Solid State Synthesis of Mo(W)–S Cluster Compounds at Low Heating Temperatures

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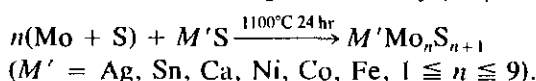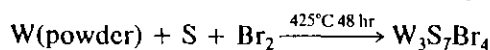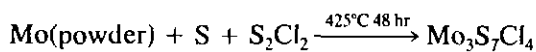*Chemistry Department, Nanjing University, Nanjing 210008, China*

A new method for synthesis of Mo(W)–S cluster compounds by solid state reactions at low heating temperatures is introduced. The factors which may influence solid state reactions are discussed. Over twenty novel structurally characterized Mo(W)–S cluster compounds including the big mixed-metal cluster compound $[(n - Bu)_4]_4[Mo_8Cu_{12}S_{32}]$ are summarized. © 1994 Academic Press, Inc.
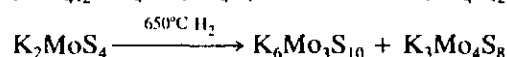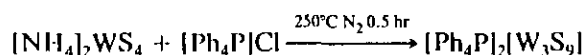
INTRODUCTION

A marked increase in both interest and research activity in synthesis of new cluster compounds has been evident in the past decade. One important direction for this has been, and continues to be, the search for new compounds and, therewith, new or unusual properties and new phenomena. Mo(W)–S cluster compounds have been very interesting kinds of compounds. Research has focused on producing Mo–Fe–S cluster compounds which can be used as models of the Mo center of the MoFe cofactor of the nitrogenase, and on producing Mo–Cu–S cluster compounds which may be important in the biological antagonism between Mo and Cu. Indeed, this field has been reviewed extensively (1–12).

So far, several hundred Mo(W)–S cluster compounds have been synthesized and structurally characterized (8–12). But almost all of the known Mo(W)–S cluster compounds were synthesized in solution. Only a few of them were prepared by solid state reactions. The following three examples are typical:
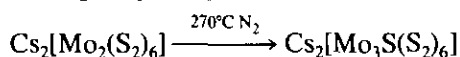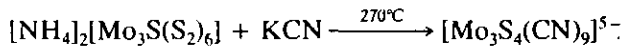
1. Preparation from elements (13, 14).

$$Mo(powder) + S + S_2Cl_2 \xrightarrow{425°C \ 48\,hr} Mo_3S_7Cl_4$$

$$W(powder) + S + Br_2 \xrightarrow{425°C \ 48\,hr} W_3S_7Br_4$$

$$n(Mo + S) + M'S \xrightarrow{1100°C \ 24\,hr} M'Mo_nS_{n+1}$$

$$(M' = Ag, Sn, Ca, Ni, Co, Fe, 1 \leq n \leq 9).$$

2. Preparation from simple compounds (15, 16).

$$[NH_4]_2WS_4 + [Ph_4P]Cl \xrightarrow{250°C \ N_2 \ 0.5\,hr} [Ph_4P]_2[W_3S_9]$$

$$K_2MoS_4 \xrightarrow{650°C \ H_2} K_6Mo_3S_{10} + K_3Mo_4S_8$$

3. Preparation from cluster compounds (17, 18).

$$[NH_4]_2[Mo_3S(S_2)_6] + KCN \xrightarrow{270°C} [Mo_3S_4(CN)_9]^{5-}$$

$$Cs_2[Mo_2(S_2)_6] \xrightarrow{270°C \ N_2} Cs_2[Mo_3S(S_2)_6]$$

In the above examples, we find that Mo(W)–S cluster compounds were prepared by solid state reactions usually at high or moderate temperatures. Because many organic or inorganic ligands are unstable at high or moderate temperatures, solid state synthesis of Mo(W)–S cluster compounds at higher temperature is limited.

METHOD OF SOLID STATE SYNTHESIS OF Mo(W)–S CLUSTER COMPOUNDS AT LOW HEATING TEMPERATURES

By exploring the solid state reactions of coordination compounds at the temperature below 100°C, or even at room temperature, we have developed a method, "Synthesis of Mo(W)–S Cluster Compounds by Solid State Reaction at Low Heating Temperatures." A typical procedure is described as follows:

Mix and grind a definite quantity of thiomolybdate (or thiotungstate) with appropriate amounts of other chemical reagents (such as CuCN, AgCl and $(n\text{-Bu})_4NBr$) in an agate mortar. Then transfer the mixture into a reaction tube and heat it in an oil bath at a temperature generally below the melting point of the reagents for several hours. Extract the product with an appropriate solvent such as CH_2Cl_2 and filter it. Add methanol or isopropanol or mixed

solvents carefully on the surface of the filtrate to yield crystalline cluster compounds.

Though this method has problems of impurity and low yield, it has the advantages of low heating temperature (about 100°C), short periods of time, and easy manipulation compared with those used at higher temperatures. It is significantly different from those used in solution by others for some of the same or related Mo(W)–S compounds. It can also be applied to preparing other types of compounds which do not contain MS_4^{2-} (M = Mo, W) (such as heteropolyacid compounds).
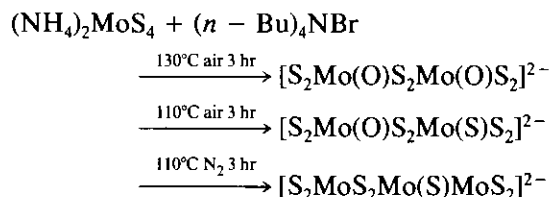
FACTORS INFLUENCING SOLID STATE REACTIONS

In the preparation of cluster compounds using the method mentioned above, one question, whether the reaction proceeds in the solid state, may arise. To answer this question, we put forward the following reasons based on a series of experimental investigations:

(1) The color of the mixture usually deepens as it is heated in the solid state. Take the system of CuCl (white powder), PPh$_3$ (white crystal), and Ph–C(S)–NH(Ph) (light yellow crystal) as an example. The main UV–DRS (Diffuse Reflectance Spectroscopy) peaks of these three compounds are 250, 290, and 410 nm, respectively. When the three compounds are ground in an agate mortar at room temperature for 5 min, the color of the yellow mixture becomes red. The UV–DRS peak of the red mixture evidently moves toward 480 nm, which indicates that a new compound is formed in the solid state reaction.

(2) There is significant difference in the IR spectra between the reagents and its heated mixture. Take the system of (NH$_4$)$_2$MoS$_4$, PPh$_3$, and CuCN as an example. The main IR absorption bands of the three compounds are 3201, 3105 (N–H), 477(Mo–S$_t$), 2160, 2120 (C≡N) cm^{-1}. When the mixture of the three compounds (molar ratio 1:3:2) is heated in the solid state at 90°C for several hours, the IR spectra changes greatly. The original IR absorptions 3201, 3105, 2160, 2120, and 477 cm^{-1} disappears, and several new bands 486, 463, and 432 cm^{-1} are

formed. These new bands show that the product contains Mo–S$_{br}$ and Mo–S$_t$ bonds (9) and certain kind of cluster compound has been formed in the solid state reaction. In some systems it has been found that there shows no significant difference between the IR spectra of the heated mixture and its CH$_2$Cl$_2$ extracted solution.
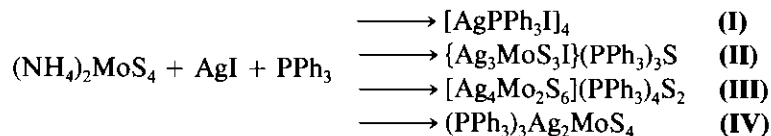
(3) By using the same chemicals and composition ratio, and extracting the products with the same solvent but under different reacting temperatures or atmospheres, different products are formed. An example is shown as follows (19–20):

$$(NH_4)_2MoS_4 + (n - Bu)_4NBr$$

$$\xrightarrow{\text{130°C air 3 hr}} [S_2Mo(O)S_2Mo(O)S_2]^{2-}$$

$$\xrightarrow{\text{110°C air 3 hr}} [S_2Mo(O)S_2Mo(S)S_2]^{2-}$$

$$\xrightarrow{\text{110°C N}_2\text{ 3 hr}} [S_2MoS_2Mo(S)MoS_2]^{2-}$$

This result and some IR spectroscopic studies on these solid state reactions (11, 19) indicate that the formation of products depends on the reaction temperature or atmosphere, and leads us to the conclusion that the reaction proceeds in the solid state.

(4) Figure 1 shows changes of the absorbances (A) of the diluted CH$_2$Cl$_2$-extracted solution (V/V 1:100) at 450 nm in the system of (NH$_4$)$_2$WS$_4$, AgI and PPh$_3$ (molar ratio 1:2.5:4) at the temperature range of 20–140°C. There is a maxium value in Fig. 1 at about 95°C, which implies that the yield of cluster compounds formed in this system is the highest at about that temperature. Similar phenomena in other systems have also been found. That is one of the important criteria of our solid state synthesis at low heating temperatures.

(5) In many cases, several cluster compounds are formed in the same solid state reaction. Take the system of (NH$_4$)$_2$MoS$_4$, AgI and PPh$_3$ as an example. As indicated by the following equations, there are at least four types of cluster compounds (21–24) formed in this solid state reaction. It is noted that not all of the four products are formed at each of the temperatures used.

$$
(NH_4)_2MoS_4 + AgI + PPh_3 \quad
\begin{cases}
\longrightarrow [AgPPh_3I]_4 & \textbf{(I)} \\
\longrightarrow \{Ag_3MoS_3I\}(PPh_3)_3S & \textbf{(II)} \\
\longrightarrow [Ag_4Mo_2S_6](PPh_3)_4S_2 & \textbf{(III)} \\
\longrightarrow (PPh_3)_3Ag_2MoS_4 & \textbf{(IV)}
\end{cases}
$$

The products are obtained by heating the mixture of these three reactants (molar ratio 1:2.5:4) in the solid state at different temperatures (20–140°C) for 8 hr extracting the products with CH$_2$Cl$_2$ (40 ml), and filtering the red colored

extract. Slow diffusion of methanol (15 ml) produces cluster compounds of various shapes which are mechanically separated. Table 1 lists the approximate yields of compounds **I, II, III,** and **IV** at different heating temperatures.
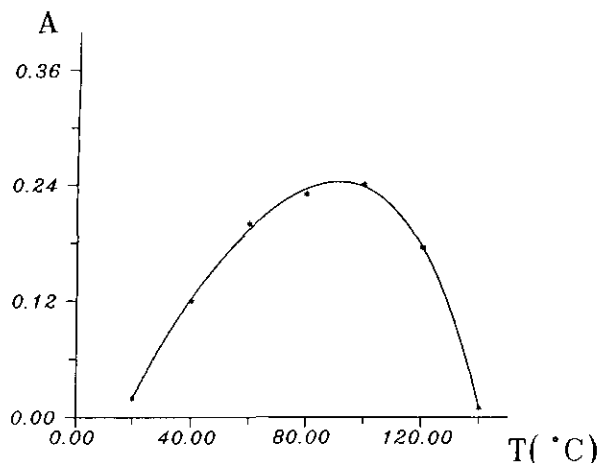
FIG. 1. Absorbances of the diluted CH_2Cl_2-extracted solution at different temperatures.

At about 80–100°C, **II** is preferably formed, while the other three types are the by-products. When reacting temperature is elevated to more than 140°C or approaches room temperature, **I** becomes the main product. When it is decreased to less than 60°C, **IV** is increased in yield. It is noted that the reaching temperature seldom affects the formation of **III** and its yield is always very poor. Interestingly, while using AgCN or AgSCN in place of AgI, **III** surprisingly becomes the main product and almost no others are formed. Though the formation mechanism of these four types of cluster compounds is unclear for the time being, the results in Table I reveal that formation of these four cluster compounds depends to certain extent on reaction temperature. Unfortunately, theory is presently in no position to assess well how the reacting temperature influences the formation of these cluster compounds in this unprincipled area.

(6) When we run the same reactions in a solvent, those obtained in the solid state reaction are greatly different from those obtained in solution. Take the system of $(NH_4)_2MoS_4$, CuCN, or Cu_2S and $(n\text{-}Bu)_4NBr$ as an example.

TABLE 1
Yields of Compounds I, II, III, and IV at Different
Heating Temperatures

	Temperature (°C)						
	20	40	60	80	100	120	140
I	>80	60	15	2	5	>80	>85
II	0	5	25	50	75	<5	<1
III	0	<1	<1	<1	<1	0	0
IV	<5	15	30	10	2	0	0

Note. Yields are calculated based on the amount of AgI as the four compounds all contain silver.

A well-ground mixture of $(NH_4)_2MoS_4$, CuCN or Cu_2S, and $(n\text{-}Bu)_4NBr$ (molar ratio 1 : 2 : 4) is heated in the solid state at about 90°C for 10 hr. The product is extracted with CH_2Cl_2 (60 ml) and filtered. Slow diffusion of a mixture of acetone (20 ml) and n-pentane (20 ml) into the filtrate deposits dark-red rhombic crystals of $[(n\text{-}Bu)_4N)_4]$ $[Mo_8Cu_{12}S_{32}]$. While the temperature is elevated up to 125°C, the smaller cluster compounds $[(n\text{-}Bu)_4N]_3[Cu_3 MoS_4Br_4]$ become the main product. This result may be explained by the formation of the smaller cluster compound at the higher reacting temperature resulting from some collapse in the bigger unstable cluster anion $[Cu_{12}Mo_8S_{32}]^{4-}$.

To a solution of CH_2Cl_2 (60 ml) is added a mixture of $(NH_4)_2MoS_4$, CuCN, and $(n\text{-}Bu)_4NBr$. Then the suspension is stirred at room temperature for 10 hr and filtered. Using the same diffusing solvents, the filtrate only produces $[(n\text{-}Bu)_4N]_2[MoS_4Cu_2(CN)_2]$. If using Cu_2S, it only produces $[(n\text{-}Bu)_4N]_2[MoS_4]$.

(7) In some reactions, the molten reagents such as PPh_3 and $(n\text{-}Bu)_4NX(X = Cl, Br, I)$ when mixed with other reagents may give eutectics that are liquid at a temperature (about 100°C) used in this method. The molten reagents may play important role in overcoming the characteristically low interphase reactivity between solids. Take the reaction of $(NH_4)_2WS_4$ and Cu_2S with $(n\text{-}Bu)_4NBr$ as an example. The melting point of $(n\text{-}Bu)_4NBr$ is 103–105°C. When the mixture of the three compounds becomes sintered at 95°C for 8 hr, the color of it changes from yellow to red. When the temperature is elevated up to 105°C, it becomes molten and the color remains red. While extracting it with CH_2Cl_2 and filtering it, the filtrate gives the reddish-orange crystals of $[(n\text{-}Bu)_4N]_4$ $[W_8Cu_{12}S_{32}]$.

EXAMPLES OF CLUSTER COMPOUNDS

By means of this method, over sixty Mo(W)–S cluster compounds and other coordination compounds have been synthesized in our laboratory, half of which have been structurally characterized: two icosanuclear Mo(W)–Cu–S clusters (Table 2), three heptanuclear polymeric Mo(W)–Cu–S clusters (Table 3), one hexanuclear open double-cubane W–Cu–S cluster and two pentanuclear Mo(W)–Cu–S clusters and one tetranuclear nido-like Mo–Cu–S cluster and one trinuclear W–Cu–S cluster (Table 4), six neutral tetranuclear cubane-like Mo(W)–Cu(Ag)–S clusters (Table 5), seven anionic tetranuclear cubane-like Mo(W)–Cu(Ag)–S clusters (Table 6) and five miscellaneous coordination compounds (Table 7).

Icosanuclear Mo(W)–Cu–S Clusters

More than 100 Mo(W)–Cu(Ag)–S cluster compounds have been reported in the literature so far. However,

TABLE 2
Summary of Crystal Data for Two Icosanuclear Mo(W)–Cu–S Clusters

Crystal sys.	Space group, Z	a	b	c	α	β	γ	V	R, R_w
1 monoclinic	C2/m, 4	22.627(3)	21.628(5)	26.259(6)	90.00	101.66(1)	90.00	12585.1	0.083, 0.090
2 triclinic	—	22.700(4)	28.961(4)	21.676(5)	112.47(2)	92.01(2)	79.93(1)	13050.0	—

the number of the metal atoms in these clusters generally are fewer than seven. Only a few bigger cluster compounds such as [(H$_2$O)$_9$Mo$_3$S$_4$Cu–CuS$_4$Mo$_3$(H$_2$O)$_9$] (CH$_3$C$_6$H$_4$SO$_3$)$_8$ · 12H$_2$O (25) and (NET)$_2$[Cu$_6$S$_6$(S$_2$)$_6$ Mo$_6$O$_6$] · DMF (26) have been reported.

We have synthesized the two cluster compounds [(n-Bu)$_4$N]$_4$[Cu$_{12}$M$_8$S$_{32}$] (1: M = Mo; 2: M = W) and structurally characterized the structure of 1 (Table 2) (27). It has a pseudo-cubane type (Mo$_8$Cu$_{12}$) core (Fig. 2) in which each Mo atom occupies the vertex of the corner and the twelve Cu atoms take the positions in the edges, and neighboring metal atoms are connected through bridge sulfur atoms and the local coordination sphere around each metal atom (Mo or Cu) approaches a tetrahedron structure. Unfortunately, we have been unable to solve the crystal structure of the corresponding tungsten compound 2, we conclude that it has the similar structure of 1 from comparison on their IR spectra, elemental analysis, and cell parameters.

Heptanuclear Polymeric Mo(W)–Cu–S Clusters

Three heptanuclear polymeric clusters (Table 3) have been prepared by the reaction of a solid state intermediate
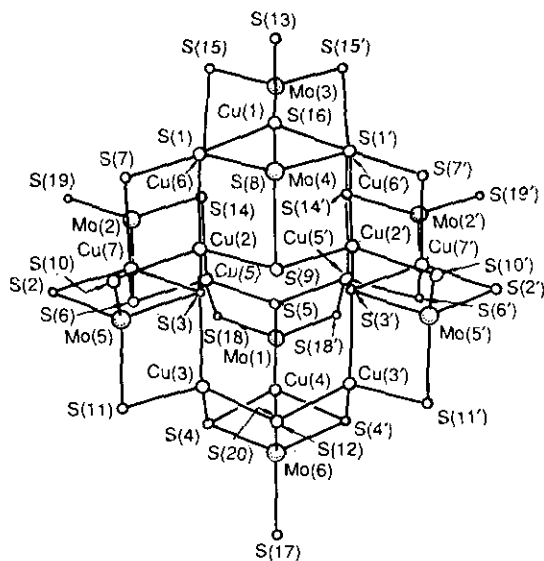

FIG. 2. Structure of cluster anion [Mo$_8$Cu$_{12}$S$_{32}$]$^{4-}$.

with pyridine. Figures 3 and 4 show the structure configuration and cell packing of [–MoS$_4$Cu$_6$Br$_4$Py$_4$–]$_n$. This compound possesses a central MoS$_4$ moiety enveloped by an octahedral array of six copper (I) atoms, forming a MoS$_4$Cu$_6$ aggregate. Linked by –Cu$_{eq}$–Br–Cu$_{eq}$–bridges, this aggregate connects with its nearest neighbors and develops a two-dimensional network.

[–WS$_4$Cu$_6$Br$_4$Py$_6$–]$_n$ and [–WS$_4$Cu$_6$I$_4$Py$_4$–]$_n$ are isostructural to the molybdenum analogue.

Hexa-, Penta-, Tetra-, and Trinuclear Mo(W)–Cu–S Clusters

A series of Mo(W)–Cu–S cluster compounds with different structure have been prepared by this method and structurally characterized (Table 4).

[Et$_4$N]$_4$[WS$_4$Cu$_5$Br$_7$] is composed of a discrete [WS$_4$Cu$_5$Br$_7$]$^{4-}$ tetraanion and four [NEt$_4$]$^+$ cations. The anion has crystallographically imposed C$_2$ symmetry. Five of the six edges of the WS$_4^{2-}$ tetrahedron are coordinated by CuBr units forming an open double-cubane structure (Fig. 5).

[Et$_4$N]$_4$[MoS$_4$Cu$_4$I$_6$] consists of a discrete [MoS$_4$Cu$_4$I$_6$]$^{4-}$ tetraanion and four (NEt$_4$)$^+$ cations. In the anion, four copper atoms are bound to the MS$_4$ tetrahedron. Two copper atoms display a distorted tetrahedral coordination geometry forming CuS$_2$I$_2$ unit (Fig. 6). [Et$_4$N]$_4$[WS$_4$Cu$_4$I$_6$] is isostructural to the molybdenum analogue.

[(n-Bu)$_4$N]$_2$[MoOS$_3$Cu$_3$(NCS)$_3$] contains a discrete [MoOS$_3$Cu$_3$(NCS)$_3$]$^{2-}$ anion and two [(n-Bu)$_4$N]$^+$ cations. The core of the anion is a nido-like skeleton composed of one Mo atom, three Cu atoms, and three S atoms. The geometry of the Mo atom is a distorted tetrahedron while the three copper atoms exhibit the same trigonal planar coordination environment (Fig. 7).

TABLE 3
Summary of Crystal Data for Three Heptanuclear
Polymeric Clusters

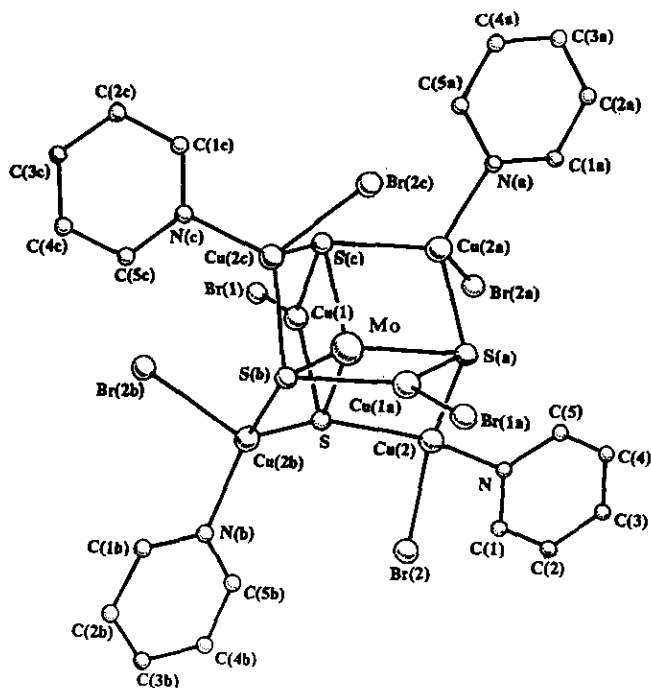| Formula	[–MoS$_4$Cu$_6$Br$_4$Py$_6$–]$_n$	[–WS$_4$Cu$_6$Br$_4$Py$_4$–]$_n$	[–WS$_4$Cu$_6$I$_4$Py$_4$–]$_n$
Space group, Z	$I\bar{4}2d$, 4	$I\bar{4}2d$, 4	$I\bar{4}2d$, 4
a(Å)	14.611(3)	14.612(2)	14.797(4)
b(Å)	14.611(3)	14.612(2)	14.797(4)
c(Å)	14.611(3)	14.612(2)	15.661(4)
V(Å^3)	3227.1	3230.0	3429.0
R, R_w	0.030, 0.027	0.040, 0.036	0.055, 0.042
Ref.	(28)	(28)	(28)

FIG. 3. Molecular structure of cluster compound [MoS$_4$Cu$_6$ Br$_4$Py$_4$]$_n$.

[WS$_4$Cu$_2$][Py]$_4$ is obtained by the reaction of a solid state intermediate product with excess pyridine. It is composed of an array of three edge-shared tetrahedra with idealized overall D$_{2d}$ symmetry. The geometries of the tungsten and the copper atoms are distorted tetrahedra (Fig. 8).

Neutral Tetranuclear Cubane-like Mo(W)–Cu(Ag)–S Clusters

Six neutral cubane-like cluster compounds (Table 5) have been synthesized in our lab in recent years. Figure 9 shows molecular configuration of [Ag$_3$WS$_3$Br][PPh$_3$]$_3$S (33), including the phenyl ring atoms. The central unit of this cluster can be described as a strongly distorted cube in which four corners are occupied by one Br atom and three Ag atoms (with a PPh$_3$ ligand being bonded to each Ag). The cube is completed by a terdenate WS$_4^{2-}$ ligand, coordinating to Ag atoms via sulfur. The geometry of the Mo (or W) atom in these clusters is a slightly distorted tetrahedron. But it is interesting to note that the geometries of the copper atoms are different from those of the silver atoms. The former has approximate trigonal coordination while the latter is distorted tetrahedron. The difference may be attributed to the bigger silver atom which
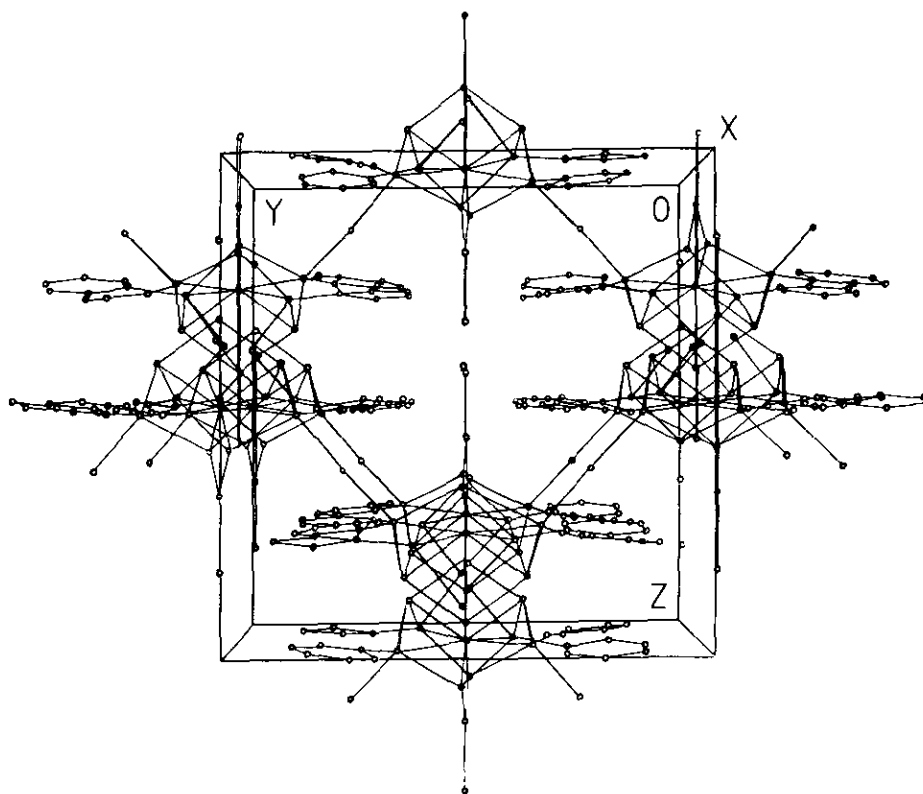

FIG. 4. Cell packing of cluster compound [MoS$_4$Cu$_6$Br$_4$Py$_4$]$_n$.

TABLE 4
Summary of Crystal Data for Five Mo(W)–Cu–S clusters

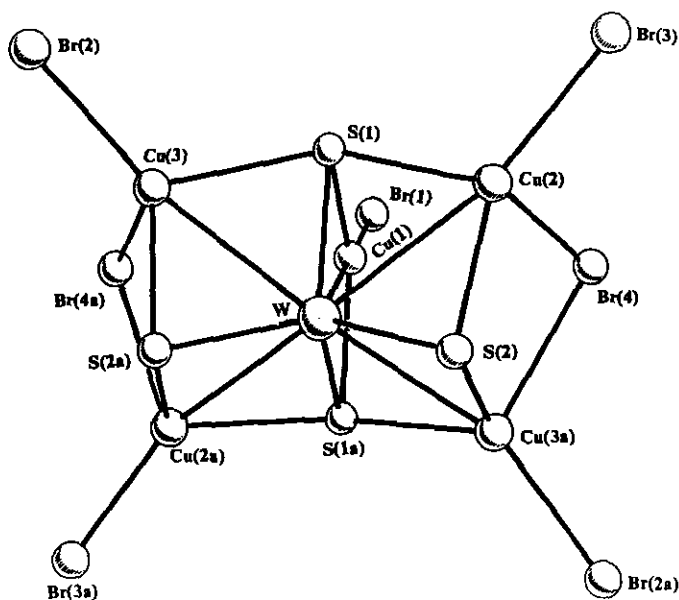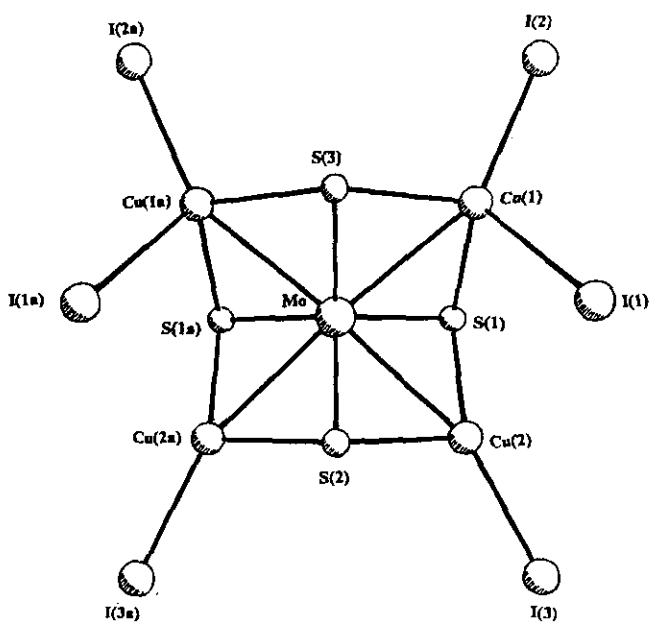| Formula	[WS$_4$Cu$_5$Br$_7$] [Et$_4$N]$_4$	[MoS$_4$Cu$_4$I$_6$] [Et$_4$N]$_4$	[WS$_4$Cu$_4$I$_6$] [Et$_4$N]$_4$	[MoOS$_3$Cu$_3$(NCS)$_3$] [(n-Bu)$_4$N]$_2$	[WS$_4$Cu$_2$] [Py]$_4$
Space group, Z	C2/c, 4	C2/m, 4	C2/m, 4	P2$_1$/n, 4	C2/c, 4
a(Å)	23.054(4)	29.688(6)	29.702(6)	16.672(9)	14.109(1)
b(Å)	10.809(2)	12.778(2)	12.787(5)	16.278(6)	12.704(1)
c(Å)	22.118(4)	15.308(2)	15.327(3)	19.608(8)	14.071(1)
β(°)	94.08(1)	99.53(2)	99.69(2)	110.05(2)	96.97(1)
V(Å^3)	5497.2	5727.2	5738.1	4999.0	2504.1
R, R$_w$	0.074, 0.062	0.052, 0.046	0.075, 0.079	0.068, 0.061	0.027, 0.027
Ref.	(28)	(28)	(28)	(29)	(30)

FIG. 5.   Structure of cluster anion [WS$_4$Cu$_5$Br$_7$]$^{4-}$.

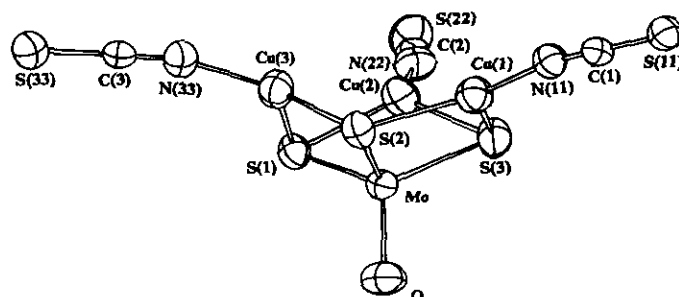FIG. 6.   Structure of cluster anion [MoS$_4$Cu$_4$I$_6$]$^{4-}$.

FIG. 7.   Structure of cluster anion [MoOS$_3$Cu$_3$(NCS)$_3$]$^{3-}$.

has enough space to meet tetrahedrally coordinated steric need.

Anionic Tetranuclear Cubane-like Mo(W)–Cu(Ag)–S Clusters

We have also synthesized seven new anionic cubane-like clusters (Table 6). Figure 10 shows the structure of the cluster anion [MoAg$_3$S$_4$Br$_4$]$^{3-}$ (28). The cluster core [Ag$_3$MoS$_3$Br] can be viewed as a cube in which the four metal atoms and four nonmetal atoms are statistically distributed by two kinds of atoms, respectively.

Miscellaneous Coordination Compounds

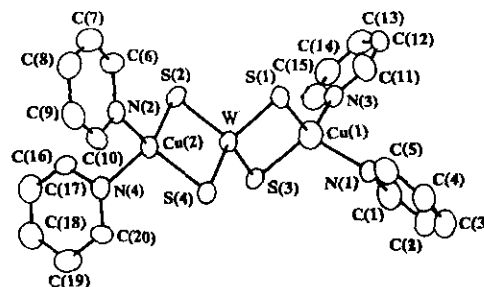We have applied this method to prepare other compounds which do not contain MS_4^{2-} (M = Mo, W). To

FIG. 8.   Molecular structure of [WS$_4$Cu$_2$][Py]$_4$.

TABLE 5
Summary of Crystal Data for Seven Neutral Cubane-like Mo(W)–Cu(Ag)–S Clusters

Formula	$[Cu_3WS_3Cl]$ $[PPH_3]_3S$	$[Cu_3MoS_3I]$ $[PPH_3]_3S$	$[Cu_3WS_3Br]$ $[PPH_3]_3S$	$[Ag_3MoS_3I]$ $[PPH_3]_3S$	$[Ag_3WS_3Br]$ $[PPH_3]_3S \cdot H_2O$	$[Ag_3WS_3Cl]$ $[PPH_3]_3S \cdot 0.5(S)Ph_3 \cdot 3H_2O$
Space group, Z	$P1$, 2	$P1$, 2	$P1$, 2	$P1$, 2	$P1$, 2	R_3, 6
a(Å)	13.049(3)	11.395(2)	11.876(1)	12.114(2)	12.129(5)	16.201(3)
b(Å)	20.351(4)	13.107(1)	13.065(2)	13.420(2)	13.340(0)	16.201(3)
c(Å)	11.876(2)	20.473(5)	20.325(2)	20.346(2)	20.228(6)	45.091(10)
α(Å)	94.75(2)	74.95(5)	74.95(1)	74.53(1)	74.48(3)	90.00
β(°)	115.97(1)	84.87(2)	85.39(1)	86.73(1)	87.17(8)	120.00
γ(°)	74.90(2)	64.27(1)	64.09(1)	63.74(1)	63.53(3)	90.00
V(Å³)	2736	2776.1	2737.3	2851.7	2814.0	10249.4
R, R_w	0.073, 0.073	0.049, 0.061	0.039, 0.055	0.048, 0.043	0.056, 0.056	0.050, 0.042
Ref.	(31)	(32)	(32)	(22)	(33)	(22)

TABLE 6
Summary of Crystal Data for Seven Anionic Cubane-Like Clusters

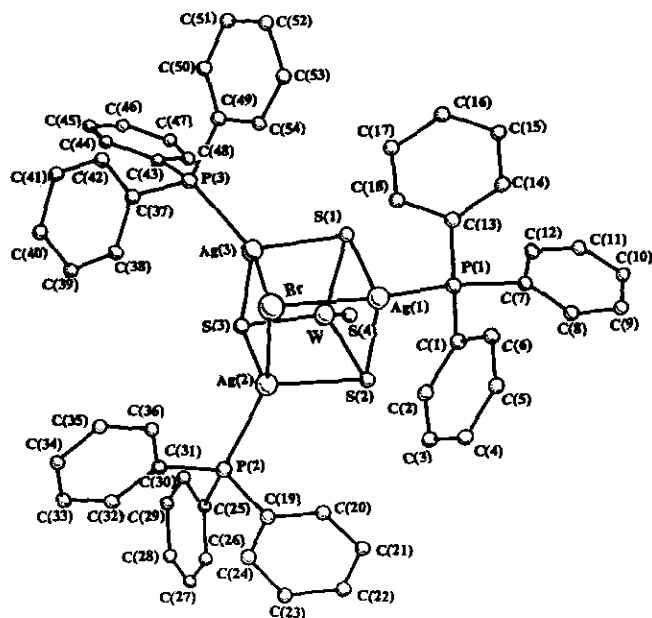| Formula	$[Ag_3MoS_4I_3Br]$ $[(n\text{-}Bu)_4N]_3$	$[WS_4Cu_3Br_4]$ $[(n\text{-}Bu)_4N]_3$	$[MoOS_3Ag_3I_3Br]$ $[(n\text{-}Bu)_4N]_3$	$[MoS_4Ag_3Br_4]$ $[(n\text{-}Bu)_4N]_3$	$[WS_4Ag_3Br_4]$ $[(n\text{-}Bu)_4N]_3$	$[MoOS_3Ag_3Br_4]$ $[(n\text{-}Bu)_4N]_3$	$[WS_4Ag_3Cl_4]$ $[(n\text{-}Bu)_4N]_3$
Space group, Z	$F43c$, 8	—	—	$F43c$, 8	$F43c$, 8	$P43m$, 1	$P43m$, 1
Crystal sys.	cubic	trigonal	tetragonal	cubic	cubic	cubic	cubic
a(Å)	24.577(6)	17.410(7)	12.224(5)	24.231(4)	24.221(4)	12.093(4)	12.059(2)
b(Å)	24.577(4)	17.410(7)	12.224(5)	24.231(4)	24.221(4)	12.093(4)	12.059(2)
c(Å)	24.577(4)	39.102(5)	12.175(9)	24.231(4)	24.221(4)	12.093(4)	12.059(2)
V(Å³)	14845.2	10265.2	1819.55	14227.0	14208.7	1768.3	1753.4
R, R_w	0.088, 0.061	—	—	0.078, 0.087	0.071, 0.068	0.076, 0.077	0.075, 0.073
Ref.	(34)	(28)	(28)	(28)	(28)	(35)	(35)

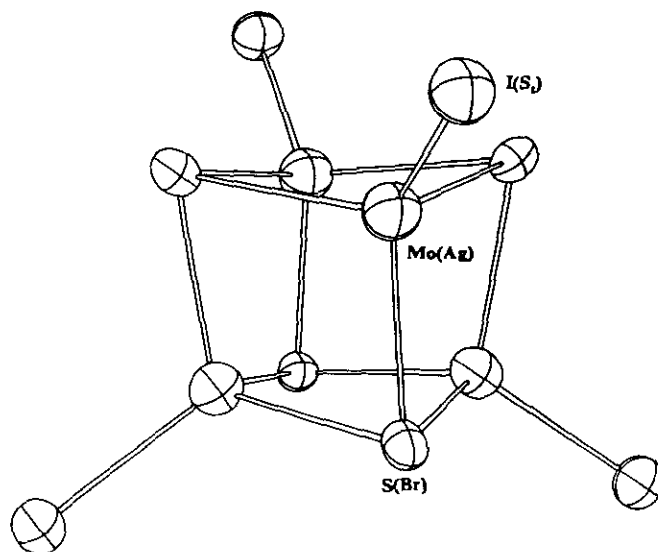FIG. 9. Molecular structure of cluster compound (Ag_3WS_3Br) $[PPh_3]_3S$.

FIG. 10. Structure of cluster anion $[Ag_3MoS_4Br_4]^{3-}$.

TABLE 7
Summary of Crystal Data for Five Coordination Compounds

Formula	[Cu(SC(Ph)NHPh)(PPh$_3$)$_2$Cl]	[Cu$_{0.84}$Au$_{0.16}$(SC(Ph)NHPh)(PPh$_3$)$_2$Cl]	[Cu$_2$(NCS)$_2$(PPh$_3$)$_4$]	[Cu$_4$Br$_8$][C$_5$H$_5$N(C$_{16}$H$_{33}$)]	[As(SiW$_{11}$O$_{39}$)]H$_2$[(n-Bu)$_4$N]$_3$
Space group, Z	$P2_1/c$, 4	$P2_1/a$, 4	$P\bar{1}$, 1	$P\bar{1}$, 1	$I\bar{4}3m$, 1
a(Å)	18.013(5)	17.231(3)	10.289(2)	9.762(2)	17.780(10)
b(Å)	14.588(5)	14.611(2)	13.098(2)	31.948(4)	17.780(10)
c(Å)	17.222(5)	18.000(3)	13.410(3)	9.143(2)	17.780(10)
α(°)	90.00	90.00	114.74(2)	94.54(1)	90.00
β(°)	105.54(3)	105.56(2)	92.95(2)	116.48(2)	90.00
γ(°)	90.00	90.00	100.79(2)	92.54(1)	90.00
V(Å^3)	4360.1	4365.1	1595.3	2533.0	5620.8
R, R$_w$	0.070, 0.071	0.052, 0.045	0.039, 0.035	0.083, 0.100	0.072, 0.083
Ref.	(28)	(28)	(28)	(36)	(28)

date, several coordination compounds have been obtained (Table 7).

[Cu(SC(Ph)NHPh)Cl(PPh$_3$)$_2$] is obtained by the reaction of CuCl, SC(Ph)NHPh and PPh$_3$ in the solid state at room temperature. It contains a tetrahedral core of copper atom which is bonded to one Cl atom, one SC(Ph)NHPh ligand and two PPh$_3$ ligands (Fig. 11). [Cu$_{0.84}$Au$_{0.16}$(SC(Ph)NHPh)Cl(PPh$_3$)$_2$] is isostructural to [Cu(SC(Ph)NHPh)(PPh$_3$)$_2$Cl].

[Cu$_2$(SCN)$_2$(PPh$_3$)$_4$] contains an eight-membered ring where the two copper atoms are bridged by the two NCS$^-$ ligands. The two copper atoms exhibit the same distorted tetrahedral environment (Fig. 12).

[C$_5$H$_5$N(C$_{16}$H$_{33}$)]$_4$[Cu$_4$Br$_8$] consists a discrete [Cu$_4$Br$_8$]$^{4-}$ tetraanion and four [C$_5$H$_5$N(C$_{16}$H$_{33}$)]$^+$ cations. The anion is a chain structure in which four copper atoms are bridged by Br atoms. The two copper atoms are distorted tetrahedral geometry while the other two are trigonal planar coordination environment (Fig. 13).

H$_2$[(n-Bu)$_4$N]$_3$[As(SiW$_{11}$O$_{39}$)] is composed of one heteropolyanion [As(SiW$_{11}$O$_{39}$)]$^{5-}$, two H$^+$ ions and three [(n-Bu)$_4$N]$^+$ cations. The anion contains a central SiO$_4$ core encapsulated by a cage composed of As, W, and O atoms. Each O atom in the SiO$_4$ tetrahedron bridges another three W atoms. The geometry of the W atom is distorted octahedron. In this anion, one As and eleven W atoms are statistically distributed (Fig. 14).

CONCLUSIONS

1. A new method for synthesis of Mo(W)–S compounds by solid state reactions at low heating temperatures has been proposed.

2. Over forty new Mo(W)–S cluster compounds were synthesized by this method, half of which have been structurally determined.

3. This method is an effective one and it can be applied to synthesize other cluster compounds and coordination compounds that contain no MS_4^{2-} (M = Mo, W).

4. Factors influencing solid state reactions have been discussed.
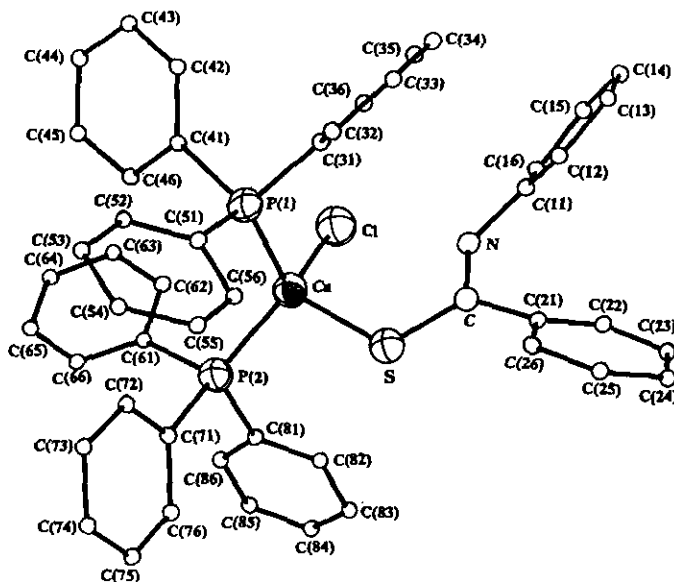
FIG. 11. Molecular structure of [Cu(SC(Ph)NHPh)(PPh$_3$)$_2$Cl].

ACKNOWLEDGMENTS
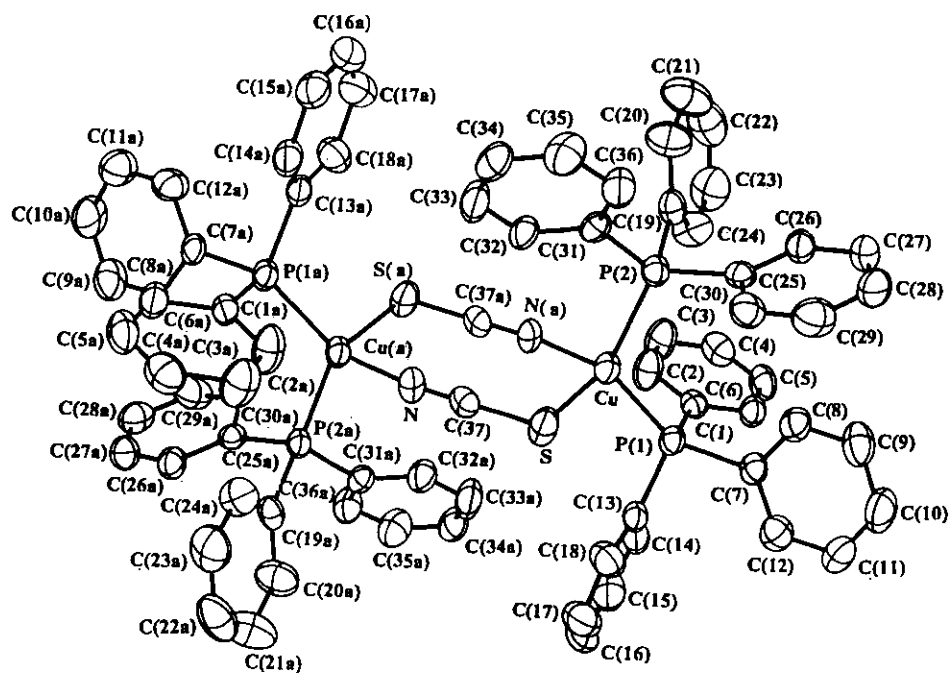
FIG. 12. Molecular structure of $[Cu_2(NCS)_2(PPh_3)_4]$.
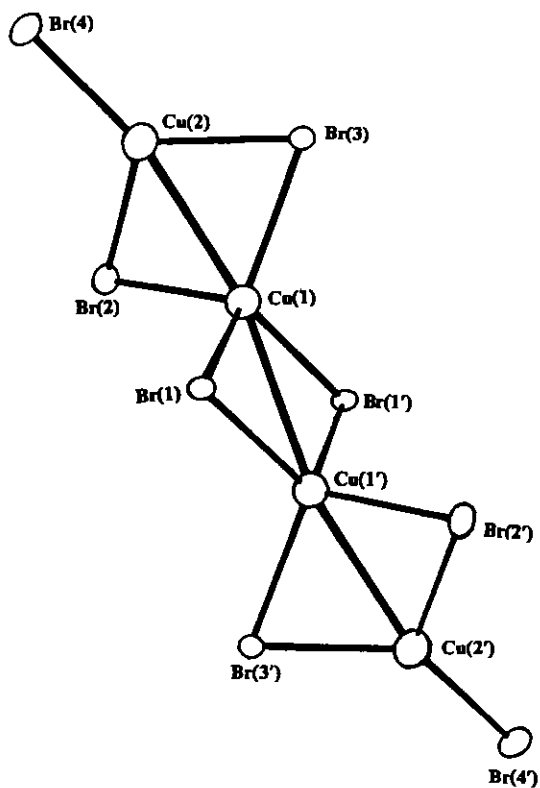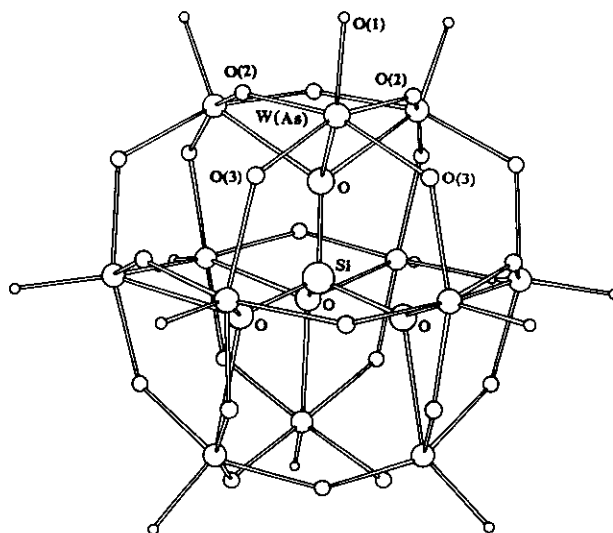
FIG. 13. Structure of $[Cu_4Br_8]^{4-}$.

FIG. 14. Structure of $[As(SiW_{11}O_{39})]^{5-}$.

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