

## Closed shell-closed shell S, S-bridged heteropolymetallic aggregates: Synthesis and characterisation

R G BHATTACHARYYA\* and R MISHRA

Department of Chemistry, Jadavpur University, Calcutta 700032, India.

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**Abstract.**  $[\text{Cu}(\text{CN})_x]^{1-x}$  in the presence of excess of KCN reacts with  $\text{MS}_4^{2-}$  and  $\text{MO}_2\text{S}_2^{2-}$  ( $\text{M} = \text{W}, \text{Mo}$ ) producing  $[\text{NC}-\text{CuS}_2\text{MS}_2]^{2-}$  and hitherto unknown  $[\text{NC}-\text{CuS}_2\cdot\text{MO}_2]^{2-}$  respectively as  $\text{PPh}_4$  salts. Complexes have been characterised by typical  $\nu\text{CN}$ ,  $\nu(\text{M}=\text{S})$ ,  $\nu(\text{M}-\text{S}-\text{M}')$  and  $\nu(\text{M}=\text{O})$  vibrations in appropriate cases. In their electronic spectra the intraligand ( $\text{MS}_4^{2-}$  or  $\text{MO}_2\text{S}_2^{2-}$ ) transitions are interestingly perturbed.  $\text{Cd}^{2+}$  affords  $[\text{Cd}(\text{WS}_4)_2]^{2-}$  and  $[\text{Cd}(\text{WO}_2\text{S}_2)_2]^{2-}$  but  $\text{Hg}^{2+}$  is reduced by  $\text{WS}_4^{2-}$  and  $\text{WO}_2\text{S}_2^{2-}$  affording  $[\text{S}_2\text{WS}_2\text{HgHgS}_2\text{WS}_2]^{2-}$  and  $[\text{O}_2\text{WS}_2\text{HgHgS}_2\text{WO}_2]^{2-}$  respectively. Besides LMCT transitions, the softer Cd and Hg complexes presumably also show MLCT type transitions.  $\text{Pb}^{2+}$  affords  $[\text{Pb}_2[\text{WS}_4)_4]^{4-}$  which is isostructural with the Sn-analogue. The copper-tungsten complexes show irreversible reduction waves in their cyclic voltammograms, indicating the reduction of W(VI) to W(V). The corresponding Mo complexes show quasi-reversibility whereby Mo(VI) is reduced to Mo(V) and then  $\text{MoS}_4^{3-}$  is reversibly oxidised. The Hg(I) centres in the mercury complexes are also reduced to Hg(0).  $[\text{NC}-\text{CuS}_2\text{WS}_2]^{2-}$  reacts with  $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$  probably forming  $[\text{CuS}_2\text{WS}_2\text{NiS}_2\text{WS}_2\text{Cu}]^{2-}$  and  $[\text{NC}-\text{CuS}_2\text{WO}_2]^{2-}$  reacts with  $\text{UO}_2^{2+}$  presumably affording  $[\text{NCCuS}_2\text{WO}_2\text{UO}_2(\text{H}_2\text{O})\text{O}_2\cdot\text{WS}_2\text{CuCN}]^{2-}$  providing evidence that besides the W=S bond, the W=O bond can also show nucleophilic character.

**Keywords.** Tetrathiometalate and dioxodithiometalate complexes; heterobimetallic complexes; heteropolymetallic complexes; sulphur-sulphur bridged metal-sulphur aggregates; electrochemistry of thio- and oxothio-metalate complexes.

### 1. Introduction

Heterobimetallic complexes, in which the metal atoms are held by S, S bridges are well-known in the closed shell-open shell systems  $[\text{S}_2\text{MS}_2\text{M}'\text{S}_2\text{MS}_2]^{2-}$  where M are  $d^0$  (closed-shell) metals, viz, Mo or W and M' stands for open shell metals, viz, Co(II), Ni(II), Pt(II), Pd(II) (Diemann and Müller 1971; Müller and Diemann 1972; Müller *et al* 1975; Callahan and Piliero 1979). Also systems of the types  $[\text{OSMS}_2\text{M}'\text{S}_2\text{MOS}]^{2-}$  (Müller *et al* 1972) and  $(\text{O}_2\text{MS}_2\text{M}'\text{S}_2\text{MO}_2)^{2-}$  (Müller *et al* 1974) do exist, though to a lesser extent, and in all the three types, bridging groups are always to sulphido ligands. Compounds with  $\text{M}' = \text{Fe}(\text{II})$  (Müller and Sarkar 1977) are, however, less well defined, and Mn(II) does not afford any such complex (Manoli *et al* 1987). The stabilizing factor in these complexes stems from the ability of the ligands, viz,  $\text{MS}_4^{2-}$ ,

\* For correspondence

$\text{MOS}_3^{2-}$  or  $\text{MO}_2\text{S}_2^{2-}$  to delocalize the electron density from  $\text{M}'$  into low-lying empty  $d$  orbitals of  $\text{M}$  (Gheller *et al* 1984, Müller *et al* 1981) and in that case  $\text{M}'$  with less than six valence electrons seems to be energetically inaccessible. The systems with  $\text{M}' =$  a closed shell ( $d^{10}$  or  $d^{10}s^2$ ) metal ion are limited in the  $\text{Zn(II)}$  (Müller and Diemann 1972; Müller *et al* 1971) complexes of the above types, and the polymeric chain-like  $\text{Cu(I)}$  complexes  $\text{NH}_4\text{CuMS}_4$  (Binnie *et al* 1970; Müller and Menge 1972). The latter is reportedly (Ghellar *et al* 1984) cleaved by aqueous cyanide to  $[(\text{CN})\text{CuS}_2\text{MS}_2]^{2-}$ , and ultimately with excess  $\text{CN}^-$  to  $[(\text{CN})\text{CuS}_2\text{MS}_2\text{Cu}(\text{CN})]^{2-}$ . It has also been reported that  $[\text{Cu}(\text{CN})_x]^{1-x}$  reacts with  $\text{MO}_2\text{S}_2^{2-}$  ( $\text{M} = \text{Mo, W}$ ) yielding  $[\text{NCCu}(\text{MOS}_3)]^{2-}$  rather than  $[\text{NCCu}(\text{MO}_2\text{S}_2)]^{2-}$ , and, with  $\text{MS}_4^{2-}$ , producing  $[\text{NCCu}(\text{MS}_4)_2]^{2-}$ . However, in the latter two cases the effect of excess  $\text{CN}^-$  in the reaction mixture was not spelled out. So we have re-examined the reaction in a bid to primarily isolate the corresponding dioxodithio complexes, and to determine whether any dicopper centre is obtainable from  $(\text{Cu}(\text{CN})_x)^{1-x}$  in the presence of excess of cyanide. Notably, inspite of the susceptibility of both  $\text{MO}$  and  $\text{MS}$  to electrophilic attack (particularly protonation, Wedd 1983), the above description indicates that only the latter is capable of undergoing nucleophilic attack, though it was earlier (Müller and Bhattacharyya 1977) noticed that  $\text{MO}$  groups are also capable of doing that towards a pronounced 'a type' acceptor.

The present paper reports the reaction of  $[\text{Cu}(\text{CN})_x]^{1-x}$  (in the presence of excess of  $\text{CN}^-$ ),  $\text{CdCl}_2$ ,  $\text{HgCl}_2$  and  $\text{Pb}(\text{NO}_3)_2$  (note that the metal ions present in these acceptor systems possess closed shell i.e.  $d^{10}$  or  $d^{10}s^2$ ) with both  $\text{MS}_4^{2-}$  and  $\text{MO}_2\text{S}_2^{2-}$  ( $\text{M} = \text{Mo, W}$ ), and the isolation and characterization of the  $\text{S, S}$ -bridged closed shell-closed shell hetero bi- or poly-metallic reaction products. Furthermore, to test the capability of the  $\text{W=S}$  function of the coordinated  $\text{WS}_4^{2-}$  ligand to undergo nucleophilic attack, the  $\text{Cu-WS}_4$  complex is allowed to react with the  $\text{Ni}^{2+}$  ion and similarly that of the  $\text{W=O}$  function in coordinated  $\text{WO}_2\text{S}_2^{2-}$ , by reaction of the  $\text{Cu-WO}_2\text{S}_2$  complex with a special type of hard acid (Majumdar and Bhattacharyya 1974) viz. the  $\text{UO}_2^{2+}$  ion.

## 2. Materials and methods

### 2.1 Materials

All chemicals used in this work were of GR (E Merck, FRG) grade. For the purification of acetonitrile and other solvents and the preparation of tetraethylammonium perchlorate see our earlier report (Bhattacharyya *et al* 1989). Ammonium salts of tetrathio- and dioxodithio-metalates were prepared by methods reported earlier (McDonald *et al* 1983). All the compounds isolated were dried under reduced pressure over  $\text{CaCl}_2$ .

### 2.2 Physical measurements

For the description of instruments for IR, electronic, and ESR spectra, solution electrical conductances, electrochemical measurements, and microanalyses (C, H, N) see Bhattacharyya *et al* (1989). The X-ray powder diffraction of the complexes was carried out by using an XRD system, Phillips (Holland) Model PW 1730/PW 1710. The  $2\theta$  range was from  $7^\circ$  to  $50^\circ$  using  $\text{CuK}_\alpha$  radiation ( $1.5418 \text{ \AA}$ ). Raman spectra

(solid, 2000–50 cm<sup>-1</sup>) were recorded with a Spex Ramalog 5 M instrument equipped with a coherent laser CR 500 K using the 647.1 nm line and with Spex model 1403 double monochromator spectrometer using the 514.5 nm line. Scattered light at 90° was detected with the help of a cooled Spex Datamate R 928/115 photomultiplier and a photon-counting processing system.

### 2.3 Preparation of the complexes

CuCl<sub>2</sub>·2H<sub>2</sub>O (0.80 g; 4.68 mmol) was dissolved in 80 ml of water and to it was added concentrated ammonia (10 ml) until a deep blue colour appeared. The solution was stirred for 30 minutes adding solid KCN (4 g; 61.5 mmol) pinchwise until a clear colourless solution was obtained. The solution was then divided into four equal portions.

2.3a (PPh<sub>4</sub>)<sub>2</sub>[CNCuWS<sub>4</sub>] (1): To the portion 1, an aqueous solution (20 ml) of (NH<sub>4</sub>)<sub>2</sub>WS<sub>4</sub> (0.42 g; 1.21 mmol) was added. It was then stirred for 15 minutes. To the clear yellow solution, an ethanolic solution (15 ml) of PPh<sub>4</sub>Cl (0.90 g; 2.4 mmol) was added with stirring when a yellow crystalline product separated out, which was filtered off, washed with water, cold ethanol and finally with ether. It was then crystallised from an acetonitrile–ether mixture. Yield, 0.95 g; 73%.

2.3b (PPh<sub>4</sub>)<sub>2</sub>[CNCuMoS<sub>4</sub>] (2): To the portion 2, an aqueous solution (20 ml) of (NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub> (0.31 g; 1.19 mmol) was added. The solution was stirred for 15 minutes. To the clear red solution, an ethanolic solution (15 ml) of PPh<sub>4</sub>Cl (0.90 g; 2.40 mmol) was added with stirring, when a bright red crystalline product separated out, which was filtered off, washed and crystallised as above. Yield, 0.80 g; 70%.

2.3c (PPh<sub>4</sub>)<sub>2</sub>[CNCuWO<sub>2</sub>S<sub>2</sub>] (3): The third portion was taken in an ice bath and to it cold aqueous solution (20 ml) of (NH<sub>4</sub>)<sub>2</sub>WO<sub>2</sub>S<sub>2</sub> (0.38 g; 1.20 mmol) was added and it was stirred for 5 minutes. To the resulting solution a cold ethanolic solution (15 ml) of PPh<sub>4</sub>Cl (0.90 g; 2.40 mmol) was added with stirring when a light yellow crystalline product separated out, which was filtered off, washed with cold water, cold ethanol and ether. It was crystallised from cold (5–8°C) acetonitrile ether mixture. Yield 0.90 g; 73%.

2.3d (PPh<sub>4</sub>)<sub>2</sub>[CNCuMoO<sub>2</sub>S<sub>2</sub>] (4): The fourth portion was taken in an ice bath and to it cold aqueous solution (20 ml) of (NH<sub>4</sub>)<sub>2</sub>MoO<sub>2</sub>S<sub>2</sub> (0.27 g; 1.18 mmol) was added and stirred for 5 minutes. The rest of the method was same as above. Yield 0.80 g; 71%.

2.3e (PPh<sub>4</sub>)<sub>2</sub>[Cd(WS<sub>4</sub>)<sub>2</sub>] (5): CdCl<sub>2</sub> (0.10 g; 0.53 mmol) was dissolved in 30 ml water and to it an aqueous solution (40 ml) of PPh<sub>4</sub>Cl (0.40 g; 1.07 mmol) was added with stirring. Stirring was continued for another 10 minutes. To the resulting solution, an aqueous solution (20 ml) of (NH<sub>4</sub>)<sub>2</sub>WS<sub>4</sub> (0.37 g; 1.06 mmol) was added when an orange product was separated out which was worked up as in 1. Yield 0.55 g; 73%.

2.3f (PPh<sub>4</sub>)<sub>2</sub>[Cd(WO<sub>2</sub>S<sub>2</sub>)<sub>2</sub>] (6): CdCl<sub>2</sub> (0.10 g; 0.53 mmol) was taken in 30 ml water and to it an aqueous solution (40 ml) of PPh<sub>4</sub>Cl (0.40 g; 1.07 mmol) was added with

stirring. Stirring was continued for another 10 minutes. To the resulting solution an aqueous solution (20 ml) of  $(\text{NH}_4)_2\text{WO}_2\text{S}_2$  (0.34 g; 1.07 mmol) was added with stirring when a greenish yellow compound separated out, which was filtered off, washed with water, ethanol and ether. The product was crystallised from dichloromethane and light petroleum (40–60)-*n*-pentane (1:1) mixture. Yield 0.41 g; 55%.

2.3g  $(\text{PPh}_4)_2[\text{Hg}_2(\text{WS}_4)_2]$  (7):  $\text{HgCl}_2$  (0.10 g; 0.36 mmol) was dissolved in 100 ml water, and to it was added an aqueous solution (50 ml) of  $\text{PPh}_4\text{Cl}$  (0.27 g; 0.72 mmol) with stirring. To the resulting solution, an aqueous solution (20 ml)  $(\text{NH}_4)_2\text{WS}_4$  (0.25 gm, 0.72 mmol) was added with stirring, when a reddish brown solid separated out, which was filtered off, washed with water, ethanol and ether. The product was crystallised from acetone–light petroleum (40–60) mixture. Yield 0.225 g; 71%.

2.3h  $(\text{PPh}_4)_2[\text{Hg}_2(\text{WO}_2\text{S}_2)_2]$  (8):  $\text{HgCl}_2$  (0.10 g; 0.36 mmol) was dissolved in 100 ml water, and to it was added an aqueous solution (50 ml) of  $\text{PPh}_4\text{Cl}$  (0.27 g; 0.72 mmol) with stirring. To the resulting solution, an aqueous solution (20 ml) of  $(\text{NH}_4)_2\text{WO}_2\text{S}_2$  (0.23 g; 0.73 mmol) was added with stirring when an orange yellow solid separated out. The product was filtered off and washed with water, ethanol and ether respectively. It was crystallised from acetone–light petroleum (40–60) mixture. Yield 0.175 g; 60%.

2.3i  $(\text{PPh}_4)_2[\text{Pb}_2(\text{WS}_4)_4]$  (9):  $\text{Pb}(\text{NO}_3)_2$  (0.20 g; 0.60 mmol) was dissolved in 40 ml of hot water and to it was added hot aqueous (20 ml) solution of  $\text{PPh}_4\text{Cl}$  (0.46 g; 1.22 mmol) with stirring. Stirring was continued for 30 minutes in the hot condition, when a clear colourless solution was obtained. To the hot solution was added a hot aqueous solution (40 ml) of  $(\text{NH}_4)_2\text{WS}_4$  (0.45 g; 1.29 mmol) with stirring when an yellow product separated out, which was filtered off while hot, washed with hot water, ethanol and ether. The product was crystallised from DMF–ether mixture. Yield 0.6 g; 65%.

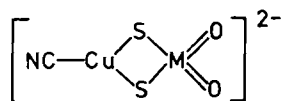
2.3j  $(\text{PPh}_4)_2[\text{NiCu}_2(\text{WS}_4)_2]$  (10):  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (0.10 g; 0.42 mmol) was dissolved in 20 ml ethanol and to it was added  $(\text{PPh}_4)_2[\text{CNCuWS}_4]$  (0.92 g; 0.85 mmol) solution in dichloromethane (30 ml) with stirring. Stirring was continued for another 15 minutes. The orange yellow compound so obtained was filtered off, washed several times with ethanol, dichloromethane and finally with ether. The product is slightly soluble only in DMSO from which a pure product could not be crystallised. Yield 0.450 g; 70%.

2.3k  $(\text{PPh}_4)_2(\text{CN})_2\text{Cu}_2(\text{WO}_2\text{S}_2)_2\text{UO}_2\text{H}_2\text{O}$  (11):  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.10 g; 0.20 mmol) was dissolved in 20 ml ethanol and to it was added a solution of  $(\text{PPh}_4)_2 \cdot [\text{CNCuWO}_2\text{S}_2]$  (0.43 g, 0.41 mmol) in dichloromethane (30 ml) with stirring. The solution was then worked up as above. Yield of the brick red compound was 0.25 g (74%).

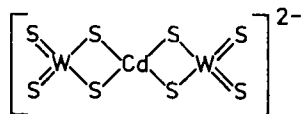
### 3. Results and discussion

#### 3.1 Synthetic aspects, IR spectroscopy and suggested structure

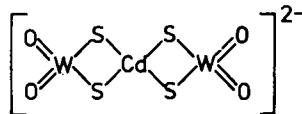
Ammoniacal  $[\text{Cu}(\text{CN})_x]^{1-x}$  reacts with  $\text{MS}_4^{2-}$  and  $\text{MO}_2\text{S}_2^{2-}$ , producing  $[\text{NCCu}(\text{MS}_4)]^{2-}$ ,  $\text{M} = \text{W}$ (1),  $\text{Mo}$ (2) and  $[\text{NCCu}(\text{MO}_2\text{S}_2)]^{2-}$ ,  $\text{M} = \text{W}$ (3),  $\text{Mo}$ (4) even in the



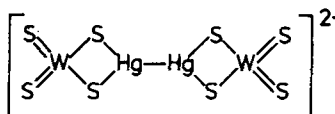
I (M=W, Mo)



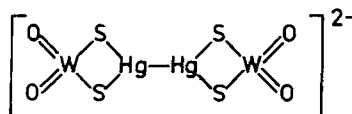
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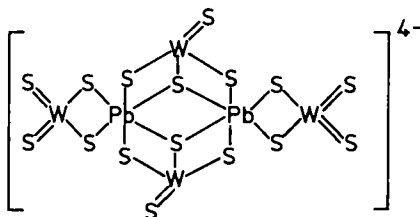
III



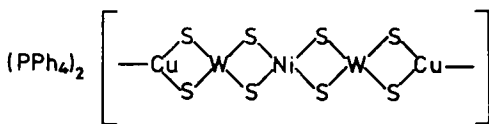
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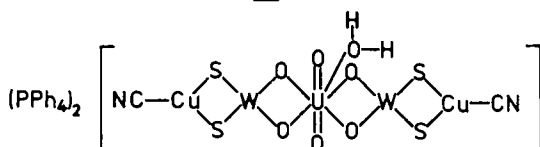
V



VI



VII



VIII

presence of excess  $\text{CN}^-$  in the reaction mixture (see §2.3), indicating that the course of the reaction in the present method is different from that of the cyanolysis of  $\text{NH}_4\text{CuMS}_4$ . It is noteworthy, under the present experimental condition, that  $\text{MO}_2\text{S}_2^{2-}$  on reaction with the cyanocuprate furnishes 3 and 4, where the identity of the ligand used is retained, contrary to what the earlier workers (Gheller *et al* 1984) otherwise observed. The infrared spectra of 3 and 4 clearly indicate two  $\nu(\text{M}=\text{O})$  vibrations which are characteristic of S, S coordinated  $\text{MO}_2\text{S}_2^{2-}$  ligands (Schmidt and Müller 1974). Complexes 1 and 2 show  $\nu(\text{M}=\text{S})$ , and  $\nu(\text{M}-\text{S}-\text{M})$ , vibrations, while 3 and 4 rightly show only the corresponding bridging vibrations (Diemann and Müller 1973). All of these complexes (1-4) are characterised by  $\nu(\text{CN})$  bands in the appropriate region (Nakamoto 1978) for coordinated  $\text{CN}^-$  ligand (table 1). On the other hand  $[\text{Cd}(\text{CN})_4]^{2-}$  when treated with  $\text{PPh}_4\text{Cl}$  in the presence

Table 1. Analytical and physico chemical data of the isolated complexes.

Compound	Analytical data <sup>a</sup>										Important IR (cm <sup>-1</sup> ) data				UV-vis (nm) data ( $\epsilon = \text{mol}^{-1} \text{cm}^{-1}$ )	Solution conductance $\Lambda_m = \text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$
	C	H	N/M <sup>b</sup>	P	M <sup>c</sup>	M <sup>d</sup>	S	$\nu_{\text{C}=\text{N}}$	$\nu_{\text{M}-\text{O}}$	$\nu_{\text{M}-\text{S}_i}$	$\nu_{\text{M}-\text{S}_h}$					
(PPh <sub>4</sub> ) <sub>2</sub> [CNCuWS <sub>4</sub> ](1)	548 (54.5)	38 (3.7)	1.4 (1.3)	5.8 (5.7)	6.0 (5.9)	17.2 (17.0)	11.7 (11.9)	2140	—	490, 485	445, 440	394(10290), 289(sh)	265			
(PPh <sub>4</sub> ) <sub>2</sub> [CNCuMoS <sub>4</sub> ](2)	59.6 (59.3)	4.0 (4.0)	1.5 (1.4)	6.4 (6.3)	6.5 (6.4)	9.8 (9.7)	12.7 (12.9)	2140	—	500, 485	450, 425	469(6560), 316(20690)	265			
(PPh <sub>4</sub> ) <sub>2</sub> [CNCuWO <sub>2</sub> S <sub>2</sub> ](3)	56.3 (56.1)	3.9 (3.8)	1.4 (1.3)	6.0 (5.9)	6.0 (6.1)	17.8 (17.8)	6.2 (6.1)	2140	875, 920	—	445	342(3045), 292(sh)	255			
(PPh <sub>4</sub> ) <sub>2</sub> [CNCuMoO <sub>2</sub> S <sub>2</sub> ](4)	61.5 (61.3)	4.3 (4.2)	1.6 (1.5)	6.6 (6.5)	6.5 (6.6)	10.2 (10.0)	6.9 (6.7)	2140	870, 900	—	450	395 (2230), 332(sh) 290(sh)	260			
(PPh <sub>4</sub> ) <sub>2</sub> [Cd(WS <sub>4</sub> ) <sub>2</sub> ](5)	40.5 (40.7)	2.7 (2.7)	8.0 (7.9)	4.5 (4.4)	—	26.2 (26.0)	18.3 (18.1)	—	—	490	435	456(4470), 393(17670)	270			
(PPh <sub>4</sub> ) <sub>2</sub> [Cd(WO <sub>2</sub> S <sub>2</sub> ) <sub>2</sub> ](6)	41.7 (42.7)	2.8 (2.9)	7.9 (8.3)	4.2 (4.6)	—	27.5 (27.3)	9.8 (9.5)	—	820, 975	—	450	413(1035), 355(3850)	265			
(PPh <sub>4</sub> ) <sub>2</sub> [Hg <sub>2</sub> (WS <sub>4</sub> ) <sub>2</sub> ](7)	33.9 (33.8)	2.3 (2.4)	23.4 (23.6)	3.5 (3.6)	—	21.8 (21.6)	15.2 (15.0)	—	—	490, 485	445	455(2730), 381(17270), 290(sh)	285			
(PPh <sub>4</sub> ) <sub>2</sub> [Hg <sub>2</sub> (WO <sub>2</sub> S <sub>2</sub> ) <sub>2</sub> ](8)	35.3 (35.1)	2.5 (2.4)	24.3 (24.5)	3.6 (3.8)	—	22.7 (22.5)	7.9 (7.8)	—	820, 975	—	450	444 (1890), 375(3290), 290(sh)	280			
(PPh <sub>4</sub> ) <sub>4</sub> [Pb <sub>2</sub> (WS <sub>4</sub> ) <sub>4</sub> ](9)	38.0 (38.2)	2.6 (2.7)	13.5 (13.7)	4.3 (4.1)	—	24.6 (24.4)	17.2 (17.0)	—	—	495, 485	440, 430	440(3210), 395(23220), 340(sh), 291(sh)	290 <sup>e</sup>			
(PPh <sub>4</sub> ) <sub>2</sub> [NiCu <sub>2</sub> (WS <sub>4</sub> ) <sub>2</sub> ](10)	39.1 (38.7)	2.8 (2.7)	3.8 (3.9)	4.7 (4.6)	8.8 (8.6)	25.1 (24.7)	17.4 (17.2)	—	—	—	445, 440	425 <sup>f</sup>	—			
(PPh <sub>4</sub> ) <sub>2</sub> [(CN) <sub>2</sub> Cu <sub>2</sub> (WO <sub>2</sub> S <sub>2</sub> ) <sub>2</sub> · UO <sub>2</sub> H <sub>2</sub> O](11)	35.2 (35.6)	2.4 (2.4)	1.6 (1.6)	4.7 (4.6)	7.6 (7.5)	22.1 (21.8)	7.8 (7.6)	2160	930, 890 810	—	465	450 <sup>f</sup> , 415 <sup>f</sup>	—			

<sup>a</sup>Calculated % in parentheses; <sup>b</sup>M<sup>+</sup> = Cd, Hg, Pb or Ni; <sup>c</sup>M<sup>+</sup> = Cu; <sup>d</sup>M = Mo, W; <sup>e</sup>Electronic spectrum and solution conductance measured in DMF; <sup>f</sup>Electronic spectrum of solids in nujol mull, absorbance arbitrary; <sup>g</sup>UO<sub>2</sub> absorption observed at 260 cm<sup>-1</sup>.

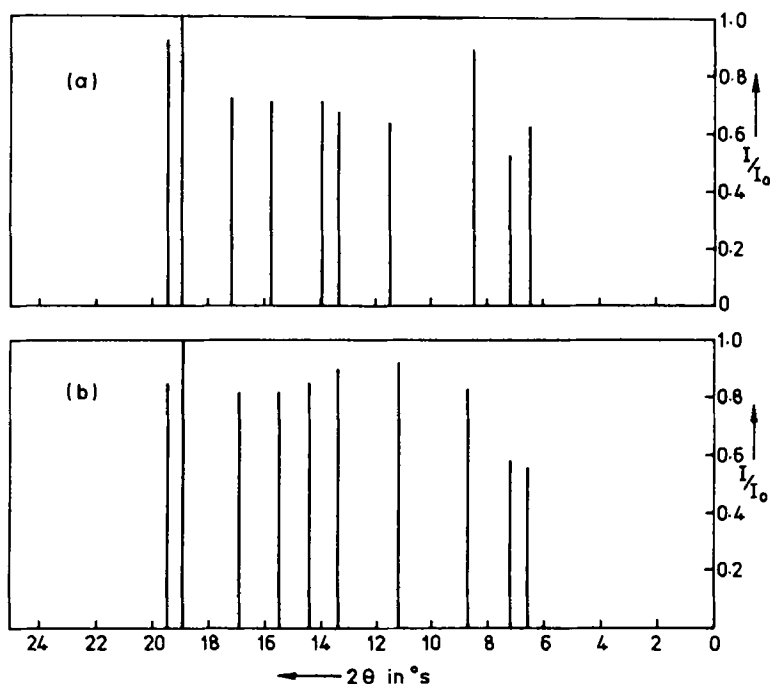


Figure 1. X-ray powder diffractograms of (a)  $(\text{PPh}_4)_4\text{Pb}_2(\text{WS}_4)_4$  (b)  $(\text{PPh}_4)_2\text{Sn}_2(\text{WS}_4)_4$ .

of  $\text{MS}_4^{2-}$  ligand, precipitates  $(\text{PPh}_4)_2(\text{Cd}(\text{CN})_4)$  and isolation of mixed cyano- $\text{MS}_4^{2-}$  complexes has not met with any success up to now. However, aqueous solution of  $\text{CdCl}_2$  on reaction with  $\text{WS}_4^{2-}$  or  $\text{WO}_2\text{S}_2^{2-}$  produces  $(\text{PPh}_4)_2[\text{Cd}(\text{WS}_4)_2]$  (5) or  $(\text{PPh}_4)_2[\text{Cd}(\text{WO}_2\text{S}_2)_2]$  (6). While 5 was earlier investigated (Müller *et al* 1981, unpublished results), 6 is a new compound. Interestingly, Hg(II) is reduced to Hg(I) when aqueous  $\text{HgCl}_2$  solution is treated with  $\text{WS}_4^{2-}$ , producing  $(\text{PPh}_4)_2[(\text{WS}_4)\text{Hg}-\text{Hg}(\text{WS}_4)]$  (7) or  $(\text{PPh}_4)_2[(\text{WO}_2\text{S}_2)\text{Hg}-\text{Hg}(\text{WO}_2\text{S}_2)]$  (8). The existence of Hg-Hg single bond in 7 and 8 has been proved by the appearance of  $\nu(\text{Hg}-\text{Hg})$  Raman vibration at  $128\text{ cm}^{-1}$  in both the cases. Besides these  $(d^{10})^+$  or  $(d^{10})^{2+}$  ions,  $\text{Pb}^{2+}$ , a  $\{d^{10}s^2\}^{2+}$  ion also reacts with  $\text{WS}_4^{2-}$  furnishing  $[\text{Pb}_2(\text{WS}_4)_4]^{4-}$ , the IR and X-ray powder diffraction pattern (figure 1) of the  $\text{PPh}_4$  salt (9) which are almost superimposable with those of the structurally characterised Sn-analogue (Müller *et al* 1976). In 9 both  $\nu(\text{W}=\text{S})_t$  and  $\nu(\text{W}-\text{S}-\text{Pb})_b$  vibrations are split like  $[\text{Sn}_2(\text{WS}_4)_4]^{4-}$ . In the light of the above discussion and citations the probable structures of the anions of the compounds 3–9 may be represented as I–VI. The nucleophilic reactivity of  $\text{W}=\text{S}$  is so pronounced that the terminal  $\text{W}=\text{S}$  functions in 1, react further with  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  producing the compound 10 (table 1) where analytical (table 1) and infrared data suggest that a structural unit of the type VII may be present. The compound may contain formally copper (0) (Bailar *et al* 1973), formed via a reductive elimination reaction whereby the  $\text{CN}^-$  ligands in two copper (I) centres escape as  $(\text{CN})_2$ . However, the complex is quite insoluble (slight solubility only in DMSO) and in the absence of other significant data a discussion on the observed magnetic moment of 3.0 BM is not possible. To test the nucleophilic reactivity of  $(\text{W}=\text{O})$  terminal groups present in 3, a special type of hard acceptor (Majumdar and Bhattacharyya

1974),  $\text{UO}_2^{2+}$ , is chosen as an electrophile, which reacts with **3** in ethanolic medium presumably producing the product **11**, also a poorly soluble (in DMF and DMSO only) compound where  $\nu(\text{C}=\text{N})$  band exists, but the  $\nu(\text{W}=\text{S})$  terminal vibration is rightly lacking (table 1). The probable structure is VIII and the  $810\text{ cm}^{-1}$  vibration can very well be attributed to  $\nu(\text{W}-\text{O}-\text{U})$  bridging vibration. The  $\nu_3$  of  $\text{UO}_2^{2+}$  (normally  $D \propto h$ ) is assigned (Majumdar and Bhattacharyya 1971) at  $930\text{ cm}^{-1}$ ,  $\nu_2$ , the bending vibration is quite apparent at  $260\text{ cm}^{-1}$ , while a weak  $890\text{ cm}^{-1}$  band may be due to the  $\nu_1$ , the symmetric  $\text{UO}_2^{2+}$  vibration, which because IR active via a slight nonlinearity of the otherwise linear cation, caused due to the accommodation of the 7th ligand,  $\text{H}_2\text{O}$  (IR,  $3500\text{ cm}^{-1}$ , TGA, DTA; water is lost endothermically at  $120^\circ\text{C}$ ) via the distortion of the octahedral  $\text{UO}_6$  framework.

### 3.2 Other characterising features and UV-visible spectra

The molar conductance values of **1**–**8** in  $\text{CH}_3\text{CN}$  solution (table 1) indicate that the complexes behave like 2:1 electrolytes while the complex **9**, shows a 4:1 electrolytic behaviour (Geary 1971) in DMF. These observations conform to the molecular formulae suggested. All the compounds excepting **10** (as mentioned earlier) are diamagnetic. The possible isostructurality of the Cu(I) complexes, viz **3** and **4** (structure I) is nicely exhibited in their respective X-ray powder diffractograms. The calculated  $d$ -spacings and their relative intensities have been recorded in table 2,

Table 2. Calculated  $d$ -spacings (in Å) and their relative intensities from the X-ray powder diffractograms of the complexes.

$d$	$I/I_0$	$d$	$I/I_0$	$d$	$I/I_0$
	<b>1</b>		<b>3</b>		<b>9</b>
10.17	0.60	10.40	0.41	13.62	0.63
9.12	0.63	7.69	1.00	12.30	0.55
6.97	1.00	7.03	0.59	10.40	0.90
5.57	0.83	6.28	0.38	7.63	0.64
4.93	0.78	6.03	0.38	6.61	0.68
4.44	1.00	5.18	0.66	6.33	0.72
3.98	0.25	4.50	0.80	5.61	0.70
3.75	0.50	4.29	0.60	5.16	0.74
3.55	0.36	4.19	0.56	4.67	1.00
3.47	0.38	3.88	0.53	4.55	0.92
	<b>2</b>		<b>4</b>		<b>10*</b>
10.29	0.58	10.78	0.39	13.40	0.56
9.21	0.83	7.89	1.00	12.29	0.63
7.03	0.47	7.14	0.53	10.17	0.89
5.61	0.67	6.37	0.41	7.90	0.83
4.95	0.66	6.06	0.43	6.61	0.90
4.44	1.00	5.18	0.63	6.02	0.85
4.00	0.20	4.50	1.00	5.72	0.82
3.77	0.33	4.29	0.59	5.25	0.82
3.55	0.40	4.17	0.54	4.72	1.00
3.30	0.26	3.88	0.42	4.55	0.85

\* Sn-analogue of (9)



where such data for the complexes **1** and **2** with known structure have also been included for ready reference.

The electronic spectra of these complexes containing essentially closed shell central atoms show only the ligand internal transitions corresponding to those of the free thio- or oxothio-metalate ions. Of the three bands normally expected for the free ligands (in the cases of ammonium or substituted ammonium salts, Müller and Diemann 1971, McDonald *et al* 1983) only two are observed here because the third one is possibly masked by  $\text{PPh}_4^+$  absorption. Comparing with free  $\text{MoS}_4^{2-}$  spectrum (Diemann and Müller 1973; Ghellar *et al* 1984) the first longest wavelength band ( $\nu_1$ ) in **2** undergoes a distinct change upon complex formation (figure 2a), while the second ( $\nu_2$ ) is practically unaltered in its position, intensity and half width. So, these absorptions can be characterised as  $n(\text{S}, 3p) \rightarrow E(\text{Mo}4d)$  ( $\nu_1$ ), and  $(\text{S}3p - \text{Mo}4d) \rightarrow E(\text{Mo}4d)$  ( $\nu_2$ ) transition (Jostes *et al* 1986). It is noteworthy that a corresponding

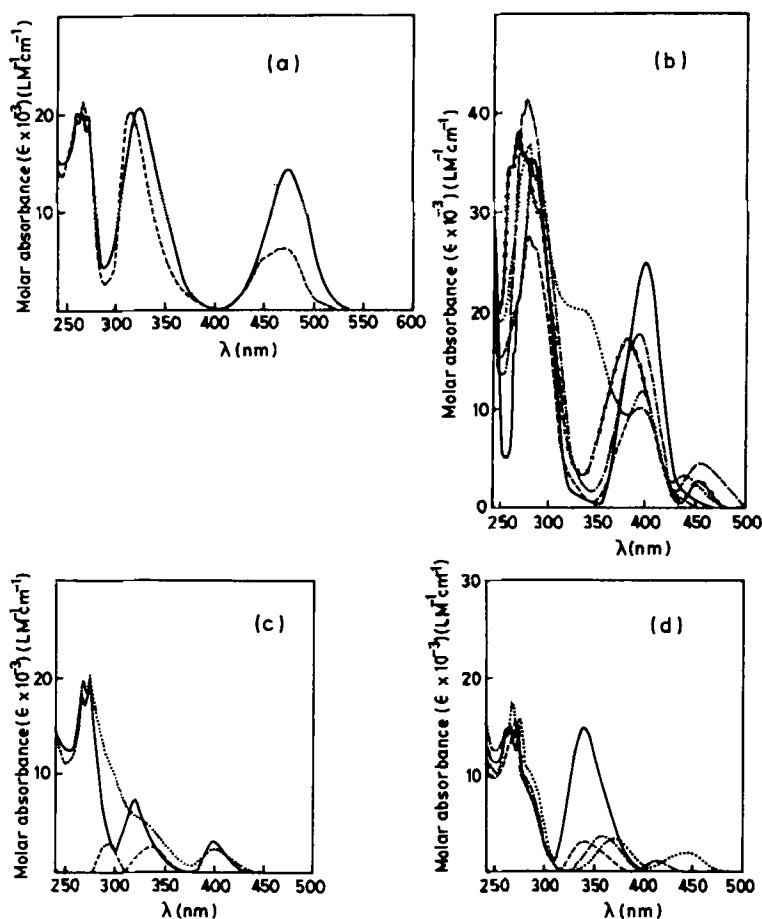


Figure 2. Electronic spectra of (a)  $(\text{PPh}_4)_2\text{MoS}_4$  (—), and  $(\text{PPh}_4)_2\text{NC-CuMoS}_4$  (----); (b)  $(\text{PPh}_4)_2\text{WS}_4$  (—),  $(\text{PPh}_4)_2\text{NC-CuWS}_4$  (----),  $(\text{PPh}_4)_2\text{Cd}(\text{WS}_4)_2$  (---),  $(\text{PPh}_4)_2\text{Hg}_2(\text{WS}_4)_2$  (-x-x-) and  $(\text{PPh}_4)_4\text{Pb}_2(\text{WS}_4)_4$  (.....); (c)  $(\text{PPh}_4)_2\text{MoO}_2\text{S}_2$  (—),  $(\text{PPh}_4)_2\text{NC-CuMoO}_2\text{S}_2$  (.....); (d)  $(\text{PPh}_4)_2\text{WO}_2\text{S}_2$  (—),  $(\text{PPh}_4)_2\text{NCCuWO}_2\text{S}_2$  (----),  $(\text{PPh}_4)_2\text{Cd}(\text{WO}_2\text{S}_2)_2$  (---) and  $(\text{PPh}_4)_2\text{Hg}_2(\text{WO}_2\text{S}_2)_2$  (.....)

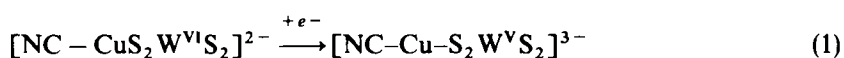
consideration would not be valid for complexes with open shell  $M'$  coordination centres (like  $Fe^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ). The above absorptions in the case of  $WS_4^{2-}$  complex are a little different. In the case of 1 the  $\nu_1$  absorption is weaker in intensity than that of free  $WS_4^{2-}$  but the position, profile and half width are not very different (figure 2b). This may be due to the fact that the  $t_1$  level (Müller *et al* 1981) in 1, mostly a pure  $S3p$  molecular orbital in free  $WS_4^{2-}$ , is much less effective to interaction with a suitable  $Cu(I)$  orbital than that of the same in  $MoS_4^{2-}$  due mainly to energy mismatch. The  $\nu_2$  absorption appears in 1 only as a shoulder on the descending portion of the  $PPh_4^+$  internal absorption (figure 2b) though in the case of  $(PPh_4)_2WS_4$  the  $WS_4^{2-}$  band is of higher intensity than that of the cation. Positionally, of course, the absorption of 1 does not differ much from that of the uncomplexed  $WS_4^{2-}$ . However, due to the lower optical electronegativity (Shriver *et al* 1990) of  $W^{6+}$  compared to that of  $Mo^{6+}$  the  $\nu_1$  and  $\nu_2$  bands in 1 are at lower wavelength regions than that of 2 (table 1 and figure 2a). The electronic spectra of  $Cd(II)$ ,  $Hg(I)$  and  $Pb(II)$  complexes (viz, in 5, 7 and 9) are widely different from that of free  $WS_4^{2-}$  in the longer wavelength regions. All the complexes show a new moderate intensity band around 450 nm otherwise absent in  $WS_4^{2-}$ . The metal ions concerned are very good soft acceptors and a good  $M'-S$  overlap may be envisaged. Also  $X_{opt}$  (optical electronegativity) values of the concerned metal ions are greater than that of  $Cu(I)$ . So these low energy bands may originate from MLCT transitions since the ligand involved possesses low energy  $\sigma$ -bonding and  $\pi$ -bonding but high energy  $\pi$ -anti-bonding molecular orbitals and metal ions involved have  $d^{10}$  or  $d^{10}S^x$  ( $x = 1$  or  $2$ ) configuration. The shoulder at 350 nm in the  $Pb-WS_4$  complex otherwise absent in the ligand may have its origin in the two different types of bridging,  $W-S-M'(Pb)$  environment (see figure 2b). This difference in bonding pattern may give rise to two different ( $S, 3p \rightarrow EW/5d$ ) transitions.

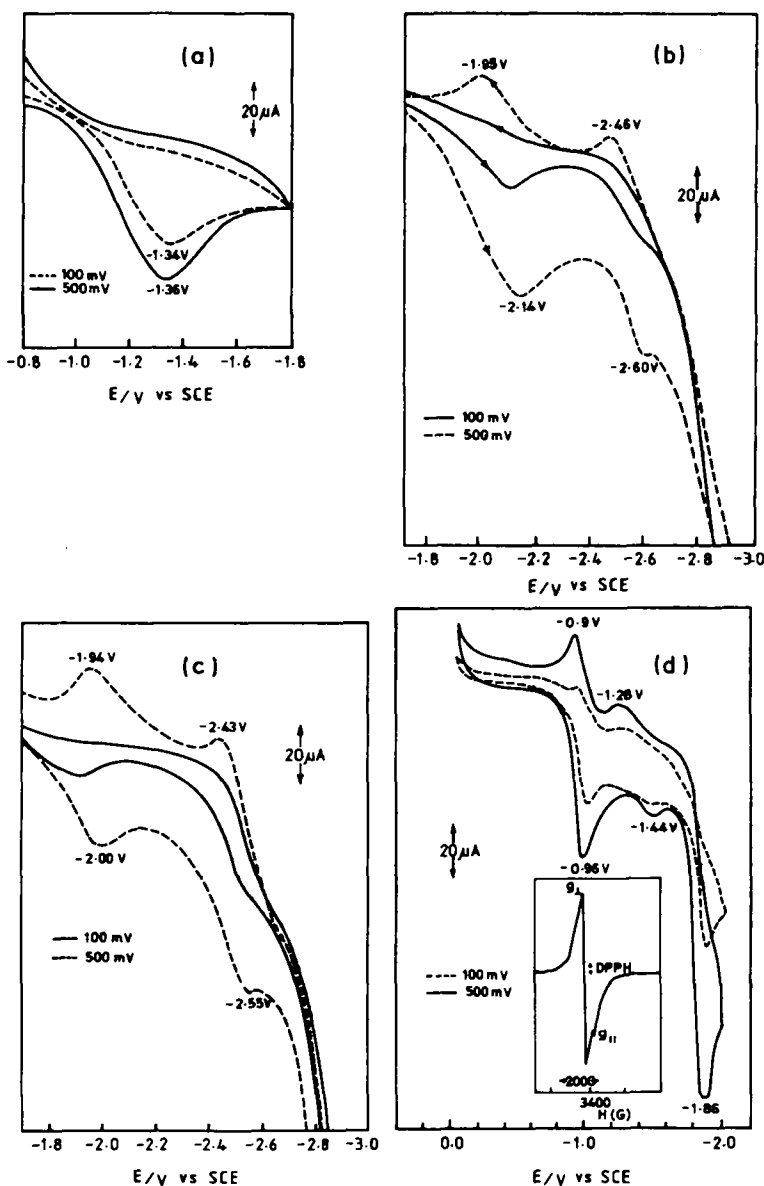
The  $MO_2S_2^{2-}$  ion has no nonbonding  $S2p$  levels. So, in 3, 4, 6 and 8 the  $\nu_1$  band may originate grossly from  $O2p \rightarrow Mo4d/W5d$  charge transfer transitions. Here again, especially in the case of the  $Hg(I)-WO_2S_2$  complex, a new band appears around 450 nm which is otherwise absent in  $WO_2S_2^{2-}$  (figure 2d). This may also be attributed to an MLCT transition involving  $Hg(I) \rightarrow WO_2S_2^{2-}$  (anti-bonding) orbitals.

### 3.3 Electrochemistry

Cyclic voltammetry was carried out in dimethylformamide solutions at a stout platinum wire working electrode and a platinum foil counter electrode. All potentials are referenced to the saturated calomel electrode (SCE). Tetraethyl ammonium perchlorate (TEAP) was used as an inert electrolyte in each case. For the reversible systems the formal potentials are also expressed (in parentheses in relevant places) relative to the  $E_{298}^0$  of the  $[Fe(\eta^5-C_5H_5)_2] \rightarrow [Fe(\eta^5-C_5H_5)_2]^+ (Fc-Fc^+)$  couple *vs.* SCE separately measured under exactly similar experimental conditions as used for the unknown products.

The copper-tungsten compound 1 shows an irreversible reductive response at  $-1.34$  V *vs* SCE at a scan rate of  $100$   $mVs^{-1}$  or above (figure 3a). This may be due to the electrode reaction (1) which shows that  $W(VI)$  is reduced to  $W(V)$ . The  $W(V)$  centre thus produced may dimerise via a chemical reaction and hence reduction becomes irreversible. The one-electron involvement as predicted in

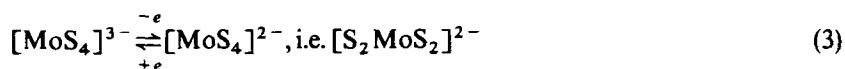
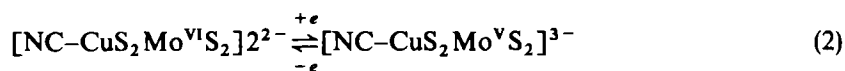




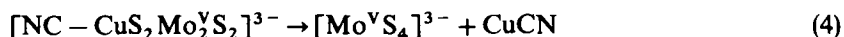
**Figure 3.** Cyclic voltammograms of (a)  $(\text{PPh}_4)_2\text{NCCuWS}_4$ ,  $100\text{ mV s}^{-1}$  (-----),  $500\text{ mV s}^{-1}$  (—); (b)  $(\text{PPh}_4)_2\text{NCCuMoS}_4$ ,  $100\text{ mV s}^{-1}$  (-----),  $500\text{ mV s}^{-1}$  (—); (c)  $(\text{PPh}_4)_2\text{NCuWO}_2\text{S}_2$ ,  $100\text{ mV s}^{-1}$  (-----),  $500\text{ mV s}^{-1}$  (—); (d)  $(\text{PPh}_4)_2\text{Hg}_2(\text{WSe}_4)_2$ ,  $100\text{ mV s}^{-1}$  (-----),  $500\text{ mV s}^{-1}$  (—). The inset shows the ESR spectrum of the electro-reduced solution of (d), i.e. compound 7.

has been corroborated by constant potential ( $-1.5\text{ V}$ ) coulometry. However the reduced solution remains EPR silent, thereby supporting the dimerization hypothesis. The corresponding Mo compound 2 on the other hand shows two reductive responses, one at  $-2.12$  and the other at  $-2.6\text{ V vs. SCE}$  at the scan rate of at least  $100\text{ mV s}^{-1}$ . Such responses show quasi-reversibility (table 2 and figure 3b) if the scan rate is

increased to  $500 \text{ mV s}^{-1}$  (difference from 1, see figures 3a and 3b). All the above observations suggest that in 2 the electrode reaction can be represented as in (2) and (3), respectively (see also Kony *et al* 1989). The details of electrochemical data including  $E_{298}^0$  of the reversible reactions are recorded in table 2. On longer time scales, the



reduced species undergo dissociation as shown in (4) and the reversibility of (2) is lost. However, the involvement of one electron in the processes (2) and (3) has also been confirmed by constant potential coulometry. However EPR detection of  $[\text{MoS}_4]^{3-}$  was



frustrated because the electrochemically reduced solution on coming in contact with a very small quantity of air changes colour instantaneously leaving behind a solution which is EPR silent. It is noteworthy, since the onset of peaks in such cases is almost at the level of overlapping potentials, that the  $I_a/I_c$  ratios recorded in table 2 are only apparent estimates and should not be taken in a very strict sense.

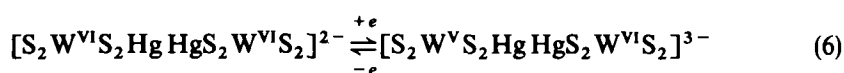
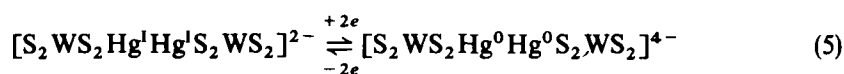
**Table 3.** Cyclic voltammetric data for the complexes 1, 2, 3, and 7 in DMF, TEAP.

Compound	Scan rate ( $\text{mV s}^{-1}$ )	$E_{pc}$ (V)	$E_{pa}$ (V)	$E_{298}^0$ (V)*	$\Delta E_p$ (mv)	Apparent $I_{pa}/I_{pc}$
(1)	100	-1.34				
	500	-1.36				
(2)	100	-2.00				
		-2.60				
	500	-2.14	-1.98	-2.06 (-2.44)	140	0.42
(3)	100	-2.60	-2.46	-2.53 (-2.91)	140	1.11
		-1.92				
	500	-2.00	-1.94	-1.97 (-2.35)	60	0.63
		-2.55	-2.43	-2.49 (-2.87)	120	1.13
(7)	100	-0.96	-0.90	-0.93 (-1.31)	60	0.35
		-1.42	-1.28	-1.35 (-1.73)	140	0.75
	500	-0.98	-0.90	-0.94 (-1.32)	80	0.43
		-1.46	-1.28	-1.37 (-1.75)	180	0.75

\*Values vs ferrocene-ferrocenium are shown in parentheses.

Interestingly, the above reversible feature which is not seen in  $WS_4^{2-}$  complexes is shown by the corresponding  $WO_2S_2^{2-}$  analogue, **3**. Figure 3c and table 2 suggest that the reductive cyclic responses in **3** can be represented by analogous sets of equations (2)–(4) by using  $S_2WO_2$  instead of  $S_2MoSO_2$ .

The Hg compound, **7**, also show interesting electroactivity. Both the Hg(I) centres were reversibly (at scan rate  $500\text{ mV s}^{-1}$ ; reversibility is poor at lower scan rates) reduced to Hg(0) at  $E_{298}^0 = -0.94\text{ V vs SCE}$  ( $-1.32\text{ V vs }fc - fc^+$ ) followed by another quasi-reversible cyclic response at  $E_{298}^0 = -1.37\text{ V vs SCE}$  ( $-1.75\text{ V vs }fc - fc^+$ ) due perhaps to the reduction at one of the W(VI) centres, since the current height, in the Hg-centre reductive response is greater than that of the latter. The process can be summarised as below.



The involvement of two electrons in (5) and one in (6) have been confirmed by constant potential coulometry. It is noteworthy, that the  $\Delta E_p$  for the reversible process (5) is 60 mV in spite of two-electron involvement; however, this type of situation is quite possible and may even occur frequently (Ammer and Saveant 1973; Flamagen *et al* 1978). It is satisfying to observe that the reduced solution, obtained by exhaustive electrolysis of **7** at  $-1.60\text{ V vs SCE}$  (equation 6) is EPR sensitive (DMF-toluene glass;  $\langle g \rangle_{\perp} = 2.01$ ,  $\langle g \rangle_{\parallel} = 1.98$ , structureless. See the inset in figure 3d).

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