

## Extended Structure Design with Simple Molybdenum Oxide Building Blocks and Urea As a Directing Agent

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We report here a simple one-pot directed synthesis of an oxomolybdate urea composite in which elementary molybdenum oxide building blocks are linked together with the aid of urea. This type of directed material design resulted in large rod-like crystals of an inorganic–organic hybrid extended structure of  $\{\text{MoO}_3(\text{NH}_2\text{-CO-NH}_2)\}_\infty$  consisting of right- and left-handed helical units. In the crystal structure urea acts both as a glue that links the inorganic molybdenum units into a helix and as a supramolecular linker for the stabilization of the crystal structure as a whole. This type of molecular topology resulted in an unexpectedly high thermal stability.

### Introduction

The directed synthesis of extended structures is a challenge in several fields of chemistry and materials sciences. Of special interest in this field are the polyoxometalates (POMs) because they combine high stability with extensive structural diversity.<sup>1</sup> In the syntheses of these types of extended structures, the literature reports several design principles. One of these is based on links between isolated large molecular moieties. In this approach organic molecules are used to direct the growth of POMs. Examples include the use of Keggin, Dawson–Wells POMs and the dimeric  $\{\text{Mo}_6\}_2$  cluster as the POM-building blocks for these types of structures.<sup>2–5</sup> Another example is the use of the large wheel-shaped molybdenum oxide based POM  $\{\text{Mo}_{154}\}$  as a building block, which can form a larger framework with the use of

urea as a structure directing agent.<sup>6,7</sup> It was shown there that urea can act as linker, holding the larger molybdenum oxide POMs together.

A second design principle based on template-directed self-assembly in hydrothermal synthesis resulted in the creation of a wide range of inorganic–organic hybrid extended structures<sup>8</sup> of which some examples contain helices.<sup>9–15</sup> Here the use of POMs and organic structure-directing agents resulted in the creation of crystal structures containing single and double stranded helices.<sup>4,15,16</sup>

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Both design principles mentioned above use POMs as the building units for the extended structures and an organic molecule as the directing agent. However, these syntheses use relatively large POMs which already have their own structural architecture. The use of more simple molybdenum oxide building blocks would allow more freedom in directing and creating extended structures with interesting structural architectures. This work makes use of much smaller and simpler building blocks for the creation of an inorganic extended structure. Moreover, the synthesis of extended structures containing helical characteristics requires high temperatures, high pressure, and often several synthesis steps. Here we report of a simple one-pot directed synthesis of an oxomolybdate urea composite in which simple molybdenum oxide building blocks are linked together with the aid of urea leading to the creation of an inorganic–organic hybrid framework consisting of helical units.

## Experimental Methods

**Synthesis.** A 5.0 g quantity of ammonium heptamolybdate(VI) tetrahydrate (Lancaster) was dissolved in 40 mL of Millipore water. To this was added 4.2 g of urea (cryst. extra pure, Acros) together with 30 mL of 1 M HCl solution. The resulting solution was kept at a constant temperature of 20 °C. After 1 day the large white crystals obtained were filtered and dried under a nitrogen flow. Yield: 4.67 g, 78.7%, based on Mo content.

**Crystal Data.**  $\text{MoO}_3(\text{NH}_2\text{-CO-NH}_2)$ ,  $\text{CH}_4\text{N}_2\text{O}_4\text{Mo}$ ,  $M = 204.00$  g/mol, monoclinic, space group  $P2_1/c$ ,  $a = 7.57090(11)$ ,  $b = 7.35570(10)$ ,  $c = 12.99040(18)\text{Å}$ ,  $\beta = 91.6093(12)^\circ$ ,  $V = 723.141(18)\text{Å}^3$ ,  $Z = 6$ ,  $\rho_c = 2.811\text{ g/cm}^3$ ,  $\mu = 2.64\text{ mm}^{-1}$ ,  $T = 100\text{ K}$ ,  $R_{\text{int}} = 0.0644$ .  $R_1 = 0.0366$  and  $wR_2 = 0.0943$  for 1352 independent reflections with  $I > 2\sigma(I)$ ;  $R_1 = 0.0414$  and  $wR_2 = 0.0976$  for all 1451 independent reflections, 103 refined parameters,  $\text{GoF} = 1.175$ ,  $\text{max/min} = 0.86/-1.00\text{ e/Å}^3$ . The structure contains two independent formula units ( $Z' = 2$ ), one in a special and the other in the general position. Therefore, the symmetry has been verified with the ADDSYM routine in PLATON.<sup>17</sup> No higher metric or crystallographic symmetry has been detected.

A single crystal of  $\sim 40\text{ }\mu\text{m}$  in width has been selected from the bulk sample and measured at the Swiss-Norwegian Beam Lines (SNBL) at the European Synchrotron Radiation Facility (ESRF). Diffraction data were collected at 100 K using the MAR345 Image Plate detector, at the wavelength  $0.72906\text{Å}$  and the crystal-to-detector distance of 110 mm. 359 frames have been collected with 30 to 60 s exposure time (fixed dose mode). Diffraction spots were indexed in a monoclinic unit cell, and 9925 diffraction intensities were integrated using the CrysAlis software,<sup>18</sup> and scaled with SADABS.<sup>19</sup> The structure was solved and refined using SHELX.<sup>20</sup> H(N) atoms were modeled in the riding model.

**Elemental Analysis.** C, 5.69 wt % (found), 5.89 wt % (calcd); N, 13.2 wt % (found), 13.7 wt % (calcd); H, 2.31 wt % (found), 1.98 wt % (calcd); Mo, 45 wt % (found), 47 wt % (calcd).

**TGA.** : For the TGA 55.316 mg of the material was heated from 293 to 773 K with a rate of 5.00 K/min, under an oxygen flow of 10.00 mL/min.

**Spectroscopic Data.** IR:  $\nu/\text{cm}^{-1}$  (KBr disk) characteristic bands: ca. 1405w, ca. 1546(sh), 1128w, ca. 1030w, ca. 956(sh), ca. 914(sh), ca. 895(sh), ca. 770(sh).

## Results and Discussion

The one-pot synthesis consists of the addition of a 2.5-fold excess of urea with respect to molybdenum to an acidified aqueous solution of  $\text{Mo}_7\text{O}_{24}^{6-}$ . After 1 day this resulted in the precipitation of rod-like single crystals of approximately 0.5 mm in length of  $\{\text{MoO}_3(\text{NH}_2\text{-CO-NH}_2)\}_\infty$  **1** at room temperature. These long rod-like crystals displayed birefringence. To ensure a good crystal quality, the synthesis was repeated at a lower concentration of the starting materials. These small ( $\sim 40\text{ }\mu\text{m}$  in size) crystals were subsequently characterized by elemental analysis, thermogravimetric analysis (TGA), IR spectroscopy, and single crystal X-ray structure analysis.

These characterizations show that the asymmetric unit of the structure consists of two independent Mo-centered octahedra and two urea units. The carbonyl oxygen of the urea acts as a  $\mu$ -2-ligand between two molybdenum centers of the two adjacent edge-shared octahedra. The fixation of the metal oxide in the highest oxidation state by urea is quite unique, not only for Mo but for all other metals. A somewhat similar case was found for dioxoneptunium(VI) chromate(VI) complex with urea,  $(\text{NpO}_2)(\text{CrO}_4)(\text{CO}(\text{NH}_2)_2)_2$ ,<sup>21</sup> where the highest oxidation state of Neptunium is stabilized by coordinated urea molecules. In this case, however, urea is coordinated only with one Neptunium atom.

As the molybdenum atoms in the structure **1** are bridged by the urea molecules, helical chains form along the crystallographic  $a$ -axis (Figure 1A). Each turn in the helix consists of three units of  $\{\text{MoO}_3(\text{NH}_2\text{-CO-NH}_2)\}$  in which the  $\text{NH}_2$  groups of urea point outward, as can be seen in the in-depth view of the helix in Figure 1B. The backbone of the helix contains the two Mo-centered octahedra Mo1 and Mo2 which alternate in the sequence  $(\text{Mo1-Mo2-Mo2})_n$ . The helical structure of the chain becomes even more evident when only the connections between the carbon atoms of the urea parts are shown (Figure 1C). This clearly illustrates the spiral formed by the urea molecules. In Figure 1A one turn in the helix has been boxed, emphasizing the tweezer-type configuration of the turn in the helix.

The crystal lattice of **1** contains left- and right-handed helices, which are mirror images of each other. The birefringence of the crystal results from the packing of the helices, which align themselves along one crystallographic axis. Figure 1 shows the crystal structure of **1** as seen along the three crystallographic axes, and the different handedness is represented by two different colors (orange and green). The pseudo- $3_1$  symmetry of the chain favors efficient packing where the helices can be placed in close proximity to each other. This is particularly evident when the crystal is viewed along the crystallographic  $b$ -axis. The hydrogen atoms of the alternating urea branches form strong hydrogen bridges

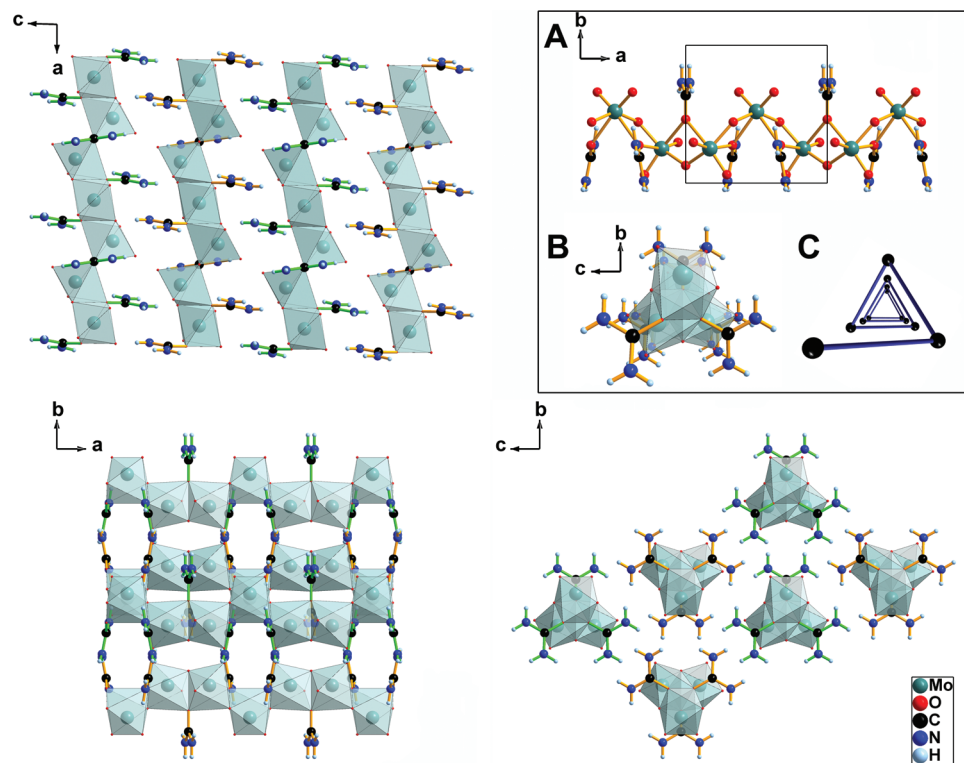
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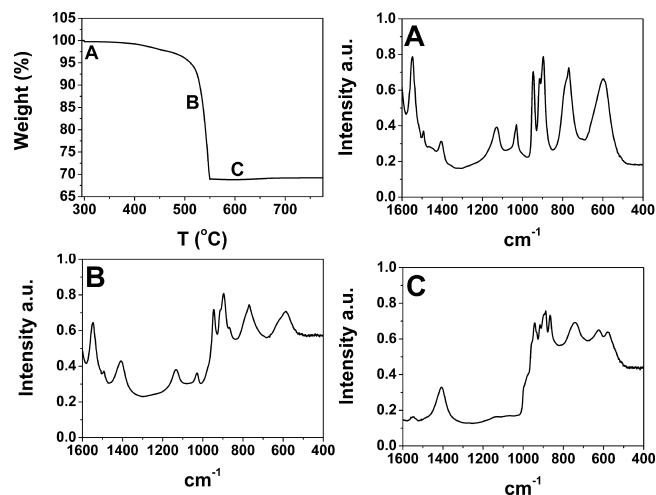
**Figure 1.** Crystal structure of **1** viewed along the three different crystallographic axes. The molybdenum backbone is given in polyhedral representation. The left- and right-handed helices present in the crystal are shown in two colors: green and orange. The helical structure of the chain is particularly clear when the chain is rotated along the crystallographic *a*-axis (see Supporting Information). Inset: (A) One helical chain with one helical turn boxed along the crystallographic *a*-axis. The turn consists of three  $\{\text{MoO}_3(\text{NH}_2\text{-CO-NH}_2)\}$  units. The tweezer-type configuration of the repetitive building unit together with the hyperconnectivity of the oxygen of urea is clearly visible. (B) In-depth view of one helical chain as seen along the crystallographic *a*-axis. (C) In-depth view of one helical chain as seen along the crystallographic *a*-axis, in which only the carbon atoms of the urea molecules have been connected. The spiral emphasizes the helicity of the chain.

with the oxygen atoms of the molybdate backbone, in this way stabilizing the structure as a whole. One hydrogen atom from the urea  $\text{NH}_2$  group even forms two hydrogen bonds with two oxygen atoms from the neighboring backbone (see Supporting Information). The role of urea in the formation of the extended structure is thus a dual one. It not only links the molybdenum oxide units into a helix, but it also connects the helices to form an extended structure.

The only other example, to our knowledge, of a crystal containing both left- and right-handed single stranded helices of molybdenum oxide is  $[\text{NH}_3(\text{CH}_2)_2\text{NH}_3(\text{CH}_2)_2\text{NH}_3]_2\text{-}[\text{Mo}_9\text{O}_{30}]$  (**2**) reported by Xu et al.<sup>15</sup> Their goal was also to use a simple molybdate as a building block for complex extended structures.  $\text{MoO}_4$  was used together with an organic polyamine in the hydrothermal synthesis, resulting in a structure made of Mo-based helical chains of linked  $\{\text{MoO}_6\}$ -octahedra, charge compensated by the protonated amine located between the helices. In this way structure **2** differs from structure **1**, as in the former case the organic template is not incorporated into the resulting crystal structure. Moreover, the helices in compound **2** are built up of  $[\text{Mo}_9\text{O}_{30}]^{6-}$  subunits, which are much larger than the simple  $\text{MoO}_6$  octahedra that form the backbone in structure **1** by edge sharing. Structure **2**, as stated earlier, was synthesized by a hydrothermal reaction. Hydrothermal reactions often result in the formation of phases which are metastable at ambient conditions. Structure **1** on the other hand, was

synthesized at room-temperature in a simple one-pot reaction, making it a thermodynamically stable phase at ambient conditions.

To determine the thermal stability of the crystal structure we carried out a TGA. A TGA of **1** was recorded up to a temperature of 773 K under a constant oxygen flow at a heating rate of 5 degrees per minute. Already at the start of the heating procedure we observed a slight loss of weight. When a temperature of about 500 K was reached, the rate of the weight loss increased to the total of 31.2% at 548 K. This amount is equivalent to the total amount of urea in the structure **1** (Figure 2). With the help of IR spectroscopy during heating, the change in the lattice structure was investigated. IR spectra at several stages during heating show that indeed urea is removed from the crystal after reaching a temperature of 548 K (as is indicated by the disappearance of the characteristic urea vibrations at 1548, 1128, and 1030  $\text{cm}^{-1}$ ) but that the structure stays intact up to this point. However, beyond 548 K other modes appear especially at the lower wavenumbers because of the reduction of the crystal symmetry (Figure 2). Solid urea itself decomposes at a temperature of 402 K, which is significantly lower than the temperature at which the crystal of **1** loses its urea. The crystal structure is clearly retained up to 548 K, revealing its unexpectedly high thermal stability which renders it attractive for potential catalytic applications.



**Figure 2.** TGA of **1** and infrared spectra taken from **1** at (A) 298 K, (B) 538 K, and (C) 594 K. The TGA shows a weight drop at 548 K. The disappearance of the characteristic urea vibrations at 1548, 1128, and 1030  $\text{cm}^{-1}$  in spectrum C shows that urea is removed from the crystal. An increase of the number of peaks in the skeletal region of the spectrum ( $<1000 \text{ cm}^{-1}$ ) suggests a symmetry reduction upon decomposition.

## Conclusion

A simple directed material design with urea and an elementary molybdenum oxide as building blocks results in

large rod-like single crystals of an inorganic–organic hybrid extended structure consisting of helical units. The structure of **1** has an interesting molecular architecture where urea links the inorganic molybdenum units in a helix and acts as a supramolecular linker for the stabilization of the crystal structure as a whole. In addition, the high thermal stability makes it an attractive agent for various materials science applications. Employing urea-based organic structure-directing agents with various alkyl spacers in a simple synthetic route reported here opens a possibility to engineer highly thermo-stable materials with interesting structural architectures.

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**Supporting Information Available:** Complete single crystal diffraction data of **1**(CIF); movie of one helical chain rotating along the crystallographic *a*-axis (AVI); list of important bond lengths and angles (PDF); Table with geometrical characteristics of hydrogen bonds (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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