进展与评述

低热固相反应合成 Mo(W)-Cu(Ag)-S 簇合物

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本文对现有中，高温固相化学反应方法合成含硫原子簇化合物作了探讨，介绍了我们实验室用低热温度固相反应合成原子簇化合物的新方法，总结了几年来我们用此法合成的 S-Mo(W)-Cu(Ag)原子簇化合物，并测定结构二十余个，其中包括了含有二十个金属原子的大核原子簇化合物 $[(n\text{-Bu})_4N]_4[Mo_8Cu_{12}S_{32}]$.

关键词: 固相反应 晶体结构 簇合物

SYNTHESIS OF Mo(W)-Cu(Ag)-S CLUSTER COMPOUNDS BY SOLID STATE REACTIONS AT LOW HEATING TEMPERATURES

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In this paper, we introduce a new method of synthesis of cluster compounds by solid state reactions at low heating temperature, and summarize Mo(W)-Cu(Ag)-S cluster compounds, we have recently obtained using this method and structurally characterize about twenty of new cluster compounds by X-ray single crystal analysis, including the bigger mixed-metal cluster compound $[(n\text{-Bu})_4N]_4[Mo_8Cu_{12}S_{32}]$.

Introduction

Research into synthesis of new cluster compounds has grown dramatically in the past de-

cade. Motivation for this research includes the search for new materials with interesting new properties. Metal sulfur containing systems have been an interesting topic because of the discovery of their conducting properties, their applications as battery materials and lubricant, their utility as hydroprocessing catalysis, and their biological relevance of polynuclear transition metal sulfur coordination compounds with different biometals (like Fe, Cu, Mo). With respect to the active sites of nitrogenase and the interrelation between Mo and Cu in numerous biological processes (the so–called Mo–Cu antagonism), many research groups in the world have devoted great efforts to those containing Fe,S and Mo systems [1–5] and to those containing Cu, S and Mo systems [6–7] . The flow of surprising discoveries in metal surful containing systems makes it clear that synthesis of new metal surful containing cluster compounds has been, and continues to be, of great importance in both inorganic chemistry and biochemistry.

So far, more than one thousand homo– and hetero–nuclear metal sulfur containing cluster compounds have been reported in the literature. Among them, several hundreds of Mo(W)–surful containing cluster compounds have been synthesized and structurally determined [8–12] . But as we know well, almost all of Mo(W)–S containing cluster compounds were synthesized in solution. Only a few of them were prepared by solid state reactions. There are five examples for preparation of cluster compounds at high or moderate temperatures.

1. Preparation from elements,

$$Mo(powder)+S+S_2Cl_2 \xrightarrow{450℃\ 48h} Mo_3S_7Cl_4$$ [13]

$$W(powder)+S+Br_2 \longrightarrow W_3S_7Br_4$$ [13]

$Mo_2(S_2)_2Cl_6$ and $[Mo_3S(S_2)_3Cl_4]$ [14] were synthesized by similar methods in the temperature range 270–750℃.

2. Preparation from simple compounds,

$$(NH_4)_2WS_4+[Ph_4P]Cl \xrightarrow{250℃\ N_2\ 0.5h} [Ph_4P]_2[W_3S_9]$$ [15]

3. Preparation from cluster compounds,

$$(NH_4)_2[Mo_3S(S_2)_6]+KCN \xrightarrow{270℃} [Mo_3S_4(CN)_9]^{5-}$$ [16]

4. Preparation from the thermodecomposition of single compounds,

$$K_2MoS_4 \xrightarrow{650℃\ H_2} K_6Mo_3S_{10}+K_3Mo_4S_8$$ [17]

$$(NH_4)_2MoS_4 \xrightarrow[r.t.]{O_2\ or\ air} (NH_4)_2[Mo_2O_2(S_2)_2]$$ [18]

5. Preparation from solid state reactions of elements and inorganic salts at high or moderate temperatures,

$$n(Mo+S)+M'S \xrightarrow{1100℃\ 24h} M'Mo_nS_{n+1}$$

(M' = Ag, Sn, Ca, Ni, Co, Fe, $1<n<9$) [19] .

Here we can see that the Mo(W)–sulfur containing cluster compounds were prepared by solid state reactions usually at high or moderate temperatures. However, many organic or

inorganic ligands in that case are unstable, the reactions of the coordination compounds at higher temperature thus are very limited.

Description of One New Method

By exploring the solid state reactions of coordination compounds at the temperature below 100℃, or even at room temperature, we have been developing a method "Synthesis of Cluster Compounds and Coordination Compounds by Solid State Reaction at Low Heating Temperature". A typical synthesis procedure is described below:

Mix and grind a definite quantity of thiomolybduate (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. Usually, the color of the mixture turns dark during the reaction. Extract the dark products with an appropriate solvent and filter it, and in many cases add methanol or isopropanol or mixed solvents on the surface of the filtrate. By standing several days, crystalline cluster compounds are always formed.

According to this method, over fourty cluster compounds have been synthesized in our lab. About twenty of them are new, and have been determined by Four Circle Single Crystal X-Ray Diffractometer.

Effect of Temperature and Atmosphere on Solid State Reactions

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 would be resulted in. This result and some IR spectroscopic studies on these solid state reactions [11,20] indicate that the formation of products depends on the reaction temperature or atmosphere, which leads us to the conclusion that the reaction proceeds in solid state and the clusters formed can not be the products which are produced in solution. Two examples are shown as follows: [20-21]

$$1.\ (NH_4)_2WS_4+(n\text{-Bu})_4NBr \xrightarrow{125℃\ \text{air}\ 3h} [S_2W(O)S_2W(O)S_2WS_2]^{2-}$$
$$\xrightarrow{130℃\ N_2\ 3h} [S_2WS_2W(S)S_2W(S)S_2WS_2]^{2-}$$
$$\xrightarrow{110℃\ N_2\ 3h} [S_2W(S)S_2W(S)S_2WS_2]^{2-}$$

$$2.\ (NH_4)_2MoS_4+(n\text{-Bu})_4NBr \xrightarrow{130℃\ \text{air}\ 3h} [S_2Mo(O)S_2Mo(O)S_2]^{2-}$$
$$\xrightarrow{110℃\ \text{air}\ 3h} [S_2Mo(O)S_2Mo(S)S_2]^{2-}$$
$$\xrightarrow{110℃\ N_2\ 3h} [S_2MoS_2Mo(S)MoS_2]^{2-}$$

Example 1 and 2 show that in the solid state synthesis of homonuclear Mo(W)-S cluster compounds, the dependence upon reacting temperature or atmosphere is evident. Different products are formed under different reacting temperatures or atmospheres.

Synthesis of New Cluster Compounds by Solid State Reaction at Low Heating Temperature

Recently, we have synthesized a great deal of cluster compounds (see Table 1,2,4,5). Based on their structures, they can be divided into four types: huge clusters (Table 1), neutral cubane–like clusters (Table 2), anionic cubane–like clusters (Table 4) and miscellaneous clusters (Table 5).

Brief Description of Structures of the Cluster Compounds

Huge clusters

More than 100 Mo(W)–Cu(Ag)–S cluster compounds have been reported in the literature so far. However, the metal atoms in these clusters generally are fewer than six. Only a few bigger cluster compounds such as $[(H_2O)_9Mo_3S_4Cu–CuS_4Mo_3(H_2O)_9](CH_3C_6H_4SO_3)_8 \cdot 12H_2O$ [29] and $(NET)_2[Cu_6S_6(S_2)_6Mo_6O_6] \cdot DMF$ [30] have been reported.

Table 1　Summary of Crystal Data for Two Huge Clusters

formula	crystal system	space group,Z	*a*	*b*	*c*	*α*	*β*	*γ*	*V*	*R*,*R*w
$[(n\text{–Bu})_4N]_4$ 1.$[Mo_8Cu_{12}S_{32}]$	monoclinic	*C*2 / *m*,4	22.627(3)	21.628(5)	26.259(6)	90.00	101.66(1)	90.00	12585.1	0.083,0.090
$[(n\text{–Bu})_4N]_4$ 2.$[W_8Cu_{12}S_{32}]$	triclinic	—	22.700(4)	28.961(4)	21.676(5)	112.47(2)	92.01(2)	79.93(1)	13050.0	—

We have synthesized the cluster compound $[Cu_{12}Mo_8S_{32}]^{8-}$ (see Fig.1) which has a pseudo–cubane type $[Mo_8Cu_{12}]$ core (1 in Table 1) [22] . Each Mo atom occupies the vertex of the corner and the twelve Cu atoms take the positions in the edges. Neighbouring metal atoms are connected through bridge sulfur atoms and the local coordination sphere around each metal atom (Mo or Cu) approaches a tetrahedron structure. The Mo–Cu distances (2.688 to

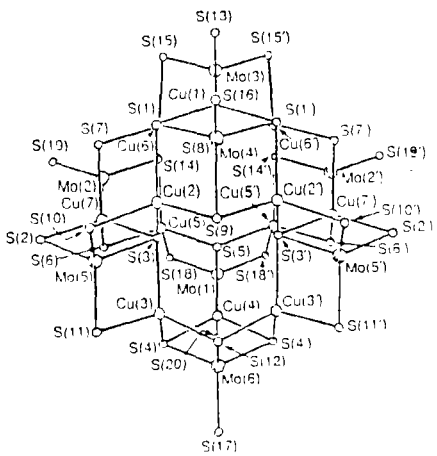

Fig.1 Structure of cluster anion $[Mo_8Cu_{12}S_{32}]^{4-}$

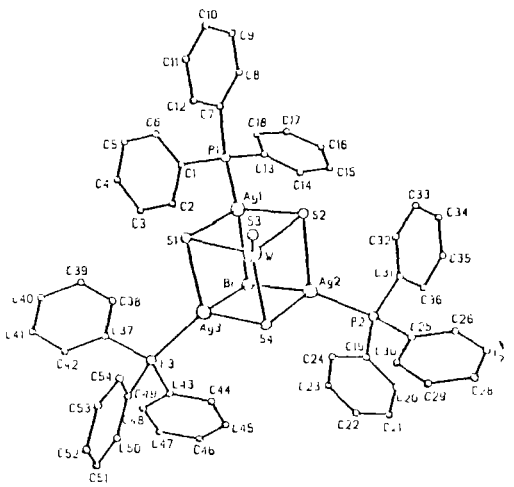

Fig.2 Molecular structure of $[Ag_3WS_3Br][PPh_3]_3S$

2.757 Å) permit the significant interaction of heteronuclear metallic atoms, and the Mo–S bond

distances vary between 2.065 and 2.301 Å. There are four types of sulfur atoms involved in this compound: S_t, μ_2–S μ_3–S and μ_4–S. And two types of molybdenum atoms and one type of copper atom are observed. All Cu atoms are coordinated by a μ_4–S, a μ_2–S and two μ_3–S atoms with a distorted tetrahedral geometry. One kind of Mo atom is coordinated by a S_t, and three μ_3–S atoms, the other one is coordinated by three μ_2–S and a μ_4–S. We have also synthesized the similar compound $[Cu_{12}W_8S_{32}]^{4-}$and determined its unit cell parameters (see Table 1).

Neutral cubane–like clusters

Seven neutral cubane–like cluster compounds (Table 2) have been synthesized in our lab. in recent years. Fig.2 shows molecular configuration of $[Ag_3WS_3Br][PPh_3]_3S$ [25] , including the phenyl ring atoms.The central unit of this cluster can be described as a strongly destorted 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. It can be described as a substitution product of $[PPh_3AgBr]_4$ [31] , where

Table 2 Summary of Crystal Data for Neutral Cubane–Like Clusters

	$[Cu_3WS_3Cl]$	$[Cu_3MoS_4]$	$[Cu_3MoS_3I]$	$[Cu_3WS_3Br]$	$[Ag_3MoS_3I]$	$[Ag_3WS_3Br]$	$[Cu_3MwS_3Cl]^*$
formula	$[PPh_3]_3S$	$[PPh_3]_3S$	$[PPh_3]_3S$	$[PPh_3]_3S$	$[PPh_3]_3S$	$[PPh_3]_3S$	$[PPh_3]_3S$
spacegroup,Z	P 1,2	$P2_12_12_1$,4	P 1,2	P 1,2	P 1,2	P 1,2	$P2_12_12_1$,4
a(Å)	13.049(3)	12.963(3)	11.395(2)	11.876(1)	12.114(2)	12.129(5)	17.764(3)
b(Å)	20.351(4)	17.793(3)	13.107(1)	13.065(2)	13.420(2)	13.340(0)	22.633(3)
c(Å)	11.876(2)	22.681(5)	20.473(5)	20.325(2)	20.346(2)	20.228(6)	12.948(2)
α(°)	94.75(2)	90.00	74.95(5)	74.95(1)	74.53(1)	74.48(3)	90.00
β(°)	115.97(1)	90.00	84.87(2)	85.39(1)	86.73(1)	87.17(8)	90.00
γ(°)	74.90(2)	90.00	64.27(1)	64.09(1)	63.74(1)	63.53(3)	90.00
V(Å^3)	2736	5231.5	2776.1	2737.3	2851.7	2814.0	5205.7
R,Rw	0.073,0.073	0.045,0.045	0.049,0.061	0.039,0.055	0.048,0.043	0.056,0.056	0.046,0.048
ref.	23	11	11	24	24	25	24

*: Mw = W : Mo = 0.556 : 0.444

Table 3 Summary of Selected Structural Data for Neutral Cubane–Like Clusters

compounds	M–S_t(Å)	M–S_{br}(Å)[a]	M–M(Å)[b]	M1–X(Å)	M2–X(Å)	M3–X(Å)
$[Cu_3WS_3Cl][PPh_3]_3S$	2.096	2.243	2.720	2.702	2.781	2.694
$[Cu_3MoS_4][PPh_3]_3S$	2.105	2.252	2.700	2.757	2.723	2.478
$[Cu_3MoS_3I][PPh_3]_3S$	2.097	2.253	2.713	2.912	2.943	2.967
$[Cu_3WS_3Br][PPh_3]_3S$	2.102	2.242	2.723	2.729	2.751	2.800
$[Ag_3MoS_3I][PPh_3]_3S$	2.106	2.253	2.979	3.103	3.019	3.070
$[Ag_3WS_3Br][PPh_3]_3S$	2.127	2.246	2.986	2.945	2.923	2.903
$[Cu_3MwS_3Cl][PPh_3]_3S$	2.100	2.256	2.714	2.481	2.738	2.706

a,b: average values

WS_4^{2-} ligand replaces one PPh_3AgBr_3 moiety. Table 3 shows a summary of the seven neutral cubane–like compounds together with some selected structural data.

Anionic cubane–like clusters

We have also synthesized five new anionic cubane–like clusters (Table 4). Fig.3 shows the structure of the cluster anion $[MoAg_3BrS_4I_3]^{3-}$ [26] . The cluster core $[Ag_3MoS_3Br]$ can be viewed as a cube in which the four metal atoms and the four non–metal atoms are statistically distributed by two kinds of atoms, respectively. Because it is situated in the specific equivalent positions in the unit cell with T_d symmetry, the three tetrahedrons $MoAg_3$, BrS_3 and SI_3 are co–centred, respectively. Mo and Ag, Br and S_{br}, S_t and I atoms are of probability statistics, respectively. Mo–Ag (or Ag–Ag), Mo–S_{br}(or Ag–S_{br}, Ag–Br), and Mo–S_t(or Ag–I) distances are 3.303(2), 2.701(1), and 2.741(3) Å, respectively.

Table 4　Summary of Crystal Data for Anionic Cubane–Like Clusters

formula	$[Ag_3MoS_4I_3Br]$ $[(n\text{–Bu})_4N]_3$	$[WS_4Cu_3Br_4]$ $[(n\text{–Bu})_4N]_3$	$[MoOS_3Ag_3I_3Br]$ $[(n\text{–Bu})_4N]_3$	$[MoS_3Ag_3Br_4]$ $[(n\text{–Bu})_4N]_3$	$[WAg_3S_4Br_4]$ $[(n\text{–Bu})_4N]_3$
space group,Z	*F*43*c*,8	—	—	*F*43*c*,8	*F*43*c*,8
crystal system	cubic	trigonal	tetragonal	cubic	cubic
a(Å)	24.577(6)	17.410(7)	12.224(5)	24.231(4)	24.221(4)
b(Å)	24.577(4)	17.410(7)	12.224(5)	24.231(4)	24.221(4)
c(Å)	24.577(4)	39.102(5)	12.175(9)	24.231(4)	24.221(4)
α(°)	90.00	90.00	90.00	90.00	90.00
β(°)	90.00	120.00	90.00	90.00	90.00
γ(°)	90.00	90.00	90.00	90.00	90.00
V(Å^3)	14845.2	10265.2	1819.55	14227.0	14208.7
R,*Rw*	0.088,0.061	—	—	0.078,0.087	0.071,0.068
ref.	26	24	24	24	24

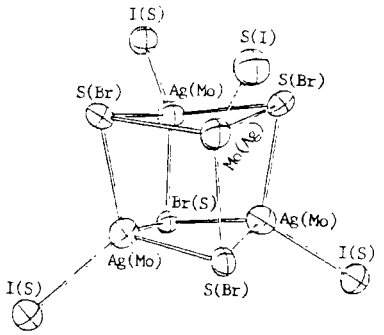

Fig.3 Structure of cluster anion $[MoAg_3BrS_4I_3]^{3-}$

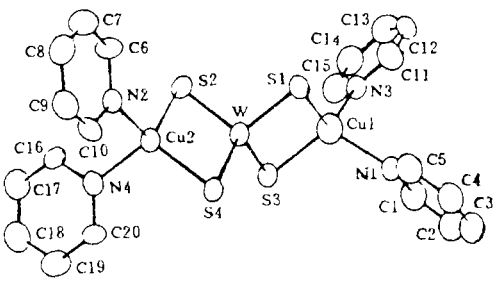

Fig.4 Molecular structure of $[WS_4Cu_2][py]_4$

Miscellaneous clusters

Several types of cluster compounds with interesting structure have been synthesized through solid state reactions in our lab. and structurally determined (Table 5). Here

we simply describe their structural characteristics.

$[WS_4Cu_2][py]_4$ is of a chain-like structure (see fig.4). Its main structural parameters are: W–S, 2.2141(8)–2.2160(8); W–Cu, 2.6564(7)–2.6856(7); Cu–S, 2.2609(9)–2.2781(1); Cu–N, 2.077(3)–2.100(3) Å.

Table 5 Summary of Crystal Data for Miscellaneous Clusters

formula	$[WS_4Cu_2]$ $[py]_4$	$[Cu_4Br_8]$ $[C_5H_5N(C_{16}H_{33})]_4$	$[Mo_4S_4Cl_4]$ $[(n\text{-}Bu)_4N]_3$	$[MoOS_3Cu_3(NCS)_3]$ $[(n\text{-}Bu)_4N]_3$
space group	$C2/c$,4	$P\bar{1}$,1	$F\bar{4}3c$,8	$P2_1/n$,4
a(Å)	14.109(1)	9.762(2)	24.212(4)	16.672(9)
b(Å)	12.704(1)	31.948(4)	24.212(4)	16.278(6)
c(Å	14.071(1)	9.143(2)	24.212(4)	19.608(8)
α(°)	90.00	94.71(1)	90.00	90.00
β(°)	96.97(1)	116.48(2)	90.00	110.05(2)
γ(°)	90.00	92.54(1)	90.00	90.00
V(Å^3)	2504.1	2533.0	14193.7	4999.0
R,Rw	0.027,0.027	0.083,0.100	0.071,0.071	0.068,0.061
ref.	27	28	11	24

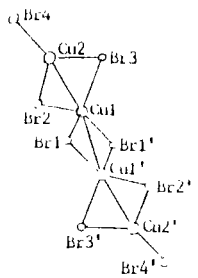

Fig.5 Structure of $[Cu_4Br_8]^{4-}$

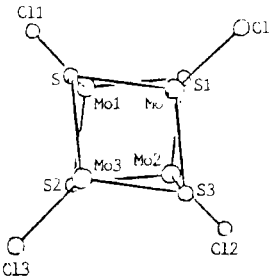

Fig.6 Structure of $[Mo_4S_4Cl_4]^{3-}$

$[C_5H_5N(C_{16}H_{33})]_4[Cu_4Br_8]$ is of a chain-like structure (see Fig.5). Its main structural parameters are: Cu–Br, 2.247(2); Cu–Cu, 2.956(3)–3.202(3) Å.

$[(n\text{-}Bu)_4N]_3[Mo_4S_4Cl_4]$ is of a cubane-like structure (see Fig.6). Its main structural parameters are: Mo–S, 2.570(5); Mo–Mo, 3.154(8); Mo–Cl, 2.587(11) Å.

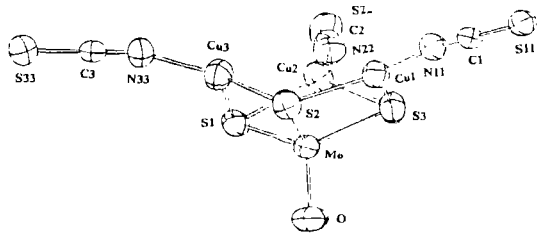

Fig.7 Structure of $[MoOS_3Cu_3(NCS)_3]^{3-}$

$[(n\text{-}Bu)_4N]_2[MoOS_3Cu_3(NCS)_3]$ is of a nido-like structure (see Fig.7). Its main structural parameters are: Mo–S_{br}, 2.248(5)–2.272(5); Mo–O_t, 2.272(5); Cu1–S, 2.252(4)–2.244(5);

Cu2-S, 2.250(4)-2.263(4), Cu3-S, 2.263(4)-2.266(4); Cu-N, 1.887(8)-1.907(8); Mo-Cu, 2.638(2)-2.652(2)Å. S-Mo-S, 107.0(2)-108.3(1); S-Mo-O, 109.1(5)-112.3(6); S-Cu-S, 107.8(2)-108.6(2); S-Cu-N, 120.1(5)-125.7(5); Mo-S-Cu, 71.4(1)-72.0(1); Cu-S-Cu, 98.0(2)-108.7(1); Cu-N-C, 166.1(3)-170.1(4); N-C-S, 176.5(2)-177.9(4)°.

Conclusion

1. A new method is proposed for synthesis of cluster and coordination compounds by solid state reactions at low heating temperatures.
2. Over fourty cluster compounds have been synthesized by this method. Among them, nearly twenty new cluster compounds have been structurally determined.
3. This new method is an effective one and it can be applied to synthesize non-sulfur containing cluster compounds.

Keywords: **solid state reaction** **crystal structure** **cluster compound**

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Reference

[1] Coucouvanis, D., *Acc. Chem. Res.*, **24**, 1 (1991).

[2] Zahello, P., *Coord. Chem. Rev.*, **87**, 1 (1988).

[3] Huang Yaozeng, Qian Yanlong, Advances in Organometallic Chemistry, p143, Chemical Industry Press, Beijing, 1987.

[4] Liu Hanqin et al., *Scientia Sinica, Ser.B*, **4**, 349 (1987).

[5] Xu Jiqing, *Hua Xue Tong Bao*, **10**, 1 (1986).

[6] Sarkar, S., Mishira, S.B.S., *Coord. Chem. Rev.*, **59**, 239 (1984).

[7] Gheller, S.F. et al., *Inorg. Chem.*, **23**, 2519 (1984).

[8] Muller, A., *Polyhedron*, **5**, 323 (1986).

[9] Muller, A. et al., *Angew. Chem. Int. Ed. Engl.*, **20**, 934 (1981).

[10] Jin Gaoxin, Ph.D. Thesis, Nanjing University, 1987.

[11] Li Jigao, Ph.D. Thesis, Nanjing University, 1990.

[12] Muller, A. et al., *Monat. Chem.*, **120**, 367 (1989).

[13] Cotton, F.A., Kibala, P.A., Matug, M., *Inorg. Chem.*, **28**, 2623 (1989).

[14] Muller, A., Jaegermann, W., Emmark, J., *Coord. Chem. Rev.*, **46**, 260 (1982).

[15] Ahlborn, E.K., Muller, A., *Angew. Chem., Int. Ed. Engl.*, **14**, 573 (1975); *Z. Anorg. Alleg. Chem.*, **476**, 171 (1981).

[16] Muller, A., Eltzner, W., unpulished results.

[17] Bronger, W., Huster, J., *Natuwissenschaften*, **56**, 88 (1969).

[18] Chandrasekaran, J., Sarkar, S., *Inorg. Chem.*, unpublished results.

[19] Chevrel, R., Sergent, M., Prigent, J., *J. Solid State Chem.*, **3**, 515 (1971).

[20] Zhu Huizhen, Cong Rongjuan, Xin Xinquan, Dai Anbang, *J. Inorg. Chem.*, **5**, 129 (1989).

[21] Gao Fengjun, M.Sc. Thesis., Nanjing University, China, 1989.

[22] Li Jigao, Xin Xinquan, Zhou Zhongyuan, Yu Kaibei, *J. Chem. Soc., Chem. Comm.*, 250 (1991).

[23] Liu Shixiong, Huang Jinling, Gao Fengjun, Zhu Huizhen, Xin Xinquan, *Chem. J. Chin. Univ.*, **11**(7), 667 (1990).

[24] Lang Jianping, Xin Xinquan, unpublished results.

[25] Lang Jianping, Zhu Huizhen, Xin Xinquan, Yu Kaibei, Zhou Zhongyuan, *J. Struct. Chem.*, **11**, 274 (1992).

[26] Cai Jinhua, Weng Linghong, Kang Beisheng, Lang Jianping, Zhu Huizhen, Xin Xinquan, *J. Struct. Chem.*, 1992, to be published.

[27] Gao Fengjun et al., *Chem. J. Chin. Univ.*, **11**, 1045 (1990).

[28] Lang Jianping, Zhu Huizhen, Xin Xinquan, Chen Mingqin, *Chem. J. Chin. Univ.*, **13**, 18 (1992).

[29] Shibahara, T., Akashi, H., Kuroya, H., *J. Am. Chem. Soc.*, **110**, 3313 (1988).

[30] Wu Xintao, Wang Bing, Zheng Yifan, Lu Jiaxi, *J. Struct. Chem.*, 7(1), 47 (1988).

[31] Teo, B.K., Calabrese, J. C., *Inorg. Chem.*, **15**, 2467 (1976).