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Hydrothermal Synthesis and Structure of a New Helical Chain Constructed from Only Molybdenum–Oxide Building Blocks

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The compound $[NH_3(CH_2)_2NH_2(CH_2)_2NH_3]_2[Mo_9O_{30}]$ was synthesized at 170 °C via hydrothermal techniques from the starting materials of $Na_2MoO_4 \cdot H_2O$, $NH_2(CH_2)_2NH(CH_3)_2NH_2$, and H_2O. The compound crystallizes in the space group *C*2/*c* of the monoclinic system with $a = 21.308(4)$ Å, $b = 9.234(2)$ Å, $c = 19.195(4)$ Å, $\beta = 120.27(3)°$, $V = 3261.9(11)$Å^3, $Z = 4$. Two novel and symmetrically related helices coexist in the centrosymmetric solid, in which the two kinds of helices appear in the left-handed and right-handed enantiomorphs, respectively. This is the first example of a helical chain structure consisting of only molybdenum–oxide building blocks. The central axis about each helical chain is a 2-fold screw axis.

The rapid progress of exploring metal oxide-based inorganic/organic hybrid materials is driven by interest in their hierarchical structures and potential applications in fields such as catalysis, sorption, electric conductivity, magnetism, and optical materials.[1] In particular, solid oxides with either helical or chiral structure are of intense interest in current chemistry.[2] The combination of inorganic components with the structure-directing properties of organic amines by a hydrothermal technique has led to the successful syntheses of many molybdenum oxide-based solid materials with 1D chain, 2D layer, 3D open-framework structures, which has been well reviewed in a recent publication by Zubieta and co-workers.[3] However, by comparison with a large number of the molybdenum oxides modified structurally by incorporating transition metal complexes or other nonmetal elements, the solid materials of one-dimensional structure with only molybdenum oxide frameworks have been reported rarely,[4−7] although they may possess potential catalytic properties related with that conventional catalyst of molybdenum trioxide.[8] Zubieta and co-workers have synthesized a molybdenum oxide $(NH_3CH_2CH_2NH_3)[Mo_3O_{10}]$; this structure consists of a one-dimensional chain of edge-, corner-, and face-sharing molybdenum octahedra.[4] The other one-dimensional structural molybdenum oxide $[NH_3(CH_2)_6NH_3][Mo_4O_{13}]$ has also been prepared by Xu and co-workers, in which this chain structure is constructed from $[Mo_4O_{13}]^{2-}$ subunits composed of edge-sharing octahedra.[5] A helical molybdenum oxide fluoride of $Zn(pyz)(H_2O)_2MoO_2F$, in which a 3_1 screw axis passes down the center of the inorganic spiral, has been recently reported by Poeppelmeier and co-workers.[9] While this type of solid materials is expected to arise more often, the exploration of unusual structures and useful properties still remains a challenge. Fortunately, it was well-known that organic templates can dramatically influence the inorganic oxide microstructure. As a result, it is possible to obtain structurally complex molybdenum oxides by template-directive self-assembly in hydrothermal synthesis. In addition, on the basis of a great quantity of research reports and our previous practical experience, we consider that the molybdenum oxide framework can be easily modified because of its high reactivity and structural flexibility.[10]

Therefore, our aim was to synthesize complex structures of molybdenum oxides using simple molybdate as the starting materials and organic polyamine as the template. Herein, we report the synthesis and X-ray crystal structure analysis of a

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(1) (a) A. K. *Science* **1994**, *264*, 794. (b) Müller, A.; Reuter, H.; Dillinger, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2328. (c) Pope, M. T.; Müller, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 34. (d) Hagrman, D.; Haushalter, R. C.; Zubieta, J. *Chem. Mater.* **1998**, *10*, 361. (e) Yaghi, O. M. *Nature* **1999**, *402*, 276. (f) Yaghi, O. M. *J. Am. Chem. Soc.* **1998**, *120*, 8571.

(2) (a) Trodjman, I.; Masse, R.; Guitel, J. C. Z. *Kristallogr.* **1974**, *139*, 103. (b) Karasawa, S. *Jpn. J. Appl. Phys.* **1974**, *13*, 799.

(3) Hagrman, P. J.; Hagrman, D.; Zubieta, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2638.

(4) Khan, M. I.; Chen, Q.; Zubieta, J. *Inorg. Chim. Acta* **1993**, *213*, 325.

(5) Xu, Y.; An, L.-H.; Koh, L.-L. *Chem. Mater.* **1996**, *8*, 814.

(6) Range, K.; Fassler, A. *Acta Crystallogr., Sect C* **1990**, *46*, 488.

(7) Gatehouse, B. M.; Leverett, P. *J. Chem. Soc. A* **1968**, 1398.

(8) (a) Skupiski, W.; Malesa, M. *Appl. Catal., A* **2002**, *236*, 223. (b) Smith, M. R.; Ozkan, U. S. *J. Catal.* **1993**, *141*, 124. (c) Machiels, C. J.; Cheng, W. H.; Chowdhry, U.; Farneth, W. E.; Hong, F.; McCarron, E. M.; Sleight, A. W. *Appl. Catal.* **1986**, *25*, 249.

(9) Maggard, P. A.; Stern, C. L.; Poeppelmeier, K. R. *J. Am. Chem. Soc.* **2001**, *123*, 7742.

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Table 1. Bond Valence Sums for Mo and O Atoms

Mo1	5.941	O1	1.667	O6	2.063	O11	1.815
Mo2	6.006	O2	1.671	O7	1.712	O12	1.789
Mo3	6.063	O3	1.717	O8	1.868	O13	1.951
Mo4	5.995	O4	1.759	O9	1.774	O14	1.600
Mo5	6.096	O5	1.823	O10	1.788	O15	2.101

helical chain molybdenum oxide $[NH_3(CH_2)_2NH_2(CH_2)_2NH_3]_2[Mo_9O_{30}]$ (**1**). Unlike those previous reported helix structures,[11] compound **1** contains a helical chain constructed from only $\{MoO_6\}$ octahedra.

Compound **1** was prepared by the hydrothermal reaction of $Na_2MoO_4 \cdot H_2O$, $NH_2(CH_2)_2NH(CH_3)_2NH_2$, and H_2O in a molar ratio 3:1:556 at 170 °C for 3 days. The crystalline product was characterized by single-crystal X-ray diffraction analysis,[12] elemental analysis, IR spectroscopy, and thermogravimetric analysis/differential thermal analysis (TGA-DTA).

A single-crystal X-ray diffraction analysis revealed that compound **1** consists of one-dimensional helical chains built up from only $\{MoO_6\}$ octahedra, and charge compensation is achieved by the protonated amine $[NH_3(CH_2)_2NH_2(CH_2)_2NH_3]^{3+}$. The 6+ oxidation state of molybdenum in **1** is consistent with the bond valance sum ($BVS_{av} = 6.02$).[13] The bond valence sums at the O and Mo sites are given in Table 1. The central axis about this helical chain is a 2-fold screw axis. As shown in Figure 1a, the helical chain of compound **1** is derived from the linkage of $[Mo_9O_{30}]$ subunits (Figure 2). Each subunit $[Mo_9O_{30}]^{6-}$ can be considered to be composed of two fragments, i.e., a $[Mo_8O_{26}]^{4-}$ cluster and a $\{MoO_6\}$ octahedron. There are three kinds of Mo−O bond lengths in $[Mo_8O_{26}]^{4-}$, related with terminal, doubly bridging, and triply bridging oxo groups, giving average values of 1.71, 1.92, 2.21 Å, respectively. In the structure of **1**, the MoO_6 octahedra are considerably distorted around the molybdenum center, with a spread of the Mo−O bond distances which range from 1.70 to 2.39 Å (see Table 2). The similar distortions of MoO_6 octahedra were also observed in other Mo(VI) polyoxoanions,[4,5] suggesting that such distortions do not result from a steric effect within the chains. A rational explanation for the origin of the strong distortion of the MoO_6 octahedron should be related with the nature of the Mo−O interaction, which changes from strongly covalent for the shortest bond to a predominantly ionic interaction for the longest bonds in the MoO_6 octahedron.[14] Therefore, such distortion of the MoO_6 octahedron, resulting from different Mo−O distances, is a requirement to stabilize the whole structure of the oxo−molybdenum framework. Virtually, the structural feature of the $[Mo_8O_{26}]^{4-}$ cluster in **1** resembles that of γ-$[Mo_8O_{26}]^{4-}$, one well-known polyoxoanion isomer.[15] The only difference is that its six Mo atoms lying in the equatorial plane are all six-coordinated, while in γ-$[Mo_8O_{26}]^{4-}$ the two Mo atoms labeled with an asterisk (*) are five-coordinated. Thus, the $[Mo_8O_{26}]^{4-}$ cluster of **1** can be designated as pseudo-γ-$[Mo_8O_{26}]^{4-}$. Such pseudo-γ-

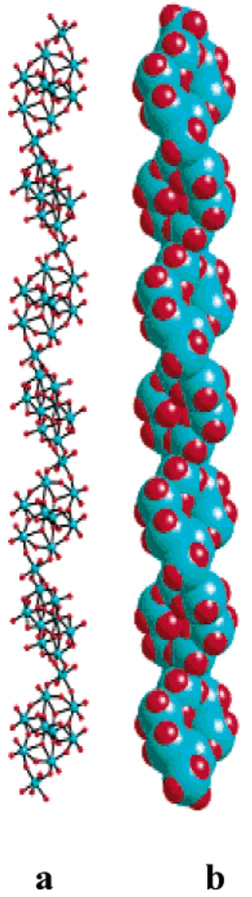

Figure 1. (a) Ball-and stick view of the helical chain of $[Mo_9O_{30}]_\infty$. (b) View of the space-filling plot of the helical chain of $[Mo_9O_{30}]_\infty$. Color code: Mo, blue; O, red.

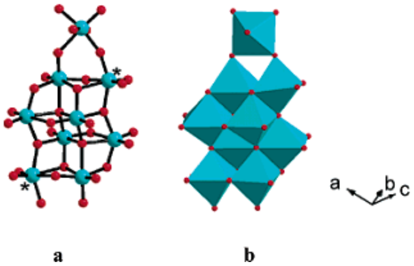

Figure 2. (a) Ball-and stick view of the subunit $[Mo_9O_{30}]^{6-}$. (b) Polyhedral view of the subunit $[Mo_9O_{30}]^{6-}$.

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(10) (a) Xu, L.; Lu, M.; Xu, B.; Wei, Y.; Peng, Z.; Powell, D. R. *Angew. Chem., Int. Ed.* **2002**, *41*, 4129. (b) Xu, L.; Sun, Y.; Wang, E. *New J. Chem.* **1999**, *23*, 1041. (c) Xu, L.; Sun, Y.; Wang, E. *J. Solid State Chem.* **1999**, *146*, 533. (d) LaDuca, R. L.; Desciak, M.; Laskoski, M.; Rarig, R. S.; Zubieta, J. *J. Chem. Soc., Dalton Trans.* **2000**, 2255. (e) Guesdon, A.; Borel, M. M.; Leclaire, A.; Raveau, B. *Chem. Eur. J.* **1997**, *3*, 1797.

(11) (a) Soghomonian, V.; Chen, Q.; Haushalter, R. C.; Zubieta, J.; O'Connor, C. J. *Science* **1993**, *259*, 1596. (b) Lii, K. H. *J. Chem. Soc., Dalton Trans.* **1996**, 815. (c) Shi, Z.; Feng, S.; Gao, S.; Zhang, L.; Yang, G.; Hua, J. *Angew. Chem., Int. Ed.* **2000**, *39*, 2325. (d) Lu, J.; Xu, Y.; Goh, N. K.; Chia, L. S. *Chem. Commun.* **1998**, 2733. (e) Lu, C.; Wu, C.; Lu, S.; Liu, J.; Wu, Q.; Zhuang, H.; Huang, J. *Chem. Commun.* **2002**, 152.

(12) Crystal data for $C_8H_{32}Mo_9N_6O_{30}$ (**1**): Crystal dimensions 0.496 × 0.456 × 0.100 mm^3, monoclinic, *C*2/*c* (No.15), $a = 21.308(4)$ Å, $b = 9.234(2)$ Å, $c = 19.195(4)$ Å, $\beta = 120.27(3)°$, $V = 3261.9(11)$ Å^3, $Z = 4$, $\rho_{calcd} = 3.168$ g cm^{-1}. Of the 7054 reflections measured ($2.21 \leq \theta \leq 27.48$), 3727 symmetry-independent reflections were used to solve the structure. On the basis of all these data and 241 refined parameters, R1 = 0.0404 (all data), wR2 = 0.0932, and GOF(F^2) = 1.184.

(13) Brown, L. D.; Altermatt, D. *Acta Crystallogr., Sect. B* **1985**, *41*, 244.

(14) Cora, F.; Patel, A.; Harrison, N. M.; Poetti, C.; Catlow, C. R. A. *J. Mater. Chem.* **1997**, *7*, 959.

(15) Hagrman, P. J.; Zubieta, J. *Inorg. Chem.* **1999**, *38*, 4480.

Table 2. Bond Lengths (Å) for Mo Atoms[a]

Mo(5)−O(9)	1.695(4)	Mo(3)−O(11)	1.805(4)
Mo(5)−O(5)	1.744(4)	Mo(2)−O(3)	1.707(5)
Mo(5)−O(12)	1.879(4)	Mo(2)−O(13)	1.955(4)
Mo(5)−O(15)	1.949(4)	Mo(2)−O(8)#1	2.239(4)
Mo(5)−O(6)	2.145(4)	Mo(1)−O(1)	1.718(5)
Mo(5)−O(15)#1	2.388(4)	Mo(1)−O(2)	1.717(4)
Mo(4)−O(7)	1.708(4)	Mo(1)−O(10)	1.875(4)
Mo(4)−O(14)	1.733(4)	Mo(1)−O(6)	1.982(4)
Mo(4)−O(13)	1.881(4)	Mo(1)−O(15)	2.222(4)
Mo(4)−O(6)	2.028(4)	Mo(1)−O(5)#1	2.392(4)
Mo(4)−(11)#1	2.165(4)	Mo(3)−O(10)	2.040(4)
Mo(4)−O(12)	2.255(4)	Mo(3)−O(15)	2.157(4)
Mo(3)−O(4)	1.698(4)	Mo(3)−(12)#1	2.329(4)

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x + 1/2, -y + 3/2, -z + 1$; #2, $-x + 1, y, -z + 3/2$; #3, $x + 1/2, -y + 3/2, z + 1/2$.

$[Mo_8O_{26}]^{4-}$ cluster was also found in the above-mentioned $[NH_3(CH_2)_6NH_3][Mo_4O_{13}]$ if two linked $[Mo_4O_{13}]$ units are considered to be a cluster.[5]

As shown in Figure 1, the formation of helical chains in **1** depends exclusively on the ingenious corner-sharing linkage between a pseudo-γ-$[Mo_8O_{26}]^{4-}$ cluster and a capping $\{MoO_6\}$ octahedron. Clearly, the capping $\{MoO_6\}$ octahedron plays a key role in the formation of the one-dimensional helical chain. Unlike the other helical compounds, such as $[(1R,2R)\text{-}C_6H_{10}(NH_3)_2][Ga(OH)(HPO_4)_2]H_2O$, $[NH_3(CH_2)_2NH_2(CH_3)_2NH_3][Zn_4(PO_4)_3(HPO_4)]$, and $[NH_3(CH_2)_3NH_2(CH_2)_2NH_3][Zn_4(AsO_4)_3(HAsO_4)]H_2O$, in which the helical moiety is built up from either the M−O−P(As) or M_1−O−M_2−O unit,[16] the helix in **1** is constructed from only the Mo−O unit, namely $[Mo_9O_{30}]_\infty$. In the meantime, it can be noted that all molybdenum atoms in **1** lie in the octahedral environment.

The most interesting feature of **1** is that two novel and symmetrically related helices coexist in the centrosymmetric solid, in which the two kinds of helices appear in the left-handed and right-handed enantiomorphs, respectively. This is first example of a helical chain structure consisting of only molybdenum-oxide building blocks. The central axis about each helical chain is a 2-fold screw axis. In addition, it is noteworthy that helical chains $[Mo_9O_{30}]_\infty$ coming from different layers do not completely overlap, as depicted in Figure 3. The layer architecture is considered to form by the overlap of the same helical chains, so the organic amine cations occupy the interlamellar space (Figure 4). Furthermore, the multipoint hydrogen-bonding links also exist between the nitrogen atoms from organic amines and the surface oxygen atoms from the $[Mo_8O_{26}]^{4-}$ cluster of the helical chains; this may make a contribution to stabilizing the helix structure of **1**.

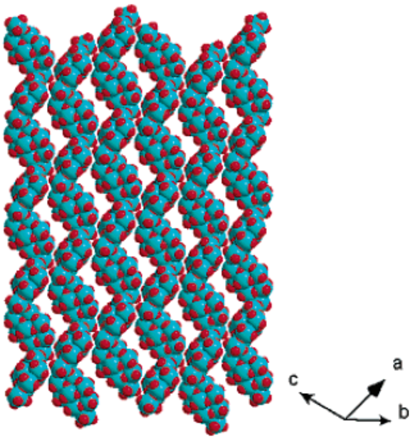

Figure 3. View of the space-filling plot of the neighboring helical chains of **1**, showing the positional difference between two neighboring helical chains. Color code: Mo, blue; O, red.

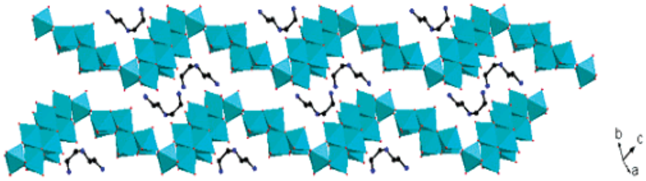

Figure 4. Polyhedral view of the layered architecture of **1** and the locations of diethylenetriamine cations.

In order to investigate the role of diethylenetriamine in the synthesis of **1**, we performed a control experiment to replace diethylenetriamine by ethylenediamine. However, the resulting product is those unidentified white needlelike crystals instead of compound **1**, suggesting that the organic template of diethylenetriamine plays an important role in the formation of the helical structure of **1**. Obviously, the protonated amine $[NH_3(CH_2)_2NH_2(CH_2)_2NH_3]^{3+}$ is not only a component for charge compensation, but also a structure-directing agent. Considering the possibility of incorporating other transition metals into the helical framework of **1**, we also attempted to modify the synthesis reaction of **1** by adding $NiCl_2$ as one of the starting materials. Interestingly, the resulting product was still **1**, but it gave larger crystal sizes than those from the original reaction. The more experimental investigations on the original reaction system are in progress so as to shed light on the reason to form the helical framework of **1**.

In conclusion, the reported inorganic solid compound is possessed of a novel helical chain structure consisting of only molybdenum−oxide building blocks. This solid material could be significant in terms of the potential applications in chiral catalysis and optical materials. The successful preparation of such a helical compound thus offers a valuable clue that other metal oxides with a helical structure may also be obtained under hydrothermal reaction by the structure-directing effect of organic templates.

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Supporting Information Available: Experimental details, table of crystallographic data, and crystallographic information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) (a) Lin, H.-M.; Lii, K.-H. *Inorg. Chem.* **1998**, *37*, 4220. (b) Neeraj, S.; Natarajan, S.; Rao, C. N. R. *Chem. Commun.* **1999**, 165. (c) Chakrabarti, S.; Natarajan, S. *J. Chem. Soc., Dalton Trans.* **2002**, 3874.