研究快报

# Synthesis of $[MoOS_3Cu_3I(3,5\text{-diMePy})_4]\cdot CH_3CN$ and $(Et_4N)_4[Mo_4Cu_8O_4S_{12}\{(Ph_2PS)_2N\}_4]$ from Solid State Product $[Et_4N]_4[Mo_2O_2S_6Cu_6I_4Br_2]$

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Treatment of iodide-bridged dimer $[NEt_4]_4[Mo_2O_2S_6Cu_6I_4Br_2]$ **1** with 3, 5-bimethylpyridine or with $K[(Ph_2PS)_2N]$ in $CH_3CN$ afforded the tetranuclear cluster $[MoOS_3Cu_3I(3,5\text{-diMePy})_4]\cdot CH_3CN$ **2** and dodecanuclear cluster $(Et_4N)_4[Mo_4Cu_8O_4S_{12}\{(Ph_2PS)_2N\}_4]$ **3**. Monomeric **2** possess a nest- shaped skeleton. The structure of oligomeric **3** can be regarded as a tetramer of nest-shaped $MoCu_3OS_3[(Ph_2PS)_2N]$ groups co-polymerized by sharing the limbic Cu atoms.

**Keywords:** solid state reaction nest-shape structure oligomeric cluster
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A well-ground mixture of $[NH_4]_2[MoS_2O_2]$, CuI, and $Et_4NBr$, was put into a reaction tube and heated at 80℃ for 4h under a nitrogen atmosphere. After extracting the resultant black solid with $CH_3CN$, the extract was filtered to afford a deep red filtrate which contains a twin-nest shape intermediate $[NEt_4]_4[Mo_2O_2S_6Cu_6I_4Br_2]$ **1**[1]. Twin-nest shape products are interesting because their bridge groups cleavage can incorporate different ligands into the cluster species with interesting skeletal structures. Taking advantage of its reactivity, we firstly succeed in introducing 3, 5-bimethylpyridine and $[Ph_2P(S)NP(S)Ph_2]^-$ into heterothiometallate system through ligand replacement (Scheme 1). Treatment of iodide-bridged dimer **1** with 3, 5-bimethylpyridine or with $K[(Ph_2PS)_2N]$ in $CH_3CN$ afforded the tetranuclear cluster $[MoOS_3Cu_3I(3,5\text{-diMePy})_4]\cdot CH_3CN$ **2** and oligomeric cluster $(Et_4N)_4[Mo_4Cu_8O_4S_{12}\{(Ph_2PS)_2N\}_4]$ **3**. The structures of **2** and **3** has been established by X-ray crystallography. Cluster **2** possess a nest-shaped skeleton. Compared to the reported nest-shaped clusters[2, 3], Cu atoms with two type of coordinated geometry coexist for the presence of the more sterically demanding iodide atom and the 3, 5-dimethylpyridine groups. In **3**

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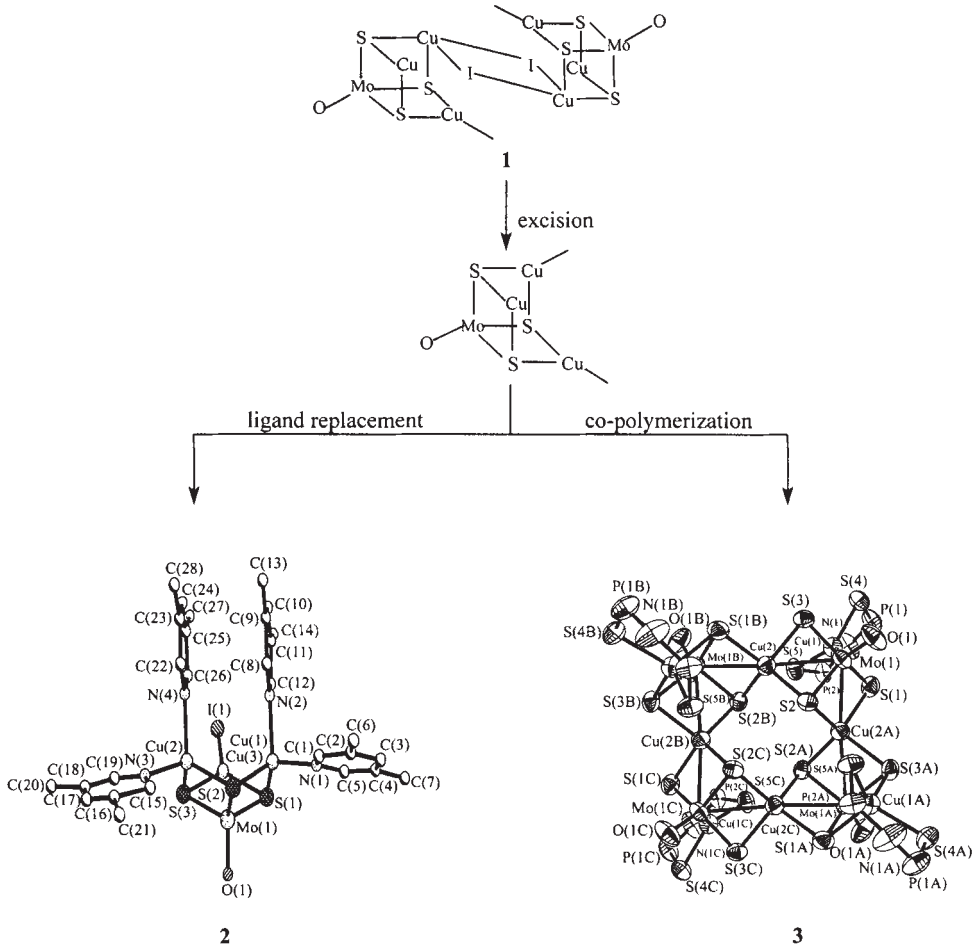
the anionic cluster consists of a square framework of $[Mo_4Cu_4O_4S_{12}]^-$, which is formed by four $MoOS_3^{2-}$ basic units linked via four Cu atoms, and four $Cu\{Ph_2P(S)NP(S)Ph_2\}$ pending units, each bound to one of the corner $MoOS_3$ moieties. The structure can also be regarded as a tetramer of nest-shaped $MoCu_3OS_3\{(Ph_2PS)_2N\}$ monomers co-polymerized by sharing the limbic Cu atoms.




Scheme 1

## References

[1] Hou H. W., Xin X. Q., Liu J., Chen M. Q., Shi S. *J. Chem. Soc., Dalton Trans.*, **1994**, 3211.

[2] Zheng H. G., Chen J. X., Xin X. Q., Leung W. H., Hong M. C. *Synth. React. Inorg. Met-Org-Chem.*, **2000**, **30** (4), 761.

[3] Ge P., Tang S. H., Ji W., Shi S., Hou H. W., Long D. L., Xin X. Q., Lu S. F., Wu Q. J. *J. Phys. Chem., B*, **1997**, **101** (1), 27.