f] Found: C, 46.0; H, 4.86; N, 4.70. Calcd: C, 46.1; H, 4.76; N, 5.12. [g] Compounds insufficiently soluble for reliable integration.

insoluble in CS_2 at room temperature, and we found no evidence of reaction after stirring for 10 h, but when the suspension (1.03 mmol) was boiled for 8–10 h, a solid of composition $Cd(SC_6H_5)_2 \cdot CS_2$ was recovered. This compound was subsequently prepared by direct electrochemical synthesis (see above). When $Cd(SC_6H_5)_2$ was dissolved at room temperature in 50 mL of CS_2/dmf mixture (2:1 v/v), a yellow solution resulted. After 24 h, the solvent was removed to reduce the volume by 60% and acetone added to precipitate a solid identified as the starting thiolate.

(ii) In the presence of bidentate neutral donors, reaction with CS_2 produces adducts of cadmium thioxanthates. When $Cd(SC_4H_9$-$n)_2$ (0.40 g, 1.38 mmol) and bpy (0.22 g, 1.41 mmol) were added to 30 mL of CS_2, a clear yellow solution was obtained. Slow evaporation in vacuo of this solution while it was being cooled in ice produced yellow crystals, which were collected and washed with diethyl ether and dried in vacuo; this material was shown to be $Cd(SC_4H_9$-$n)_2 \cdot 2CS_2 \cdot$bpy, and subsequent X-ray crystallographic analysis (see below) identified the structure as $Cd(S_2CSC_4H_9$-$n)_2 \cdot$bpy. Similar reactions with excess tmen gave $Cd(S_2CSC_4H_9$-$n)_2 \cdot$tmen.

(iii) Solutions of 1,10-phenanthroline (0.23 g, 1.28 mmol) in CS_2 (30 mL) readily dissolved $Cd(SC_4H_9$-$n)_2$ (0.37 g, 1.28 mmol). Slow evaporation in vacuo of the resultant yellow solution gave a yellow solid, which was collected and washed with diethyl ether and dried in vacuo; this product is $Cd(SC_4H_9$-$n)_2 \cdot CS_2 \cdot$phen. The remaining solution phase was evaporated to dryness, and the solid produced was redissolved in 3 mL of CS_2; addition of n-pentane caused the precipitation of a yellow solid, which was collected, washed with n-pentane, and dried in vacuo. This material was identified as $Cd(S_2CSC_4H_9$-$n)_2 \cdot$phen.

(iv) The addition of CS_2 was shown to be readily reversible. A suspension of $Cd(S_2CSC_4H_9$-$n)_2 \cdot$bpy in 40 mL of mixed xylenes (bp 137–144 °C) was refluxed for 30 min, during which time the yellow of the thioxanthate adduct disappeared, leaving a colorless residue. No further color change was detected on further refluxing over 5–6 h. The mixture was filtered, and the solid was collected, washed with benzene, and dried in vacuo; metal analysis (Cd 38.1%) and infrared spectroscopy showed that quantitative conversion to $Cd(SC_4H_9$-$n)_2$ had occurred, with loss of both CS_2 and 2,2′-bipyridine.

(v) When CS_2 (40 mL) was added to a solution of $Cd(SC_6H_5)_2$ (0.5 g, 1.52 mmol) and phen (1 g, 5.56 mmol) in dmf (10 mL), the solution immediately became deep yellow; after 1 h at room temperature, a yellow precipitate formed from the stirred solution. Infrared analysis showed the presence of SC_6H_5 and phen, and analysis suggested the formula $Cd(SC_6H_5)_2 \cdot$(phen)$_2 \cdot 0.5CS_2$. Anal. Found: Cd, 16.1; C, 60.0; H, 4.15; N, 7.35. Calcd: Cd, 15.4; C, 60.1; H, 3.56; N, 7.68. The filtrate from this procedure was stirred for a further 48 h and further precipitate removed. Addition of acetonitrile to the cooled filtrate caused the precipitation of a yellow solid, with infrared bands characteristic of SC_6H_5 and phen and a strong absorption at 1679 cm^{-1}(ν(C=O); the ^{1}H NMR spectrum (slightly soluble in Me$_2$SO) showed broad bands in the aromatic region and a methyl resonance at 3 ppm. This substance is apparently the dmf solvate $Cd(SC_6H_5)_2 \cdot$(phen)$_2 \cdot$dmf. Anal. Found: Cd, 13.9; C, 60.6; H, 4.44; N, 8.26. Calcd: Cd, 14.7; C, 61.3; H, 4.35; N, 9.16.

A similar procedure using 2,2′-bipyridine in place of 1,10-phenanthroline yielded no precipitate. After 48 h at room temperature, petroleum ether (30–50 °C) was added to the mixture, precipitating an oil, which was collected and triturated with ethanol to give a solid, which on the basis of spectroscopy and metal analysis is formulated as $[Cd(SC_6H_5)_2]_2 \cdot$bpy (cf. Table I).

Table II. Crystal and Experimental Data for $Cd(S_2CSC_4H_9$-$n)_2 \cdot$bpy

mol formula	$C_{20}H_{26}CdN_2S_6$
M_r	550.1
space group	$C2/c$ (confirmed by successful refinement)
a	22.184 (3) Å
b	9.001 (2) Å
c	12.687 (6) Å
β	99.90 (3)°
V	2550.8 Å^3
D_c	1.565 g cm^{-3}
Z	4
λ	0.7093 Å
μ(Mo Kα_1)	13.39 cm^{-1}
transmissn coeff	0.947, 0.998
θ_{min}; θ_{max}	0°; 22.5°
data collcn range	$\pm h,+k,+l$
N_{total}	1831
N_{obsd}	1457
R[a]	0.025
R_w[b]	0.029
weighting scheme	$w = 1/[\sigma(F_o)^2 + 0.0001F_o^2]^{1/2}$
goodness of fit[c]	1.984

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|^2$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum F_o^2]^{1/2}$. [c] $GOF = [\sum w(|F_o| - |F_c|)^2/n]^{1/2}$ (n = no. of degrees of freedom).

Crystallographic Analysis. A suitable pale yellow crystal of $Cd(S_2CSC_4H_9$-$n)_2 \cdot$bpy, of dimensions 0.24 × 0.24 × 0.45 mm, was cleaved from a larger crystal and sealed in a Lindeman tube. After preliminary photographic studies, the crystal was mounted on an Enraf-Nonius CAD4 diffractometer. Data were collected in the $\omega/2\theta$ scan mode with graphite-monochromated Mo $K\alpha$ radiation. A total of 1831 reflections were measured, of which 1457 were considered to be observed ($I > 3\sigma(I)$). The structure was solved routinely by the heavy-atom method and refined by full-matrix least squares using counter-derived weights ($w = [\sigma(F)^2 + 0.0001F^2]^{-1}$) to a final R value of 0.025 ($R_w = 0.029$); the function minimized was $\sigma w(|F_o| - |F_c|)^2$. A final difference Fourier map showed no significant features ($\rho_{max} = 0.28$ e Å^{-3}). Calculations were carried out by using the programs of Larson and Gabe[5] and scattering factors including anomalous dispersion.[6] There was no evidence for extinction, and corrections were therefore unnecessary.

Pertinent crystal and experimental data are given in Table II, fractional atomic coordinates in Table III, and bond lengths and bond angles

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Table III. Fractional Atomic Parameters and B_{eq} of Non-Hydrogen Atoms of $Cd(S_2CSC_4H_9\text{-}n)_2\cdot$bpy with Estimated Standard Deviations in Parentheses

atom	x	y	z	B_{eq},[a] Å^2
Cd	0.00000	0.11020 (4)	0.25000	3.82
S(1)	−0.17910 (5)	−0.13603 (13)	0.07799 (8)	5.76
S(2)	−0.09517 (4)	−0.05264 (10)	0.27855 (7)	4.13
S(3)	0.07475 (5)	0.04335 (12)	0.43522 (7)	5.23
N	0.03518 (12)	0.32187 (30)	0.17421 (22)	4.11
C(1)	−0.1148 (2)	−0.0466 (3)	0.1450 (3)	3.9
C(2)	0.0190 (1)	0.4512 (3)	0.2084 (3)	3.9
C(3)	0.0380 (2)	0.5780 (4)	0.1651 (4)	5.5
C(4)	0.0731 (2)	0.5701 (5)	0.0864 (4)	6.5
C(5)	0.0893 (2)	0.4379 (5)	0.0511 (3)	6.1
C(6)	0.0694 (2)	0.3164 (4)	0.0981 (3)	5.1
C(11)	−0.2137 (2)	−0.2257 (4)	0.1788 (3)	5.4
C(12)	−0.2520 (2)	−0.1326 (4)	0.2378 (4)	5.9
C(13)	−0.2811 (2)	−0.2175 (5)	0.3157 (5)	8.0
C(14)	−0.3160 (3)	−0.1322 (6)	0.3819 (5)	9.0

[a] $B_{eq} = {}^1/_3(U_{11} + U_{22} + U_{33})$.

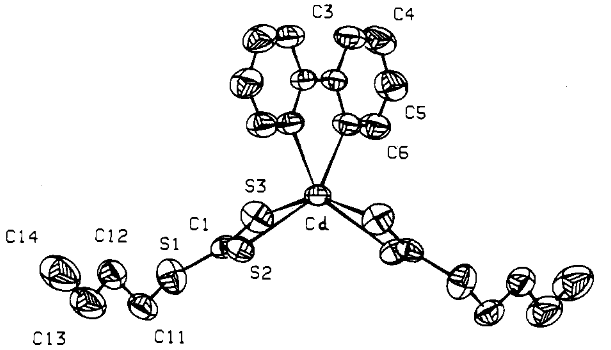

Figure 1. Stereochemistry of $Cd(S_2CSC_4H_9\text{-}n)_2\cdot$bpy, showing the atomic numbering scheme. Hydrogen atoms have been omitted for clarity.

Table IV. Interatomic Distances (Å) and Angles (deg) for $Cd(S_2CSC_4H_9\text{-}n)_2\cdot$bpy[a]

Cd–S(2)	2.664 (1)	C(2)–C(2)*	1.460 (6)
Cd–S(3)	2.704 (1)	C(2)–C(3)	1.386 (4)
Cd–N	2.363 (3)	C(3)–C(4)	1.371 (7)
S(1)–C(1)	1.738 (3)	C(4)–C(5)	1.365 (7)
S(1)–C(11)	1.801 (4)	C(5)–C(6)	1.375 (6)
S(2)–C(1)	1.676 (3)	C(11)–C(12)	1.495 (6)
S(3)–C(1)	1.679 (3)	C(12)–C(13)	1.491 (6)
N–C(2)	1.336 (4)	C(13)–C(14)	1.464 (7)
N–C(6)	1.327 (4)		
S(2)–Cd–S(2)*	111.6 (1)	C(2)–N–C(6)	119.3 (3)
S(2)–Cd–S(3)	97.8 (1)	S(1)–C(1)–S(2)	121.8 (2)
S(2)–Cd–S(3)*	66.9 (1)	S(1)–C(1)–S(3)	114.4 (2)
S(2)–Cd–N	147.5 (1)	S(2)–C(1)–S(3)	123.8 (2)
S(2)–Cd–N*	94.8 (1)	N–C(2)–C(2)*	117.1 (3)
S(3)–Cd–S(3)*	153.7 (1)	N–C(2)–C(3)	120.3 (3)
S(3)–Cd–N	110.2 (1)	C(2)*–C(2)–C(3)	122.6 (3)
S(3)–Cd–N*	91.7 (1)	C(2)–C(3)–C(4)	119.6 (4)
N–Cd–N*	69.0 (1)	C(3)–C(4)–C(5)	120.0 (4)
C(1)–S(1)–C(11)	106.5 (2)	C(4)–C(5)–C(6)	117.4 (4)
Cd–S(2)–C(1)	85.3 (1)	N–C(5)–C(6)	123.5 (4)
Cd–S(3)–C(1)	84.0 (1)	S(1)–C(11)–C(12)	116.2 (3)
Cd–N–C(2)	118.4 (2)	C(11)–C(12)–C(13)	112.3 (3)
Cd–N–C(6)	122.3 (2)	C(12)–C(13)–C(14)	115.5 (4)

[a] An asterisk denotes a 2-fold symmetry-related atom within the molecule.

in Table IV. Tables of thermal parameters, hydrogen atom coordinates, and observed and calculated structure factor amplitudes are available as supplementary data. The structure is shown in Figure 1.

Reaction of $Cd(SR)_2$ with Acid Chlorides. A suspension of $Cd(SR)_2$ (R = n-C_4H_9, C_6H_5) in 30 mL of dry benzene was treated with R′COCl (R′ = CH_3, C_6H_5), and the mixture was refluxed for 4–5 h. The cooled solution was filtered, and solvent and unreacted R′COCl were removed from the reaction mixture by slow evaporation to yield the product R′COSR, whose purity was confirmed by thin-layer chromatography (liquid phase 95/5 petroleum ether/diethyl ether mixture); it was identified by NMR and mass spectroscopy.

(i) $Cd(SC_6H_5)_2$ (1.02 g, 3.1 mmol) and CH_3COCl (1.1 g, 14 mmol): the product was a yellow liquid; ^1H NMR ($CDCl_3$) 7.45 (s), 2.35 (s) ppm; mass spectrum, m/e 152 (molecular ion), 109 ($C_6H_5S^+$), 43 (CH_3CO^+); identified as $CH_3COSC_6H_5$. Yield: 96%, based on $Cd(SC_6H_5)_2$.

(ii) $Cd(SC_6H_5)_2$ (1.83 g, 5.5 mmol) and C_6H_5COCl (2.4 g, 17 mmol): white crystalline solid product; ^1H NMR ($CDCl_3$) 7.42–8.15 m; mass spectrum, m/e 214 (molecular ion), 109 ($C_6H_5S^+$), 105 ($C_6H_5CO^+$); corresponding to $C_6H_5COSC_6H_5$. Yield: 98%. The solid recovered from this reaction had 59.3% Cd and 34.6% Cl; $CdCl_2$ requires 61.3% Cd and 38.7% Cl. This water-soluble material dissolved in Me_2SO-d_6 to give a green solution, which did not show any ^1H resonances other than those of the solvent.

(iii) $Cd(SC_4H_9\text{-}n)_2$ (0.31 g, 1.07 mmol) and CH_3COCl (0.15 g, 1.94 mmol): the product was a yellow-green liquid; ^1H NMR ($CDCl_3$) 2.34, 2.91 (q), 1.51 (m), 0.91 (t); mass spectrum showed no molecular ion, peaks at m/e 57 ($C_4H_9^+$), 43 (CH_3CO^+); product identified as $CH_3COSC_4H_9$-n.

(iv) $Cd(SC_4H_9\text{-}n)_2$ (0.43 g, 1.49 mmol) and C_6H_5COCl (0.34 g, 2.45 mmol): the product was a yellow liquid; ^1H NMR ($CDCl_3$) 7.35–8.27 (m), others 3.21 (q), 1.45 (m), 0.92 (t); mass spectrum, m/e 194 (molecular ion), 105 ($C_6H_5CO^+$); identified as $C_6H_5COSC_4H_9$-n.

Results and Discussion

Adducts of $Cd(SC_6H_5)_2$. Previous work[1] showed that cadmium thiolates (R = C_6H_5, n-C_4H_9, t-C_4H_9) are insoluble in a wide variety of organic solvents, and this behavior together with the infrared spectra led to the formulation of these compounds as homopolymers with CdS_4 coordination through bridging sulfur atoms. We have now shown that $Cd(SC_6H_5)_2$ is soluble in dimethylformamide (dmf) and that the addition of bidentate nitrogen donors to that solution produces adducts that have 2:1 (tmen, phen), 1:1 (phen, bpy), or 1:2 (phen) stoichiometry. Ligand coordination was confirmed in each case by the identification of the appropriate features in the infrared spectra. The 1:2 stoichiometry is reasonably assigned to a CdS_2N_4 kernel, since six-coordinate species are already known for Cd(II)[7,8] and for the isoelectronic In(III)[9] and Sn(IV) ions. The 2:1 and 1:1 species presumably represent stabilization of dimeric or monomeric, or higher, residues of the initial $Cd(SR)_2$ polymer as stabilized under different reaction conditions. The compound $Cd(SC_6H_5)_2\cdot(\text{phen})_2\cdot$dmf may be a coordination complex or a solvate in which dmf is not coordinated to the metal atom, but here as with the 2:1 and 1:1 species no structural information is yet available. Apart from this dmf species, no compounds could be obtained with oxygen donors by the techniques used in this work, although the solubility in dmf and Me_2SO imply the presence of solvated species in the solution phase. The triphenylphosphine adduct $[Cd(SC_6H_5)_2]_4\cdot P(C_6H_5)_3$ may well be a cage structure, but again a detailed structure is presently lacking.

The n-butyl thiolate compound $Cd(SC_4H_9)_2$ is insoluble in dmf and in solutions of bpy in dmf or acetonitrile, so that this homopolymer resists dissociation under the conditions used. We return to this point below.

Structure of $Cd(S_2CSC_4H_9\text{-}n)_2\cdot$bpy (1). The crystallographic results (Table II and Figure 1) show that the product of the reaction between $Cd(SC_4H_9\text{-}n)_2$, 2,2′-bipyridine, and CS_2 is the bpy adduct of bis(n-butyl thioxanthato)cadmium(II), with a CdN_2S_4 coordination kernel. The molecule has a crystallographic 2-fold axis of symmetry. The Cd–bpy distances are similar to those in $Cd(bpy)_2(ONO_2)_2$ (Cd–N range 2.33 (1)–2.43 (1) Å) and $Cd(bpy)_2(ONO_2)(H_2O\cdot ONO_2)$ (Cd–N range 2.34 (1)–2.39 (1) Å, as is the N–Cd–N bite angle (69.5 (4)–71.2 (4)°).[10] The C–C and C–N distances and angles within the ligand are close to those found in other bpy complexes of zinc.[11]

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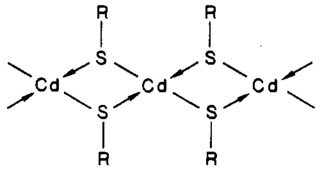
The Cd-S distances are in the middle of the range of 2.52–2.85 Å found for other six-coordinate compounds.[9] A recent study[12] of the $\{Cd[S_2CN(C_2H_5)_2]_3\}^-$ anion gave Cd–S distances in the range 2.655 (3)–2.755 (3) Å, while in $\{Cd[S_2P(OC_3H_7)_2]_3\}^-$ the values are 2.658 (1)–2.777 (2) Å, so that the bond distances in all these compounds are quite consistent. The bite angle S(3)–Cd–S(2) in **1** is also similar to that in the above-mentioned thiocarbamate anionic complex,[12] while the C–S distances and angles in the ligand are close to those reported for the $[Fe(S_2CSC_2H_5)_3]^-$ anion[13] and the $W(S_2CSC_2H_5)_4$ complex.[14]

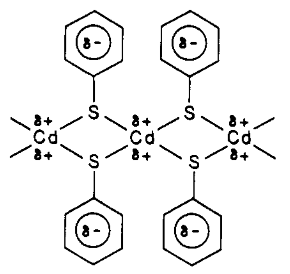
Comparison of the present results with those for a series of five-coordinate cadmium(II) species shows that the Cd–S bond distances are apparently dependent on the coordination number. Thus in the dimeric $\{Cd[S_2CN(C_2H_5)_2]_2\}_2$, the Cd–S bond distances are in the range 2.536 (4)–2.644 (3) Å, with a fifth Cd–S bond of substantially greater length (2.800 (3) Å) being involved in bridging.[15-17] Similar values have been reported for $\{Cd[S_2CN(CH_2)_6]_2\}_2$ (2.539–2.631 and 2.873 Å),[18] so that apart from the bridging S atom, the Cd–S bonds in the latter are shorter than in the present six-coordinate structure. In the six-coordinate *O*-ethyl xanthate complex $Cd(S_2COC_2H_5)_2$·phen, the bond lengths (Cd–S 2.647, 2.727 Å; Cd–N 2.386 Å)[19] are close to those reported in Table IV, suggesting that coordination number may be more important than the nature of the groups bonded to CS^-_2 in affecting Cd–S distances.

Reaction with Carbon Disulfide. The crystal structure of **1** clearly establishes that the reaction of CS_2 with $Cd(SC_4H_9\text{-}n)_2$ involves the insertion of the former into the M–S bond. The reactions of CS_2 with thiolate or alkoxide anions to give the appropriate $ROCS_2^-$ or $RSCS_2^-$ species are well-known as being important in the synthesis of complexes of these ligands,[20] but examples of in situ insertion into an existing complex are still rare. The insertion was shown to be reversible at 140 °C (see Experimental Section), as is commonly found with other thioxanthate compounds.[20]

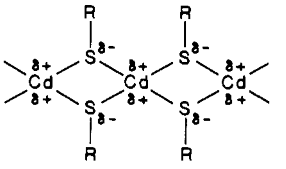
There is a clear difference in reactivity between $Cd(SC_4H_9\text{-}n)_2$, which reacts readily and completely, and $Cd(SC_6H_5)_2$, which gives the presumed $Cd(SC_6H_5)(S_2CSC_6H_5)$ only after prolonged reaction at the boiling point (46 °C) or by direct electrochemical synthesis; in the latter case it is probable that a reaction in situ between CS_2 and $C_6H_5S^-$ produces $C_6H_5SCS_2^-$, which then reacts at the cadmium anode (cf. ref 1–4). The differing reactivity toward CS_2 is the inverse of the ease with which $Cd(SC_4H_9\text{-}n)_2$ and $Cd(SC_6H_5)_2$ react with neutral donors, and we suggest that these differences have a common origin in the structures of these compounds, which are best formulated as sulfur-bridged homopolymers.[1]



The most important difference between the *n*-butyl and phenyl derivatives lies in the charge distribution, which in the latter case will include a significant contribution from the delocalized resonance form



compared to that for the alkyl compound



where any partial negative charge must be centered on the sulfur atom. This difference has three important consequences. First, the sulfur bridging should be stronger in the alkyl case. Second, nucleophilic reagents such as donor ligands will react more readily with the benzenethiolato compound, since to form mononuclear or other adducts of low nuclearity requires the breakdown of the sulfur bridging that stabilizes the homopolymer. Third, an electrophilic reagent such as CS_2 is more likely to attack the sulfur atom of $[Cd(SC_4H_9\text{-}n)_2]$, with its localized negative charge, than that in the phenyl derivative. These deductions are in keeping with the results reported in the Experimental Section.

Finally, we note that when reaction does occur between CS_2 and $Cd(SC_6H_5)_2$, the product involves attack at only one of the two sulfur atoms, to give a product that can be formulated as $[Cd(SC_6H_5)(S_2CSC_6H_5)]_n$. Other examples of such reactions are known.[20] It has been suggested elsewhere[21] that such species may be the result of structural requirements in the product; in the case of $Cu(SC_5H_{11})$, the stable cage $Cu_8(SC_5H_{11})_4(S_2CSC_5H_{11})_4$ satisfies the structural requirements of the metal and two different ligands in a way that would not occur if $Cu_n(S_2CSC_5H_{11})_n$ were formed. Similar arguments may apply in the present case.

Reactions with Acid Chlorides. The use of SR^- salts of alkali metals, or the equivalent solution of RSH in alkaline solution, to produce R′COSR is well-known.[22] The brief investigations reported in the Experimental Section show that $Cd(SR)_2$ compounds can also be used in such reactions to give high yields of the thio ester. There may be circumstances under which the long storage life of $Cd(SR)_2$, or the use of a solid in nonaqueous nonpolar solvents, will offer experimental advantages over the standard procedure.

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Registry No. **1**, 104506-94-7; $Cd(SC_6H_5)_2$, 21094-83-7; $[Cd(SC_6H_5)_2]_2$·tmen, 104506-88-9; $Cd(SC_6H_5)_2$·bpy, 104506-89-0; $[Cd(SC_6H_5)_2]_2$·bpy, 104506-90-3; $Cd(SC_6H_5)_2$·phen, 97567-25-4; $[Cd(SC_6H_5)_2]_2$·phen, 104506-91-4; $Cd(SC_6H_5)_2(phen)_2$, 104506-92-5; $Cd(SC_6H_5)_2\cdot CS_2$, 104531-51-3; $Cd(SC_4H_9)_2$, 72575-99-6; $Cd(S_2CSC_4H_9)_2$·tmen, 104506-93-6; $Cd(S_2CSC_4H_9)_2$·phen, 104506-95-8; $Cd(SC_4H_9)_2\cdot CS_2$·phen, 104506-96-9; $Cd(SC_4H_9)_2\cdot CS_2$, 104506-97-0; CS_2, 75-15-0; *n*-C_4H_9SH, 109-79-5; C_6H_5SH, 108-98-5; CH_3COCl, 75-36-5; C_6H_5COCl, 98-88-4; $CH_3COSC_4H_9$-*n*, 928-47-2; $C_6H_5COSC_4H_9$-*n*, 7269-35-4; $CH_3COSC_6H_5$, 934-87-2; $C_6H_5COSC_6H_5$, 884-09-3.

Supplementary Material Available: Tables of hydrogen atom coordinates and anisotropic temperature factors (2 pages); a table of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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