The Direct Electrochemical Synthesis of Zinc and Cadmium Derivatives of α,ω-Alkanedithiols and their Reaction with Carbon Disulphide

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Abstract

The anodic oxidation of zinc or cadmium in non-aqueous solutions of α,ω-alkanedithiols, $HS(CH_2)_nSH$ ($n = 2$–6) gives the corresponding $M[S_2(CH_2)_n]$ species in high yield. When 2,2'-bipyridine or 1,10-phenanthroline are present in the cell, the products are the appropriate 1:1 adducts. These compounds react with carbon disulphide, but in general only one of the two M–S–C sites undergoes attack. The products are complexes involving one thiolato and one thioxanthato group in the ligand, and the thioxanthate is in the exocyclic M–S–C–S– mode.
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Introduction

The chemistry of metal thiolates continues to present challenges in the fields of synthesis and structure [1, 2] and much of the interest in the transition metal is derived from the potential biological information which may become available. Less attention has been paid to those compounds in which the metal ion is formally a d^{10} species, although here again there are challenging problems, as exemplified by the stereochemistry of $(Cu^ISR)_n$ derivatives [1, 2]. The present paper is concerned with the synthesis of compounds of zinc and cadmium with bidentate dithiolato ligands derived from α,ω-alkanedithiols $HS(CH_2)_nSH$ ($n = 2$–6). Studies of such compounds of certain transition metal ions have appeared [3–7] but again little attention has been given to d^{10} derivatives. Of special interest to the present report is the work of Dean and Stillman, who prepared $Cd[SC_3H_6S]$ by the reaction of $Cd(NO_3)_2$ and the parent diol in aqueous solution [8].

The method of synthesis used here involves the simple and efficient electrochemical oxidation of a metal anode in a non-aqueous solution of $HS(CH_2)_nSH$, and follows previous work in this laboratory on thiolato derivatives of zinc, cadmium,

mercury [9, 10], indium, thallium [11], tin, lead [12], copper [13, 14], silver, gold [13], cobalt and nickel [15]. The products, $M[S_2(CH_2)_n]$ (M = Zn, Cd) undergo insertion reactions with carbon disulphide to give compounds in which one M–S– and one M–S–C–S– group are formed for each original

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$$M\!\!\begin{array}{c} \diagup S \\ \diagdown S \end{array}\!\!\Big) \text{ unit.}$$
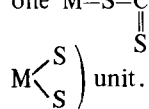
Experimental

Materials

Zinc and cadmium were in the form of rods, *ca.* 0.5 cm diameter. Acetonitrile (Reagent Grade) was distilled before use, and stored over phosphorus pentoxide. All other reagents were used as supplied.

Analysis and Spectroscopy

Metals were determined by atomic absorption spectrophotometry. Microanalysis was by Guelph Chemical Laboratories Ltd. Infrared spectra were recorded on a Nicolet 5DX spectrometer using KBr discs.

Electrochemical Procedures

As in previous work, the electrochemical cell consisted of a 100 ml tall-form beaker containing an acetonitrile solution of the dithiol; a platinum cathode and the sacrificial anode (Zn or Cd) attached to a platinum wire served as the electrodes and were connected to a d.c. power supply. In some cases, either 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen) were added to the electrolyte phase. All preparative work was carried out under dry nitrogen, which bubbled slowly through the solution and so served to mix the contents gently. We observed that the surface of the anodes disintegrated in some cases, thereby depositing metal particles along with the product, making the final analysis difficult. This problem was easily overcome by placing a small glass cup or mini-beaker (approx. 1 cm diam., 2 cm height) below the anode; any metal particles fell into this cup, and could be removed before collecting the required product.

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The solution composition, electrochemical conditions and yields are given in Table I, and analytical results for the products are given in Table II. Since these products are insoluble in the reaction mixture, the collection procedure involved filtration, after which the solid was washed with acetonitrile and dried *in vacuo*. Characterization depended on analysis, and on identification of the ligand(s) present by infrared spectroscopy. Since the products are insoluble in common organic solvents, no ^{1}H NMR spectra could be recorded (see below). The compounds are air stable.

Reaction with Carbon Disulphide

(i) $Zn(S_2C_2H_4)$ (0.15 g, 0.96 mmol) was added to a solution of phen (0.17 g, 0.96 mmol) in acetone

TABLE I. Experimental Conditions for the Electrochemical Synthesis of $M[S_2(CH_2)_n]$ and Adducts (M = Zn, Cd)

Thiol	Amount[a] (ml)	Ligand[b]	Voltage[c] (V)	Time of electrolysis (h)	Metal consumed (mg)	Yield[d] (%)
A. Zinc						
$1,2\text{-}C_2H_4(SH)_2$	0.10		10	3.5	80	98
	0.10	bpy	15	3	72	79
	0.10	phen	10	3	69	74
$1,2\text{-}C_3H_6(SH)_2$	0.15		10	2.5	67	94
	0.15	bpy	10	3	72	80
	0.15	phen	10	3	70	95
$1,3\text{-}C_3H_6(SH)_2$	0.15		10	2.5	65	100
	0.15	bpy	10	3	80	75
	0.15	phen	10	2.5	65	80
$1,4\text{-}C_4H_8(SH)_2$	0.16		10	2.5	63	100
	0.16	bpy	10	2.5	64	79
	0.16	phen	10	2.5	64	78
$2,3\text{-}C_4H_8(SH)_2$	0.16		10	3.5	87	100
	0.16	bpy	10	3	78	85
	0.16	phen	10	3	75	84
$1,5\text{-}C_5H_{10}(SH)_2$	0.20		10	2.5	66	96
	0.20	bpy	10	3	84	76
	0.20	phen	10	3	76	80
$1,6\text{-}C_6H_{12}(SH)_2$	0.17		10	3	72	100
	0.15	bpy	10	2.5	78	90
	0.15	phen	10	3	75	82
B. Cadmium						
$1,2\text{-}C_2H_4(SH)_2$	0.10		15	2	89	93
	0.10	bpy	10	2	83	75
	0.10	phen	10	2	90	78
$1,2\text{-}C_3H_6(SH)_2$	0.10		10	2	84	90
	0.10	bpy	25	2	82	65
	0.10	phen	25	2	90	72
$1,3\text{-}C_3H_6(SH_2)$	0.10		20	2	80	87
	0.10	bpy	10	2	90	80
	0.10	phen	10	2	90	73
$1,4\text{-}C_4H_8(SH)_2$	0.10		20	2.5	100	94
	0.10	bpy	20	2	84	79
	0.10	phen	20	2	85	76
$2,3\text{-}C_4H_8(SH)_2$	0.11		15	2	80	91
	0.11	bpy	10	2	77	70
	0.11	phen	10	2	79	86
$1,5\text{-}C_5H_{10}(SH)_2$	0.15		10	2	83	90
	0.15	bpy	12	2	85	71
	0.15	phen	10	2	87	82
$1,6\text{-}C_6H_{12}(SH)_2$	0.12		20	2	82	85
	0.12	bpy	15	2	84	77
	0.12	phen	10	2	85	82

[a]Dissolved in 50 ml CH$_3$CN containing *ca.* 30 mg Et$_4$NClO$_4$. [b]0.20 ± 0.01 g for Zn, 0.15 ± 0.01 for Cd. [c]Voltage to give an initial current of 20 mA. [d]Based on metal consumed.

TABLE II. Analytical Results for $M[S_2(CH_2)_n]$ and Derivatives (M = Zn, Cd)

Compound	Colour	M (%) Found	M (%) Calculated
A. Zinc			
$Zn(S_2C_2H_4)$	colourless	41.7	41.5
$Zn(S_2C_2H_4)$bpy	off-white	20.8	20.8
$Zn(S_2C_2H_4)$phen	yellow	19.5	19.4
$Zn(S_2C_3H_6-1,2)$	colourless	38.2	38.1
$Zn(S_2C_3H_6-1,2)$bpy	off-white	20.1	19.9
$Zn(S_2C_3H_6-1,2)$phen	yellow	18.5	18.6
$Zn(S_2C_3H_6-1,3)$	colourless	38.1	38.1
$Zn(S_2C_3H_6-1,3)$bpy	pale yellow	20.1	19.9
$Zn(S_2C_3H_6-1,3)$phen	yellow	18.6	18.6
$Zn(S_2C_4H_8-1,4)$	colourless	35.2	35.2[a]
$Zn(S_2C_4H_8-1,4)$bpy	pale yellow	19.3	19.1
$Zn(S_2C_4H_8-1,4)$phen	yellow	18.1	17.9
$Zn(S_2C_4H_8-2,3)$	colourless	35.0	35.2
$Zn(S_2C_4H_8-2,3)$bpy	off-white	19.5	19.1
$Zn(S_2C_4H_8-2,3)$phen	yellow	17.6	17.9
$Zn(S_2C_5H_{10}-1,5)$	colourless	32.7	32.7
$Zn(S_2C_5H_{10}-1,5)$bpy	cream	18.5	18.4
$Zn(S_2C_5H_{10}-1,5)$phen	yellow	17.4	17.2
$Zn(S_2C_6H_{12}-1,6)$	colourless	30.7	30.6
$Zn(S_2C_6H_{12}-1,6)$bpy	yellow	17.6	17.7
$Zn(S_2C_6H_{12}-1,6)$phen	yellow	16.7	16.6
B. Cadmium			
$Cd(S_2C_2H_4)$	colourless	55.0	54.9
$Cd(S_2C_2H_4)$bpy	off-white	31.4	31.2
$Cd(S_2C_2H_4)$phen	cream	29.3	29.2
$Cd(S_2C_3H_6-1,2)$	colourless	51.4	51.4[b]
$Cd(S_2C_3H_6-1,2)$bpy	off-white	30.0	30.0
$Cd(S_2C_3H_6-1,2)$phen	yellow	27.8	28.2
$Cd(S_2C_3H_6-1,3)$	colourless	51.7	51.4
$Cd(S_2C_3H_6-1,3)$bpy	cream	30.3	30.0
$Cd(S_2C_3H_6-1,3)$phen	yellow	28.0	28.2
$Cd(S_2C_4H_8-1,4)$	colourless	48.2	48.3
$Cd(S_2C_4H_8-1,4)$bpy	pale yellow	29.1	28.9
$Cd(S_2C_4H_8-1,4)$phen	yellow	27.1	27.2
$Cd(S_2C_4H_8-2,3)$	colourless	48.3	48.3
$Cd(S_2C_4H_8-2,3)$bpy	cream	29.1	28.9
$Cd(S_2C_4H_8-2,3)$phen	yellow	27.2	27.2
$Cd(S_2C_5H_{10}-1,5)$	colourless	45.8	45.6
$Cd(S_2C_5H_{10}-1,5)$bpy	pale yellow	28.1	27.9
$Cd(S_2C_5H_{10}-1,5)$phen	yellow	26.5	26.3
$Cd(S_2C_6H_{12}-1,6)$	colourless	43.3	43.2[c]
$Cd(S_2C_6H_{12}-1,6)$bpy	cream	27.0	27.0
$Cd(S_2C_6H_{12}-1,6)$phen	yellow	25.6	25.5

[a]Found C, 26.9; H, 4.30. Calc. C, 25.9; H, 4.34%. [b]Found C, 16.9; H, 2.95. Calc. C, 16.4; H, 3.21%. [c]Found C, 26.2; H, 4.56. Calc. C, 27.6; H, 4.64%.

TABLE III. Carbon Disulphide Insertion Products of $M[S_2(CH_2)_n]$ (M = Zn, Cd)

Compound	Colour	M (%) Found	M (%) Calculated
$Zn(S_2C_2H_4)CS_2 \cdot$phen	golden yellow	15.3	15.8
$Zn(S_2C_3H_6-1,3)CS_2 \cdot$phen	yellow	15.4	15.3
$Zn(S_2C_4H_8-1,4)CS_2 \cdot$phen	golden yellow	14.9	14.8[a]
$Zn(S_2C_6H_{12}-1,6)CS_2 \cdot$phen	deep yellow	14.3	13.9
$Cd(S_2C_6H_{12}-1,6) \cdot 2CS_2$	green—yellow	27.5	27.2
$Cd(S_2C_3H_6-1,3)CS_2 \cdot$phen	deep yellow	23.8	23.7
$Cd(S_2C_6H_{12}-1,6)CS_2 \cdot$phen	deep yellow	21.6	21.8
$Cd(S_2C_4H_8-1,4)CS_2 \cdot$tmen	deep yellow	26.7	26.5
$Cd(S_2C_6H_{12}-1,6)CS_2 \cdot$tmen	yellow	25.0	24.8[b]

[a]Found C, 46.8; H, 3.81; N, 6.82. Calc. C, 46.2; H, 3.65; N, 6.34%. [b]Found C, 34.3; H, 6.25. Calc. C, 34.5; H, 6.23%.

was collected by filtration, washed with acetone (25 ml) and dried *in vacuo*; identified as $Zn(S_2C_2H_4)$-$CS_2 \cdot$phen. Yield 0.27 g, 70%. (See Table III for analytical results.) Essentially identical procedures with $Zn(S_2C_3H_6-1,3)$, $Zn(S_2C_4H_8-1,4)$ and $Zn(S_2C_6H_{12}-1,6)$ gave the corresponding CS_2 addition compounds ligated by 1,10-phenanthroline.

(ii) A suspension of $Zn(S_2C_6H_{12}-1,6)CS_2 \cdot$phen (0.20 g, 0.43 mmol) in toluene (30 ml) was refluxed for 4 h. The colour of the solid changed from deep to pale yellow during this time. The suspended material was collected, washed with toluene and dried *in vacuo*. *Anal.* Found: Zn, 16.5. Calc. for $Zn(S_2C_6H_{12})$phen: Zn, 16.6%. Yield 0.16 g, 0.41 mmol, 95%. Infrared spectroscopy (see below) confirmed the absence of CS_2 in the final product.

(iii) The addition of excess CS_2 (0.7 ml, 0.9 g, 11.7 mmol) to $Cd(S_2C_6H_{12}-1,6)$ (0.2 g, 0.77 mmol) suspended in acetone (20 ml) caused the solid to change colour immediately to green—yellow. After 4 h stirring at room temperature under nitrogen, the solid was collected, washed with acetone (2 X 10 ml) and dried *in vacuo*. Yield of $Cd(S_2C_6H_{12}) \cdot$ $2CS_2$, 0.25 g, 79%.

(iv) $Cd(S_2C_3H_6-1,3)$ (0.2 g, 0.91 mmol) was suspended in acetone (50 ml) containing phen (0.17 g, 0.95 mmol), CS_2 (0.7 ml, 11.7 mmol) added, and the mixture stirred overnight at room temperature. The deep yellow suspended solid was collected, washed and dried. Analysis and infrared spectroscopy identified this compound as $Cd(S_2C_3$-$H_6-1,3)CS_2 \cdot$phen. Yield 0.38 g, 88%. Similar experiments with $Cd(S_2C_6H_{12}-1,6)$ also gave an insoluble CS_2 insertion product, as did reactions in which the starting material was $Cd(S_2C_6H_{12}-1,6) \cdot$phen prepared electrochemically.

(v) A suspension of $Cd(S_2C_4H_8-1,4)$ (0.2 g, 0.85 mmol) in acetone (10 ml) containing CS_2 (1 ml,

(40 ml) under nitrogen. After stirring (*ca.* 1 h), carbon disulphide (0.2 ml, 0.25 g, 3.3 mmol) was added and the stirring continued for 1 h; the colour of the suspended solid changed to golden yellow almost immediately on addition of CS_2. The product
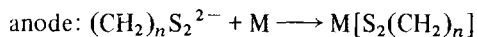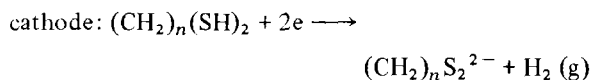
16.7 mmol) was treated with N,N,N',N'-tetramethyl-ethanediamine (tmen) (0.1 g, 0.86 mmol). As the mixture was stirred at room temperature, the solid dissolved after about 10 min to give a yellow—orange solution. After 2 h, the solvent was removed *in vacuo* to reduce the volume by 60%, and diethyl ether (10 ml) added dropwise to precipitate a deep yellow solid which was collected, washed and dried. Yield of $Cd(S_2C_4H_8)CS_2 \cdot$tmen 0.25 g, 0.59 mmol, 70%. Similar procedures yielded $Cd(S_2C_6H_{12}$-1,6)-$CS_2 \cdot$tmen in 91% yield from the final green reaction mixture.

Results and Discussion

Preparation of $M[S_2(CH_2)_n]$ and Adducts

The results show that the electrochemical synthesis of α,ω-dithiolato derivatives of zinc and cadmium is a very efficient and simple route to these compounds. Adducts are obviously easily obtained by suitable adjustment of the electrolyte phase. The experiments reported were carried out on a small scale, but it is a simple matter to scale up the experiment, or to run a number of cells in series. There is little doubt that adducts other than those of phen or bpy could also be obtained. In summary, the electrochemical route is obviously a convenient route to these, and probably other, $M(S_2R)_n$ compounds.

The electrochemical efficiency for the consumption of the anode, defined as moles of metal dissolved per Faraday of charge, was found to have an average value of 0.52 ± 0.02 mol F^{-1} for Zn, irrespective of the dithiol used or of the presence or absence of neutral ligand. For those experiments involving cadmium, the average E_F value was 0.50 mol F^{-1}. These results, together with the evolution of hydrogen gas at the cathode, implies that the electrode reactions are

cathode: $(CH_2)_n(SH)_2 + 2e \longrightarrow$

$$(CH_2)_nS_2^{2-} + H_2 \text{ (g)}$$

anode: $(CH_2)_nS_2^{2-} + M \longrightarrow M[S_2(CH_2)_n]$

These reactions parallel those identified previously for the electrochemical synthesis of $M(SR)_2$ compounds [9, 12]. An alternative reaction scheme would involve the formation of a singly charged anion $HS(CH_2)_nS^-$ at the cathode. This could then migrate in the form of hydrogen-bonded anion with a neutral $(CH_2)_n(SH)_2$, *i.e.* $[(HS)_2(CH_2)_n$-$HS(CH_2)_nS]^-$ $(=A^-)$, which decomposes at the anode.

cathode: $(CH_2)_n(SH)_2 + e \longrightarrow$

$$HS(CH_2)_nS^- + \tfrac{1}{2}H_2 \text{ (g)}$$

solution: $HS(CH_2)_nS^- + (CH_2)_n(SH)_2 \longrightarrow A^-$

anode: $A^- + \tfrac{1}{2}M \longrightarrow \tfrac{1}{2}M[S_2(CH_2)_n] + (CH_2)_n(SH)_2$
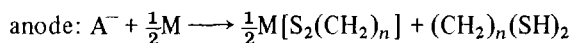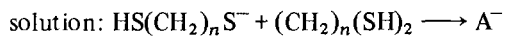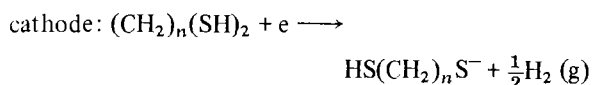
This sequence also gives $E_F = 0.5$ mol F^{-1}. Studies of the solution phase interactions of thiolate anions are planned.

In the absence of NMR spectra, caused by the insolubility of the products in all common solvents, the infrared spectra are especially important. Comparison of the spectra of the parent dithiol and of the products confirmed the loss of the acidic hydrogens of the —SH groups in every case, since the characteristic $\nu(S-H)$ bands at 2550–2650 cm^{-1} were invariably absent in the products. The $\nu(C-S)$ mode in the dithiols occurs at 670–620 cm^{-1}, and changes only slightly on formation of the metal dithiolate; average values in $Zn[S_2(CH_2)_n]$ are 630–680, in the bpy and phen adducts 610–670, in $Cd[S_2(CH_2)_n]$ 610–670 and in their bpy and phen adducts 620–660 cm^{-1}. Equally the spectra of the bpy and phen adducts confirmed the presence of these ligands unambiguously.

In previous papers [9, 16] it has been suggested that the solid state structure of $M(SR)_2$ (M = Zn, Cd) involves extensive sulphur-bridging to form homo-polymers. By the same argument, the most likely structure of $M[S_2(CH_2)_n]$ also involves this type of polymerization which in its simplest two-dimensional form can be written as
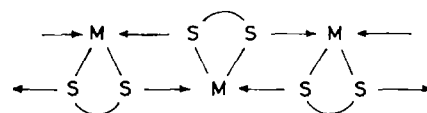
and this is supported by the structure of $Pb[S_2C_2H_4]$ in which homopolymerization has been demonstrated by X-ray crystallography [17]. The previous argument [16] emphasized the importance of the polarity of the $M^{\delta+}-S^{\delta-}$ bond in strong sulphur bridging in metal—alkylthiolato compounds. The α,ω-dithiolato derivatives differ from the alkyl thiolates in that adducts can be formed, (*cf.* refs. 9, 16) but the insolubility of these adducts suggests that the sulphur bridging is intact, so that a probable structure for the phen and bpy adducts would be
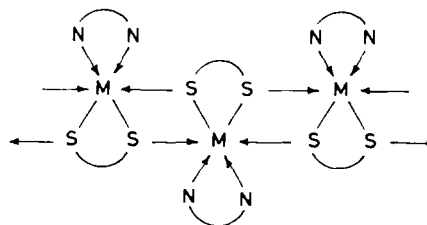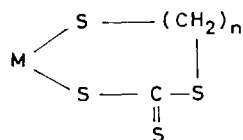

The same structural arguments then apply to both monothiolato and α,ω-dithiolato derivatives of zinc and cadmium, and also explain the facile attack of carbon disulphide on these $M[S_2(CH_2)_n]$ species.

Reaction with Carbon Disulphide

The preparative results show that carbon disulphide reacts easily with both $M[S_2(CH_2)_n]$ and adducts, and the products are in fact the result of *in situ* insertion reaction at the M—S bond. As emphasized earlier [16], synthesis of $RSCS_2^-$ complexes by the reaction of CS_2 with RS^- prior to complexation with a metal is well-established [18], but examples of *in situ* insertion into an existing thiolato complex are still relatively rare. In all the cases studied, the results show that with the exception of $Cd(S_2C_6H_{12}-1,6)$, only one of the two M—S bonds is attacked.

There are no significant differences between the zinc and cadmium insertion products on the basis of the infrared spectra. In each case, the spectrum of the insertion product shows a strong vibration at ~1010 cm^{-1}, absent from the spectrum of the parent dithiolate. This is assigned to $\nu(C=S)$ and is evidence that the thioxanthate moiety of the ligand is monodentate with an exocyclic C=S group. The $\nu(C-S)$ mode is little changed, appearing at 620—650 cm^{-1} in all these compounds. In these compounds then the bonding of the bifunctional thioxanthate—thiolate ligand is

$$
\begin{array}{c}
\text{S} \longrightarrow (\text{CH}_2)_n \\
\text{M} \\
\text{S} \longrightarrow \text{C} - \text{S} \\
\quad\quad\quad \parallel \\
\quad\quad\quad \text{S}
\end{array}
$$

In general, the reaction with carbon disulphide follows the model proposed earlier [16], whereby such electrophilic attack on the sulphur atom of the M—S—C bond is aided by the polarity of the $M^{\delta+}-S^{\delta-}$ bond. As noted above, the present results show that with one exception only one M—S bond reacts, and similar observations have been made in the cases of $Cd(SC_6H_5)_2$ [16] and $CuSC_5H_{11}$ [19], and there seems no way of rationalizing these results in detail at present. For $Cd[S_2(C_6H_{12}-1,6)]$, the results show that double insertion of CS_2 occurs, and this may show that the size of the metal-containing ring is important. All of the products of these insertion reactions are insoluble in common organic solvents, so that homopolymerization by M—S cross-linking is apparently still important, as it is in the parent dithiolates.

Finally, we note that in the one case investigated, carbon disulphide is extruded from the thioxanthate group on heating to give back the original α,ω-dithiolate, again in keeping with the behaviour of related monothiolato compounds [16].

Acknowledgement

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