Pergamon

PII: S0277-5387(96)00561-X

Polyhedron Vol. 16, No. 14, pp. 2483–2490, 1997

0277-5387/97 $17.00+0.00

Heterobimetallic *S,S*-bridged complexes, $[S_2MS_2M'I_2]^{2-}$ (M = Mo, W; M′ = Cd^{II}, Hg^{II}, Zn^{II}): synthesis, structure and redox properties

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(Received 7 May 1996; accepted 15 November 1996)

Abstract—Heterobinuclear complexes, $[S_2MS_2M'I_2]^{2-}$ (M = Mo, W; M′ = Cd, Hg, Zn), have been synthesized as PPh_4^- salts by reacting $[M'I_4]^{2-}$ with $[MS_4]^{2-}$. The complexes are characterized by ν (metal–sulphur) terminal, ν (metal–sulphur) bridging and ν (metal–iodine) terminal vibrations in their IR spectra. The single-crystal X-ray structure analysis of $(PPh_4)_2\,[S_2WS_2CdI_2]$ (**1**) reveals a two-fold anionic disorder. The coordination geometries about the metal centers in the anions $[S_2WS_2CdI_2]^{2-}$, containing planar $[WS_2Cd]$ cores, are best described as distorted edge-shared bitetrahedra. The oxidation states of cadmium and tungsten in a sulfur environment in **1** have been confirmed by X-ray photoelectron spectroscopy. Zn^{II} and Cd^{II} complexes each show a single metal centered irreversible cyclic voltammetric response essentially localised within $[MS_4]^{2-}$ ligands. © 1997 Elsevier Science Ltd

Keywords: heterobimetallic complexes; *S,S*-bridged complexes; diiodo-tetrathiometalato; mercurate(II); diiodo-tetrathiometalato cadmate(II); diiodo-tetrathiometalato zincate(II).

Multimetallic sulfido complexes play integral roles in the current context due to their solid-state properties [1] and applications in catalysis [2] and biology [3]. Coordination of $[MS_4]^{2-}$ (M = Mo, W) ions to transition and post-transition metals affords three important classes of compounds; (i) square-planar d^8 complexes $[S_2MS_2M'S_2MS_2]^{n-}$, M′ = Ni^{II}, Pd^{II}, Pt^{II} [4,5] for $n = 2$; Fe^I and Co^I [6] for $n = 3$, (ii) tetrahedral d^7 and d^{10} complexes for $n = 2$ and M′ = Co^{II} and Zn^{II} [7,8], and (iii) tris complexes with d^6 metals $[S_2WS_2M'(S_2WS_2)_2]^{3-}$, where M′ = Rh^{III} and Ir^{III} [9]. The stability of the complexes largely depends on the ability of the $[MS_4]^{2-}$ ligands to delocalize electron density from M′ into low-lying empty *d*-orbitals of M [10]. The delocalization becomes energetically favorable when M′ possesses five [11] or more [12] valence electrons. In the organometallic domain, however, a d^1 metal ion, *viz.*, osmium(VII) in a $\{Os{\equiv}N\}^{4+}$ core also forms stable $[MS_4]^{2-}$ complexes [13].

Several mixed tetrathiometalato complexes of copper(I) and silver(I) are known, but the corresponding complexes of other closed shell metal ions *viz.* Zn^{II}, Cd^{II} and Hg^{II} have not yet been reported, although mixed-ligand Zn^{II} and Cd^{II} complexes in sulfur coordination are highly relevant in the biological context [14].

We have recently reported [15] the synthesis of $[S_2MS_2HgCl_2]^{2-}$. The present paper records that although our attempts to synthesize the corresponding chloro compounds of Cd^{II} and Zn^{II} were unsuccessful,

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stable complexes $[S_2MS_2M'I_2]^{2-}$ M′ = Cd (**1**), Hg (**2**), Zn (**3**), with M = W, M′ = Cd (**4**), Hg (**5**) and Zn (**6**), with M = Mo, can be obtained as PPh_4^+ salts, by reacting MI_4^{2-} with MS_4^{2-} ions.

EXPERIMENTAL

Materials

All the reagents used for the preparation of the complexes were of analytical (E. Merck, India) grade, unless otherwise mentioned. Tetraphenyl phosphonium chloride (PPh_4Cl) was obtained from E. Merck (Germany). The ligands $(NH_4)_2WS_4$ and $(NH_4)_2MoS_4$ were synthesized using standard literature procedures [16]. For physico-chemical studies analytical grade solvents were further purified by literature methods [17]. Triply distilled water (all glass still) was used throughout the experimental procedures. Dinitrogen used for electrochemical work was passed through an alkaline dithionite solution before use.

Physical measurements

IR spectra were recorded as KBr discs on a Perkin–Elmer Model 597 IR spectrophotometer and electronic absorption spectra on a Hitachi Model U-3400 UV–vis–NIR spectrophotometer. Solution conductances were measured on a Systronics (India) Model 304 digital conductivity meter. Voltammetric measurements were carried out on a Bioanalytical systems Model BAS-100B electrochemical analyzer in acetonitrile solution. The experiments were conducted at 298 K under dinitrogen using a glassy carbon working electrode, a platinum wire auxilliary electrode and Ag–AgCl reference electrode. Elemental analyses (C and H) were performed using a Perkin–Elmer model 240C elemental analyzer, phosphorus and iodine as $P_2O_5 24MoO_3$ and AgI, respectively, and cadmium, mercury and zinc by atomic absorption spectroscopy (AAS) employing a Perkin–Elmer 2820 atomic absorption spectrometer. The XPS studies were carried out on an ESCALAB 503 spectrometer. Al-K_α line (1486.6 eV) was used as the excitation source. The spectra were calibrated by using the $Cls_{1/2}$ binding energy (at 285.0 eV) from pump oil as an internal standard. FAB mass spectra at room temperature were recorded on a JEOL SX 102/DA-6000 Mass spectrometer/data system using argon as the FAB gas and *m*-nitrobenzyl alcohol (NBA) as the matrix.

Preparation of the complexes

$(PPh_4)_2[I_2CdS_2MS_2]$[M = W (**1**) or Mo (**4**)]. $CdCl_2 \cdot 2H_2O$ (0.1 g, 0.45 mmol) was dissolved in 30 cm^3 of water and to it was added potassium iodide (4.0 g, 24 mmol) and stirred for 25 min. The resultant solution was then added with stirring to a solution of $(NH_4)_2WS_4$ (0.20 g, 0.57 mmol) in 15 cm^3 of water or $(NH_4)_2MoS_4$ (0.16 g, 0.60 mmol) in 20 cm^3 water followed by PPh_4Cl (0.25 g, 0.67 mmol) in 20 cm^3 of water when bright yellow (**1**) or red–brown (**4**) products precipitated. The compounds were filtered off, washed thoroughly with water, ethanol and diethylether and dried *in vacuo* over fused $CaCl_2$. Yield: 0.45 g (65%) for **1**; 0.35 g (60%) for **4**. Orange–yellow or red–brown crystals were obtained from slow diffusion of light-petroleum (40–60°C) through an acetone solution of **1** or **4**. Yield, 55% in both the cases. Found: C, 42.4; H, 2.9; S, 10.9; W, 13.0; Cd, 8.0; I, 18.5; P, 4.3. Calc. for $C_{48}H_{20}P_2I_2S_4CdW$ (**1**): C, 42.5; H, 3.0; S, 10.0; W, 13.6; Cd, 8.3; I, 18.7; P, 4.6%. IR, cm^{-1} 490(m), 495(sh) $\nu(W—S_t)$; 435(sh), 430(m), $\nu(W—S—Cd)_b$; 150(m), 140(m) $\nu(Cd—I_t)$. Found: C, 45.0; H, 2.9; S, 9.9; Mo, 7.1; Cd, 8.5; I, 19.5; P, 4.6. Calc. for $C_{48}H_{20}P_2I_2S_4CdMo$ (**4**): C, 45.4; H, 3.2; S, 10.1; Mo, 7.3; Cd, 8.8; I, 20.0; P, 4.9%. IR, cm^{-1}: 498(m), $\nu(Mo—S_t)$; 440(m), 420(sh), $(Mo—S—Cd)_b$; UV–vis λ nm (ε): 545 (4800), 466 (6200), 312 (14,446), 428 (547), 384 (320), 344 (550), 274 (10,030).

$(PPh_4)_2[I_2HgS_2MS_2]$ [M = W(**2**), or Mo (**5**)]. $HgCl_2 \cdot 2H_2O$ (0.1 g, 0.33 mmol) was dissolved with stirring in 30 cm^3 of H_2O. Potassium iodide (4.0 g, 24 mmol) was then added to the solution with constant stirring which was continued for another 30 min. An aqueous solution of $(NH_4)_2WS_4$ (0.14 g, 0.40 mmol) or $(NH_4)_2MoS_4$ (0.12 g, 0.45 mmol) dissolved in 25 cm^3 of water was added to the above solution. Addition of PPh_4Cl (0.25 g, 0.66 mmol) in 20 cm^3 of water deposited orange–yellow (**2**) or dark-brown (**5**) complexes. Yields: 0.40 g (80%) for **2**; 0.35 g (65%) for **5**. Red–orange (**2**) and dark-brown (**5**) microcrystalline products were obtained upon crystallization of **2** and **5**, respectively, from acetone light-petroleum (40–60°C) mixture. Yield: 0.25 g (52%) for **2**; 0.25 g (56%) for **5**. Found: C, 39.5; H, 2.5; S, 8.5; Hg, 13.5; W, 12.1; I, 17.0; P, 4.1; Calc. for $C_{48}H_{20}P_2I_2S_4HgW$ (**2**): C, 40.0; H, 2.8; S, 8.9; Hg, 13.9; W, 12.7; I, 17.6; P, 4.3%. IR, ν cm^{-1}: 485(sh), 480(m) $\nu(W—S_t)$, 440(m), $\nu(Hg—S—W)_b$. Found: C, 42.1; H, 2.9; S, 8.9; Hg, 14.2; Mo, 6.8; I, 18.1; P, 4.2. Calc. for $C_{48}H_{20}P_2I_2S_4MgMo$ (**5**): C, 42.5; H, 3.0; S, 9.5; Hg, 14.8; Mo, 7.1; I, 18.8; P, 4.6%. IR, cm^{-1}: 495(m), $\nu(Mo—S_t)$, 450(m), $\nu(Mo—S—Hg)_b$.

$(PPh_4)_2[I_2ZnS_2MS_2]$ [M = W (**3**) or Mo (**6**)]. $ZnCl_2 \cdot 2H_2O$ (0.1 g, 0.40 mmol) was dissolved in 25 cm^3 of H_2O with stirring. Potassium iodide (4.0 g, 24 mmol) was then added to it and stirring was continued for 20 min. The resultant solution was filtered and to the filtrate was added an aqueous solution of $(NH_4)_2WS_4$ (0.16 g, 0.45 mmol) or $(NH_4)_2MoS_4$ (0.12 g, 0.45 mmol) dissolved in 20 cm^3 of water with stirring when an orange–red or dark red solution was obtained. Addition of an aqueous PPh_4Cl (0.25 g, 0.66 mmol) solution in 25 cm^3 of H_2O to the above solutions yielded complexes **3** or **5**, respectively.

Yields: 0.30 g (80%) for **3**; 0.34 g (70%) for **6**. Orange–red or red–brown crystalline products were obtained from crystallization of **3** or **6** from acetone–light petroleum (40–60°C) mixture. Yields: 0.25 g (75%) for **3**; 0.30 g (65%) for **6**. Found: C, 42.9; H, 2.9; S, 9.8; W, 13.8; Zn, 4.9; I, 19.0; P, 4.8. Calc. for $C_{48}H_{20}P_2I_2S_4ZnW$ (**3**): C, 43.9; H, 3.1; S, 10.1; W, 14.1; Zn, 5.0; I, 19.4; P, 4.9%. IR, cm^{-1}: 490(s$_t$), 480(sh), ν(W—S$_t$), 445(s), ν(W—S—Zn)$_b$, 138(m), 124(m), ν(Zn—I$_t$). Found: C, 46.9; H, 3.2; S, 10.1; Mo, 7.2; Zn, 4.8; I, 19.5; P, 5.0. Calc. for $C_{48}H_{20}P_4I_2S_4ZnMo$ (**6**): C, 47.1; H, 3.3; S, 10.5; Mo, 7.8; Zn, 5.4; I, 21.0; P, 5.1%. IR, cm^{-1}: 500(m), ν(Mo—S$_t$), 460(m), 440(m), (Mo—S—Zn)$_b$.

X-ray crystallography and structure solution of 1

A prismatic crystal of **1** was selected and mounted on a Enraf–Nonius CAD-4 diffractometer. Crystallographic data are summarized in Table 1. The accurate unit-cell parameters were determined from automatic centering of 20 reflections ($12 \leqslant \theta \leqslant 16°$) and refined by the least-squares method. Intensity data were collected in the ω–2θ mode using graphite monochromated Mo-K_α radiation. Three standard reflections monitored periodically showed negligible variation in intensity during data collection. The intensities were corrected for Lorentz and polarization effects and an empirical absorption correction [18] based on azimuthal scans was applied. Density measurement indicated that there was only one complex molecule per unit cell. Of the two possible space groups $P1$ and $P\bar{1}$, the latter one, with one $(PPh_4)^+$ cation and half of the $[S_2WS_2CdI_2]^{2-}$ anion comprising the asymmetric unit, was favoured from *E*-statistics and deemed satisfactory by successful refinement. Since the anion containing two dissimilar metals (W, Cd) and different terminal ligands (S, I) has no center of inversion, a disorder was introduced to accommodate the centrosymmetric space group $P\bar{1}$. The single metal site M (W/Cd) was obtained from a Patterson synthesis. The remaining non-hydrogen atoms, including the disordered terminal S/I of the anion involving different sites, were located from successive Fourier syntheses. Full-matrix least-squares refinement (SHELXL 93) [19] with W and Cd atoms disordered over same position and having identical thermal parameters revealed a splitting of the bridging sulfur atom into S(3) and S(4). The observed asymmetry between M—S(3)/S(4) and M′—S(3)/S(4) (M′ = $-x+1$, $-y+1$, $-z$) distances, 2.20 and 2.66 Å, respectively, coupled with the reported M—S (bridging) bond lengths in related homobimetallic complexes [20,21] was used in selecting W—S$_{\text{bridging}}$ and Cd—S$_{\text{bridging}}$ bonds. As a consequence of the postulated center of symmetry the occupancy factors of W, Cd, terminal S(1), S(2), I(1), I(2) and bridging S(3), S(4) atoms were fixed at 0.5. In the final least-squares cycles all non-hydrogen atoms were refined anisotropically keeping M—S (bridging) and M—S/I (terminal) distances restrained by DFIX. The hydrogen atoms of the cation were held fixed at geometrically calculated positions. The largest peak (2.44 e/Å^{-3}) and the deepest hole (2.70 e Å^{-3}) in the final difference-Fourier map were 0.93 and 1.12 Å, respectively, away from the metal atom site. Selected bond lengths and angles are given in Table 2.

Table 1. Crystal data for $(PPh_4)_2[I_2CdS_2WS_2]$ (**1**)

Formula	$C_{40}H_{40}CdI_2P_2S_4W$
Formula weight	1357.03
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	9.923(6)
b (Å)	10.089(3)
c (Å)	13.171(4)
α (°)	108.62(4)
β (°)	94.65(2)
γ (°)	100.24(3)
V (Å)^3	1216.2(9)
Z	1
Radiation	Mo-K_α
λ (Å)	0.71073
F(000)	650
μ (mm^{-1})	4.339
D_{calc} (g cm^{-3})	1.853
Crystal size (mm)	0.3 × 0.2 × 0.15
θ range (°)	$2 \leqslant \theta \leqslant 25$
Index ranges	$0 \leqslant h \leqslant 11$
	$-11 \leqslant k \leqslant 11$
	$-15 \leqslant l \leqslant 15$
No. of reflections collected	4582
Unique reflections	4248
Observed reflections $I \geqslant 2\sigma(I)$	3394
R_1,^{a} WR_2^{b}	0.0506, 0.1233
Weighting parameters^c (A, B)	0.0916, 0.00
GOF^{d}S	1.054

[a] $R_1 = \Sigma \| F_o| - |F_c \| / \Sigma | F_o|$.

[b] $WR_2 = [\Sigma\{w(F_o^2 - F_c^2)^2\} / \Sigma\{w(F_o^2)^2\}]^{1/2}$.

[c] $w = 1/[\sigma^2(F_o^2) + (AP)^2 + BP$, where $P = (F_o^2 + 2F_c^2)/3$.

[d] $s = [\Sigma\{w(F_o^2 - F_c^2)^2\} / (N - P)]^{1/2}$, where N is the number of data and P is the total number of parameters refined.

Tables of atomic coordinates, anisotropic thermal parameters, full listing of bond lengths and angles, observed and calculated structure factors are available as supplementary material.

X-ray powder diffraction studies of 2–6

Since all attempts to obtain suitable single crystals of **2–6** failed, the complexes were examined by X-ray powder diffraction. Accurate *d*-spacings (Å) were obtained from powder patterns recorded on a Philips XRD diffractometer (PW 1730/1710) at 22°C operating at 40 KV and 20 mA with 2° min^{-1} scan rate. A

Table 2. Selected bond distances (Å) and angles (°) in complex **1**

M—M′	3.171(1)	M—S(1)	2.282(5)
M—S(2)	2.156(4)	M—S(3)	2.197(3)
M—S(4)	2.208(4)	M—S(3)	2.646(4)
M—S(4)	2.684(3)	M—I(1)	2.582(2)
M—I(2)	2.715(1)		
S(1)—M—S(2)	104.55(16)	S(1)—M—S(3)	110.33(16)
S(1)—M—S(4)	106.96(12)	S(2)—M—S(3)	110.12(16)
S(2)—M—S(4)	112.58(14)	S(3)—M—S(4)	111.99(9)
S(3)—M—S(4)	86.47(8)	I(1)—M—S(3)	117.29(8)
I(1)—M—S(4)	113.57(8)	I(2)—M—S(3)	108.11(9)
I(2)—M—S(4)	110.86(8)	I(1)—M—I(2)	113.43(5)
M—S(3)—M′	81.22(10)	M—S(4)—M′	80.16(10)

M = M′ = (1/2) (W+Cd).

comparison of the powder data of **1–6** (Table 3) revealed that the complexes were not isostructural.

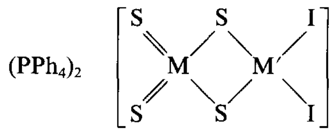
RESULTS AND DISCUSSION

Synthetic aspects

Zn^{II} ions react with $[MS_4]^{2-}$ (M = W, Mo) ligands producing the complex $[S_2MS_2ZnS_2MS_2]^{2-}$, but detailed reports on the corresponding Cd^{II} and Hg^{II} analogues are still unpublished [22]. It is observed that while $[M'(CN_4]^{2-}$ (M′ = Zn, Cd, Hg) complexes on reaction with $[MS_4]^{2-}$ do not yield any mixed-ligand tetrathiometalato complexes, $[M'I_4]^{2-}$ as the starting material resulted in the isolation of $[I_2M'S_2MS_2]^{2-}$ with PPh_4^+ counterions. Interestingly, $[M'Cl_4]^{2-}$ and $[M'Br_4]^{2-}$ do not respond to such a reaction, indicating that the covalency of the iodide ligands stabilizes the complexes by a soft–soft symbiotic effect [23]. It has been recently reported [15] that $HgCl_2$ in the presence of twice its molar proportion of CN^- ions forms $[Cl_2Hg(CN)_2]^{2-}$, which reacts with $[MS_4]^{2-}$ ions to afford $[S_2MS_2HgCl_2]^{2-}$ rather than a cyano-derivative, indicating that the cyano-complexes of the closed shell metal ions are quite labile.

General and spectroscopic characterization and structural assessment

All the complexes, as expected, behave as 2 : 1 electrolytes in acetonitrile [24] (molar conductance *ca* 250 Ω^{-1} cm^2) and in the solid state (as KBr pellets) show $\nu(M—S)_t$, $\nu(M—S_b)$, $\nu(M'—S_b)$ and $\nu(M'—I_t)$ stretching vibrations in the normal regions [25] (see experimental section) in their IR spectra, indicating the possible structures of **1–6** as I. Small changes are observed for $\nu(M—S_t)$ or $\nu(M—S—M')_b$ vibrations as M and M′ vary from W to Mo and Zn to Hg, respectively. The shifts are not always commensurate with the reduced masses of M and M′, presumably due to the changes in the force constants of the metal–sulfur bonds and the mixing of several vibrational modes.



Comparison of electronic spectra of **1–6** with those of $(PPh_4)_2MS_4$ (M = Mo, W), recorded in CH_3CN and DMF [26] solvents reveals that the main features of the spectra remain almost unaltered except for the enhancement of the intensities of the bands (Table 4). The spectra of two representative compounds **1** and **4** are shown in Fig. 1. Noticable changes occur in the long-wavelength region bands, *viz.* at 450 nm for $[WS_4]^{2-}$ and 550 nm for $[MoS_4]^{2-}$ complexes, which appear only as shoulders in the respective tetraphenyl phosphonium salts.

Crystal structure of $(PPh_4)_2[S_2WS_2CdI_2]$ (**1**)

The structure consists of well-separated tetraphenyl phosphonium $[PPh_4]^+$ cations and disordered heterobinuclear $[S_2WS_2CdI_2]^{2-}$ anions. An ORTEP II [27] view of the anion with atom labeling scheme is shown in Fig. 2. A crystallographically imposed inversion center in the anions resulted in half of the dimer and one $[PPh_4]^+$ cation comprising the asymmetric unit. The geometry of the anion containing a planar $W(\mu\text{-}S)_2Cd$ core and coordinated by terminal S^{2-} and I^- ligands, can be best described as two edge-shared tetrahedra. The M—M′ [3.171(1) Å], $W—S_{bridging}$ [2.197(3), 2.208(4) Å], $Cd—S_{bridging}$ [2.646(4), 2.684(3) Å] distances and $S_{bridging}—M—S_{bridging}$ (M = W, Cd) angles [111.99(9), 86.47(8)°] are comparable to the corresponding parameters reported for related homobimetallic systems [20,21]. The discrepancies between the two W—S (terminal) 2.156(4), 2.282(5) Å and two Cd—I 2.582(2), 2.715(1) Å bond distances can be attributed to the unresolved anionic disorder at the terminal sites. The

Table 3. X-ray powder diffraction data for $(PPh_4)_2[S_2MS_2M'I_2]$, (M = W, Mo ; M′ = Cd, Hg, Zn) ; (**2–6**) ; $\lambda = 1.5418$ Å

$[I_2CdS_2WS_2]^{2-}$ d_{obs} (Å)	(1) I/I_o (%)	$[I_2HgS_2WS_2]^{2-}$ d_{obs} (Å)	(2) I/I_o (%)	$[I_2ZnS_2WS_2]^{2-}$ d_{obs} (Å)	(3) I/I_o (%)	$[I_2CdS_2MoS_2]^{2-}$ d_{obs} (Å)	(4) I/I_o (%)	$[I_4HgS_2MoS_2]^{2-}$ d_{obs} (Å)	(5) I/I_o (%)	$[I_2ZnS_2MoS_2]^{2-}$ d_{obs} (Å)	(6) I/I_o (%)
8.192	14	9.686	45	6.970	25	7.098	8	8.758	30	7.254	40
7.900	10	8.889	26	6.758	38	6.006	31	7.512	40	6.657	90
6.487	22	8.253	29	6.109	40	5.363	6	7.351	39	6.067	16
6.326	18	7.701	32	5.717	8	4.793	10	6.937	75	5.985	10
4.955	15	7.345	26	5.216	16	4.693	13	5.887	29	5.574	15
4.611	25	6.779	100	5.068	25	4.506	14	5.659	25	5.126	10
4.552	58	6.281	45	4.720	55	4.418	14	5.395	49	4.796	36
4.291	9	5.856	44	4.552	100	4.252	100	4.912	21	4.695	17
3.969	71	5.191	42	4.191	60	4.071	21	4.700	100	4.848	100
3.770	35	4.928	45	4.040	58	3.792	31	4.578	23	4.396	7
3.493	18	4.740	76	3.867	10	3.684	8	4.439	18	4.210	58
3.327	9	4.592	44	3.802	5	3.527	32	4.330	50	4.004	18
3.290	33	4.236	78	3.739	11	3.468	30	4.015	15	3.934	5
3.232	13	4.058	16	3.414	4	3.230	13	3.857	23	3.786	19
2.755	7	3.897	13	3.198	32	3.151	6	3.613	20	3.723	20
2.637	7	3.754	11	3.028	6	3008	28	3.424	33	3.466	18
2.585	16	3.494	16	2.969	5	2.833	6	3.347	15	3.326	6
2.455	100	3.440	14	2.858	8	2.685	26	3.157	13	3.243	26
2.392	82	3.330	24	2.652	13	2.578	11	3.039	36	3.121	9
2.270	33	3.275	22	2.637	3	2.505	18	2.921	12	3.038	7
2.254	42	3.071	21	2.281	4	2.355	4	2.901	11	2.988	16
		3.039	18			2.276	10	2.751	23	2.903	10
		2.979	37					2.646	16	2.771	13
		2.930	32					2.535	13	2.675	23
		2.837	16					2.466	16	2.652	8
		2.700	15					2.408	21	2.564	7
		2.621	18					2.346	20	2.344	6
		2.562	8					2.293	23	2.309	3
		2.498	13							2.265	12
		2.464	11								
		2.393	13								
		2.355	10								
		2.291	16								

Table 4. Electronic spectral data[a] of the isolated complexes

Complex	Spectral bands λ nm (ε)						
1	453 (5123)	390 (14,943)	364 (sh)	320 (sh)	274 (23,000)		
4	454 (4800)	466 (6200)	312 (14,446)	428 (sh)	384 (sh)	344 (sh)	274 (23,200)
2[b]	453 (3890)	393 (14,590)	330 (sh)	297 (sh)	284 (22,213)		
5[b]	550 (3790)	464 (1668)	446 (sh)	300 (17,490)	274 (23,000)		
3	448 (4812)	394 (14,290)	369 (sh)	274 (23,075)			
6	540 (5840)	471 (6310)	440 (sh)	330 (12,000)	278 (23,000)		

[a] In CH_3CN medium.
[b] In DMF medium.

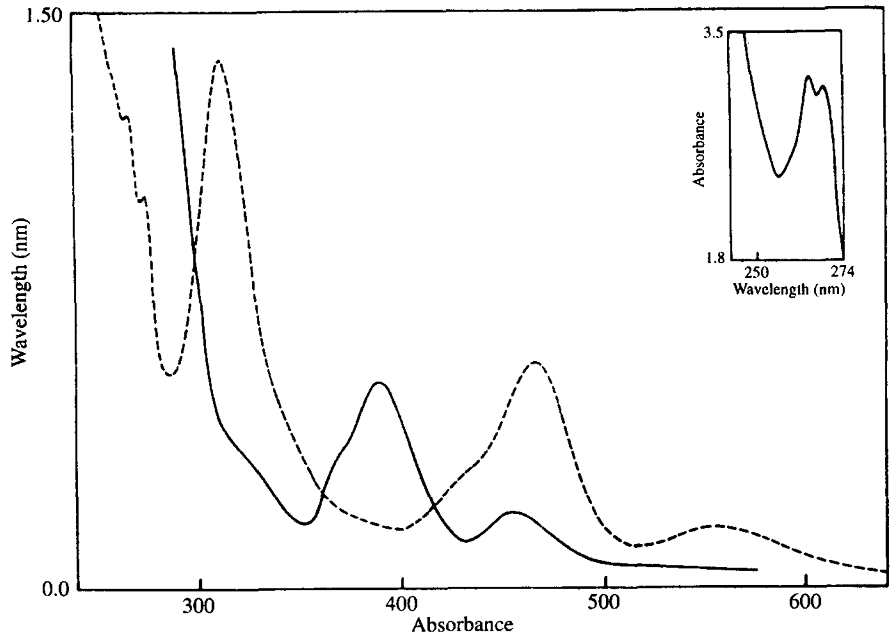


Fig. 1. Electronic absorption spectra of **1** (—) and **4** (---) in CH_3CN medium.

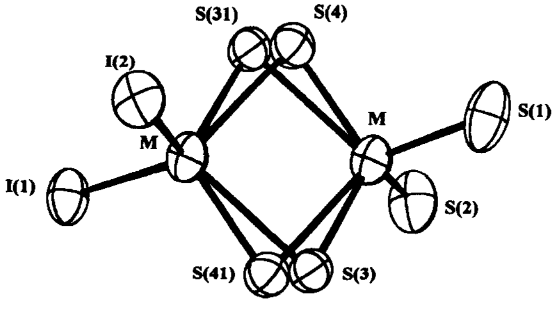


Fig. 2. ORTEP view of the anion of **1** with atom-labeling scheme.

$[PPh_4]^+$ cations, with P—C distances, ranging between 1.785(7) and 1.800(7) Å are of usual geometries.

X-ray photoelectron spectroscopy and FAB mass spectroscopy

The metal oxidation states are further corroborated by $Cd3d_{3/2}$, $Cd3d_{5/2}$ (411.5 and 405.5 eV), W $4f_{5/2}$ and W $4f_{7/2}$ (35.0 and 32.5 eV, respectively) binding energies obtained from the X-ray photoelectron spectrum of **1**. The binding energy values indicate that in the sulfur environment cadmium is present as Cd^{II} and tungsten as W^{VI} [28]. The structural formulae assigned

Table 5. Cyclic voltammetric data[a] of the isolated complexes

Complex		Irreversible reductive waves (V *vs* Ag—AgCl) E_{pc}[b]			E_{pa}[c]
$(PPh_4)_2[I_2CdS_2WS_2]$	**(1)**	−0.98,	−1.60,	—	—
$(PPh_4)_2[I_2CdS_2MoS_2]$	**(4)**	−0.70,	−1.2,	−1.4	—
$(PPh_4)_2[I_2ZnS_2WS_2]$	**(3)**	−0.98,	−1.4,	−1.6	+0.80
$(PPh_4)_2[I_2ZnS_2MoS_2]$	**(6)**	−0.78,	−1.10,	−1.50	+0.39

[a] In CH_3CN TEAP medium.

[b] E_{pc} = peak potential on cathodic sweep.

[c] E_{pa} = peak potential on anodic sweep.

have been corroborated also by FAB-MS data of two representative complexes (**1** and **4**) in both positive and negative ion modes. The negative-ion FAB-MS spectrum of complex **1** shows a medium intensity peak at $m/z = 1019$, corresponding to the parent molecular ion $\{(PPh_4)[I_2CdS_2WS_2]\}^-$. Several other peaks are observed in the spectrum at $m/z = 961$ for $\{(PPh_4)[CdI_4]\}^-$; $m/z = 1114$ for $\{(PPh_4)WS_4I\}^-$ and at $m/z = 650$ for $\{PPh_4WS_4\}^-$ fragment ions. The peaks in the corresponding spectrum of **4** are observed at $m/z = 930$ assigned to $\{(PPh_4)[I_2CdS_2MoS_2]\}^-$ and at $m/z = 961$ for the $\{(PPh_4)CdI_4\}^-$ moiety. The positive-ion FAB-MS spectra of complexes **1** and **4** show intense peaks at $m/z = 340$ for the $[PPh_4]^+$ ion, medium peaks at $m/z = 1696$ and a weak peak at $m/z = 1608$ corresponding to $\{(PPh_4)_3I_2CdS_2WS_2\}^+$ and $\{(PPh_4)_3[I_2CdS_2MoS_2]\}^+$ molecular ions, respectively.

Electrochemical studies

All the complexes show multi-step irreversible reductive responses in their cyclic voltammograms scanned in the potential range 0.0 to −2.0 V in acetonitrile TEAP medium using glassy-carbon as working electrode and Ag—AgCl as reference electrode. The positions of the actual responses (Table 5) indicate that the reduction waves are localized within the $[WS_4]^{2-}$ cores. [4c,29] In the Zn^{II} cases, however, single irreversible oxidative responses observed at *ca* +0.80 V for **3** and +0.39 V for **6** *vs* Ag—AgCl are attributable to the oxidations at the sulfur centers of the respective $[MS_4]^{2-}$ ligand [29].

Acknowledgments—We thank the Head, RSIC (Regional Sophisticated Instrumentation Centre), I.I.T., Madras, for X-ray crystallographic data collection (by Dr Manisekaran) facilities and the Alexander Von Humbolt Foundation, Bonn, for the donation of the IR spectrophotometer used in this work. We also thank the Department of Geological Sciences, Jadavpur University, for X-ray powder diffraction data. Financial assistance from D.S.T. and U.G.C., New Delhi is acknowledged.

REFERENCES

1. Rakowski Dubois, M., *Chem Rev.* 1989, **89**, 1.
2. Gates, B. C., *Catalytic Chemistry*, John Wiley and Sons, New York, 1991.
3. (a) *Iron–Sulphur Proteins*, ed. T. G. Spiro. Wiley, New York, 1982; (b) *Metalloproteins Chemical Properties and Biological Effects*, ed. S. Otsuka and T. Yamanaka. Elsevier, New York, 1987.
4. (a) Müller, A. and Diemann, E., *J. Chem. Soc., Chem. Commun.* 1971, 65; (b) Søtofte, I., *Acta Chem. Scand. Ser. A* 1976, **30**, 157; (c) Callahan, K. P. and Piliero, P. A., *Inorg. Chem.* 1980, **19**, 2619.
5. Müller, A., Chakravorti, M. C. and Dornfeld, H., *Z. Naturforsch., B., Inorg. Chem. Org. Chem.* 1975, **30B**, 162.
6. (a) Müller, A., Hellmann, W., Schneider, J., Schimanski, J., Demmer, U., Trautwein, A. and Bender, U., *Inorg. Chim. Acta* 1982, **65**, L41; (b) Stremple, P., Baenziger, N. C. and Coucouvanis, D., *J. Am. Chem. Soc.* 1981, **103**, 4601.
7. Paulat-Böschen, I., Krebs, B., Müller, A., Königer-Ahlborn, E., Dornfeld, H. and Schultz, H., *Inorg. Chem.* 1978, **17**, 1440.
8. Müller, A., Hellmann, W., Schimanski, U., Jostes, P. and Newton, W. E., *Z. Naturforsch* 13: *Inorg. Chem. Org. Chem.* 1983, **38**, 528.
9. Howard, K. E. and Rauchfuss, T. B., *Inorg. Chem.* 1988, **27**, 3561.
10. Müller, A. and Diemann, E., *Coord. Chem. Dev.* 1973, **10**, 79.
11. Manoli, J. M., Potvin, C. and Sécheresse, F., *Inorg. Chem.* 1987, **26**, 340. (See also ref. 26)
12. Müller, A., Diemann, E., Jostes, R. and Bögge, H., *Angew, Chem. Int. Ed. Engl.* 1981, **20**, 934.
13. Shapley, P. A. Gebeyehu, Z. and Wilson, S. R., *Inorg. Chem.* 1993, **32**, 5646.
14. (a) Otvos, J. D., Olafson, R. W. and Armitage, I. M. *J. Biol. Chem.* 1982, **257**, 2427; (b) Gierdroe, D. P., Johnson, B. A., Armitage, I. M. and Coleman, J. E., *Biochem.* 1989, **28**, 2410.
15. Ghosh, I., Mishra, R., Poddar, D., Mukherjee, A. K., Mukherjee, M. and Bhattacharyya, R., *J. Chem. Soc., Chem. Commun.* 1996, 435.
16. McDonald, J. W., Friesen, G. D., Rosenhein, L. D. and Newton, W. E., *Inorg. Chim. Acta* 1983, **72**, 205.

17. Perrin, D. D., Armergo, W. L. F. and Perrin, D. R., *Purification of Laboratory Chemicals*. Pergamon, New York, 1966.
18. North, A. T. C., Phillips, D. C. and Mathews, F. S., *Acta Cryst.* 1968, **A24,** 351.
19. Sheldrick, G. M., *SHELXL* 93, *Program for Crystal Structure Refinement*. University of Göttingen, Germany, 1993.
20. Müller, A., *Polyhedron* 1986, **5,** 323.
21. (a) Shibahara, T., *Coord. Chem. Rev.* 1993, **123,** 73; (b) Garry, S. H. L., Fisher, K. J., Vasallo, A. M., Hanna, J. V. and Dance, I. G., *Inorg. Chem.* 1993, **32,** 66, and refs therein.
22. Müller, A. and Schimanski, U., unpublished results.
23. Klopman, G., *J. Am. Chem. Soc.* 1968, **90,** 223.
24. Clark, R. J. H. and Williams, C. S., *Inorg. Chem.* 1965, **4,** 350.
25. (a) Coucouvanis, D., Stremple, P., Simhon, E. D., Baenjiger, N. C., Draganjac, M., Chan, L. T., Simopoulos, A., Papaefthymiou, V., Kostikas, V. and Petrouleas, U., *Inorg. Chem.* 1983, **22,** 293; (b) Cormier, A., Nakamoto, K., Königer-Ahlborn, E. and Müller, A., *J. Mol. Struct.* 1975, **25,** 43.
26. Bencini, A., Cecconi, F., Ghilardi, C. A., Midolleni, S., Nuzzi, F. and Oriandini, A., *Inorg. Chem.* 1992, **31,** 5329.
27. Johnson, C. K., ORTEP-II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, U.S.A., 1976.
28. Sakane, G., Shibahare, T., Hou, H. W., Yin, X. Q. and Shi, S., *Inorg. Chem.* 1995, **34,** 4785.
29. Sécheresse, F., Salis, M., Potvin, C. and Manoli, J. M., *Inorg. Chim. Acta* 1986, **114,** L19.