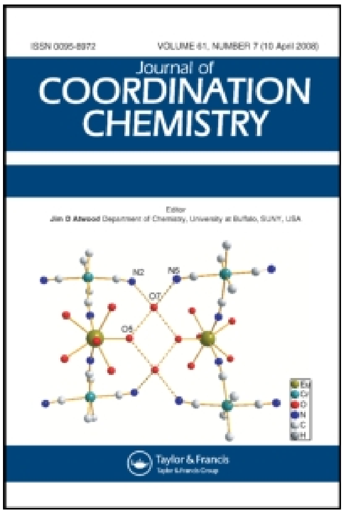

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SYNTHESIS OF TWO NOVEL POLYMERIC HETERONUCLEAR CLUSTER COMPOUNDS, $[MoS_4Cu_6X_4\ (Py)_4]_n$ (X = Br, I). CRYSTAL STRUCTURE OF $[MoS_4Cu_6Br_4\ (Py)_4]_n$

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The title compounds $[MoS_4Cu_6X_4(Py)_4]_n$ (**1**:X = Br; **2**: X = I) were obtained by the reaction of $[NH_4]_2\ [MoS_4]$, CuX, and $[Bu_4^nN]X$ (X = Br, I) in the solid state and pyridine substitution of the solid state product in acetonitrile. Dark crystals of 1 are tetragonal, space group $I\bar{4}2d$ with unit cell parameters a = 14.611 (3), c = 15.119 (13) Å; V = 3227.1 Å^3; Z = 4, D_{calc} = 2.55 g cm^{-3}, R = 0.030 for 586 observed reflections. The X-ray analysis confirms that the structure, which possesses a crystallographic $\bar{4}$ symmetry axis situated at the Mo atom, consists of a tetrahedral MoS_4 core enveloped by an octahedral array of six copper atoms, forming an MoS_4Cu_6 aggregate. Linked by $-Cu_{eq}-Br-Cu_{eq}-$ bridges, this aggregate connects with its nearest, neighbours and develops a two-dimentional network. The Mo-Cu lengths range from 2.645(1) to 2.668(1) Å.

KEYWORDS: tetrathiomolybdate, copper, solid state reaction, cluster compounds, X-ray structure

INTRODUCTION

The tetrathiometallate anions MS_4^{2-} (M = Mo, W, V, Re) have been shown to act as multidentate ligands with a wide variety of metal ions[1] and particularly with copper. The reaction of Cu^+ with MS_4^{2-} has led to a large number of heteronuclear compounds.[2–12] The number of polymeric heteronuclear Mo (W, V, Re) -Cu-S clusters is small.[7,9,11] We have recently undertaken investigations of cluster compounds formed by reaction of $[NH_4]_2[MS_4]$ (M = Mo, W) with CuX (X = Cl, Br, I, CN, NCS) in the solid state and have prepared and structurally characterized

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a number of mixed-metal cluster compounds.[13–17] As a novel extension of this research, we report the synthesis and structural characterization of the two new polymeric heptanuclear cluster compounds $[MoS_4Cu_6X_4(Py)_4]_n$ (**1**:X = Br; **2**: X = I). The substitution of the solid state products with strong ligands such as pyridine and triphenylphosphine is discussed.

EXPERIMENTAL

$[NH_4]_2[MoS_4]$ was prepared by a literature method.[18] Other reactants and solvents were used as purchased. Infrared spectra (KBr pellets) were recorded on a Nicolet FT-170 SX spectrophotometer and electronic spectra on a Shimadzu UV-240 spectrophotometer (CH_3CN solution, $10^{-3}M^{-1}$). Carbon and hydrogen analyses were performed on a PE-240C elemental analyser. Molybdenum and copper analyses were performed on a JA-1100 ICP spectrophotometer. All solid state reactions were carried out under a pure argon atomsphere.

Preparation of $[MoS_4Cu_6Br_4(Py)_4]_n$ *(1)*

A well-ground mixture of $[NH_4]_2$ $[MoS_4]$ (0.25 g, 1.0 mmol), CuBr (0.29 g, 2.0 mmol), and $[Bu^n_4N]Br$ (1.48 g, 4.0 mmol) was placed in a reaction tube. A dark red solid was obtained by heating the mixture at 95°C for 15h. After extracting the product with CH_2Cl_2 (40 cm^3), filtering the dark red extract and layering the filtrate with CH_3OH (15 cm^3), 0.14 g of dark crystals of **1a** (as an intermediate) were obtained several days later. The product thus obtained was dissolved in CH_3CN (20 cm^3) in a tube, which was then put into a closed beaker containing a small amount of pyridine. Slow diffusion of pyridine vapour into the tube at room temperature formed dark, octahedral crystals of **1** during a month. Yield: 0.10 g (24.2%). Anal: calcd. for $C_{20}H_{20}Br_4Cu_6MoN_4S_4$: C, 19.34; H, 1.63; N, 4.51; Cu, 30.71; Mo, 7.73%. Found: C, 19.31; H, 1.62; N, 4.59; Cu, 30.63; Mo, 7.55%.

Preparation of $[MoS_4Cu_6I_4(Py)_4]_n$ *(2)*

2 was prepared as above, starting from CuI (0.38 g, 2.0 mmol). Yield: 0.12 g of dark crystals of **2a** (as an intermediate) 0.07 g (14.7%) of dark crystals of **2**. Anal.: calc. for $C_{20}H_{20}Cu_6I_4MoN_4S_4$: C, 16.80; H, 1.41; N, 3.92; Cu, 26.40; Mo, 6.71%. Found: C, 16.70; H, 1.37; N, 4.07; Cu, 26.40; Mo, 6.32%. Attempts to grow single crystals failed.

X-ray crystallography of $[MoS_4Cu_6Br_4(Py)_4]_n$

Crystals of **1** suitable for X-ray determinations were obtained directly from the preparation. All measurements were made on samples mounted in random orientation on the tip of a glass fibre with exoxy, using a Nicolet R/3m four-circle diffractometer operating in the θ-2θ scan mode with graphite-monochromated Mo-K_α radiation at 293K. The cell constants and orientation matrix for data collection for **1** were based on 24 carefully centered reflections in the range $6.77° < 2\theta < 23.61°$. Details of the data collection together with structure refinement are summarized in Table 1.

Table 1 Summary of crystal data, intensity collection and structure refinement parameters for **1**.

Compound	$[MoS_4Cu_6Br_4(Py)_4]_n$
Chemical formula	$C_{20}H_{20}Br_4Cu_6MoN_4S_4$
Formula weight	1241.51 (for the monomer)
Crystal system	tetragonal
Space group	$I\bar{4}2d$
a (Å)	14.611(3)
b (Å)	14.611(3)
c (Å)	15.119(3)
V (Å^3)	3227.1
Z	4
μ(cm^{-1})	93.39
F (000)	2351
$D_{calc.}$ (g cm^{-1})	2.55
Crystal dimensions (mm)	0.34 × 0.38 × 0.45
Radiation	Mo-$K\alpha$ (λ = 0.71073 Å)
Scan mode	θ-2θ
Scan width (°)	1.6
Scan rate (° min^{-1})	8
2θ limits (°)	2-45
Unique data measured	2439
Unique data used	585 ($I > 3.0\sigma(I)$)
No. of variables	91
$(\Delta/\sigma)_{max}$	0.27
R (int)	0.055
R^a, R_w^b	0.030, 0.027
G	1.022
largest/smallest peaks in final diff. map (e Å^{-3})	0.520/-0.422

$^a R = \Sigma \mid \mid Fo \mid - \mid Fc \mid \mid / \Sigma \mid Fo \mid$.

$^b R_w = [\Sigma w(\mid Fo \mid - \mid Fc \mid)^2 / \Sigma w \mid Fo \mid^2]^{1/2}$; $w = 1/[\sigma^2(\mid Fo \mid + 0.00001 \mid Fo \mid^2)]$.

Intensity data were corrected for LP factors and for absorption empirically based on the DIFABS program.[19] 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 Patterson maps revealed the position of the Mo atom. Successive least-squares refinements and difference Fourier calculations revealed the positions of the remaining non-hyrdrogen atoms. Anisotropic temperature factors were introduced for these. Hydrogen atoms were not included in the calculations. Neutral atom scattering factors with anomalous dispersion corrections were taken from ref. 20. All calculations were performed on an Eclipse S/140 computer using the SHELXTL program package (Nicolet Corperation, 1986). Atomic coordinates and isotropic thermal parameters are given in Table 2.

RESULTS AND DISCUSSION

Selected bond distances and bond angles for **1** are listed Table 3. Figures 1 and 2 show the configuration and the molecular arrangment of **1** in the unit cell, respectively. The structure consists of an essentially tetrahedral MoS_4 moiety encapsulated by a slightly distorted octahedron of six copper atoms, forming an MoS_4Cu_6 aggregate with a crystallographic $\bar{4}$ symmetry axis situated at the Mo atom. Linked by -Cu_{eq}-Br-Cu_{eq}- bridges, this aggregate connects with its nearest

Table 2 Atomic coordinates (× 10^4) and isotropic thermal parameters (Å^2 × 10^3) for **1**.

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U*
Mo	5000	0	2500	25(1)
Cu(1)	5000	0	750(1)	52(1)
Cu(2)	3505(1)	- 1032(1)	2676(1)	43(1)
Br(1)	5000	0	- 758(1)	64(1)
Br(2)	2500	- 89(1)	3750	50(1)
S	3744(1)	107(2)	1629(1)	33(1)
N	2755(5)	- 2142(5)	2522(7)	43(2)
C(1)	1864(8)	- 2087(9)	2438(13)	79(4)
C(2)	1317(10)	- 2858(11)	2389(18)	112(4)
C(3)	1705(9)	- 3704(9)	2481(16)	98(4)
C(4)	2623(9)	- 3763(7)	582(11)	75(3)
C(5)	3137(7)	- 2993(8)	2644(8)	53(3)

*Equivalent isotropic *U* defined as one third of the trace of the orthogonalised U_{ij} tensor.

neighbours and forms a two-dimensional network. The latter can be described as infinite sheets comprising the diagonal (101) plane as the mean plane. There is no unusually short van der Waals contact between the neutral two-dimensional sheets. It is worth noting that the structure of the core [MoCu$_6$] in **1** is very different from the core [MoCu$_6$] in the heptanuclear cluster. [NMe$_4$]$_5$ [MoS$_4$Cu$_6$Cl$_9$][6] or the core [VCu$_6$] in [VS$_4$Cu$_6$(PPh$_3$)$_5$Cl$_3$] · CH$_2$Cl$_3$.[10] The symmetry of the [MoCu$_6$] core in **1** is D_{4h}, while the symmetry of the [MoCu$_6$] core in [NMe$_4$]$_5$ [MoS$_4$Cu$_6$Cl$_9$][6] is C_{3v} and the [VCu$_6$] core in [VS$_4$Cu$_6$(PPH$_3$)$_5$Cl$_3$]·CH$_2$Cl$_2$[10] possesses practically no symmetry element.

The MoS$_4$ core has retained the ideal geometry of free thiomolybdate with the same Mo-S length (2.263(2)Å) and similar S-Mo-S angles (108.9(1)–109.8(1)°). Each copper atom is bound across an edge of the MoS$_4$ tetrahedron, giving each sulfur atom a μ_4 - S coordination. There are two types of copper atoms in the Cu$_6$ octahedron: two axial Cu(1) atoms and four equatorial Cu(2) atoms. Each axial Cu(1) atom has one terminal bromine atom and two μ_4S atoms, forming a trigonal geometry. Each equatorial Cu(2) atom is four-coordinated by a pair of μ_4-S atoms, one μ_2-Br atom, and one nitrogen atom of a pyridine molecule with a distorted tetrahedral BrCu(μ_4-S)$_2$N unit. It is of interest to note that the Cu$_{eq}$-Br length (2.587(1)Å) is about 0.30Å longer than Cu$_{ax}$-Br (2.280(2) Å), but is shorter than values observed in other Mo-Cu-S compounds containing tetrahedrally-coordinated

Table 3 Selected bond distances (Å) and angles (°) for **1**.

Mo-Cu(1)	2.645(1)	Mo-Cu(2)	2.668(1)	Mo-S	2.263(2)
Cu(1)-Br(1)	2.280(2)	Cu(2)-Br(2)	2.587(1)	Cu(1)-S	2.270(2)
Cu(2)-S	2.322(2)	Cu(2)-S(a)	2.308(3)	Br(2)-Cu(2d)*	2.587(1)
Cu(2)-N	1.970(8)				
S-Mo-S(a)	109.8(1)	S-Mo-S(b)	109.8(1)	S-Mo-S(c)	108.9(1)
Br(1)-Cu(1)-S	125.8(1)	S-Cu(1)-S(c)	108.4(1)	Br(1)-Cu(1)-S(c)	125.8(1)
Br(2)-Cu(2)-S	97.6(1)	Br(2)-Cu2-N	101.3(3)	S-Cu(2)-N	126.4(3)
Br(2)-Cu(2)-S(a)	106.8(1)	S-Cu(2)-S(a)	105.5(2)	N-Cu(2)-S(a)	115.2(2)
Mo-Cu(1)-Br(1)	180.0(1)	Cu(1)-Mo-Cu(1a)	180.0(1)	Cu(2)-Mo-Cu(2a)	90.6(1)
Cu(2)-Mo-Cu(2)	90.6(1)	Cu(2)-Mo-Cu(2c)	168.6(1)	Cu(2)-Br(2)-Cu(2d)	115.6(1)
Cu(1)-Mo-Cu(2)	95.7(1)	Cu(1)-Mo-Cu(2c)	84.3(1)	Cu(1)-Mo-Cu(2a)	84.3(1)
Cu(1)-Mo-Cu(2b)	95.7(1)				

*Equatorial copper atom in the nearest [MoCu$_6$] unit.

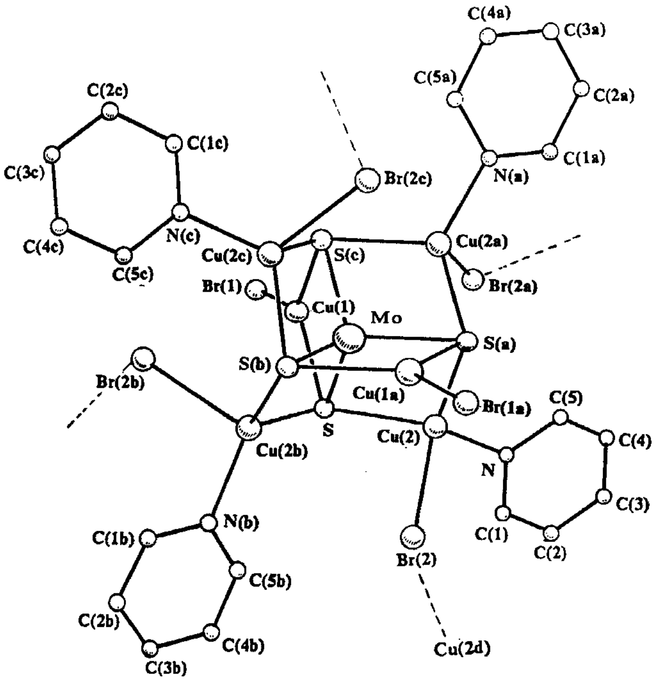

Figure 1 The molecular structure of $[MoS_4Cu_6Br_4(Py)_4]_n$.

Cu (*e.g.*, 2.776(2)–2.840(3)Å in $\{Cu_3MoS_3Br\}$ $(PPh_3)_3S \cdot 0.5\ Me_2CO)$.[2] This difference, which results from different coordination of two kinds of copper in **1** was reported in other similar compounds (*e.g.*, $(Cu\text{-}Cl)_{av}$ = 2.17(1)Å for trigonally planar coordinated Cu $(Cu\text{-}Cl)_{av}$ = 2.49(1)Å for tetrahedrally coordinated Cu in $[NMe_4]_5$ $[MoS_4Cu_6Cl_9]$[6]. The Cu-S lengths also reflect the mode of coordination of the copper atoms, 2.270(2)Å for trigonal geometry, 2.308(3)–2.322(2)Å for a tetragonal environment. These Cu-S lengths are very similar to those reported for $[NMe_4]_5$ $[MoS_4Cu_6Cl_9]$[6] and $[VS_4Cu_6(PPh_3)_5Cl_3] \cdot CH_2Cl_2$.[10] Owing to the slight distortion of the Cu_6 octahedron, the Mo-Cu lengths are slightly different, 2.645(1) Å for $Mo\text{-}Cu_{ax}$ and 2.668(1)Å for $Mo\text{-}Cu_{eq}$, respectively. These values are typical of corresponding bonds observed in other Mo-Cu-S clusters (*e.g.*, 2.633(4)–2.703(3)Å in $[NEt_4]_5[MoS_4Cu_6Cl_9]$)[6]. Since the Br(1a)-Cu(1a)-Mo, Cu(1a)-Mo-Cu(1) and Mo-Cu(1)-Br(1) angles are very close to 180° and the Mo atom remains situated on the $\bar{4}$ symmetry axis, the Br(1), Cu(1), Mo, Cu(1a) and Br(1a) atoms are colinear. The Cu(2)-Mo-Cu(2c) angle is about 170°, showing that the Mo atom is slightly displaced from the mean plane composed of the four equatorial copper atoms.

Since a nearly perfect T_d symmetry is observed for the MoS_4 core in **1** and **2**, only one strong ν (Mo-S) frequency is observed in the i.r. spectra of **1** and **2**, located at 438s cm^{-1} and 437s cm^{-1}, respectively. These absorptions are lower than in $[NH_4]_2[MoS_4]$ (ν(Mo-S), 472 cm^{-1}).[1] The electronic spectra (Figure 3) of **1** and **2** are characterized by absorptions at 530 (3.4), 350 (sh) and 295 (12.9) nm for **1**, and

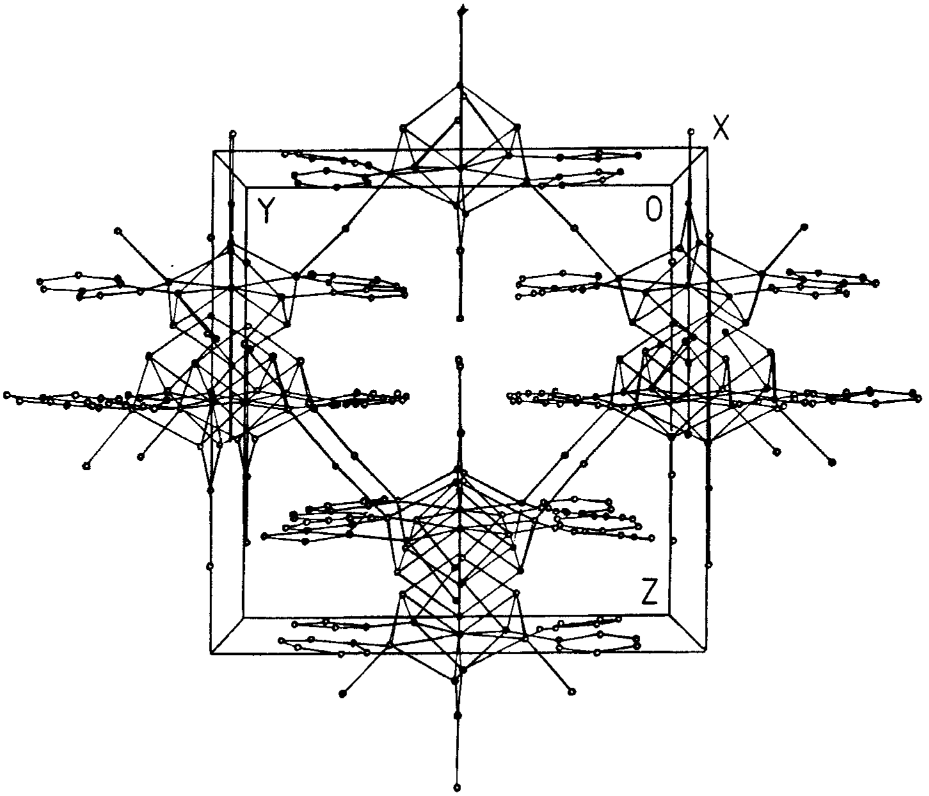

Figure 2 Stereoview of the molecular packing of [MoS$_4$Cu$_6$Br$_4$(Py)$_4$]$_n$.

535 (3.3), 340 (sh) and 285 (13.3) nm for **2**. The principal features are attributed to charge- transfer transitions of MoS$_4^{2-}$.[1,21,22] The polymeric structure mentioned above has little influence on the electronic spectra of **1** and **2** compared with those of related compounds (*e.g.*, 512 (3.7), 360 (sh), 308 (10.5) nm in [NEt$_4$]$_4$ [MoS$_4$Cu$_5$Cl$_7$];[5a] 512 (3.3), 372 (sh) nm in [NEt$_4$]$_5$ [MoS$_4$Cu$_6$Cl$_9$])[6].

In the synthesis of the title compounds, the formula of the intermediate products **1a** or **2a** was concluded to be [Bu$_4^n$N]$_4$ [MoS$_4$Cu$_6$X$_8$] by i.r. spectra [for **1a**: ν (Mo-S) 437s, 419s cm^{-1}; for **2a**: ν (Mo-S) 445s, 419s cm^{-1}] and elemental analysis [for **1a**: calcd. for C$_{64}$H$_{144}$Br$_8$CU$_6$MoN$_4$S$_4$: C, 34.63; H, 6.51; N, 2.57; Cu, 17.32; Mo, 4.73% . Found: C, 34.51; H, 6.50; N, 2.61; Cu, 17, 18; Mo, 4.21%. For 2a: calcd. for C$_{64}$H$_{144}$Cu$_6$I$_8$MoN$_4$S$_4$: C, 30.10; H, 5,41; N, 2.12; Cu, 13.76; Mo, 4.12%. Found: C, 29.31; H, 5.37; N, 2.25; Cu, 13.14; Mo, 3.18%]. Attempts to obtain single crystals of good quality failed. Interestingly, when pyridine vapour slowly diffused into the acetonitrile solution of **1a** or **2a** and partly substituted four of the eight X groups, beautiful octahedral crystals of the title compounds formed.

When the intermediate product **1a** or **2a** was dissolved in excess pyridine, one dark prismatic crystal was formed in a couple of days and needles were doposited on standing in air a month later. Based on elemental analysis and i.r. spectra of

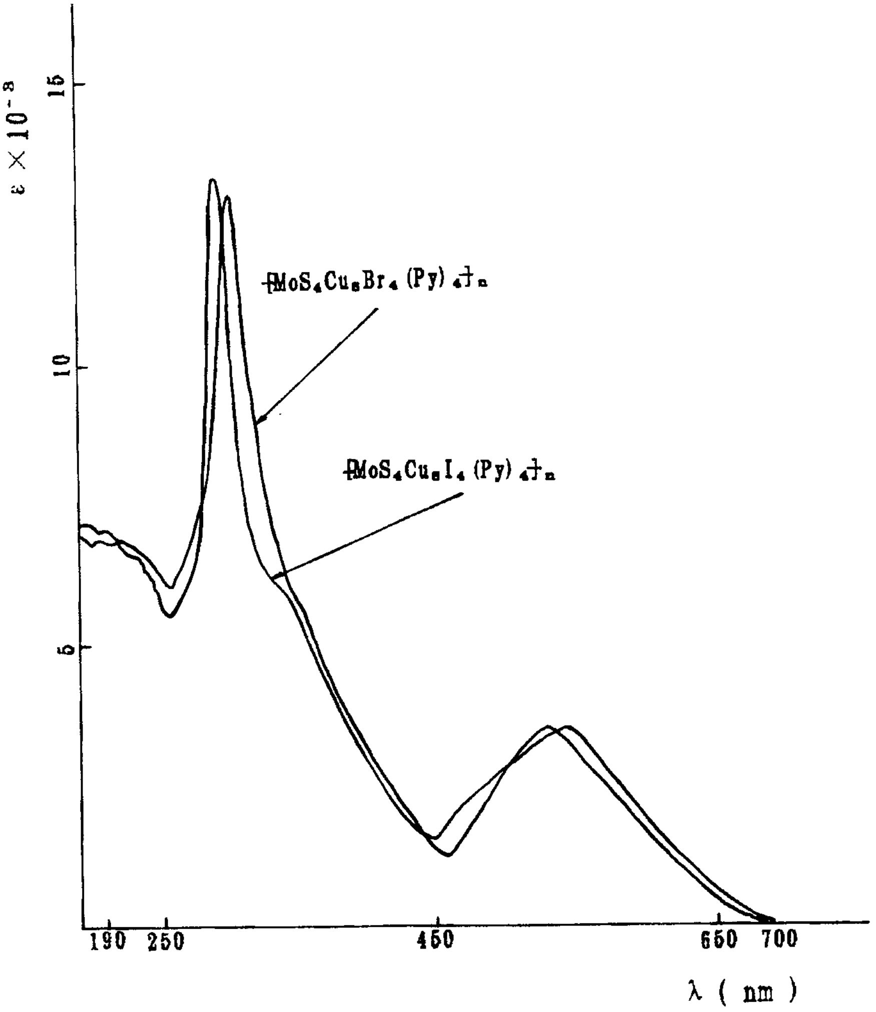

Figure 3 Electronic spectra of $[MoS_4Cu_6X_4(Py)_4]_n$ (X = Br, I) in CH_3CN solution.

these products, the prisms and needles were concluded to be the known compounds $[MoS_4Cu_4X_2(Py)_6]$ (X = Br, I)[23] and $[MoS_4Cu_2(Py)_4]$,[24] respectively. The formation of these two cluster compounds was attributed to the collapse of the framework of the cluster core MoS_4Cu_6. Use of PPh_3 or phen in CH_3CN led to the formation of $[MoS_4Cu_2(PPh_3)_4]$[23] or $[MoS_4Cu_2(phen)_2]$.[25]

Mixing acetonitrile solutions of **1a** or **2a** with pyridine-2-thione (Py-2-SH) in acetone, produced two kinds of compounds, $[MoS_4Cu_3X(Py\text{-}2\text{-}SH)_3]$ and $[MoS_4Cu_2(Py\text{-}2\text{-}SH)_2]$. The structure of the former is supposed to be similar to that of the known cubane-like compounds $[MoS_4Cu_3X(PPh_3)_3]$ (X = Br[2], I[15a]) while the structure of the latter is currently being studied by X-ray analysis.

It is expected that a series of new cluster compounds can be prepared from substitution of the X groups in the intermediate product **1a** or **2a** with other strong ligands such as dppm, $S_2CNR_2^{-1}$ (R_2 = Me_2, Et_2, C_5H_{10}). Research on this respect of the work is under way.

Supplementary material

Complete lists of anisotropic thermal parameters, bond distances, bond angles and observed and calculated factors for the title compound are available from the authors upon request.

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References

1. A. Muller, E. Diemann, R. Jostes and H,. Bogge, *Angew. Chem., Int. Ed. Engl.*, **20**, 934 (1981).
2. A. Muller, H. Bogge, M. Penk, K. Nieradzik, M. Dartmann, E. Krickemeyer, J. Schimanski, C. Romer, M. Romer. H. Dornfeld, U. Wienboker, W. Hellamnn and M. Zimmermann, *Monats. Chem.*, **120**, 367 (1989).
3. F. Secheresse, S. Bernes, F. Robert and Y. Jeannin, *J. Chem. Soc., Dalton Trans.*, 2875 (1991).
4. F. Secheresse, J.M. Manoli, C. Potvin and S. Marzak, *J. Chem. Soc., Dalton Trans.*, 3055 (1988).
5. (a) F. Secheresse, F. Robert, S. Marzak, J.M. Manoli and C. Potvin, *Inorg, Chim, Acta*, **182**, 221 (1991); (b) F. Secheresse, M. Salis, C. Potvin and J. M. Manoli, *Inorg. Chim. Acta*, **114**, L19 (1986).
6. S. Bernes, F. Secheresse and Y. Jeannin, *Inorg. Chim. Acta*, **191**, 11 (1992).
7. J.R. Nicholson, A.C. Flood, C.D. Garner and W. Clegg, *J. Chem. Soc., Chem. Commun.*, 1179 (1983).
8. S.F. Gheller, T.W. Hambley, J.R. Rodgers, R.T.C. Brownlee, M.J. O'Connor, M.R. Snow and A. Wedd, *Inorg. Chem.*, **23**, 2519 (1984).
9. J.M. Manoli, C. Potvin, F. Secheresse and S. Marzak, *Inorg. Chim. Acta*, **150**, 257 (1988)
10. C.D. Scattergood, P.G. Bonney, J.M. Slater, C.D. Garner and W. Clegg, *J. Chem. Soc., Chem Commun.*, 1749 (1987).
11. A. Muller, E. Krickemeyer, A. Hildebrand, H. Bogge, K. Schneider and M. Lemke, *J. Chem. Soc., Chem Commun.*, 1685 (1991).
12. A. Muller, E. Krickemeyer and H. Bogge, *Z. Anorg. Allg. Chem.*, **554**, 61 (1987); *Angew, Chem.*, **98**, 987 (1986); *Angew. Chem., Int. Ed. Engl.*, **25**, 990 (1986).
13. J.G. Li, X.Q. Xin, Z.Y. Zhou and K.B. Yu, *J. Chem. Soc., Chem. Commun.*, 250 (1991).
14. X.Q. Xin, J.P. Lang, K.B. Yu, Z.Y. Zhou, M.Q. Chen, P.J. Zheng, J.H. Cai and B.S. Kang, *J. Inorg. Chem.*, **8**, 472 (1992).
15. (a) J.P. Lang, H.Z. Zhu, X.Q. Xin, M.Q. Chen, K. Liu and P.J. Zheng, *Chin. J. Chem.*, **10**, 521 (1992); (b) J.P. Lang, S.A. Bao, H.Z. Zhu, X, Q, Xin and K.B. Yu, *Chin. J. Chem.*, **11**, 126 (1993); (c) J.P. Lang, W.Y. Zhou, X.Q. Xin, J.H. Cai, B.S. Kang and K.B. Yu, *Polyhedron*, **12**, 1647 (1993).

16 J.P. Lang, S.A. Bao, H.Z. Zhu, X.Q. Xin, J.H. Cai, L.H. Weng, Y.H. Hu and B.S. Kang, *Chem. J. Chin. Univ.*, **13**, 889 (1992).

17 F.J. Gao, H.Z. Zhu, X.Q. Xin, A.B. Dai, W.X. Liu, B.Y. Wang and P.J. Zheng, *Chem. J. Chin. Univ.*, **11** 1045 (1990).

18. J.W. McDonald, G.D. Friesen, L.D. Rosenhein and W.E. Newton, *Inorg. Chim Acta*, **72** 205 (1983).

19. N. Walker and D. Stuart, *Acta Crystallogr.*, **A39**, 158 (1983).
20. *International Tables for X-ray Crystallography*, Vol. IV. pp. 72–98. (Kynoch Press, Birmingham, 1974).
21. R.J.H. Clark, T.J. Dimes and M.L.J. Wolf, *J. Chem. Soc., Faraday Trans.*, **2**, 679 (1982).
22. R.J.H. Clark, T.J. Dimes and G.P. Proud, *J. Chem. Soc., Dalton Trans.*, 2019 (1983).
23. G.X. Jin, *Ph.D. Thesis*, Nanjing University, China (1987).
24. X.L. Jin., K.L. Tang, L. Tong and Y.Q. Tang, *ZIRAN*, **7**, 314 (1984).
25. C. Potvin, J.M. Manoli, F. Secheresse and S. Marzak, *Inorg. Chim. Acta*, **134**, 9 (1987).