Available online at www.sciencedirect.com

SCIENCE DIRECT®

Microporous and Mesoporous Materials 78 (2005) 225–234

MICROPOROUS AND MESOPOROUS MATERIALS

www.elsevier.com/locate/micromeso

Chiral open-framework uranyl molybdates. 3. Synthesis, structure and the $C222_1 \rightarrow P2_12_12_1$ low-temperature phase transition of $[C_6H_{16}N]_2[(UO_2)_6(MoO_4)_7(H_2O)_2](H_2O)_2$

Sergey V. Krivovichev [a,*], Th. Armbruster [b,c], Dmitry Yu. Chernyshov [b,c],
Peter C. Burns [d], Evgeniy V. Nazarchuk [a], Wulf Depmeier [e]

[a] Department of Crystallography, St. Petersburg State University, University Emb. 7/9, 199034 St. Petersburg, Russia
[b] Laboratorium für chemische and mineralogische Kristallographie, Universität Bern, Freiestrasse 3, CH-3102 Bern, Switzerland
[c] Petersburg Nuclear Physics Institute, Orlova Grove, Gatchina, Leningrad District 188350, Russia
[d] Department of Civil Engineering and Geological Sciences, University of Notre Dame, 156 Fitzpatrick Hall, Notre Dame, IN 46556, USA
[e] Institut für Geowissenschaften, Kiel Universität, Olshausenstrasse 40, D-24118 Kiel, Germany

Received 5 April 2004; received in revised form 7 October 2004; accepted 8 October 2004
Available online 30 November 2004

Abstract

A new chiral 6:7 open-framework uranyl molybdate, $[C_6H_{16}N]_2[(UO_2)_6(MoO_4)_7(H_2O)_2](H_2O)_2$, has been synthesized by hydrothermal methods. The structure has been refined using single-crystal X-ray diffraction data collected at 20 and −127 °C. The 20 °C structure [orthorhombic, $C222_1$, $a = 11.3045(14)$, $b = 19.962(6)$, $c = 24.416(5)$ Å, $V = 5510(2)$ Å^3] has been refined to $R_1 = 0.046$ on the basis of 6093 unique observed reflections. The −127 °C structure [orthorhombic, $P2_12_12_1$, $a = 11.211(4)$, $b = 19.880(10)$, $c = 24.421(8)$ Å, $V = 5443(4)$ Å^3] has been refined to $R_1 = 0.047$ on the basis of 6951 unique observed reflections. The structures are based upon topologically identical frameworks of corner-sharing UO_7 pentagonal bipyramids and MoO_4 tetrahedra. The extra-framework H_2O groups and protonated triethylamine molecules reside in the framework cavities. In the $C222_1$ structure at 20 °C, H_2O and $[C_6H_{16}N]^+$ molecules filling the chiral channels along [001] are disordered, whereas, in the $P2_12_12_1$ structure at −127 °C, they are perfectly ordered. The symmetry difference between structures at 20 °C and −127 °C is the result of a $C222_1 \rightarrow P2_12_12_1$ second order phase transition that involves ordering of extra-framework protonated amine molecules and H_2O groups, and distortion of the flexible $[(UO_2)_6(MoO_4)_7(H_2O)_2]^{2-}$ uranyl molybdate framework. On the basis of measurements of intensities of reflections that violate absence conditions of C-centering cell, the temperature of the phase transition is estimated as −11 °C.

Keywords: Uranyl molybdates; Open framework; Crystal structure; Phase transition; Order–disorder

---

1. Introduction

Chiral open-framework uranyl molybdates are of potential interest for a number of applications, including ion-exchange, catalysis and radioactive waste remediation [1–3]. They also represent an interesting group of materials that are based upon heteropolyhedral frameworks with corner-sharing between polyhedra of different types. In the case of uranyl molybdates, UO_7 pentagonal bipyramids and MoO_4 tetrahedra are the most common structural subunits. The U–O_{br}–Mo links (O_{br} = bridging oxygen atoms) are flexible and result in observed interesting physical behavior of structures of

---

[*] Corresponding author. Address: Institute für Mineralogie and Petrographie, Leopold-Franzens-Universität Innsbruck, Innrain 52, Innsbruck 6020, Austria.
E-mail address: skrivovi@mail.ru (S.V. Krivovichev).

doi:10.1016/j.micromeso.2004.10.020

uranyl molybdates such as highly anisotropic thermal expansion and phase transitions [4]. As shown in [3], uranyl molybdate frameworks are sufficiently flexible to be able to adapt to the geometrical shape of extra-framework cations.

In this paper, we report the synthesis, structure and low-temperature phase transition of $[C_6H_{16}N]_2[(UO_2)_6(MoO_4)_7(H_2O)_2](H_2O)_2$, a new chiral open-framework uranyl molybdate with protonated amine molecules within framework cavities. The flexibility of the framework allows the structure to adapt to different degrees of order of the guest molecules during the structural phase transformation.

2. Experimental

2.1. Synthesis

Crystals of $[C_6H_{16}N]_2[(UO_2)_6(MoO_4)_7(H_2O)_2](H_2O)_2$ were synthesized by a hydrothermal method from a solution of UO_2 $(CH_3COO)_2 \cdot 2H_2O$ (0.1568 g), MoO_3 (0.0576 g), triethylamine (0.054 g) and HCl (0.040 g) in 5 ml of H_2O (with an approximate U:Mo:triethylamine:HCl:H_2O molar gel ratio of 4:4:9:11:2780). The solution was placed in a Teflon-lined Parr bomb and heated to 180 °C for 43 h, followed by cooling to ambient temperature. The crystals occur as aggregates of yellow needles.

2.2. Single-crystal structure analysis

A crystal of $[C_6H_{16}N]_2[(UO_2)_6(MoO_4)_7(H_2O)_2](H_2O)_2$ was selected for X-ray data collection and mounted on a thin glass fiber. More than a hemisphere of X-ray diffraction data were collected at 20 °C using a Bruker SMART APEX CCD diffractometer with MoKα radiation. The data were integrated and corrected for absorption using an empirical ellipsoidal model supplied by the Bruker programs SAINT and XPREP. The absence conditions and reflection statistics indicated the orthorhombic space group $C222_1$, which was in agreement with previous studies of uranyl molybdates with $[(UO_2)_6(MoO_4)_7(H_2O)_2]$ frameworks [3,5]. The structure was solved by direct methods, yielding the positions of U, Mo and O atoms of the uranyl molybdate framework. Analysis of the difference Fourier maps revealed the presence of several partially-occupied positions in the framework cavities that can be assigned to disordered organic and H_2O molecules. Attempts to refine these positions were unsuccessful. Thus, they were introduced into the refinement, but their positional coordinates were not refined, whereas their isotropic thermal parameters were fixed at 0.15 Å^2; occupancies were fixed at the values corresponding to the heights of the residual peaks in the difference Fourier map. Later, the same crystal was measured at −127 °C using a Bruker SMART 1K CCD diffractometer with MoKα radiation. At this temperature, analysis of the diffraction pattern revealed the presence of several hundred relatively weak reflections that violate the $h + k = 2n$ absence conditions of the C-centered orthorhombic cell. The data were integrated and corrected for absorption using an empirical ellipsoidal model supplied by the Bruker programs SAINT and XPREP. The absence conditions and reflection statistics indicated the orthorhombic space group $P2_12_12_1$ which is a subgroup of the $C222_1$ space group found for the same crystal at room-temperature. The structure was solved by direct methods and refined in the space group $P2_12_12_1$ The refinement included not only the positions of U, Mo and O atoms of the uranyl molybdate framework, but also the positions of extra-framework protonated triethylamine molecules and H_2O groups (guest molecules).

Additional information pertinent to the data collections and structure refinements is given in Table 1. Atomic coordinates and displacement parameters for the structures at 20 and −127 °C are given in Tables 2 and 3, respectively. Selected bond-lengths for the structures at 20 and −127 °C are given in Tables 4 and 5, respectively. Table 6 provides values of the U–O–Mo bond angles for both temperatures studied.

The difference in symmetry of the structure at 20 and −127 °C provides evidence of a $C222_1 \rightarrow P2_12_12_1$ structural phase transition. To characterize the phase transition, the crystal was transferred to a CAD4 Enraf-Nonius four-circle single crystal diffractometer. A conventional liquid nitrogen device with an accuracy ±2 °C was

Table 1
Crystallographic data and refinement parameters for $[C_6H_{16}N]_2[(UO_2)_6(MoO_4)_7(H_2O)_2](H_2O)_2$ at 20 and −127 °C

	20 °C	−127 °C
a (Å)	11.3045(14)	11.211(4)
b (Å)	19.962(6)	19.880(10)
c (Å)	24.416(5)	24.421(8)
V (Å^3)	5510(2)	5443(4)
Space group	$C222_1$	$P2_12_12_1$
μ (cm^{-1})	192.90	194.33
Z	4	4
Diffractometer	SMART APEX CCD	SMART 1K CCD
Radiation	MoKα	MoKα
Total Ref.	31,126	31,610
Unique Ref.	11,422	12,009
Unique $\lvert F_o \rvert \geqslant 4\sigma_F$	6093	6951
R_1	0.046	0.047
wR_2	0.096	0.068
S	0.812	0.832

Note: $R_1 = \sum \lVert F_o \rvert - \lvert F_c \rVert / \sum \lvert F_o \rvert$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP^2 + bP)]$, where $P = (F_o^2 + 2F_c^2)/3$; $s = \{\sum[w(F_o^2 - F_c^2)]/(n - p)\}^{1/2}$ where n is the number of reflections and p is the number of refined parameters.