The Direct Electrochemical Synthesis of some Thiolates of Zinc, Cadmium and Mercury

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The electrochemical oxidation of anodic Zn, Cd or Hg (=M) into acetonitrile solutions of RSH (or R_2S_2) gives the corresponding $M(SR)_2$ compounds in high yield. The mechanism of the electrochemical reactions is discussed. The insolubility, and the far infrared spectra ($500–50$ cm^{-1}), are compatible with a polymeric structure for $M(SR)_2$ in the solid state.

Introduction

Complexes involving ligands in which sulphur is the donor atom are of considerable interest for a number of reasons, amongst which are the nature of the metal–sulphur bonding interaction, and the importance of sulphur in many molecules of biological interest. For the elements of Group IIB, complexes formed by such ligands and organomercury groups have been reviewed [1, 2], and there have been some recent investigations of cadmium complexes in solution by means of ^{113}Cd NMR [3, 4]. Surprisingly little has been published on the preparation of the neutral $M(SR)_2$ compounds or their derivatives, although as has been emphasized elsewhere [4], such species present the simplest possible systems for the study of metal–ligand interactions.

We have now extended our applications of the method of direct electrochemical synthesis [5] to the preparation of the simple bis-thiolato complexes of zinc, cadmium and mercury. These species are formed in high yield in a one-step route by the electrochemical oxidation of the metal into aceto-nitrile solution of the parent thiol or disulphide. The method has also been used for the preparation of analogous compounds of indium, thallium, tin, and lead [6], and with suitable modification for the direct synthesis of an anionic zinc(II) thiophenolate cluster containing a Zn_4S_{10} core [7].

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Experimental

General

Acetonitrile was dried and stored over molecular sieve and/or calcium hydride. Thiols, and di-t-butyl-disulphide, were used as supplied (Aldrich). Zinc and cadmium were the mossy granulated materials; mercury was triple-distilled.

Electrochemical

The electrochemical preparation followed essentially the same procedure in each case, with the metal forming the anode of a simple cell

$$Pt_{(-)}/CH_3CN + RSH/M_{(+)}$$
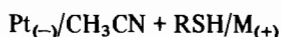
In the case of zinc or cadmium, the anode was a piece of metal, approx. 2 cm^2 area, suspended on a platinum wire; for mercury, a pool of the element was in contact with a platinum wire sealed through the glass wall. We have found that RSH can be successfully replaced by R_2S_2 for R = t-C_4H_9 with zinc, but not with cadmium or mercury.

The solution composition and electrochemical conditions used in these experiments are detailed in Table I. When the electrolysis began, a white solid formed at the anode almost immediately, save that in the case of Zn/C_6H_5SH a few hours elapsed before any precipitate was visible. When the solute was RSH, the formation of hydrogen gas at the cathode was observed. Details of two typical experiments are given below.

Preparation of $Zn(SC_4H_9^n)_2$

The cell was a 100 ml tall-form beaker filled with a rubber stopper through which the electrodes were suspended. The composition of the electrolyte is given in Table I. Solid precipitated continuously throughout the electrolysis, and was subsequently collected, washed several times with acetonitrile and petroleum ether, and dried.

TABLE I. Experimental Conditions for the Direct Electrochemical Synthesis of $M(SR)_2$ Compounds.

System		Solution composition		Initial[b] Voltage (V)	Time of electrolysis (h)	Metal dissolved (mg)
Sulphur compound	M	(ml) RSH	CH_3CN^a			
$n\text{-}C_4H_9SH$	Zn	5	50	25	6	130
	Cd	5	40	20	5	150
	Hg	1	10^c	15	5	d
$t\text{-}C_4H_9SH$	Zn	1	10^c	15	4.5	80
	Hg	1	10^c	7	3	d,e
$(t\text{-}C_4H_9)_2S_2$	Zn	1	10^c	20	4.5	70
	Cd	1	10^c	35	1	40^e
	Hg	1	10^c	10	2.5	d,e
C_6H_5SH	Zn	5	45	30	20	400
	Cd	5	40	20	5	220
	Hg	1	10^c	15	5	d

[a]Plus 20 mg $(C_2H_5)_4NClO_4$ in each case.   [b]Voltage required to produce a current of 20 mA.   [c]Experiment performed in H-cell (see text).   [d]Not recorded.   [e]Product of these experiments not $M(SR)_2$; see text.

TABLE II. Analytical Results for Thiolate Complexes of Zinc, Cadmium and Mercury.

Compound	Metal %	
	Found	Calculated
$(n\text{-}C_4H_9)_2Zn$	26.8^a	26.8
$(n\text{-}C_4H_9)_2Cd$	38.8	38.7
$(n\text{-}C_4H_9)_2Hg$	53.2	52.9
$(t\text{-}C_4H_9)_2Zn$	$26.6^{b,c}$	26.8
	27.3^d	26.8
$(t\text{-}C_4H_9)_2Cd$	$57^{d,e}$	38.7
$(C_6H_5)_2Zn$	22.6	23.0
$(C_6H_5)_2Cd$	33.8	34.0
$(C_6H_5)_2Hg$	48.3	47.9

[a]Found: C, 39.7; H, 7.4; calc.: C, 39.4; H, 7.4%.   [b]Sample prepared *via* $t\text{-}C_4H_9SH$.   [c]Found: C, 37.9; H, 7.4; calc.: C, 39.4; H, 7.4%.   [d]Sample prepared *via* $(t\text{-}C_4H_9)_2S_2$.   [e]See text.

Preparation of $Hg(SC_4H_9^n)_2$

The cell in this case was the two-arm H-cell described earlier [8]. An unweighed quantity of mercury, *ca.* 1 ml volume, was placed in the bottom of the cell, and a solution of $n\text{-}C_4H_9SH$ in acetonitrile decanted onto the mercury from the second arm of the vessel. Electrolysis produced a solid which deposited on the mercury surface. At the end of the electrolysis the contents of the cell were poured into a beaker; the solution was decanted from the mercury and product, and the latter then washed away from

the mercury with pure solvent. The resultant solid was collected, washed with petroleum ether, and dried. No attempt was made to measure the product yield in these circumstances, since losses in the decantation and washing are not easily controlled.

The use of this H-cell is convenient for handling small quantities of material, and has the further advantage of minimising the severe social problems associated with the odour of thiols.

Characterisation

The reaction products were analysed for metal by atomic absorption spectrophotometry, with the results shown in Table II. Microanalysis was carried out on two compounds by Guelph Chemical Laboratories Ltd. The presence of the ligand was also confirmed by infrared spectroscopy. Far infrared spectra were recorded on a Beckman IR-180 instrument. Mass spectra were obtained on a Varian MAT CH5 DF instrument operating in the field ionisation mode.

Results and Discussion

General

The results show that dithiolates of zinc, cadmium and mercury are readily prepared by the direct electrochemical oxidation of the metal into solutions of the appropriate thiol, with chemical yields in the 85–95% range, based on the quantity of metal dissolved. The compounds are air-stable solids, insoluble in a wide range of solvents, including carbon tetrachloride, benzene, toluene, nitromethane, aceto-

nitrile, acetone, methanol and dimethyl sulphoxide. Decomposition occurs with conc. nitric acid, with the formation of foul-smelling products; the resultant solution was used after suitable dilution for metal analysis. The n-butyl thiolates are soluble in carbon disulphide; the solution subsequently deposits a substance which is not the starting material, which contains the metal in question but which has not yet been fully characterised. Further work on this topic is proceeding.

The metal-thiolate compounds are apparently not good electron pair acceptors. In addition to the insolubility in donor solvents (see above), they are insoluble in solutions of 2,2'-bipyridine in benzene. Similarly addition of this ligand to an electrochemical cell containing n-C_4H_9SH in acetonitrile gave $Zn(SC_4H_9^n)_2$ as the only identifiable product.

The ligands investigated include aryl, straight chain alkyl and tertiary alkyl thiolates. Metal dithiolates were obtained in all but two of the systems investigated (see Table I). For Hg/t-C_4H_9SH, the product was a black powder, containing essentially no organic groups, and tentatively identified as HgS. Similarly for $Cd/(C_4H_9)_2S_2$ the reaction product had an unreasonably high metal content (see Table II), although the far infrared spectrum was similar to that of $Zn(SC_4H_9^t)_2$. We believe that the material probably contained $Cd(SC_4H_9^t)_2$ and CdS. We return to this below.

Electrochemistry

The electrochemical efficiency E_F, defined as moles metal dissolved per Faraday, was determined for the following systems:

Zn/n-C_4H_9SH E_F 0.47 mol F^{-1}
$Zn/(t$-$C_4H_9)_2S_2$ 0.48 mol F^{-1}
Cd/C_6H_5SH 0.51 mol F^{-1}
$Cd/(t$-$C_4H_9)_2S_2$ 0.46 mol F^{-1}

For the thiols, the simplest mechanism compatible with these results, bearing in mind the cathodic formation of hydrogen gas, is

cathode: $2RSH + 2e^- \rightarrow 2RS^- + H_2$ (1)

anode: $2RS^- + M \rightarrow M(SR)_2$ (2)
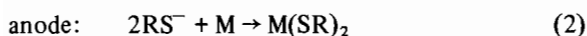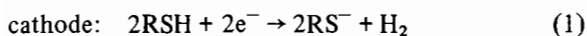
For the disulphides, which are known to undergo cathodic cleavage [9], reaction (1) is obviously replaced by

$$R_2S_2 + 2e^- \rightarrow 2RS^-$$ (3)

These reactions should apply in principle for all thiols, provided that RS^- is sufficiently stable for the anion to migrate to the anode without prior decomposition. The most important competing process is that exemplified by the Hg/t-C_4H_9SH system,

TABLE III. Predominant Ions in the Field Ionisation Mass Spectra of n-Butylthiolates of Zinc, Cadmium and Mercury.

Metal	Temperature (°C)		Relative Intensities[a]			
	Probe	Ion Source	M^+	$R_2S_2^+$	R_2S^+	RSH^+
Zn	27	220	0.2	0.6	100	2.1
Cd	30	290	0.3	0.1	100	2.5
Hg	30	230	69.6	100	1.7	12.3

[a]Integrated values for the manifold of isotopic species for each ion.

in which no dithiolate was obtained, apparently because of desulphurisation of either RS^- or RS at the anode. It is perhaps not surprising that this process is most easily observed for a thiolate in which sulphur is bonded to a tertiary carbon atom.

Mass Spectra

The field ionisation mass spectra of the n-butyl-thiolato derivatives of zinc, cadmium and mercury were recorded in the hope of obtaining some information on the structures of these solids. In the event, the results (Table III) confirm the identity of the species but do not help in elucidating the structure, so that no further spectra of this type were run.

The mode of decomposition of the compounds, or of their ions, cannot be inferred from these results. Perhaps the most interesting features are the relative intensities of the molecular ions (Hg $\gg$ Cd $\approx$ Zn), and the concomitant changes in the abundance of the $R_2S_2^+$ and R_2S^+ ions.

Infrared Spectra

The infrared spectra of the compounds in the sodium chloride region serve to confirm the presence of the appropriate organic radicals, but are otherwise not significant except for the identification of the $\nu(C-S)$ mode at 657 ± 3 cm^{-1} in $Zn(SC_4H_9^t)_2$ and its cadmium analogue. No attempt was made to identify the $\nu(C-S)$ absorption in the phenylthiolates in view of the difficulties associated with the assignment of this mode in aromatic compounds [10].

The assignment of $\nu(M-S)$ has been a matter of some discussion, with frequencies between 160 and 400 cm^{-1} being proposed (See ref. [3] for a
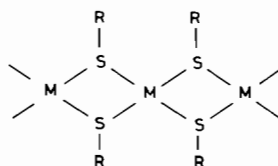
TABLE IV. Far Infrared Absorptions of n-C_4H_9SH and $M(SC_4H_9^n)_2$ (M = Zn, Cd, Hg). (cm^{-1}).

n-C_4H_9SH	Zn	Cd	Hg
465w	475w		460vw
395w	410w		410w
	355m	348m	345m
	335m	325m	320m
	295s		
255m,br	255m,br	260m,vbr	250m,vbr
		226m	240?
170m,br	170m,vbr	170m,vbr	170m,vbr

[a]Nujol mulls between polythene plates.

TABLE V. Far Infrared Spectra of t-C_4H_9SH, and Zn-$(SC_4H_9^t)_2$ (in cm^{-1}).

t-C_4H_9SH	Zn
478m	
414w	414mw
392m	
	384m
368m	
	344s
	317m
300m	
	217sh
190vs,br	209s
	135w,br

TABLE VI. Far Infrared Spectra of C_6H_5SH, and $M(SC_6-H_5)_2$ (M = Zn, Cd, Hg) (in cm^{-1}).

C_6H_5SH	Zn	Cd	Hg
460s	478s	476s	485s
398m	422s	418s	424m
	358sh	342sh	
	328s	324s	
280m,vbr	292s	286m	
	258m	260m,br	262m
		244m	
	208sh	190sh	195m
185m,vbr	182s,br	170m,br	
		104m	90m

tions of the polymeric MS_2M ring systems. These show little dependence on the metal involved, but this is perhaps not surprising in view of the structure proposed. Similar conclusions can be reached from the results in Tables V and VI. A more detailed analysis does not seem justified at this stage.

Acknowledgement

summary). We note first that the properties of the compounds prepared, and especially the solubilities, are compatible with a polymeric solid in which each metal atom is surrounded by four sulphur atoms, probably in a pseudo-tetrahedral environment. Such four-coordination is in keeping with the known stereochemical properties of these elements in the solid state [11, 12, 13]. If this proposal is correct, the problem of identifying the M–S stretching modes is then similar to that encountered in systems such as metal diketonates, namely the mixing of stretching and bending modes.

The far infrared spectra of the three groups of metal dithiolates, and of the parent thiols, are given in Tables IV–VI. Table IV shows that certain features are common to the spectrum of each n-butylthiolate-metal complex, and can be related to absorptions of similar frequency in n-C_4H_9SH. Elimination of these then leaves modes at 300–350 cm^{-1} and possibly at $\sim$230 cm^{-1}, which are assigned to vibra-

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