

**Toward Quantum Line–Self-Assembly Process of Nanomolecular Building Blocks Leading to a Novel One-Dimensional Nanomolecular Polymer: Single-Crystal X-ray Structure of  $\{[\text{H}_3\text{O}]^+_{12}\{(\text{H}_2\text{O})\text{MoO}_{2.5}[\text{Mo}_{36}\text{O}_{108}(\text{NO})_4(\text{H}_2\text{O})_{16}]\text{O}_{2.5}\text{Mo}(\text{H}_2\text{O})\}^{12-}\}_n$**

Shi-Wei Zhang,\* Yong-Ge Wei, Qing Yu, Mei-Cheng Shao, and You-Qi Tang

Department of Chemistry, Peking University  
Beijing 100871, People's Republic of China

Received May 15, 1996

Revised Manuscript Received October 26, 1996

Nanostructured materials with mesoscopic dimensions have been intensely studied in recent years because they may exhibit novel electronic, optical, magnetic, and chemical properties.<sup>1–5</sup> However, almost all of the mesoscopic materials reported in literature<sup>6</sup> have a distribution of molecular weights, which prevents an understanding of mesophysical behavior.<sup>5–7</sup> The preparation of nanoparticles with little or no molecular weight distribution is still largely undeveloped.<sup>5,7</sup> We have evolved the so-called “reduction–oxidation–reconstitution” self-assembly processes to prepare well-defined, discrete nanomolecules of polyoxometalates,<sup>8–11</sup> and Müller et al.<sup>12–14</sup> have studied further this kind of synthetic route. Investigations of this subject in our laboratory recently revealed that these nanospecies<sup>8–14</sup> could be used to make nanomolecular polymers by such a self-assembly process. Here, we report the synthesis and structure of a novel one-dimensional nanopolymer,  $\{[\text{H}_3\text{O}]^+_{12}\{(\text{H}_2\text{O})\text{MoO}_{2.5}[\text{Mo}_{36}\text{O}_{108}(\text{NO})_4(\text{H}_2\text{O})_{16}]\text{O}_{2.5}\text{Mo}(\text{H}_2\text{O})\}^{12-}\}_n \cdot 44n\text{H}_2\text{O}$ , obtained from the discrete nanomolecule  $[\text{H}_3\text{O}]^+_{12}[\text{Mo}_{36}\text{O}_{108}(\text{NO})_4(\text{H}_2\text{O})_{16}]^{12-}$ . The syntheses and properties of this kind of polyoxometalates may lead to new quantum lines based on molecular quantum dots.

The compound  $\{[\text{H}_3\text{O}]^+_{12}\{(\text{H}_2\text{O})\text{MoO}_{2.5}[\text{Mo}_{36}\text{O}_{108}(\text{NO})_4(\text{H}_2\text{O})_{16}]\text{O}_{2.5}\text{Mo}(\text{H}_2\text{O})\}^{12-}\}_n \cdot 44n\text{H}_2\text{O}$  was prepared by the reaction of  $[\text{H}_3\text{O}]^+_{12}[\text{Mo}_{36}\text{O}_{108}(\text{NO})_4(\text{H}_2\text{O})_{16}]^{12-}$  (0.5 g) with  $\text{NH}_2\text{OH}\cdot\text{HCl}$  (0.2 g) in 20 mL of water in an approximate mole ratio of 1:40 at reflux temperature for no more than 30 min. In a typical experiment,  $\{[\text{H}_3\text{O}]^+_{12}\{(\text{H}_2\text{O})\text{MoO}_{2.5}[\text{Mo}_{36}\text{O}_{108}(\text{NO})_4$

**Table 1.** Synthesis and Crystallographic Properties of Mo38

Synthesis	
Mo36 + $\text{NH}_2\text{OH}\cdot\text{HCl}$	$\xrightarrow[\text{reflux}]{\text{water}}$ green solution $\xrightarrow[\text{precipitate}]{\text{filter}}$ red solution
red solution	$\xrightarrow{\text{open air } \sim 1 \text{ week}}$ Mo38 (80% yield)
X-ray Structural Data	
formula	$\text{H}_{320}\text{N}_8\text{O}_{382} \text{Mo}_{76}$
unit cell (Å)	$a = 27.960(6)$ $b = 17.877(4)$ $c = 32.130(6)$
space group	$C2/c$
Z	2
$R^a$	0.0489
$wR^b$	0.0485
goodness of fit	2.53

<sup>a</sup>  $R = \sum||F_o| - |F_c||/\sum|F_o|$ , <sup>b</sup>  $wR = [\sum|w(F_o^2 - F_c^2)|/\sum|w(F_o^2)|]$  and  $w = [\sigma^2(F) + 0.00001F^2]^{-1}$ . Where  $R$  and  $wR$  are the crystallographic residuals and  $F_o$  and  $F_c$  are observed and calculated structure factors, respectively. The structure was solved from single-crystal X-ray diffraction data by conventional direct methods and difference Fourier techniques followed by the blocked full-matrix least-squares anisotropic refinement of all non-hydrogen atoms.

$(\text{H}_2\text{O})_{16}]\text{O}_{2.5}\text{Mo}(\text{H}_2\text{O})\}^{12-}\}_n \cdot 44n\text{H}_2\text{O}$ <sup>16</sup> was obtained as well-defined red-brown monoclinic block crystals in about 80% yield (Table 1). A long reflux time and an excess of reductant led to the formation of a large number of greenish precipitates, which greatly reduced the yield of product. It is surprising that not only is this very novel inorganic polymer self-assembled from the discrete nanomolecule as starting material but also formed in quantitative yield. These optimized synthetic conditions were determined empirically after the observation of the product in other reactions with the same starting materials but with different mole ratios and reflux times. The role of  $\text{NH}_2\text{OH}\cdot\text{HCl}$  is presumably to reduce some Mo atoms of  $[\text{H}_3\text{O}]^+_{12}[\text{Mo}_{36}\text{O}_{108}(\text{NO})_4(\text{H}_2\text{O})_{16}]^{12-}$  to afford several active positions which could be employed by the self-assembly process induced by air oxidation.

The structure of  $\{[\text{H}_3\text{O}]^+_{12}\{(\text{H}_2\text{O})\text{MoO}_{2.5}[\text{Mo}_{36}\text{O}_{108}(\text{NO})_4(\text{H}_2\text{O})_{16}]\text{O}_{2.5}\text{Mo}(\text{H}_2\text{O})\}^{12-}\}_n \cdot 44n\text{H}_2\text{O}$  was determined by the single-crystal X-ray diffraction method (Table 1) and consists of a one-dimensional covalently bonded chainlike framework built up from a polyoxometalate cluster containing 38 Mo atoms. As shown in Figures 1 and 2, this 38-molybdate repeating unit, which actually is the “monomer” of this inorganic polymer, is made up of two 19-molybdate subunits, which are related by a crystallographic center of symmetry. In each subunit, there are an enormous variety of polyhedra: one  $\text{Mo}^{\text{VI}}\text{O}_6$ , two  $(\text{O}=\text{Mo}^{\text{VI}}\text{O}_4(\text{H}_2\text{O}))$ , one  $(\text{O}=\text{Mo}^{\text{VI}}\text{O}_3(\text{H}_2\text{O}))$ , four  $(\text{O}=\text{Mo}^{\text{VI}}\text{O}_3(\text{H}_2\text{O}))$ , four  $(\text{O}=\text{Mo}^{\text{VI}}\text{O}_6)$ , one  $(\text{O}=\text{Mo}^{\text{VI}}\text{O}_4)$  octahedra, and two pentagonal  $\text{Mo}^{\text{II}}(\text{NO})^+\text{O}_6$  bipyramids and two  $\text{Mo}^{\text{VI}}_2\text{O}_8(\mu\text{-O})(\mu\text{-H}_2\text{O})$  units consisting of edge-shared octahedron. The underlying feature of the structure is that this 19-molybdate subunit originates from the same building block of 17-molybdate unit,  $[\text{Mo}^{\text{VI}}_{15}(\text{MoNO})^3_2\text{O}_{58}(\text{H}_2\text{O})]^{20-}$ , as those of the 18-molybdate subunit  $[\text{Mo}_{36}\text{O}_{108}(\text{NO})_4(\text{H}_2\text{O})_{16}]^{12-}$  and the 19-molybdate 2-vanadate subunit of  $[\text{Mo}_5^{\text{VI}}\text{V}_6\text{O}_{183}(\text{NO})_6(\text{H}_2\text{O})_{18}]^{24-}$  (cf., Figures in refs 8–13). Since it is a highly negatively charged moiety, the 17-molybdate unit could behave as a polydentate ligand. When these two units are linked in transpositions by two  $[\text{MoO}_2]^+$  centers with their two terminal oxygen atoms in cis-positions,  $[\text{Mo}_{36}\text{O}_{108}(\text{NO})_4(\text{H}_2\text{O})_{16}]^{12-}$  was formed under suitable conditions. Apparently, the formation of  $[\text{Mo}_{36}\text{O}_{108}(\text{NO})_4(\text{H}_2\text{O})_{16}]^{12-}$  makes use of only half of the active positions of the 17-molybdate unit owing to its  $C_{2v}$  symmetry. When the remaining active positions in  $[\text{Mo}_{36}\text{O}_{108}$

(16) Anal. Calcd: Mo, 53.20; N, 0.76; H, 2.15. Found for  $\text{H}_{160}\text{N}_4\text{O}_{191}\text{Mo}_{38}$ : Mo, 52.69; N, 0.81; H, 2.33.

(1) Drexler, K. E. *Nanosystems, Molecular Machinery, Manufacturing and Computation*. New York, Wiley 1992.

(2) Ozin, S. A. *Adv. Mater.* **1982**, *4*, 612–648.

(3) Bruce, D. W.; O'Hare, D. *Inorganic Materials*. New York, Wiley 1992.

(4) Rao, C. N.; Gopalakrishnan, J. *New Directions in Solid State Chemistry*. Cambridge University Press: Cambridge, 1986.

(5) Schmid, G. *Chem. Rev.* **1992**, *92*, 1709–1727.

(6) Wang, Y.; Herron, N. *J. Phys. Chem.* **1991**, *95*, 525–532.

(7) Herron, N.; Calabrese, J. C.; Farneth, W. E.; Wang Y. *Science* **1993**, *259*, 1426–1428.

(8) Zhang, S.-W.; Liao, D.-Q.; Shao, M.-C.; Tang, Y. Q. *J. Chem. Soc., Chem. Commun.* **1986**, 835–836.

(9) Zhang, S.-W.; Huang, G.-Q.; Shao, M.-C.; Tang, Y. Q. *J. Chem. Soc., Chem. Commun.* **1993**, 37–38.

(10) Huang, G.-Q.; Zhang, S.-W.; Shao, M.-C. *Polyhedron* **1993**, *12*, 2067–2068.

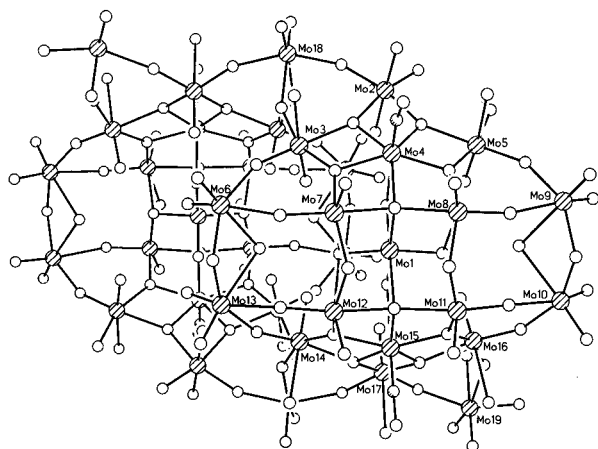
(11) Huang, G.-Q.; Zhang, S.-W.; Shao, M.-C. *Chin. Sci. Bull.* **1995**, *40*, 1438–1441.

(12) Müller, A., et al. *Z. Anorg. Allg. Chem.* **1994**, *620*, 599–619.

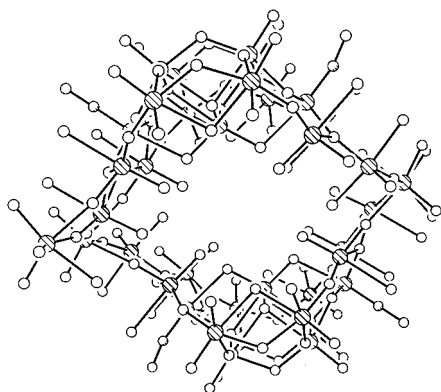
(13) Müller, A., et al. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 849–851.

(14) Müller, A., et al. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2122–2124.

(15) This compound was prepared according to ref 8. A pH = 2 aqueous solution of  $\text{Na}_2\text{Mo}_4\cdot 2\text{H}_2\text{O}$  (3.0 g) and  $\text{NH}_2\text{OH}\cdot\text{HCl}$  (1.9 g) in 40 mL of water at an approximate mole ratio of 1:2.25 was refluxed for about an hour. However, the charge and formula given in this reference are incorrect and the present formula was confirmed by the elemental analyses, determination of oxidation number for Mo, and ref 12. In addition, this compound is different in component and structure from that reported by A. Müller et al. in ref 12 owing that they prepared their 36-Mo compound in an acidic solution containing ammonium chloride.



**Figure 1.** Ball-and-stick model of the polymeric 38-molybdate anion (view parallel to *C* axis).



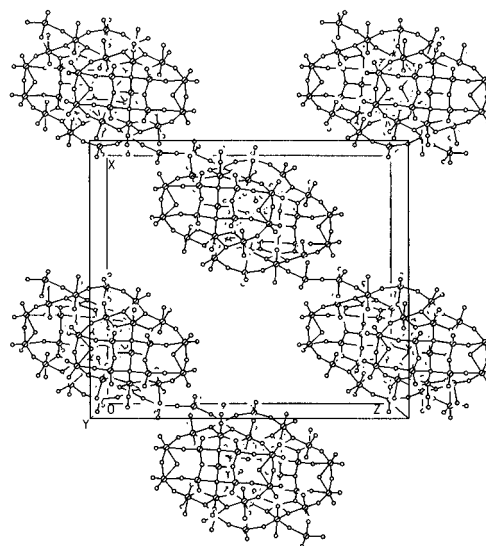
**Figure 2.** Ball-and-stick model of the polymeric 38-molybdate anion (view along the *a* axis perpendicular to *C* axis).

$(\text{NO})_4(\text{H}_2\text{O})_{16}]^{12-}$  are further linked in the same trans manner by two vertex-shared polyhedra,  $[(\text{H}_2\text{O})_2\text{O}_2\text{Mo}^{\text{V}}\text{OMo}^{\text{V}}\text{O}_2(\text{H}_2\text{O})]$  in the present case, the novel polymeric species,  $\{[\text{H}_3\text{O}]^{+12-}\{(\text{H}_2\text{O})\text{MoO}_{2.5}[\text{Mo}_{36}\text{O}_{108}(\text{NO})_4(\text{H}_2\text{O})_{16}]\text{O}_{2.5}\text{Mo}(\text{H}_2\text{O})\}^{12-}\}_n$ , is obtained. It looks like a beautiful string of “pearls” (see Figure 3), where the “pearls” are exactly the 36-molybdate clusters.

Compared with their constituting building blocks, large clusters or nanomolecules show the presence of electrons with low binding energy in the HOMO region, since the interactions between the blocks lead to strong delocalization effects and exchange interactions in mesoscopic size. For example, in the discrete nanospecies  $[\text{Mo}_{36}\text{O}_{108}(\text{NO})_4(\text{H}_2\text{O})_{16}]^{12-}$  and  $[\text{Mo}_{57}\text{V}_6\text{O}_{183}(\text{NO})_6(\text{H}_2\text{O})_{18}]^{24-}$  very strong delocalization effects have been observed by Müller et al.<sup>12</sup> This type of effect could stabilize “rich” electrons in these nanospecies and make them

(17) There are two UV–vis absorption bands in Mo36 monomer and Mo38 polymer: One band in the UV region at 209 nm found in the Mo38 polymer is the same as that of Mo36 monomer owing to the same “core” structures of these two compounds. However, another band in the visible region at 408 nm found in the Mo36 monomer shifts to 418 nm in the Mo38 polymer owing to the polymeric linkage of the Mo36 monomer by covalent bonds.

(18) Coronado, E., et al. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1460–1461.



**Figure 3.** View of crystal packing of the polymeric 38-molybdate anion along the *b* axis.

“reservoirs” of electrons. Furthermore, they perhaps drive the jump of electrons between these nanospecies in the solid state under suitable conditions. This jumping of electrons may become more visible in the crystals of  $\{[\text{H}_3\text{O}]^{+12-}\{(\text{H}_2\text{O})\text{MoO}_{2.5}[\text{Mo}_{36}\text{O}_{108}(\text{NO})_4(\text{H}_2\text{O})_{16}]\text{O}_{2.5}\text{Mo}(\text{H}_2\text{O})\}^{12-}\}_n \cdot 44n\text{H}_2\text{O}$ , owing to its nanopolymeric structure compared to the discrete nanospecies  $[\text{Mo}_{36}\text{O}_{108}(\text{NO})_4(\text{H}_2\text{O})_{16}]^{12-}$ . Red-shift has indeed been observed in the UV–vis spectra<sup>17</sup> of these two nanospecies. In order to increase the electron conductivity of this kind of nanopolymers, hybridizing them with conducting organic donors<sup>18</sup> is under investigation in our laboratory.

In conclusion, we believe that large clusters or nanospecies generated from small moieties could be further reconstituted as starting materials by self-assembly processes under suitable conditions to prepare new nanostructured compounds, especially to prepare 1D, 2D, and 3D nanomolecular-species-based polymeric materials with novel optical, electronic, magnetic, and chemical properties. The present polymer  $\{[\text{H}_3\text{O}]^{+12-}\{(\text{H}_2\text{O})\text{MoO}_{2.5}[\text{Mo}_{36}\text{O}_{108}(\text{NO})_4(\text{H}_2\text{O})_{16}]\text{O}_{2.5}\text{Mo}(\text{H}_2\text{O})\}^{12-}\}_n$  offers a successful example of this kind of nanosynthetic method by a reduction–oxidation–self-assembly process developed in our laboratory. In addition, this type of polymer also provides a chance to make molecular quantum lines, even quantum faces and bodies, if the cations are replaced by conducting organic donors.<sup>18</sup>

**Acknowledgment.** We thank the National Natural Science Foundation of China, the Key Project in Climbing Program from the State Science and Technology Commission, and the Doctorial Foundation of the State Educational Committee for financial support. Thanks are also given to professor S. J. Lippard and the reviewers for their help in modifying this manuscript.

**Supporting Information Available:** Crystallographic details and UV–vis spectra (20 pages). See any current masthead page for ordering and Internet access instructions.

JA961637E