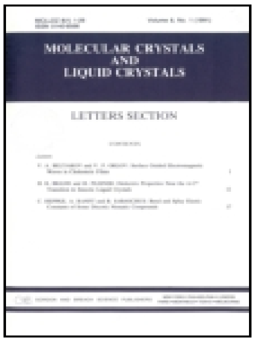

MOLECULAR CRYSTALS AND LIQUID CRYSTALS

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Hierarchical Self-Assembly of Oxomolybdate Monomers into a Stable Polyoxomolybdate Crystal with an Ordered Nanochannel Array

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A highly ordered nanochannel array consisting of giant-ring-shaped polyoxomolybdate (POMo) was prepared via self-assembly of the oxomolybdate monomers. Concentration and pH optimization of the reaction solution favored the self-assembly; the nanochannel structure spontaneously self-constructed during the crystallization process. The obtained crystal showed a highly ordered nanochannel with a diameter of 2.0 nm and no distribution in the channel size. In addition, the material was found to be very stable at ambient temperature in atmospheric air due to the formation of three-dimensional crosslinks via Mo–O–Mo covalent bonds between neighboring molecules in the crystal.

Keywords Polyoxomolybdate; Nanochannel Array; Self-Assembly.

Introduction

Nanomaterials, which are defined as materials with unique properties arising from their nanoscale dimensions, are recognized for their utility in advancing the fields of electronics, fuel cells, and solar cells [1]. In particular, materials with nanometer-size channels in the matrix core have attracted much attention as ion-exchange membranes, molecular adsorbents, transport, and storage materials owing to their unique characteristics such as high ion conductivity, mechanical strength, and molecular confinement properties in their channels [2].

Herein, we demonstrate that a highly ordered nanochannel-array structure with a channel diameter of 2.0 nm can be formed in polyoxomolybdate (POMo) crystals by hierarchical self-assembly of oxomolybdate monomers. POMo is a molybdenum-oxide cluster that consists of molybdenum-oxide polyhedra bridged through corners, edges, and faces. POMos with a giant-ring structure have been recently developed [3–5]; these are mixed-valence inorganic molecules consisting of 154 or 176 units of Mo(V) and Mo(VI) oxides; because of their blue coloration, they are also known as “molybdenum blue”. To date, such compounds can be obtained by a simple one-pot synthetic method developed

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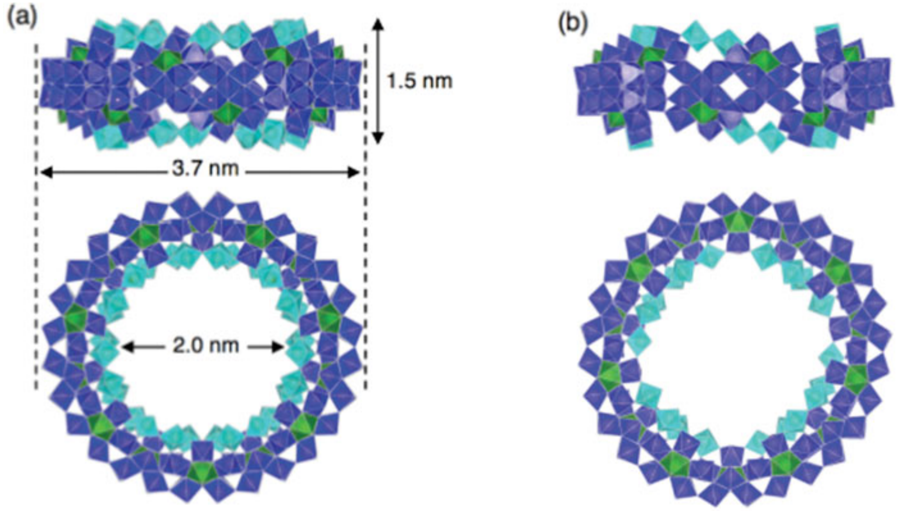

Figure 1. The POMo molecular structure observed with single-crystal X-ray diffraction carried out with (a) a four-circler-axis diffractometer at 23°C, and (b) with synchrotron radiation at -173°C (b). Color legends of atoms: blue, six-coordinated Mo atoms with octahedral structure; green, seven-coordinated Mo atoms with decahedral structure; light blue, occupancy-refined Mo atoms with octahedral structure. Na^+ cations are omitted for clarity.

by Müller et al [6]. According to this method, oxomolybdate monomers spontaneously assemble into nanometer-size macromolecules with well-defined giant-ring structures. We suggest that the giant-ring-shaped POMo structures might serve as a building block for nanochannel materials; in particular, a nanochannel array with a strictly defined channel size can be obtained by stacking up the giant rings of POMo. Such a material has already been obtained by using giant-ring-shaped POMos as building blocks [5,7]. However, it is known that the POMo crystals are unstable in air at ambient temperature, and that a fast weathering process takes place due to the loss of crystal water, when isolating the crystal from the mother liquor [6]. Thus, the POMo crystals recovered from the mother liquor have to be immediately cooled to liquid-nitrogen temperature to allow the analysis of the crystal structure and other physical properties. Therefore, it is necessary to develop a method to obtain stable POMo crystals with a nanochannel structure at ambient temperature in air. In this work, we demonstrate that an extremely stable nanochannel array can be obtained from giant-ring-shaped POMo; in addition, its well-defined nanostructure at room temperature in air was reported in this study for the first time.

Results and Discussion

The POMo molecular structure determined by single-crystal X-ray diffraction at 23°C in atmospheric air is shown in Fig. 1a. Our data confirmed that the molecules obtained in this study have a giant-ring structure. The single-crystal X-ray analysis also revealed that the studied compound is characterized by several structural defects, which were typically localized inside the giant rings. The low-temperature experiment carried out with the synchrotron radiation clearly confirmed that the defects are localized inside the rings

Table 1. Polyoxomolybdate (POMo) crystallographic data[a]

Radiation type	Cu $K\alpha$ radiation	Synchrotron radiation
λ (Å)	1.54178	0.61769
T (K)	296	100
Crystal size (mm)	0.34 × 0.15 × 0.05	0.10 × 0.04 × 0.03
Molecular formula	$Mo_{141.94}O_{480.92}\cdot 4(Na)$	$Mo_{139.58}O_{472.32}\cdot 4(Na)$
Molecular weight	21404.40	21040.00
Crystal system	Monoclinic	Monoclinic
Space group	*C2/m*	*C2/m*
a (Å)	26.035 (14)	25.6830 (7)
b (Å)	50.13 (2)	49.7459 (12)
c (Å)	28.327 (18)	28.344 (2)
α (deg)	90	90
β (deg)	105.01 (5)	104.933 (7)
γ (deg)	90	90
V (Å^3)	35709 (34)	34990 (3)
Z	2	2
R [$F^2 > 2\sigma(F^2)$]	0.079	0.050
$wR(F^2)$	0.223	0.130
Oxidation number of Mo	5.6	5.8

[a] These data were treated with SQUEEZE.

(Fig. 1b). Therefore, the site occupancy of the Mo and O atoms was refined on the basis of their displacement parameters (Fig. 1). Additionally, the disordered crystal water molecules were treated with the SQUEEZE technique [8]. We omitted 5003 electrons per unit cell. Since two POMo molecules are contained in the unit cell, 2502 electrons were omitted for each molecule. Assuming that all of these electrons originate from water, we concluded that one POMo molecule contains 250 water molecules; the POMo molecular formula and molecular weight are shown in Table 1.

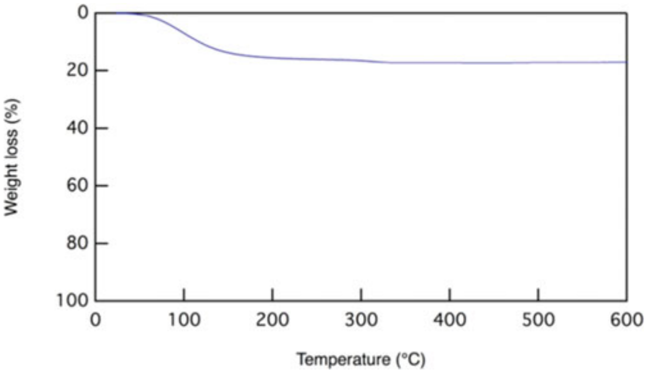

Figure 2. POMo TGA thermogram measured at a heating rate of 10°C/min. α-Alumina powder was used as the reference.

A thermogravimetric analysis (TGA) of the crystals showed a weight loss of 17%; this was assigned to the loss of crystal water (Fig. 2). This suggests that one POMo molecule contains about 240 water molecules as crystal water, which is in good agreement with the data obtained from the single-crystal X-ray structure analysis. This confirms our assumption that the 2502 electrons per molecule omitted with the SQUEEZE technique originated from the crystal water.

From these data, we concluded that POMo molecules synthesized in this study contain 142 units of oxomolybdates on average. As shown in Fig. 1a, the outer diameter, inner diameter, and the thickness of the POMo molecule are 3.7 nm, 2.0 nm, and 1.5 nm, respectively. The oxidation state of each Mo atom was also estimated by the bond-valence sum (BVS) calculation; POMo was found to be a mixed-valence compound containing Mo(V) and Mo(VI) atoms [9,10].

The crystallographic data of POMo are summarized in Table 1. Because the crystal shows large lattice constants, comparable to those of proteins, the entire process of X-ray diffraction data collection required 122 h. In contrast, data collection was completed much quicker (about 15 h) when the cylindrical imaging-plate camera with synchrotron radiation at -173°C was used. Despite this difference, the two experiments led to the same results, i.e., the POMo single crystals are extremely stable, and the crystal structure is not affected by long periods of exposure to X-rays at 23°C in atmospheric air. This is in clear contrast to previous studies, which reported that the crystals of giant-ring-shaped POMo are unstable, due to the weathering of the crystals occurring at room temperature upon exposure to air. In particular, the crystals were degraded within 2 h when they were allowed to stand in contact with air at room temperature [6]. Therefore, single-crystal structure analysis has been typically carried out at very low temperatures and, in some cases, with the mother liquors. In contrast, the single crystals obtained in this study showed a long-term stability (for at least several months) at room temperature in air; we were thus able to determine the precise structure of the POMo molecules under such conditions.

In particular, our data showed that the giant-ring molecules are stacked along the crystallographic *a* axis, and that the rectangular arrangement of the one-dimensional nanometer-size channels were bored through the crystal along the *a* axis (Fig. 3a). Since the nanochannel array structure was formed by self-assembly of the POMo molecules, the channels had the same inner diameter as the POMo molecules (2.0 nm) and showed no distribution in the channel size.

Interestingly, the molecules in this crystal polymerized further, i.e., neighboring molecules bonded together via Mo–O–Mo covalent bonds. In the crystallographic *ac* plane, each molecule was linked at two opposite sites and formed a one-dimensional linear polymer structure along the *c* axis (Fig. 3b). In addition, a two-dimensional sheet structure was formed via the formation of links at four sites per molecule in the *ab* plane (Fig. 3c). These intermolecular covalent crosslinks possibly resulted from the dehydration polycondensation of the Mo–OH groups during the crystallization process in the mother liquor and drying process after isolation; this led to the stabilization of the crystal structure, which, to the best of our knowledge, resulted in a crystal significantly more stable than those previously reported.

In the crystal studied in this work, the crosslinks between the molecules were formed by several Mo–O–Mo bonds. At each crosslinking site, the linkage consisted of about three Mo–O–Mo bonds on average, both in a one-dimensional linear structure along the *c* axis and in the two-dimensional sheet structure in the *ab* plane (Fig. 3b,c) [11]. As a result of the high crosslinking density, the molecules were strongly bonded. In the giant-ring-shaped POMo crystals previously reported, only a few examples of the formation of

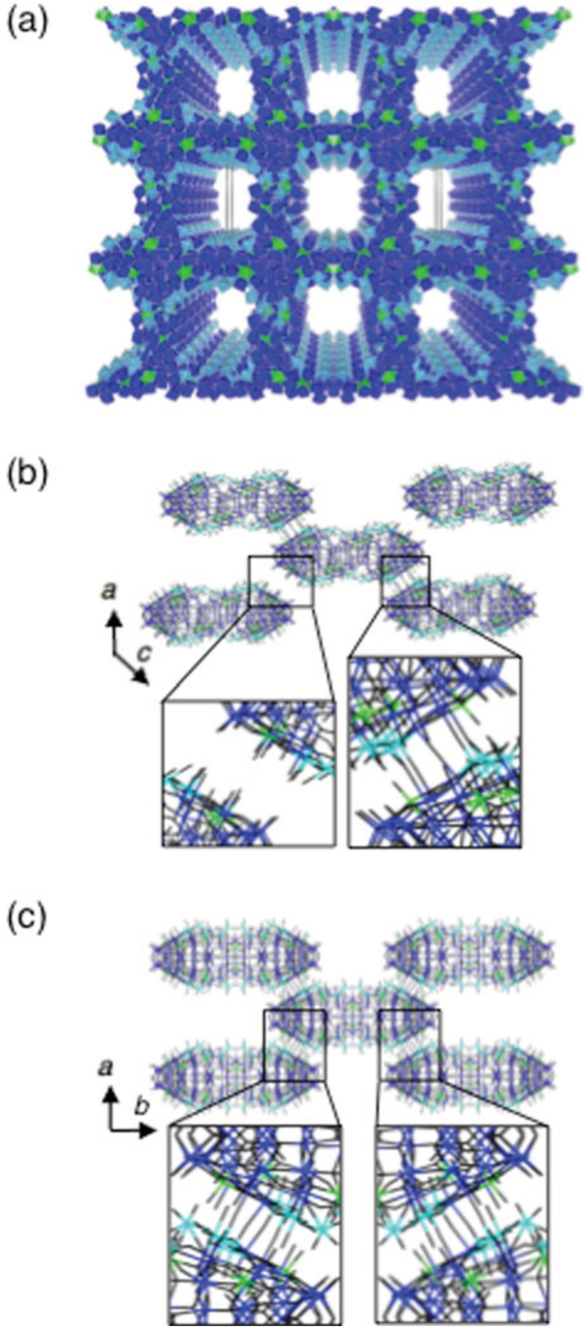

Figure 3. POMo crystal-packing structure obtained from single-crystal X-ray diffraction with a four-circler-axis diffractometer at 23°C: (a) Perspective view of the highly ordered nanochannel structure along the *a* axis (channel size = 2.0 nm); (b) view along the *b* axis; (c) view along the *c* axis.

one- or two-dimensional crosslinks, and only one example of a three-dimensional crosslink have been proposed [5,7]. In addition, such crystals were unstable at room temperature, and the crystal structures were observed only at around liquid-nitrogen temperature. The crosslinking density in the present crystal is higher than that in the three-dimensionally crosslinked crystals previously reported [7]. Thus, we concluded that the high density of three-dimensional crosslinks is the main factor that causes the high room-temperature stability of the POMo crystal presented in this work. In addition, we also confirmed that the crystals are soluble in water, despite the presence of three-dimensional crosslinks. Because the crosslinks between molecules were easily hydrolyzed by water, we concluded that the polycondensation reaction was reversible.

To date, investigations on the structure and properties of giant-ring-shaped POMo molecules have been performed only at low temperature because of the instability of the crystals; this has limited their practical application to functional materials. Owing to the high stability under ambient conditions and the absence of a distribution in the channel size, the POMo systems studied in this work may be employed as selective heterogeneous catalysts, molecular-storage materials, ion-conductive materials and so on. For this purpose, further studies on the structure-property relationship of these materials are being carried out in our laboratory.

Experimental Section

Synthesis and Characterizations of POMo

Synthesis of POMo [6]. $Na_2MoO_4 \cdot 2H_2O$ (3.05 g, 12.6 mmol) and $Na_2S_2O_4$ (152 mg, 0.87 mmol) were dissolved in 40 mL of aqueous hydrochloric acid (0.7 mol/L). In this reaction, the pH of the reaction mixture was adjusted to 0.85; we confirmed that the pH range of 0.8 and 1.2 is optimal for this reaction. After the reaction mixture was stored in an open vessel at room temperature (~20°C) for 6 d, dark-blue trapezoidal POMo single crystals separated out at the air-solution interface together with a certain amount of amorphous material; the latter was manually removed from the reaction mixture. After the reaction mixture was left for an additional 4 d, the trapezoidal crystals were obtained together with square-plate crystals; both crystals were then completely air-dried at room temperature. The square-plate crystals were effloresced in air during the air-drying process. We selected the trapezoidal crystals under a stereoscopic microscope to obtain 204 mg of air-stable POMo single crystals in 9% yield. The obtained trapezoidal crystals were characterized by single-crystal X-ray structure analysis as well as by TGA.

Single-Crystal X-Ray Structure Analysis. A single crystal was mounted on a glass fiber at room temperature in atmospheric air. The reflection data was measured with the ω-scan technique on a Rigaku automated four-circler-axis diffractometer AFC-5R with graphite monochromatized Cu $K\alpha$ radiation ($\lambda = 1.54178$ Å). All measurements were performed at room temperature (296 K). We also carried out single-crystal X-ray diffraction experiments at 100 K using synchrotron radiation ($\lambda = 0.61769$ Å) and a large cylindrical imaging-plate camera at SPring-8 BL02B1 (Hyogo, Japan).

The initial structure of the POMo giant-ring framework in the unit cell was determined by a direct method using SIR92 [12]. The structure model was refined by full-matrix least-squares methods using SHELXL97 [13]. Mo and O atoms of POMo were refined with anisotropic and isotropic displacement parameters, respectively. The site occupancies of the Mo atoms placed at the inner ring (determined on the basis of the refinement of their displacement parameters) were refined. From a difference Fourier map, we assigned Na cations and O atoms of crystal water (several of which could not be determined due to disorder); their displacement parameters were then refined isotropically. Hydrogen atoms were not included in the refinement. All calculations were performed with the crystallographic software package WinGX [14].

The obtained crystallographic data are listed in Table 1. The oxidation state of the Mo atoms was estimated by BVS calculation of the Mo–O bonds of the giant-ring framework. The BVS values were derived from the parameters given by Brown and Altermatt [9]; the average BVS values of the 70 Mo atoms on the periphery of the ring ranged between 5.6 and 5.8, in line with previously reported values [4]. Data listed in Table 1 have been indexed and included in the Cambridge Crystallographic Centre (CCDC) database with the following reference numbers: CCDC 1019709 for the data collected with the four-circler-axis diffractometer; 1019710 for the crystal treated with SQUEEZE; CCDC 1019711 for the data corrected with the imaging-plate camera using synchrotron radiation; 1019712 for the crystal treated with SQUEEZE. The indexed database contains additional supplementary crystallographic data for this paper and may be accessed without charge at http://www.ccdc.cam.ac.uk/conts/retrieving.html. The CCDC may contacted by mail at 12 Union Road, Cambridge CB2 1EZ, U.K., by fax at (44)1223-336-033, or by e-mail at deposit@ccdc.cam.ac.uk.

Thermogravimetric Analysis

TGA was performed on a DTG-60AH thermogravimetric analyzer (Shimadzu) at a heating rate of 10°C/min to estimate the amount of crystal water. Powder of α-alumina was used as the reference.

Acknowledgments

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[10] Based on BVS calculation we estimated that the average oxidation number of the Mo atoms ranges between 5.6 and 5.8.

[11] Our data suggested that the molecules were bonded together via four Mo–O–Mo bonds at a crosslinking site along the *c* axis; however, occupancy of the Mo atoms involved in this intermolecular linkage was found to be 73%. We thus concluded that the molecules are bonded via about three Mo–O–Mo bonds on average. Similarly, the two-dimensional sheet structure in the *ab* plane was apparently formed via five Mo–O–Mo bonds (i.e., 56% occupancy for four Mo atoms, and 100% occupancy for one Mo atom); we concluded that the actual linkage consists of about three Mo–O–Mo bonds on average.

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