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Hydrothermal Synthesis of a New Molybdate with a Layered Structure, $(NMe_4)Mo_{4-\delta}O_{12}$

Jingdong Guo, Peter Zavalij, and
M. Stanley Whittingham*

*Department of Chemistry and
Materials Research Center
State University of New York at Binghamton
Binghamton, New York 13902-6000*

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Hydrothermal techniques have been extensively used in the synthesis of zeolitic materials[1] and recently have found broader application in solid-state synthesis such as in the formation of metal phosphates. Thus, Haushalter et al.[2] have reported many reduced molybdenum phosphates with octahedral–tetrahedral frameworks. The Nasicon structure type $MTi_2(PO_4)_3$, where M is a monovalent cation, traditionally made at temperatures from 700 to 900 °C, can be prepared hydrothermally at 250 °C[3,4] and below.[5] More recently we have synthesized a series of tungstates $M_xWO_{3+x/2}{\cdot}nH_2O$ with pyrochlore and hexagonal tungsten bronze (HTB) structures.[6,7] This work has been extended by the use of templating organic cations such as tetramethylammonium (TMA) to the synthesis of new titanium phosphates and tungstates.[8,9] Here we report the use of the TMA template in the synthesis of molybdates and the formation of a new layered molybdate $(NMe_4)Mo_{4-\delta}O_{12}$.

There is much interest in molybdates and molybdenum oxides due to their catalytic activity and their capability of forming a variety of crystal structures which allow a rich intercalation chemistry like their tungsten analogs. In the various forms of molybdenum trioxide, MoO_6 octahedra join in different ways through corners and/or edges to form chains, layers or packets. In α-MoO_3, MoO_6 octahedra connect by edge sharing, resulting in a zigzag chain and a unique layered structure.[10] β-MoO_3, an analog of WO_3, has a ReO_3-related structure where MoO_6 octahedra share only corners to form a monoclinically distorted symmetry.[11] There are also a number of molybdenum trioxide hydrates having different arrangements of MoO_6 octahedra.[12,13]

Here we report the formation of a layered molybdate structure type with a new MoO_6 octahedra arrangement. It was synthesized by mixing molybdic acid H_2MoO_4 from Fisher Scientific with 25% tetramethylammonium hydroxide aqueous solution in a 1:2 Mo:TMA molar ratio. The mixture was acidified with 3 M HCl under stirring conditions to pH = 3–4. A yellowish gel resulted. This gel was transferred to a 125-mL Teflon-lined autoclave (Parr Bomb), sealed, and reacted hydrothermally for 4 days at 200 °C and autogenous pressure.[14] The resulting microcrystallites which have a dark brown color with bright metallic luster were filtered out, washed, and dried in air. The yield was around 60% based on Mo.

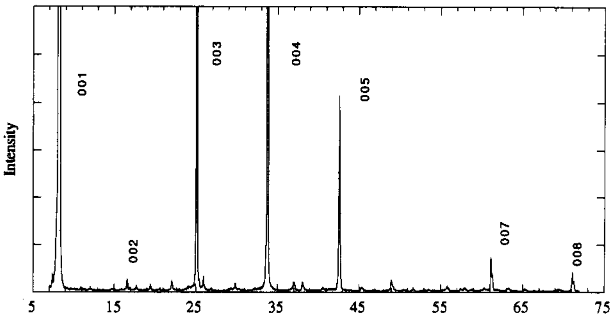

Figure 1. Powder XRD pattern from a wet pressed sample of $(NMe_4)Mo_{4-\delta}O_{12}$ showing the 001 preferentially oriented reflections.

X-ray diffraction of a pressed wet powder sample showed a series of 001 reflections indicative of a layered topology (Figure 1). This is supported by SEM images (Figure 2) which showing sheet stacking of rectangular microcrystallites. EDS elemental analysis showed no chlorine. The Mo content, 59 wt %, was determined by ignition on a TGA to MoO_3 at 600 °C under an O_2 atmosphere. The TMA content, 11.5 wt %, was calculated from the TGA weight loss around 400–450 °C (the typical decomposition temperature for TMA in a solid,[8,15] and the oxidation state of Mo was determined as above 5.5[16] by Ce^{4+}/Ce^{3+} titration.[17] This analysis gives the composition of the new layered compound as $(NMe_4)Mo_{4-\delta}O_{12}$, where $\delta \le 0.2$.

As we were unable to grow large enough crystals for a single-crystal experiment, powder XRD was applied to solve the structure of $(NMe_4)Mo_{4-\delta}O_{12}$. The pattern was indexed with monoclinic symmetry and lattice parameters: $a = 11.331(1)$, $b = 11.949(1)$, $c = 11.140(1)$ Å, and $\beta = 108.11(2)°$. Systematic extinction suggested a space group $C2/m$. Two other space groups Cm and $C2$ did not give better results. After minimizing the effect of preferred orientations by side loading, the best pattern was then chosen for the refinement work. The powder XRD data are tabulated in Table 1.

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(14) The synthesis temperature must be carefully controlled. Whereas higher temperatures cause some of the product to turn to MoO_2, lower temperatures produced two crystals in the millimeter size range. One was yellow with hexagonal symmetry; $a = 10.073$ and $c = 14.318$ Å; space group $P6/mcm$. The other was transparent with monoclinic symmetry; $a = 11.231$, $b = 16.337$, $c = 10.034$ Å, and $\beta = 110.3°$; space group $C2/m$. Single-crystal experiments are being carried out to further determine the crystal structures of these two crystals.

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(16) The titration indicated an overall molybdenum oxidation state of 5.5. Both TGA and X-ray structural analysis showed four Mo per NMe_4^+ cation. X-ray analysis also indicated the presence of trace amounts, <2 wt %, of MoO_2. To balance the charge, we anticipate that there are molybdenum vacancies as found in related molybdates.[23] However, an alternative mechanism would be hydrogen species giving the composition $NMe_4H_xMo_4O_{12}$, where $x \le 1$. Resolution must await a neutron diffraction study or the obtaining of single crystals for an X-ray study.

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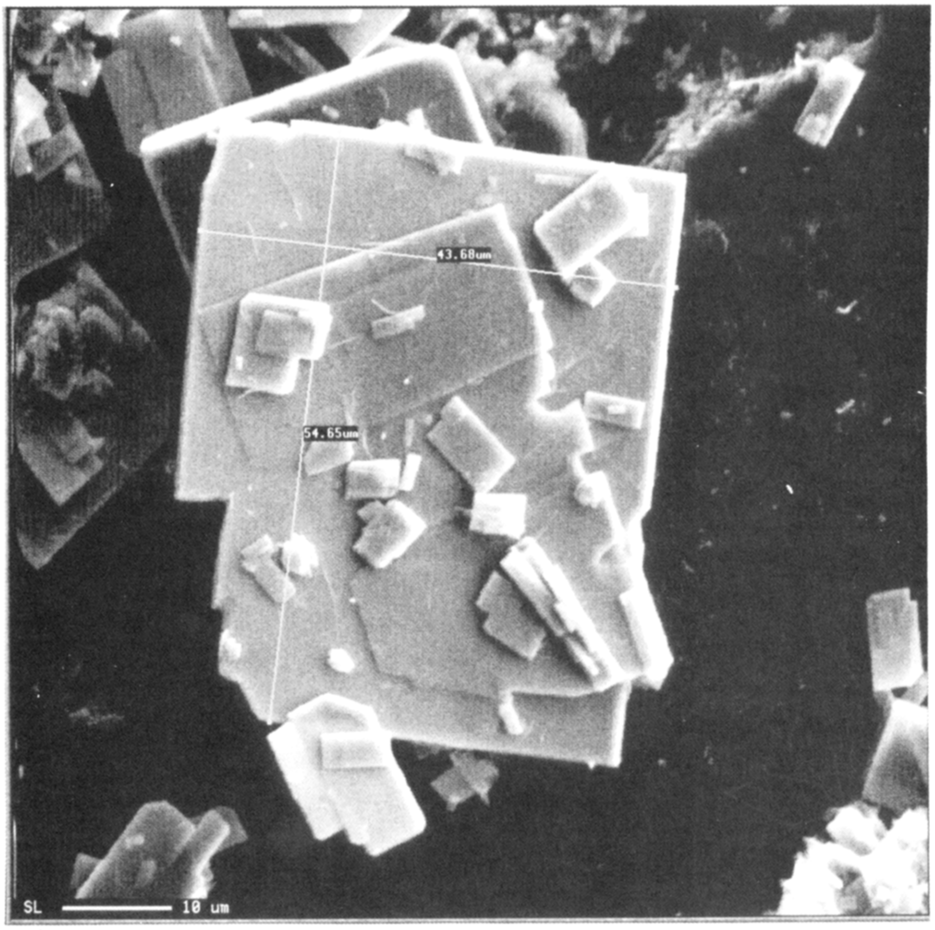

Figure 2. Secondary electron image of $(NMe_4)Mo_{4-\delta}O_{12}$. Scale is shown on the picture.

Table 1. XRD Powder Table for Monoclinic $(NMe_4)Mo_{4-\delta}O_{12}$[a]

h	*k*	*l*	*I*(obs)	2*θ*(obs)	*d*(obs)	*d*(calc)	*h*	*k*	*l*	*I*(obs)	2*θ*(obs)	*d*(obs)	*d*(calc)
0	0	1	1000	8.345	10.595	10.605	3	1	0	32	25.989	3.4284	3.4422
1	1	0	29	11.043	8.0120	8.0120	3	1	−2	25	26.296	3.3891	3.3832
1	1	−1	48	12.194	7.2582	7.2470	2	0	2	6	26.965	3.3065	3.3011
0	2	0	25	14.801	5.9848	5.9820	1	3	−2	4	27.632	3.2281	3.2236
2	0	−1	19	15.958	5.5535	5.5542	0	2	3	6	29.343	2.0437	3.0419
0	2	1	53	17.010	5.2124	5.2096	3	1	1	14	29.582	3.0196	3.0203
1	1	−2	18	17.797	4.9836	4.9811	0	4	0	34	29.879	2.9903	2.9904
2	0	−2	60	19.508	4.5503	4.5528	1	1	3				2.9809
2	0	1	22	20.648	4.3016	4.2964	3	1	−3	16	30.348	2.9451	2.9416
2	2	−1	7	21.848	4.0678	4.0698	1	3	2	9	30.775	2.9053	2.9046
1	1	2	23	22.153	4.0125	4.0139	0	4	1	17	31.043	2.8808	2.8780
1	3	0	22	23.817	3.7358	3.7399	4	0	−1	11	31.604	2.8309	2.8310
1	3	−1	28	24.342	3.6565	3.6525	4	0	0	12	33.215	2.6972	2.6955
2	2	−2	3	24.619	3.6159	3.6225	3	3	0	20	33.562	2.6701	2.6695
0	0	3	80	25.203	3.5335	3.5332	0	0	4	93	33.833	2.6493	2.6497
2	0	−3	9	25.597	3.4800	3.4948							

[a] I_{obs} accuracy was hindered somewhat by the 001 preferred orientation effect.

The structure was solved by direct method and refined using full profile refinement (Rietveld method); the CSD[18] and DBWS[19] programs were used. Final refinement gave $R_{profile} = 10.3\%$, and the measured and calculated data are compared in Figure 3. The atomic positions are given in Table 2 and show three Mo–O distances: Mo=O 1.68–1.69 Å, Mo–O–Mo 1.87–2.07 Å, and O–(Mo)$_3$ 2.22–2.38 Å. The results showed that $(NMe_4)Mo_{4-\delta}O_{12}$ exhibits a new structural type and a new arrangement of MoO_6 octahedral which lead to a layered stacking along the 001 direction with NMe_4^+ cations located between the layers. The basic building block of the layers is the Mo_4O_{16} unit; the layer consists of these Mo_4O_{16} units which share corners and edges with one another. The structure viewed along (010) is shown in Figure 4a. What is particularly intriguing are the tunnels along 101 which can be seen in the 001 projection shown in Figure 4b; they are about 3 Å in diameter. These would appear to permit the diffusion of ionic and small molecular species not only in the interlayer planes but from one plane to the neighboring ones. Additional XRD work and neutron powder diffraction are under way to reveal more details about this structure.

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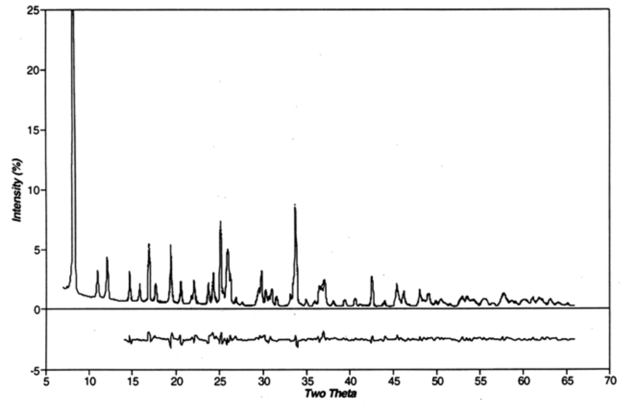

Figure 3. Experimental, calculated, and difference X-ray diffraction plots for $(NMe_4)Mo_{4-\delta}O_{12}$; the first three peaks were not used for the refinement because of the high intensity of the background and the very high intensity of peak 1.

Table 2. Atomic Positions in $(NMe_4)Mo_{4-\delta}O_{12}$

atom	x/a	y/b	z/c	N
Mo(1)	0.2059(5)	0.1552(6)	0.3780(4)	8
Mo(2)	0.0356(5)	0.3406(6)	0.3643(4)	8
O(1)	0.386(3)	0.153(4)	0.422(3)	8
O(2)	0.206(3)	0.310(3)	0.401(3)	8
O(3)	−0.033(2)	0.343(3)	0.206(3)	8
O(4)	0.160(3)	0.134(3)	0.221(3)	8
O(5)	0.035(3)	0.172(4)	0.403(3)	8
O(6)	0.515(4)	0	0.343(4)	4
O(7)	0.216(5)	0	0.406(5)	4
N	0.800	0	0.075	4[a]
C(1)	0.908	0	0.183	4[a]
C(2)	0.812	0	−0.063	4[b]
C(3)	0.725	−0.101	0.085	8

[a] Determined by differential Fourier synthesis. [b] Determined by geometrical calculation.

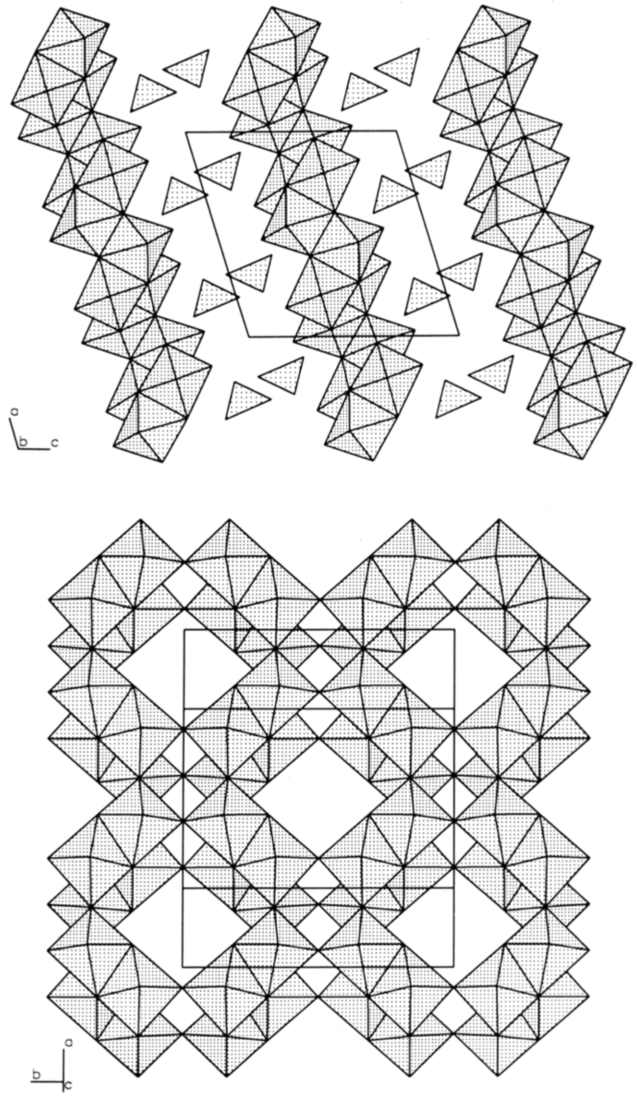

Figure 4. Polyhedral representation of the proposed structure of $(NMe_4)Mo_{4-\delta}O_{12}$ viewed from (a, top) and (010) direction and (b, bottom) the 001 direction; open circles represent the TMA ions.

The FTIR spectrum showed a sharp strong band at 1482 cm^{-1} due to CH_3 asymmetric deformation; skeletal C–N stretching gave characteristic frequencies at 956, 941 cm^{-1} and 473, 456 cm^{-1} as seen in tetramethylammonium halides.[20] The IR data also support the presence of three different kinds of Mo–O bonds with a band at 970 cm^{-1} characteristic of the Mo=O double bond stretching,[21] indicating a terminal oxygen in the framework.

The molybdenum bronzes, M_xMoO_3, have been intensively studied[22] because of their complex structural and electronic properties. Despite a similar apparent metallic luster the conductivity of $(NMe_4)Mo_{4-\delta}O_{12}$ is very low (10^{-11} S/cm) in contrast to the molybdenum bronzes, which usually have metallic conductivity. It would be worthwhile to further study the electronic properties of $(NMe_4)Mo_{4-\delta}O_{12}$ to provide insight into the relation between structure and properties. Moreover, molybdenum oxides are known to undergo ion exchange[23] and redox reactions by, for example, H^+ or Li^+ insertion.[24] Structurally there is ample space in $(NMe_4)Mo_{4-\delta}O_{12}$ to allow these reactions to occur and preliminary experiments with Li^+ insertion indicate ready reaction, as evidenced by color change. However, we must first find a way to remove or replace the TMA ion without changing the structure. Currently, further experiments are being performed to explore the chemical, electronic, structural, and catalytic properties of this new compound.

In summary, the hydrothermal reaction of H_2MoO_4 and TMA produces a novel molybdate with a layered structure, exhibiting a new MoO_6 octahedra arrangement. This hydrothermal route is expected to be general, and initial data suggest it can be extended to tungsten and vanadium and to the use of long-chain amines as in zeolites.[25]

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