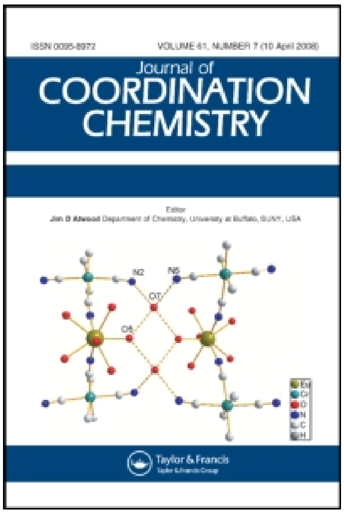

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SYNTHESIS OF TWO NOVEL HETEROBIMETALLIC CLUSTER COMPOUNDS $[NEt_4]_4[MS_4Cu_4I_6]$ (M = Mo, W). CRYSTAL STRUCTURE OF $[NEt_4]_4[MoS_4Cu_4I_6]$

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SYNTHESIS OF TWO NOVEL HETEROBIMETALLIC CLUSTER COMPOUNDS $[NEt_4]_4[MS_4Cu_4I_6]$ (M = Mo, W). CRYSTAL STRUCTURE OF $[NEt_4]_4[MoS_4Cu_4I_6]$

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Two new cluster compounds $[NEt_4]_4[MS_4Cu_4I_6]$ (**1**: M = Mo; **2**: M = W) have been obtained by the reaction of $[NH_4]_2[MS_4]$ (M = Mo, W), CuBr, $[NEt_4]I$ and $[Bu^n_4N]I$ in the solid state. Dark red crystals of **1** are monoclinic, space group *C2/m* with cell dimensions a = 29.686(6), b = 12.778(2), c = 15.308(3)Å, β = 99.53(2)°, Z = 4, D_{calc} = 2.04g cm^{-3}, R = 0.052 for 4021 observed reflections. The X-ray analysis shows that four edges of the tetrahedral MoS_4^{2-} core are coordinated by four copper atoms, giving a MoS_4Cu_4 aggregate of approximate C_{2v} symmetry. The Mo–Cu lengths range from 2.650(2) to 2.686(1)Å.

KEYWORDS: Tetrathiomolybdate and tungstate, copper, solid state reaction, cluster compounds, X-ray crystal structure

INTRODUCTION

The chemistry of the tetrathiometallates MS_4^{2-} (M = Mo, W) has been extensively developed.[1] This interest has been caused by the ability of tetrathiometallates to coordinate to transition metals[2] and particularly with copper. The reaction of CuCl,[3–8] CuBr,[9] CuCN[10] and CuNCS[11–12] with MS_4^{2-} has led to a large number of heterometallic cluster compounds which have been crystallographically characterized. So far, almost all of these Mo(W)–Cu–S cluster compounds reported in the literature have been prepared in solution. Recently, we have studied mixed-metal cluster compounds formed by the reaction of CuX (X = Cl, Br, I, CN, NCS) with $[NH_4][MYS_3]$ (M = Mo, W; Y = O, S) in the solid state at low temperatures; a number of mixed metal cluster compounds have been obtained.[13–16] The synthesis

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and structural charaterization of the two new cluster compounds $[NEt_4]_4[MoS_4Cu_4I_6]$ (**1**: M = Mo; **2**: M = W) are described here.

EXPERIMENTAL

All solid state reactions were carried out in an atmosphere of pure argon. IR spectra (KBr pellets) were recorded with a Fourier Nicolet FT-170 SX spectrophotometer and electronic spectra on a shimada UV-240 spectrophotometer (CH_3CN solution, $10^{-3}M^{-1}cm^{-1}$). Carbon and hydrogen analyses were performed on a PE-240C Elemental Analyser. Molybdeum, tungsten and copper analyses were performed on a JA-1100 ICP spectrophotometer. Cyclic voltammetry measurements were performed on a PAR Model 370 electrochemical apparatus equipped with an X–Y recorder at room temperature under anaerobic conditions, using a three electrode system with a vitreous carbon working electrode, a platinum wire auxiliary electrode and a SCE reference electrode. The supporting electrolyte was $(n\text{-}Bu)_4NBF_4$ (0.1 M) and the samples were dissolved in DMF solution (2.5×10^{-3}M). The scan rate was 100 mV/s. $[NH_4]_2[MS_4]$ (M = Mo, W) was prepared to the literature.[17] Other reactants and solvents were used as purchased.

Synthesis of $[NEt_4]_4[MoS_4Cu_4I_6]$ (1)

A well-ground mixture of $[NH_4]_2[MoS_4]$ (0.26 g, 1.0 mmol), CuI (0.19 g, 1.0 mmol), $[NEt_4]I$ (0.26 g, 1.0 mmol) and $[Bu^n_4N]I$ (0.37 g, 1.0 mmol) was put into a reaction tube. A dark red solid was obtained by heating the mixture in the solid state at 110°C for 15h. After extracting the product with CH_2Cl_2 (40 cm^3) and filtering the dark red coloured extract, the filtrate, on slow evaporation by standing in air at room temperature, deposited 0.12 g (27.3%) of the dark red crystals of **1**. Anal. Calcd. for $C_{32}H_{80}Cu_4I_6MoN_4S_4$: C, 21.8; H, 4.6; N, 3.2; Cu, 14.4; Mo, 5.5%. Found: C, 21.7; H, 4.6; N, 3.4; Cu, 14.1; Mo, 5.1%.Crystals of the title compound prepared as described proved suitable for X-ray crystallographic studies.

Synthesis of $[NEt_4]_4[WS_4Cu_4I_6]$ (2)

The homologous cluster compound of tungsten was prepared as above starting from $[NH_4]_2[WS_4]$ (0.36 g, 1.0 mmol). Yield: 0.08 g (17.3%) of reddish-orange crystals of **2**. Anal. Calcd. for $C_{32}H_{80}Cu_4I_6N_4S_4W$: C, 20.8; H, 4.4; N, 3.0; Cu, 13.8; W, 9.9%. Found: C, 20.7; H, 4.3; N, 3.3; Cu, 13.6; W, 9.4%. Attempts to cultivate its single crystal failed.

Intensity data collection and structure analysis

A single crystal of **1** was mounted in a random orientation on a glass fibre. Data were collected using a Nicolet R3m/E four-circle diffractometer with graphite-monochromated Mo–K$_\alpha$ (λ = 0.71073Å1) at room temperature. Cell contants were obtained by least-squares analysis on 24 diffraction maxima (the search limits of 2θ: 7.65°–23.70°). Details of the data collection together with structure refinement are summarized in Table 1.

Table 1 Summary of crystal data and data collection parameters for 1.

Compound	$[NEt_4]_4[MoS_4Cu_4I_6]$
Chemical formula	$C_{32}H_{80}Cu_4I_6MoN_4S_4$
Formula weight	1760.9
Crystal system	monoclinic
Space group	C 2/m
a(Å)	29.686(6)
b(Å)	12.778(2)
c(Å)	15.308(3)
β(°)	99.53(2)
V(Å^3)	5727(2)
Z	4
μ(cm^{-1})	50.43
F(000)	3359
$D_{calc.}$ (g cm^{-3})	2.04
Crystal dimension (mm)	0.16 × 0.20 × 0.52
Radiation	Mo-K_α (λ = 0.71074 Å)
Transmission factors	0.672–0.932
Scan mode	θ–2θ
Scan width	1.6
Scan rate (° min^{-1})	8
2θ range (°)	2–50
Unique data measured	5451
Unique data used	4021 ($I > 3.0\sigma(I)$)
No. of variables	308
$(\Delta/\sigma)_{max}$	−0.175
R(int)	0.0225
R^a, R_w^b	0.0520, 0.0464
Goof(or S)	1.192
largest/smallest peaks in final diff. map (e Å^{-3})	1.060/ − 1.074

$^a R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$.

$^b R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$. $w = 1/[\sigma^2(|F_o| + 0.00015|F_o|^2)]$.

Intensity data were corrected for LP factors and for absorption empirically based on DIFABS program[18]. There was no evidence of crystal decay from standard reflections monitored every 1.5h of exposure. The structure was solved by the heavy-atom method. Three dimensional paterson maps revealed the position of the molybdenum atom. Successive least-squares refinements and difference Fourier calculations revealed the positions of the remaining non-hydrogen atoms. For the title compound, the summation of the cations was kept four as cations containing N(4) and N(5) atoms are given site occupancy factors of 0.5 and 0.5, respectively. Cations containing N(3), N(4) and N(5) are disordered. In the cation containing N(3) atom, atoms C(13)–C(20) are disordered. In the cations containing N(4) and N(5) atoms, atoms C(21)–C(25) and C(26)–C(30) are also disordered. The refinements of occupancy factors converged respectively to 0.5 and 0.5. Anisotropic temperature factors were introduced for all atoms of the anion and the cations. Hydrogen atoms were not included in the refinements. Neutral atom scattering factors with anomalous dispersion corrections were taken from ref. **19**. Atomic parameters were refined by full-matrix least-squares method using SHELXTL program package (Nicolet corporation, 1986) on an Eclipse S/140 computer. Atomic coordinates and isotropic thermal parameters are given in Table 2. Selected bond lengths and bond angles are listed in Table 3.

Table 2 Atomic coordinates (× 10^4) and isotropic thermal parameters ($Å^2$ × 10^3).

Atom	X	Y	Z	U*
Mo	3675(1)	0	2001(1)	30(1)
Cu(1)	3773(1)	1626(1)	3128(1)	56(1)
Cu(2)	3699(1)	1508(1)	821(1)	72(1)
I(1)	4413(1)	2769(1)	2331(1)	58(1)
I(2)	3549(1)	2428(1)	4512(1)	66(1)
S(1)	3233(1)	1437(2)	1861(1)	42(1)
S(2)	4106(1)	0	941(2)	43(1)
S(3)	4117(1)	0	3315(2)	42(1)
N(1)	643(3)	5000	2787(7)	53(4)
N(2)	2179(3)	0	3474(7)	45(4)
N(3)[a]	2067(3)	0	8365(6)	41(3)
N(4)[a]	0	0	5000	45(5)
N(5)[a]	0	0	0	46(5)
C(1)	327(6)	5000	3480(1)	95(8)
C(2)	598(8)	5000	4419(1)	122(1)
C(3)	297(5)	5000	1929(1)	74(6)
C(4)	524(8)	5000	1079(1)	113(1)
C(5)	957(3)	4045(8)	2846(7)	67(4)
C(6)	727(4)	2984(1)	2797(1)	92(5)
C(7)	2229(8)	0	2489(1)	99(9)
C(8)	1748(1)	0	1893(2)	140(1)
C(9)	2690(7)	0	3937(2)	103(9)
C(10)	2715(2)	0	4954(2)	199(9)
C(11)	1926(4)	944(1)	3715(9)	86(5)
C(12)	2133(4)	1999(9)	3471(9)	85(5)
C(13)[a]	1975(7)	702(2)	7626(1)	65(7)
C(14)[a]	1519(7)	0	6876(1)	104(9)
C(15)[a]	1733(6)	-709(1)	8740(1)	56(7)
C(16)[a]	1361(5)	0	9100(1)	82(7)
C(17)[a]	2284(7)	783(2)	9067(1)	70(8)
C(18)[a]	2570(8)	0	9839(2)	161(2)
C(19)[a]	2402(6)	-696(2)	8010(1)	62(7)
C(20)[a]	2766(7)	0	7599(6)	114(1)
C(21)[a]	169(8)	0	4056(2)	59(1)
C(22)[a]	699(6)	0	4237(2)	112(1)
C(23)[a]	207(6)	-963(2)	5503(1)	51(6)
C(24)[a]	0	-2011(1)	5000	91(8)
C(25)[a]	-501(7)	0	4735(2)	56(1)
C(26)[a]	-275(7)	-954(2)	185(1)	66(8)
C(27)[a]	0	-2009(1)	0	94(8)
C(28)[a]	470(1)	0	581(2)	77(1)
C(29)[a]	391(8)	0	1623(1)	117(1)
C(30)[a]	119(1)	0	-938(2)	76(1)

*Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.
[a]occupancy factor = 0.5.

RESULTS AND DISCUSSION

The crystal structure of **1** consists of a discrete $[MoS_4Cu_4I_6]^{4-}$ independent tetranion and four $[NEt_4]^+$ cations. Figure 1 depicts the structure of the anion $[MoS_4Cu_4I_6]^{4-}$.

The structure of the anion contains an essentially tetrahedral MoS_4 moiety bound by four copper atoms, forming a MoS_4Cu_4 aggregate showing nearly a C_{2v}

Table 3 Selected bond lengths (Å) and bond angles (°).

Mo–Cu(1)	2.686(1)	Mo–Cu(2)	2.560(2)	Mo–S(1)	2.247(2)
Mo–S(2)	2.226(4)	Mo–S(3)	2.211(3)	Mo–Cu(1a)	2.686(1)
Mo–Cu(2a)	2.650(2)	Mo–S(1a)	2.247(2)	Cu(1)–I(1)	2.828(1)
Cu(1)–I(2)	2.539(1)	Cu(1)–S(1)	2.315(2)	Cu(1)–S(3)	2.312(2)
Cu(2)–I(3)	2.488(1)	Cu(2)–S(1)	2.276(3)	Cu(2)–S(2)	2.265(2)
S(2)–Cu(2a)	2.266(2)	S(3)–Cu(1a)	2.313(2)		
Cu(1)–Mo–Cu(2)	82.1(1)	Cu(1)–Mo–S(1)	55.1(1)	Cu(2)–Mo–S(1)	54.7(1)
Cu(1)–Mo–S(2)	117.0(1)	Cu(2)–Mo–S(2)	54.5(1)	S(1)–Mo–S(2)	109.1(1)
Cu(1)–Mo–S(3)	55.3(1)	Cu(2)–Mo–S(3)	122.8(1)	S(1)–Mo–S(3)	109.6(1)
S(2)–Mo–S(3)	109.7(1)	Cu(1)–Mo–Cu(1a)	101.4(1)	Cu(2)–Mo–Cu(1a)	171.2(1)
S(1)–Mo–Cu(1a)	133.9(1)	S(2)–Mo–Cu(1a)	117.0(1)	S(3)–Mo–Cu(1a)	55.3(1)
Cu(1)–Mo–Cu(2a)	171.2(1)	Cu(2)–Mo–Cu(2a)	93.3(1)	S(1)–Mo–Cu(2a)	127.6(1)
S(2)–Mo–Cu(2a)	54.6(1)	S(3)–Mo–Cu(2a)	122.8(1)	Cu(1)–Mo–S(1a)	133.9(1)
Cu(2)–Mo–S(1a)	127.6(1)	S(1)–Mo–S(1a)	109.6(1)	S(2)–Mo–S(1a)	109.1(1)
S(3)–Mo–S(1a)	109.6(1)	Mo–Cu(1)–I(1)	97.5(1)	Mo–Cu(1)–I(2)	146.4(1)
I(1)–Cu(1)–I(2)	116.0(1)	Mo–Cu(1)–S(1)	52.8(1)	I(1)–Cu(1)–S(1)	96.5(1)
I(2)–Cu(1)–S(1)	120.0(1)	Mo–Cu(1)–S(3)	51.9(1)	I(1)–Cu(1)–S(3)	101.7(1)
I(2)–Cu(1)–S(3)	115.5(1)	S(1)–Cu(1)–S(3)	103.9(1)	Mo–Cu(2)–I(3)	157.1(1)
Mo–Cu(2)–S(1)	53.6(1)	I(3)–Cu(2)–S(1)	126.4(1)	Mo–Cu(2)–S(2)	53.2(1)
I(3)–Cu(2)–S(2)	119.0(1)	S(1)–Cu(2)–S(2)	106.7(1)	Mo–S(1)–Cu(1)	72.1(1)
Mo–S(1)–Cu(2)	71.7(1)	Cu(1)–S(1)–Cu(2)	99.5(1)	Mo–C(2)–Cu(2)	72.3(1)
Mo–S(2)–Cu(2a)	72.3(1)	Cu(2)–S(2)–Cu(2a)	116.5(2)	Mo–S(3)–Cu(1)	72.8(1)
Mo–S(3)–Cu(1a)	72.8(1)	Cu(1)–S(3)–Cu(1a)	128.0(1)		

symmetry. The MoS_4 core has retained the tetrahedral coordination geometry (bond lengths between 2.211(3)–2.247(2) Å and angles between 109.1(1)°–109.7(1)°) with Mo and two sulphur S(2) and S(3) atoms lying a crystallographic mirror plane. There are two types of copper atoms in the MoS_4Cu_4 aggregate. The two copper Cu(1) and Cu(1a) atoms have a distored tetrahedral geometry giving a S_2CuI_2 arrangement involving two bridging sulphur atoms and two iodine atoms. The another two copper Cu(2) and Cu(2a) atoms thave a trigonal planar coordination forming S_2CuI unit. It is noted that the Cu(1)–I(1) length (2.828(1) Å) is 0.29 Å longer than that of the Cu(1)–I(2) lenght (2.539(1) Å), or 0.34 Å longer than that of the Cu(2)–I(3) length (2.488(1) Å). The I(1) and I(1a) atoms involved in the longer Cu–I bonds do not serve as bridging ligands with Cu(2) and Cu(2a), respectively, because the shortest I(1)–Cu(2) or I(1a)–Cu(2a) contact of 3.29 Å precludes any μ_2-I bridges, as observed for the Cl atoms in $[NMe_4]_4[MoS_4Cu_5Cl_7]$[7] and $[NMe_4]_5[MoS_4Cu_6Cl_9]$[8]. The Cu–S lengths also reflects the mode of coordination of the copper atoms, av. 2.313 Å for the tetrahedral environment, av. 2.270 Å for the trigonal geometry. These Cu–S lengths are very similar to those reported in $[NMe_4]_5[MoS_4Cu_6Cl_9]$ (2.268(15)–2.339(2) Å)[8] or in $[NEt_4]_2$ $[MoS_4(CuNCS)_4]$ (2.275(2)–2.291(2) Å)[11]. Owing to the different coordination mode of the copper atoms, the Mo–Cu lengths are slightly different, 2.686(1) Å for the tetrahedrally-coordinated Cu(1) and Cu(1a) and 2.650(2) Å for the trigonally-coordinated Cu(2) and Cu(2a), respectively. These values are typical of corresponding lengths observed in other Mo(W)–Cu–S clusters (e.g. 2.658(1)–2.6997(1) Å in $[MoS_4Cu_4I_2(Py)_6]$[20] or 2.674(1)–2.682(1) Å in $[NEt_4]_2[MoS_4(CuNCS)_4]$[11] or 2.618(3)–2.685(3) Å in $[PPh_4]_2[MoS_4(CuBr)_4]\cdot Me_2CO)$[9].

In the i.r. spectra of **1** and **2**, bands at 442s cm^{-1} (**1**) and 432s cm^{-1} (**2**) are assigned to the bridged MoS_4 group and WS_4 group, respectively. The electronic

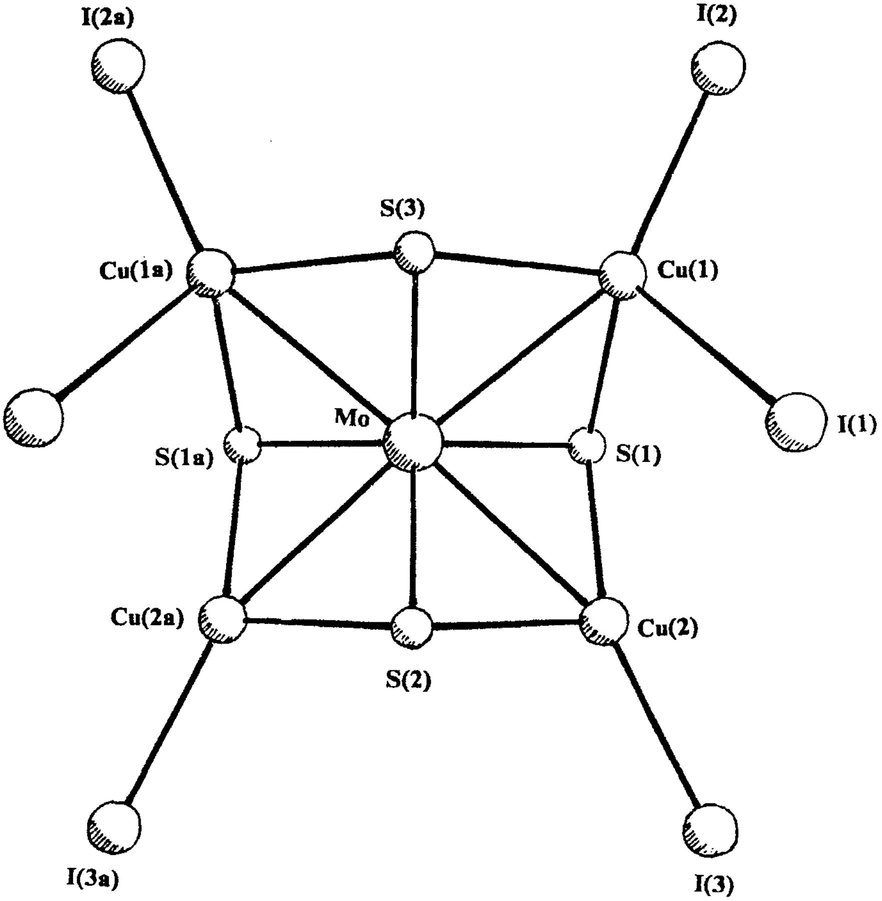


Figure 1 Structure of the cluster anion $[\mathrm{MoS_4Cu_4I_6}]^{4-}$.

spectra (Figure 2) of **1** and **2** is characterized by absorption at 515 (3.0), 403 (sh), 301 (15.3) and 269 (25.9)nm for **1**, at 506 (3.4), 399 (sh), 297 (16.5) and 260 (26.7)nm for **2**. The principal features are attributed to the charge-transfer transitions of $\mathrm{MS_4^{2-}}$ (M = Mo, W)[1,21,22].

Cyclic voltammetric measurement for **1** in DMF in the range −2.0–0.0 V displays one irreversible oxidation wave ($\mathrm{Ep_a}$ = −0.20 V) and three irreversible reduction waves ($\mathrm{Ep_{c1}}$ = −0.69 V, $\mathrm{Ep_{c2}}$ = −1.23 V, $\mathrm{Ep_{c3}}$ = −1.41 V) (Figure 3). While **2** shows one irreversible oxidation wave ($\mathrm{Ep_a}$ = −0.17 V) and one irreversible reduction wave ($\mathrm{Ep_c}$ = −0.75 V) (Figure 4).

The compound $[\mathrm{Bu^n_4N}]\mathrm{I}$ is used to decrease the melting point of the solid mixture in the solid state reaction. It is noted that there contains no $[\mathrm{Bu^n_4N}]^+$ but $[\mathrm{NEt_4}]^+$ cations in the title compound. The fact may be due to solubility difference in $\mathrm{CH_2Cl_2}$. It is of interest to note that, because the fifth and sixth edges of the $\mathrm{MoS_4}$ tetrahedron in the anion are uncoordinated, another one or two copper atoms may

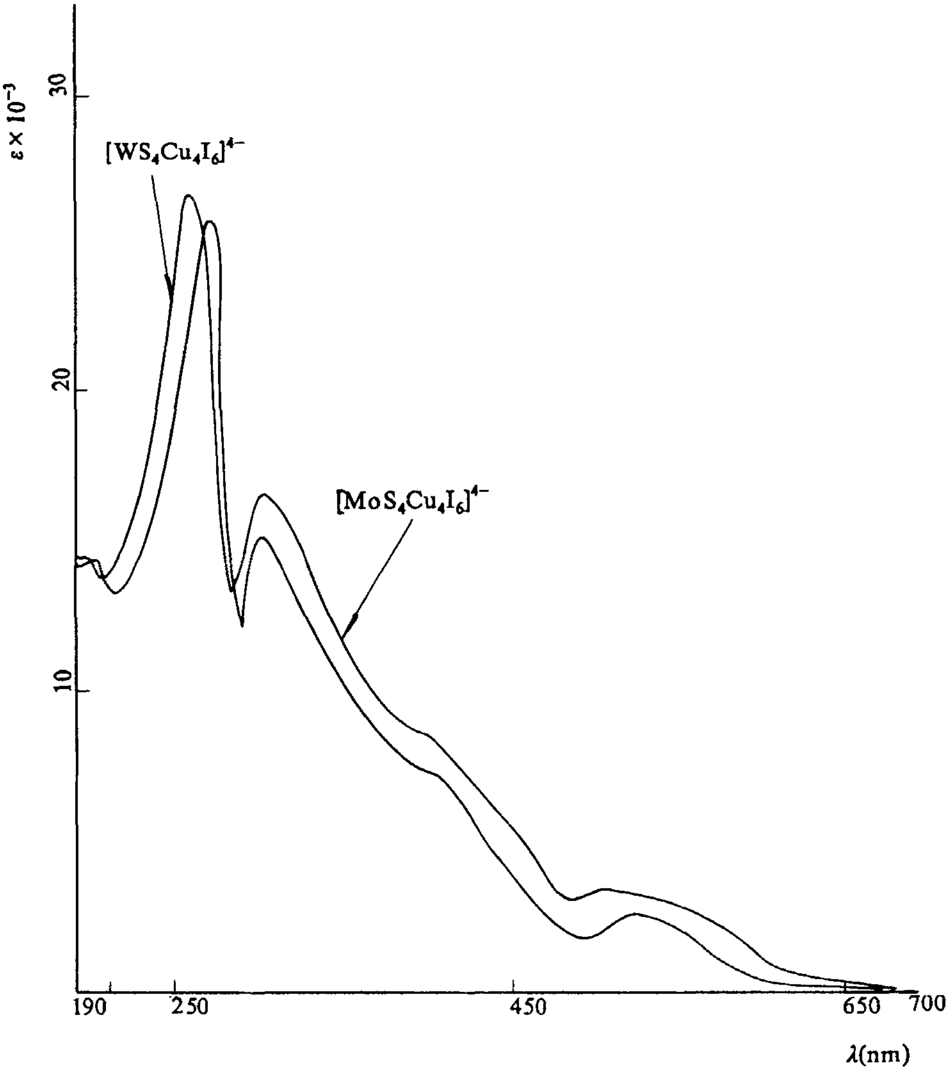


Figure 2 Electronic spectra of $[NEt_4]_4[MS_4Cu_4I_6]$ (M = Mo W) in acetonitrile solution.

attach to them and form MoS_4Cu_5 or MoS_4Cu_6 aggregate. As a matter of fact, Secheresse et al. has recently prepared and structurally characterized two hexanuclear compouns $[NMe_4]_4[MS_4Cu_5Cl_7]$ (M = Mo, V)$^{6-7}$ and one heptanuclear compound $[NEt_4]_5[MoS_4Cu_6Cl_9]^8$. We have also obtained and structurally determined one hexanuclear compound $[NEt_4]_4[WS_4Cu_5Br_7]^{23}$ and three heptanuclear compounds $[MS_4Cu_6X_6]_n$ (1: M = Mo, X = Br; 2: M = W, X = Br; 3: M = W, X = I)^{24} by the reaction of $[NH_4]_2[MS_4]$(M = Mo, W), CuX (X = Br, I) and $[NR_4]$X (R = Et, n–Bu; X = Br, I) in the solid state and pyridine substitution of the solid state product in acetonitrile.

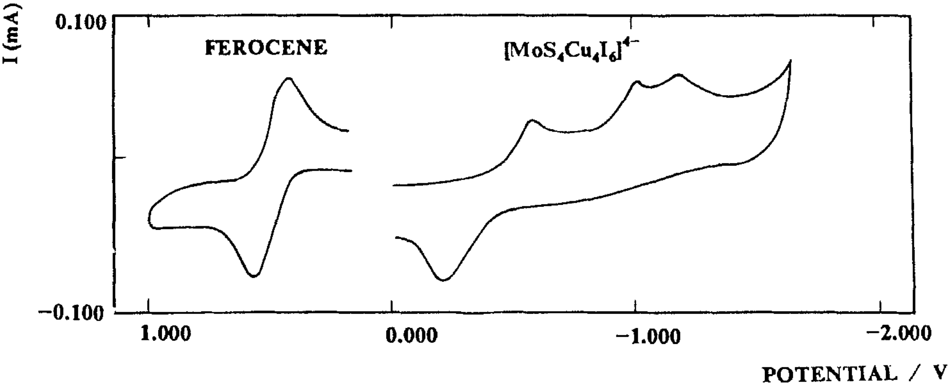


Figure 3 Cyclic voltammogram of ca. 2.5×10^{-3} M $[NEt_4]_4[MoS_4Cu_4I_6]$ and ferrocene in a solution of 0.1 M $[Bu_4N]BF_4$ in DMF at room temperature; scan rate 100 mVs^{-1}.

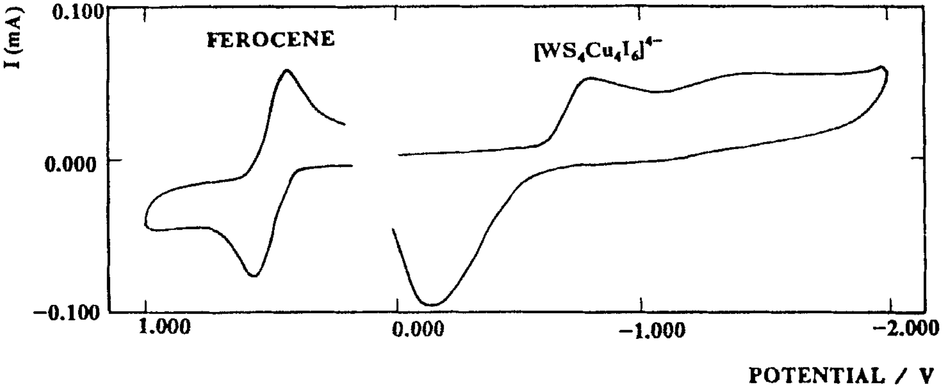
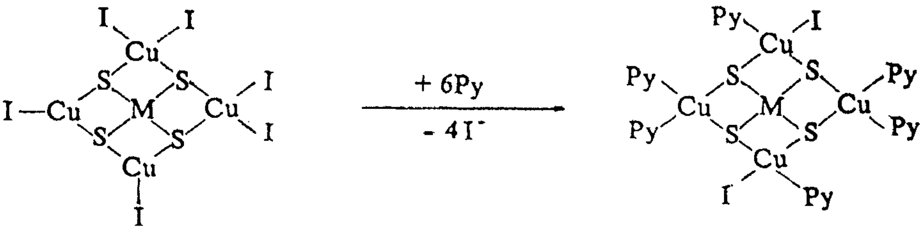


Figure 4 Cyclic voltammogram of ca. 2.5×10^{-3} M $[NEt_4]_4[MoS_4Cu_4I_6]$ and ferrocene in a solution of 0.1 M $[Bu_4N]BF_4$ in DMF at room temperature; scan rate 100 mVs^{-1}.

Another interesting reaction is the substitution of the iodine groups in anion $[MS_4Cu_4I_6]^{4-}$ in solution with strong ligands such as pyridine, forming one kind of substitution product $[MS_4Cu_4I_2(Py)_6]$.[20,25] This reaction can be described as follows:



While using PPH_3 in CH_3CN, the substitution reaction led to a different product $[MS_4Cu_2(PPh_3)_3]$ (M = Mo, W),[26,27] the formation of which are considered as collapse of the aggregate $[MS_4Cu_4I_6]^{4-}$. This substitution reaction can be described as follows:

$$[MS_4Cu_4I_6]^{4-} + 3PPh_3 \longrightarrow [MS_4Cu_2(PPh_3)_3] + 2CuI + 4I^-$$

It is expected that substitution of the I groups in the anion $[MS_4Cu_2I_6]^{4-}$ with other strong ligands ($PPh_2CH_2PPh_3$, S_2CNR^{-1}, etc.) may produce a series of new interesting cluster compounds. Research on this respect of the work is under way.

Supplementary material

Complete lists of bind lengths, bond angles, thermal parameters and observed and calculated structure factors for the title compound have been deposited with the editor and are available upon request.

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