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研究简报

$\{(n\text{-}Bu_4N)_2[Mo_2O_2S_6Cu_6Br_4(4,4'\text{-bipy})_3]\cdot 0.5H_2O\}_n$ 的合成与晶体结构

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Synthesis, Crystal Structure of a Zigzag Cluster Coordination Polymer $\{(n\text{-}Bu_4N)_2[Mo_2O_2S_6Cu_6Br_4(4,4'\text{-bipy})_3]\cdot 0.5H_2O\}_n$

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Abstract: Cluster coordination polymer $\{(n\text{-}Bu_4N)_2[Mo_2O_2S_6Cu_6Br_4(4,4'\text{-bipy})_3]\cdot 0.5H_2O\}_n$ (4,4′-bipy=4,4′-bipyridine), has been synthesized and characterized by X-ray crystallography. The polymeric anion $\{[Mo_2O_2S_6Cu_6Br_4(4,4'\text{-bipy})_3]^{2-}\}_n$ is composed of secondary building units (SBUs) $[MoOS_3Cu_3]$, Br atoms and 4,4′-bipy ligands. Two secondary building units $[MoOS_3Cu_3]$ and a double parallel 4,4′-bipy ligands form an octanuclear rectangular metallamacrocycle with the dimension of 1.13×0.39 nm^2, which is further connected by single bridging 4,4′-bipy ligands to form a 1D zigzag structure. Crystal data for compound **1**: $C_{62}H_{97}N_8O_{2.50}S_6Br_4Cu_6Mo_2$, M=2 079.68, Triclinic, $P\bar{1}$, a=0.982 40 (10) nm, b=1.293 70(10) nm, c=1.737 4(2) nm, α=97.810(10)°, β=101.390(10)°, γ=108.520(10)°, V=2.005 1(4) nm^3, Z=2, D_c=1.722 g·cm^{-3}, F(000)=1 039, μ (Mo $K\alpha$)=4.055 mm^{-1}, the final R=0.040 7, wR_2=0.097 2. CCDC: 236407.

Key words: coordination polymer; clusters; crystal structure

Recently, the concept of coordination polymer has become a focus for their great potential applied value in the fields of supramolecular chemistry, crystal engineering, nonlinear optical materials, porous material and catalytic reactions[1~4]. The coordination polymers were usually constructed by using metal ions or metal clusters as nodes and suitable multi-dentate bridging ligands as linkers, to form 1D infinite chains, 2D sheets and 3D frameworks[5~12]. The metal clusters have multiple metal sites available than single metal ion, could be designed as secondary building units (SBUs). The transition metal sulfur clusters have been developed for a long time[13~15]. The thiometallates core $[MO_nS_{4-n}]^{2-}$ (M=Mo, W; n=0~2) can easily bond to M′L (M′=Cu, Ag; L=Cl, Br, I, SCN, CN) to form a series of polymeric heterothiometallates[16]. For example, the reaction of

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$[MOS_3]^{2-}$ (M=Mo, W) with CuBr and 4-picoline produce $[MOS_3Cu_3]$ nest-shaped center containing 4-picoline[17]. These heterothiometallates $[MO_nS_{4-n}M'L]$ may be further designed as SBUs to produce many fascinating cluster coordination polymer than expected [18~23]. Herein we reported the structure of a 1D zigzag anionic cluster coordination polymer $\{(n\text{-}Bu_4N)_2[Mo_2O_2S_6Cu_6Br_4(4,4'\text{-bipy})_3]\cdot 0.5H_2O\}_n$ containing rectangular metallamacrocycle with nanometer-sized cavities.

The crystallographic data and other pertinent information are summarized in Table 1. Selected bond lengths and bond angles are listed in Table 2.

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The complex **1** was synthesized by self-assembly of $(NH_4)_2MoO_2S_2$, CuBr, $(n\text{-}Bu)_4NBr$ and 4,4′-bipy with the mol ratio 1∶2∶2∶2. The single crystal structure reveals that the complex **1** consists of interesting infinite zigzag polymeric anionic chains $[Mo_2O_2S_6Cu_6Br_4(4,4'\text{-bipy})_3]^{2-}_n$ and $[n\text{-}Bu_4N]^+$ cations. The cation has its expected structure as well as normal distances and angles, which will not be discussed further. The anion of cluster coordination polymer **1** consists of the nest-shaped SBU $[MoOS_3Cu_3]$, Br atoms and 4,4′-bipy ligand (Fig.1). In each of SBUs, one Mo atom, three μ_3-S atoms and three Cu atoms, assumes a nest-shaped structure similar to that of $[MoOS_3Cu_3X(py)_5]$ (X=Br, I) reported before[22]. The coordination circumstance of the three Cu atoms is different each other: Cu(1) is tetrahedrally coordinated with N(1), N(3) atoms from two 4,4′-bipy ligands and S(1), S(2) atoms from $[MoOS_3]^{2-}$; Cu(2) atom is triangularly coordinated by S(2), S(3) and Br(1) atoms, whereas Cu(3) is tetrahedrally coordinated by S(1), S(3), N(2) and Br(2) atoms. The bond distance of Mo-Cu(3) (0.268 94(9) nm) is a little longer than Mo-Cu(1) 0.264 30(8) nm and Mo-Cu(2) 0.263 60(10) nm . The center-to-center distance between two parallel 4,4′-bipy planes is about 0.39 nm indicating there are face-to-face weak π-π interactions between the two 4,4′-bipy

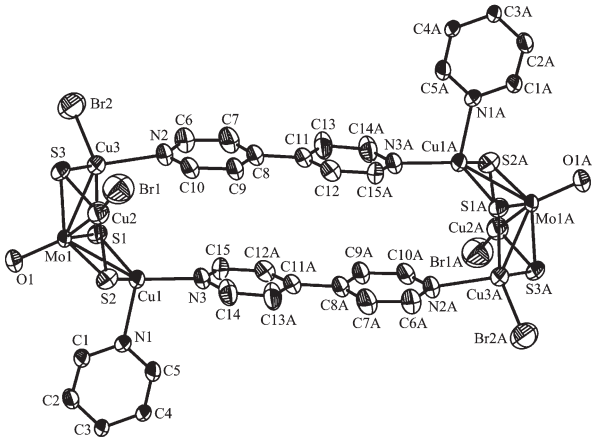
Table 1 Crystallographic data and structure refinement for complex 1

Empirical formula	$C_{62}H_{97}N_8O_{2.50}S_6Br_4Cu_6Mo_2$	Z	1
Formula weight	2 079.68	D_c / (g·cm^{-3})	1.722
Crystal system	Triclinic	F(000)	1 039
Space group	$P\bar{1}$	μ / mm^{-1}	4.054
Temperature / K	293(2)	θ range / (°)	1.87~25.00
a / nm	0.982 40(10)	R_{int}	0.03
b / nm	1.293 70(10)	Reflections collected	10 051
c / nm	1.737 4(2)	Independent reflections	6 936
α / (°)	97.810(10)	Reflections [$I>2\sigma(I)$]	4 631
β / (°)	101.390(10)	Goodness-of-fit on F^2	0.941
γ / (°)	108.520(10)	R indices [$I>2\sigma(I)$]	R_1=0.040 7, wR_2=0.097 2
V / nm^3	2.005 1(4)		

Table 2 Selected bond distances (nm) and angles (°) for complex 1

Mo(1)-O(1)	0.170 6(3)	Mo(1)-S(1)	0.224 85(16)	Mo(1)-S(2)	0.227 56(16)
Mo(1)-S(3)	0.225 39(15)	Mo(1)-Cu(1)	0.264 30(8)	Mo(1)-Cu(2)	0.263 60(10)
Mo(1)-Cu(3)	0.268 94(9)	Cu(1)-S(1)	0.226 56(17)	Cu(1)-S(2)	0.227 46(18)
Cu(2)-S(2)	0.223 67(17)	Cu(2)-S(3)	0.223 96(17)	Cu(3)-S(1)	0.230 32(16)
Cu(3)-S(3)	0.225 81(18)	Cu(1)-N(1)	0.212 4(4)	Cu(1)-N(3)	0.201 1(4)
Cu(3)-N(2)	0.212 5(4)	Cu(2)-Br(1)	0.223 92(12)	Cu(3)-Br(2)	0.237 08(11)
O(1)-Mo(1)-S(1)	108.96(15)	O(1)-Mo(1)-S(3)	111.67(13)	S(1)-Mo(1)-S(3)	108.16(6)
O(1)-Mo(1)-S(2)	111.94(14)	S(1)-Mo(1)-S(2)	108.73(6)	S(3)-Mo(1)-S(2)	107.27(6)
N(3)-Cu(1)-N(1)	100.21(17)	N(3)-Cu(1)-S(1)	117.27(16)	N(1)-Cu(1)-S(1)	106.60(13)
N(3)-Cu(1)-S(2)	120.41(17)	N(1)-Cu(1)-S(2)	101.60(13)	S(1)-Cu(1)-S(2)	108.17(6)

rings in the metallamacrocycle. The attractive character of this anion is that it has a wavelike zigzag chain with single 4,4′-bipy bridges and double parallel 4,4′-bipy bridges alternately (Fig.2). In this wavelike zigzag structure, the two SBUs of $[MoOS_3Cu_3]$ and two 4,4′-bipy molecules form a metallamacrocycle with the dimension of 1.13×0.39 nm^2, and the distance between the adjacent metallamacrocycles is about 1.13 nm. In the structure, the cations and the polymeric anions are stacked alternately viewing along *a* axis (Fig.3).



Symmetric code A: $-x$, $-y+1$, $-z+1$

Fig.1　ORTEP diagram (30% probability ellipsoids) showing structure unit of the anion $[Mo_2O_2S_6Cu_6Br_4(4,4\text{-bipy})_3]^{2-}{}_n$

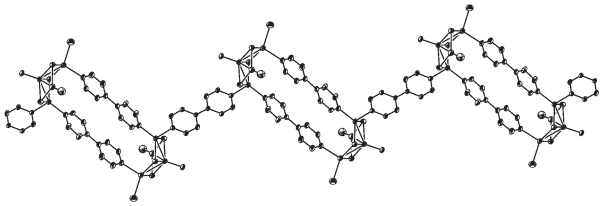
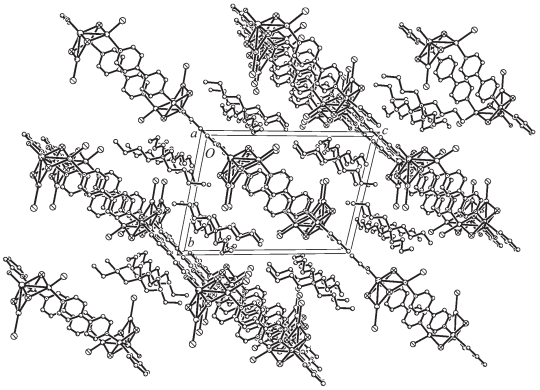


Fig.2　One-dimensional zigzag structure of anionic cluster coordination polymer **1**



H atoms and H_2O molecules are omitted for clarity

Fig.3　Packing picture along a axis of complex **1**

In conclusion, we have described a cluster coordination polymer based on the $[MoOS_3Cu_3]$ nest-shaped SBUs and 4,4′-bipy ligands, which possessing an interesting zigzag chain structure. It currently represents a great challenge to synthesis more and more cluster coordination polymers using the unique SBU with other organic ligands.

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