An Unprecedented One-Dimensional Chain Constructed from β-Octamolybdate Clusters and Two Kinds of Silver Complex Fragments

Zhenyu Shi,[a] Xiaojun Gu,[a] Jun Peng,*[a] and Zhifeng Xin[a]

Keywords: Chainlike compound / Hydrothermal synthesis / Octamolybdate cluster / Ag complex

An unprecedented one-dimensional chainlike compound with green fluorescent emission, $(H_3O)[Ag_3(2,2'\text{-bpy})_2(\text{phnz})_2(\beta\text{-}Mo_8O_{26})]$ (bpy = bipyridine, phnz = phenazine) has been synthesized under hydrothermal conditions. The compound is constructed from β-octamolybdate clusters linked through two kinds of silver-ligand subunits, $[Ag(2,2'\text{-bpy})(\text{phnz})]^+$ and $[Ag(\text{phnz})]^+$.

Introduction

The significant contemporary interest in the crystal engineering of inorganic-organic hybrid materials not only originates from their diverse structural flexibility, but also from their widely promising potential applications in catalysis, medicine, photochemistry and electromagnetism.[1] Up to now, although a number of inorganic-organic hybrid compounds have been reported,[1f,2] the design and synthesis of novel hybrid materials with highly specific and cooperative functions are still a great challenge. Recently, one synthetic strategy for controlling structure-function relationship has been extensively investigated by choosing suitable building blocks and exploiting the selected or designed organic ligands with the structure-directing properties during the preparation of inorganic-organic hybrid materials, in which the features of the components can be combined to form unique architectures and new properties.[3] An attractive choice of building blocks is polyoxometalate (POM) clusters which, similar to organic ligands, can coordinate to metal centers to construct novel inorganic-organic hybrids.[4] However, among the reported POM-based hybrids, few POM clusters bridged by silver complex fragments have been reported.[5] On the other hand, silver coordination polymers not only are good candidates for potential conducting materials, but also show interesting photophysical and photochemical properties.[6]

As is already known, aromatic chelate ligands such as 2,2′-bipyridine are capable of "passivating" metal sites via the N donors, thus inhibiting expansion of the polymeric frameworks.[7] The polycyclic aromatic bridging ligands such as phenazine with bigger steric hindrance can induce metal ions with flexible coordination spheres to form a complex with a lower coordination number.[1i,8] Therefore, the introduction of two such kinds of organodiamine ligands at a Ag^I site may lead to low-dimensional coordination polymers consisting of π–π stacking interactions and other intermolecular forces which contribute to the physical and chemical behavior of Ag^I complexes.

In this study, we choose 2,2′-bipyridine as a chelate ligand, phenazine as a bridging ligand and Ag^I as the secondary metal, to hydrothermally synthesize a novel one-dimensional chainlike compound with photoluminescence activity, $(H_3O)[Ag_3(2,2'\text{-bpy})_2(\text{phnz})_2(\beta\text{-}Mo_8O_{26})]$ (bpy = bipyridine, phnz = phenazine). The compound represents the first example of octamolybdate clusters bridged by two kinds of organic aromatic amine ligands coordinated to Ag complex fragments.

Results and Discussion

Hydrothermal synthesis has been proved to be a powerful method for the construction of organic-inorganic hybrid materials. Although, in most cases, the reaction mechanisms under hydrothermal conditions are not clear and the control and prediction of crystal structures are difficult, the architecture of the final product directly depends on the interplay of the characteristics of metal ion, ligand, pH values and reaction temperature.[9] In the family of POMs, molybdenum polyoxoanions have received widespread attention owing to their different structures and versatile stoichiometry. It has been documented that the formation of different molybdenum oxoanion subunits can be controlled by the pH values.[3a,10] Generally, mononuclear molybdate $\{MoO_4\}$ exists in basic reaction conditions, while polyoxomolybdate clusters, such as $\{Mo_2O_7\}$, $\{Mo_3O_{10}\}$, $\{Mo_6O_{19}\}$ and $\{Mo_8O_{26}\}$, are most likely isolated under

---

[a] Institute of Polyoxometalate Chemistry, Department of Chemistry, Northeast Normal University,
Changchun, 130024, P. R. China
E-mail: jpeng@nenu.edu.cn
pjun56@yahoo.com

Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

DOI: 10.1002/ejic.200500330

acidic reaction conditions. The β-octamolybdate cluster anion is commonly crystallized from aqueous solutions of molybdate acidified to pH 3–4.

The single-crystal X-ray analysis reveals that the structure of the compound could be described as chains constructed from β-octamolybdates bridged by 2,2′-bipy- and phnz-coordinated Ag^I fragments. As shown in Figure 1, the centrosymmetric octamolybdate $\{Mo_8O_{26}\}$ moiety, which is built up from eight distorted $\{MoO_6\}$ edge-shared octahedrals, is a typical β-octamolybdate. The valence sum calculations show that all molybdenum atoms are in the +6 oxidation state.[11] According to the type of oxygen atoms bonded to the molybdenum atoms, the Mo–O bond lengths are divided into four categories: 1.692(5)–1.706(5) Å for Mo–O(t), 1.754(4)–2.267(4) Å for Mo–O(μ_2), 1.947(4)–2.340(4) Å for Mo–O(μ_3) and 2.135(4)–2.468(4) Å for Mo–O(μ_5) bonds, respectively. All these bond lengths are within the normal ranges and in close agreement with those described in the literature.[4]

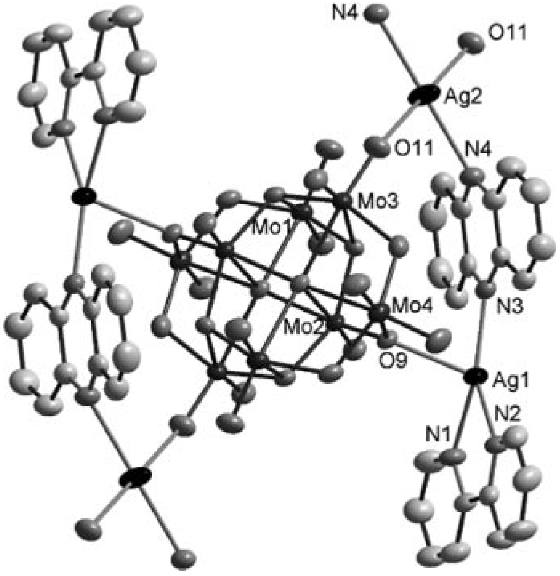

Figure 1. ORTEP drawing of the fundamental building block of the compound with the 50% probability level, showing the coordination environment around Ag and Mo. Only parts of atoms are labeled, and all the hydrogen atoms and water molecules are omitted for clarity.

There are two coordinated dinuclear Ag^I fragments around each β-octamolybdate cluster anion. Two crystallographically independent Ag sites comprise two different distinct environments (see Figure 1). One (Ag1) is coordinated by two nitrogen atoms (N1 and N2) from one 2,2′-bipy ligand, one nitrogen atom (N3) from one phnz ligand, and one bridging oxygen atom (O9) from one β-octamolybdate cluster to complete a trigonal-pyramidal coordination geometry (see Supporting Information, S1a). The atoms N1, N2, N3 and Ag1 nearly lie in the same plane [N3–Ag1–N2 = 144.3(2)°, N2–Ag1–N1 = 71.7(2)°, and N3–Ag1–N1 = 143.2(2)°], while the O9 atom is almost perpendicular to the plane, with the O9–Ag1–N3 angle of 81.5(2)°. The other (Ag2) is coordinated by two nitrogen atoms from two phnz ligands [Ag–N = 2.364(5) Å] and two terminal oxygen atoms from two β-octamolybdate clusters [Ag–O = 2.405(5) Å]. The N4–Ag2–O11 and N4#–Ag2–O11 angles are 82.38(2)° and 97.62(2)°, respectively. The sum of the four N–Ag–O angles is 360.00(4)°, which shows that the Ag(2) site exhibits a distorted square-planar coordination geometry (see Supporting Information, Figure S1b). As is already known, Ag^I generally adopts linear, trigonal, tetrahedral and octahedral coordination geometries, whereas the trigonal-pyramidal and square-planar coordination geometries are less reported. Furthermore, examples of two such kinds of coordination modes existing in the same Ag^I compound have not been documented. The two silver atoms (Ag1 and Ag2) are joined together by one phnz ligand, which acts as a bidentate bridging ligand.

The interesting structural feature of the compound is that β-octamolybdate clusters are linked together by Ag^I fragments through both terminal and bridging oxygen atoms to form a one-dimensional chain (see Figure 2). Interestingly, all the Ag^I ions in the same chain are coplanar. The adjacent one-dimensional chains in the compound are stacked into a two-dimensional supramolecular network (see Figure 3) through offset π–π aromatic stacking interactions with the closest face-to-face distance of ca. 3.40 Å. Protonated water molecules (Ow1) are positioned between the adjacent two-dimensional supramolecular networks and form the hydrogen bonding interactions with the terminal oxygen atoms coming from β-octamolybdate clusters, thus resulting in a three-dimensional supramolecular array (see Supporting Information, Figure S2). The typical hydrogen bonds are as follows: O(6)···Ow(1) 2.892 Å, Ow(1)···O(5) 2.854 Å, Ow(1)···O(8) 2.897 Å, Ow (1)···O(13) 3.001 Å.

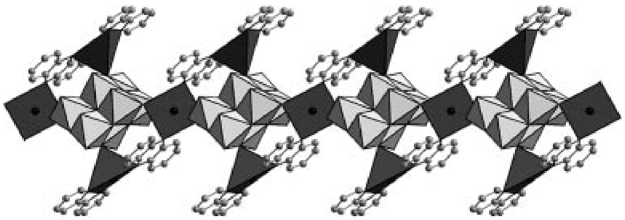

Figure 2. A view of the one-dimensional chain in the compound, all hydrogen atoms and water molecules are omitted for clarity.

Another interesting structural feature is that π–π stacking and Ag^I–π interactions coexist in the compound. To the best of our knowledge, no POM-based Ag^I complexes consisting of π–π stacking and Ag^I–π interactions have been reported. In the compound, the offset face-to-face distance is ca. 3.40 Å. The closest Ag···C contact between adjacent molecules is 3.37(2) Å, which is longer than those found for Ag^I complexes of other polycyclic aromatic compounds (see Figure 4).[6a]

In the infrared spectrum of the compound (as shown in Figure S3), the strong bands at 909, 831, 760, 691, 557 cm^{-1} are attributed to the μ(Mo=O) or μ(Mo–O–Mo) vibrations, while bands in the 1683–1419 cm^{-1} regions can be assigned to characteristic peaks of ligands 2,2′-bipy and phnz.

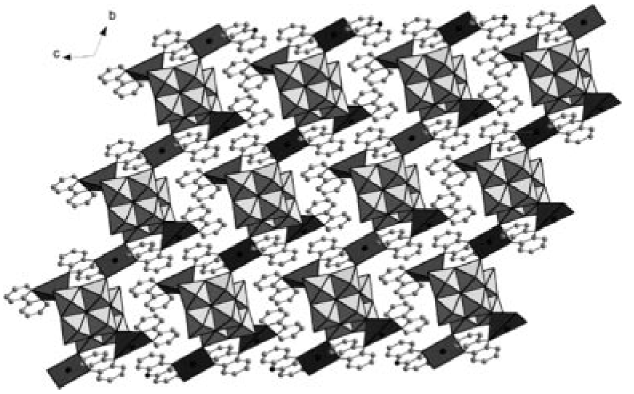

Figure 3. A view of the one-dimensional $\{Ag_3(2,2'\text{-bpy})_2(\text{phnz})_2(\beta\text{-}Mo_8O_{26})\}^-$ chains linked into a two-dimensional layer through supramolecular interactions. All hydrogen atoms are omitted for clarity.

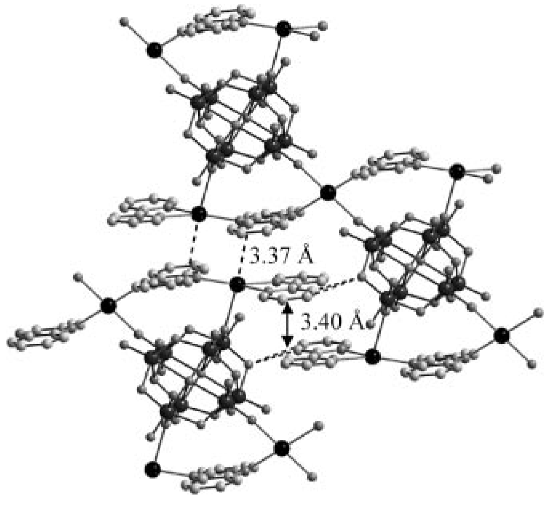

Figure 4. View of the compacted aromatic stacking interactions and significant interactions between the Ag^I ion and aromatic group in the compound.

The thermal gravimetric (TG) curve of the compound exhibits two steps of weight loss in the temperature range 30 to 700 °C (see Figure S4). The first weight loss of 0.63% in the temperature range 40–110 °C corresponds to the release of crystalline water. The second weight loss of 31.08% at 290–430 °C is ascribed to decomposition of organic ligands 2,2′-bipy and phnz. The total weight loss of 31.71% is in good accordance with the calculated value 31.52%.

Generally, Ag^I complexes may emit weak photoluminescence at low temperature.[6b] Whereas, at room temperature the compound in the powdered solid state displays intense photoluminescence with an emission maximum that occurs at 517 nm upon excitation at 420 nm (see Supporting Information, Figure S5). Comparably, the emission bands of the free ligands in the solid state are centered at about 394 nm (λ_{ex} = 330 nm) for 2,2′-bipy and 480, 512 nm (λ_{ex} = 445 nm) for phnz (see Figure S6). It is worth noting that the luminescent properties of the ligands 2,2′-bipy and phnz are very weak, therefore the strong photoluminescence of the compound may originate from the Ag^I–π interactions between Ag^I and the phnz ligand. Since the compound is insoluble in water and common solvents such as ethanol, acetone, acetonitrile and benzene, it may be a good candidate for solvent-resistant green fluorescent material.

In conclusion, a new one-dimensional chainlike compound with green fluorescent emission, constructed from β-octamolybdates linked by two kinds of organic aromatic amine ligands coordinated to Ag^I units, has been successfully synthesized. It represents the first example of POM-based inorganic-organic hybrids in which π–π stacking and Ag^I–π interactions coexist.

Experimental Section

Materials: All reagents and solvents for the syntheses were purchased from commercial and used as received.

Physical Methods: Elemental analyses (C, H, and N) were performed on a PerkinElmer 2400 CHN Elemental Analyzer. Ag and Mo were determined by a Leaman inductively coupled plasma (ICP) spectrometer. IR spectra were obtained on Alpha Centaurt FT/IR spectrometer with KBr pellets in the 400–4000 cm^{-1} region. The TG analyses were performed on a Perkin–Elmer TGA7 instrument in flowing N_2 with a heating rate of 10 °C min^{-1}. Excitation and emission spectra were obtained on a Cary Eclipse.

Synthesis of $(H_3O)[Ag_3(2,2'\text{-bpy})_2(\text{phnz})_2(\beta\text{-}Mo_8O_{26})]$: A mixture of $(NH_4)_6Mo_7O_{24}\cdot 2H_2O$ (0.4140 g, 0.335 mmol), $AgNO_3$ (0.1138 g, 0.67 mmol), 2,2′-bpy (0.1046 g, 0.67 mmol), phnz (0.0603 g, 0.335 mmol) and H_2O (12 mL) in a mol ratio of 1:2:2:1:2000 was sealed in a Teflon-lined stainless autoclave and heated at 165 °C for 5 days. Yellow crystals of the compound were filtered, washed with water and dried at room temperature. Yield 0.162 g (33% based on silver). Initial pH, 3.8; final pH, 3.3. Elemental analysis for the compound $C_{44}H_{35}Ag_3Mo_8N_8O_{27}$ (2198.91): calcd. C 24.02, H 1.59, N 5.10, Ag 14.73, Mo 34.92; found C 23.96, H 1.46, N 5.18, Ag 14.67, Mo 34.88. IR (KBr): $\tilde{\nu}$ = 3446 (m), 1683 (m), 1558 (m), 1540 (m), 1521 (m), 1490 (m), 1472 (m), 1437 (m), 1419 (m), 909 (m), 831 (w), 760 (w), 691 (m), 557 (w) cm^{-1}.

X-ray Crystallography: Crystal data for the compound was collected on a Rigaku R-AXIS RAPID IP diffractometer, with Mo-K_α-monochromated radiation (λ = 0.71073 Å) at 293 K. An empirical absorption correction was applied.[12] The structure was solved by directed methods and refined by full-matrix least-squares on F^2 using the SHELXTL crystallographic software package.[13] All the non-hydrogen atoms were refined anisotropically. Ow1 was located from difference maps and refined anisotropically, while the hydrogen atoms attached to Ow1 were not located. The positions of hydrogen atoms on carbon atoms were calculated theoretically. Selected bond lengths and angles are listed in Table S1 (see Supporting Information). Crystal data: $C_{44}H_{35}Ag_3Mo_8N_8O_{27}$, triclinic, $P\bar{1}$, M_r = 2198.91 $g\,mol^{-1}$, a = 10.132(2) Å, b = 12.106(2) Å, c = 13.283(3) Å, α = 114.43(3)°, β = 107.76(3)°, γ = 90.76(3)°, V = 1394.3(5) $Å^3$, Z = 1, D_c = 2.615 $g\,cm^{-3}$, $F(000)$ = 1045, θ range 2.61–27.48°. A total of 9334 reflections were collected and 6204 were independent (R_{int} = 0.0293). The final refinement including hydrogen atoms converged to R = 0.0456, wR = 0.0944, $(\Delta\rho)_{max.}$ = 0.98 $e\,Å^{-3}$ (0.72 Å from Mo4), $(\Delta\rho)_{min.}$ = –0.98 $e\,Å^{-3}$ (0.88 Å from Ag2).

CCDC-267510 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

This research was supported financially by the National Science Foundation of China (20271011).

---

[1] a) V. Soghomonian, Q. Chen, R. C. Haushalter, J. Zubieta, *Science* **1993**, *259*, 1596–1599; b) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003**, *423*, 705–714; c) P. S. Halasyamani, M. J. Drewitt, D. O'Hare, *Chem. Commun.* **1997**, 867–868; d) Z. Shi, S. H. Feng, S. Gao, L. R. Zhang, G. Y. Yang, J. Hua, *Angew. Chem. Int. Ed.* **2000**, *39*, 2325–2327; e) A. Müller, H. Reuter, S. Dillinger, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2328–2361; f) S. T. Zheng, J. Zhang, G. Y. Yang, *Inorg. Chem.* **2005**, *44*, 2426–2430; g) E. Coronado, C. J. G. Garcia, *Chem. Rev.* **1998**, *98*, 273–296; h) Y. G. Wei, B. B. Xu, C. L. Barnes, Z. H. Peng, *J. Am. Chem. Soc.* **2001**, *123*, 4083–4084; i) A. N. Khlobystov, A. J. Blake, N. R. Champness, D. A. Lemenovskii, A. G. Majouga, N. V. Zyk, M. Schröder, *Coord. Chem. Rev.* **2001**, *222*, 155–192.

[2] a) C. M. Liu, D. Q. Zhang, M. Xiong, D. B. Zhu, *Chem. Commun.* **2002**, 1416–1417; b) J. Y. Niu, D. J. Guo, J. P. Wang, J. W. Zhao, *Cryst. Growth Des.* **2004**, *4*, 241–247; c) L. M. Duan, C. L. Pan, J. Q. Xu, X. B. Cui, F. T. Xie, T. G. Wang, *Eur. J. Inorg. Chem.* **2003**, 2578–2581; d) A. Dolbecq, P. Mialane, L. Lisnard, J. Marrot, F. Sécheresse, *Chem. Eur. J.* **2003**, *9*, 2914–2920.

[3] a) E. Burkholder, V. Golub, C. J. O'Connor, J. Zubieta, *Inorg. Chem.* **2003**, *42*, 6729–6740; b) M. E. Davis, W. B. Lin, *J. Am. Chem. Soc.* **2001**, *123*, 10395–10396.

[4] a) A. Kitamuura, T. Ozeki, A. Yagasaki, *Inorg. Chem.* **1997**, *36*, 4275–4279; b) J. Q. Xu, R. Z. Wang, G. Y. Yang, Y. H. Xing, D. M. Li, W. M. Bu, L. Ye, Y. G. Fan, G. D. Yang, Y. Xing, Y. H. Lin, H. Q. Jia, *Chem. Commun.* **1999**, 983–984; c) D. Hagrman, C. Zubita, D. J. Rose, J. Zubieta, R. C. Haushalter, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 873–876; d) C. D. Wu, C. Z. Lu, H. H. Zhuang, J. S. Huang, *Inorg. Chem.* **2002**, *41*, 5636–5637; e) J. Lü, E. H. Shen, Y. G. Li, D. R. Xiao, E. B. Wang, L. Xu, *Cryst. Growth Des.* **2005**, *5*, 65–67; f) D. G. Allis, E. Burkholder, J. Zubieta, *Polyhedron* **2004**, *23*, 1145–1152; g) D. Hagrman, H. D. Hagrman, J. Zubieta, *Inorg. Chim. Acta* **2000**, 212–224.

[5] a) H. Abbas, A. L. Pickering, D. L. Long, P. Kögerler, L. Cronin, *Chem. Eur. J.* **2005**, *11*, 1071–1078; b) S. M. Chen, C. Z. Lu, Y. Q. Yu, Q. Z. Zhang, X. He, *Inorg. Chem. Commun.* **2004**, *7*, 1041–1044; c) E. Burkholder, J. Zubieta, *Solid State Sci.* **2004**, 1421–1428.

[6] a) S. L. Zheng, J. P. Zhang, W. T. Wong, X. M. Chen, *J. Am. Chem. Soc.* **2003**, *125*, 6882–6883; b) M. L. Tong, X. M. Chen, B. H. Ye, L. N. Ji, *Angew. Chem. Int. Ed.* **1999**, *38*, 2237–2240.

[7] Y. G. Li, N. Hao, Y. Lu, E. B. Wang, Z. H. Kang, C. W. Hu, *Inorg. Chem.* **2003**, *42*, 3119–3124.

[8] a) H. Miyasaka, R. Clérac, C. S. Campos-Fernándz, K. R. Dunbar, *J. Chem. Soc., Dalton Trans.* **2001**, 858–861; b) A. J. Blake, N. R. Champness, A. N. Khlobystov, D. A. Lemenovskii, W. S. Li, M. Schröder, *Chem. Commun.* **1997**, 1339–1340.

[9] S. O. H. Gutschke, M. Molinier, A. K. Powell, R. E. P. Winpenny, P. T. Wood, *Chem. Commun.* **1996**, 823–824.

[10] C. Z. Lu, C. D. Wu, H. H. Zhuang, J. S. Huang, *Chem. Mater.* **2002**, *14*, 2649–2655.

[11] I. D. Brown, D. Altermatt, *Acta Crystallogr., Sect. B* **1985**, *41*, 244–247.

[12] R. H. Blessing, *Acta Crystallogr., Sect. A* **1995**, *51*, 33–37.

[13] a) G. M. Sheldrick, *SHELXL 97, Program for Crystal Structure Refinement*, University of Göttingen, Germany, **1997**; b) G. M. Sheldrick, *SHELXL 97, Program for Crystal Structure Solution*, University of Göttingen, Germany, **1997**.

Received: April 20, 2005