Synthesis and Structure of the Novel Layered Oxide $BiMo_2O_7OH\cdot 2H_2O$

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The novel layered oxide $BiMo_2O_7OH\cdot 2H_2O$ was prepared under very mild hydrothermal conditions and the structure determined by *ab initio* methods from synchrotron X-ray powder diffraction data. The cell is monoclinic, $P2_1/m$, $Z = 2$, with dimensions $a = 6.343\,21(3)$ Å, $b = 11.597\,03(5)$ Å, $c = 5.792\,44(3)$ Å, and $\beta = 113.329(1)°$. Refinement using the Rietveld technique converged with $R_{F^2} = 5.99\%$, $R_P = 12.67\%$, $R_{wP} = 16.92\%$, and $\chi^2 = 5.44$ for 34 variables and 453 reflections. The structure is composed of infinite chains of edge-shared molybdenyl dimers which are corner-linked along [010]. These are connected via hexacoordinated bismuth atoms to form sheets parallel to $(10\bar{1})$ which are loosely held together via a hydrogen-bonding network.

Introduction

The bismuth molybdates are of great industrial importance as selective oxidation and ammoxidation catalysts.[1] The structural relationships between the known phases were recently described, and the catalytic activity was discussed in relation to the cation and anion vacancies.[2] There are several known binaries in the $Bi_2O_3\cdot MoO_3$ system,[3] and the structures of the so-called α-($Bi_2Mo_3O_{12}$),[4,5] β-($Bi_2Mo_2O_9$),[6,7] and γ-(Bi_2MoO_6)[8,9] phases have been elucidated. These are all known to be catalysts for the partial oxidation of hydrocarbons. In addition, two other materials have been synthesized but not yet fully characterized, the δ-($Bi_6Mo_2O_{15}$)[10] and ϵ-($Bi_{38}Mo_7O_{78}$)[11] phases.

More recently, a new hydrous phase of nominal composition $Bi_2Mo_3O_{12}\cdot 4.75H_2O$ and monoclinic crystal symmetry was reported.[12,13] This was shown to transform to an amorphous phase between 150 and 250 °C and then to $Bi_2Mo_3O_{12}$ above 300 °C. Treatment with pyridine leads to what appears to be an intercalation compound, which indicates the parent structure is probably layered.[13] The monoclinic unit cell matches that obtained for a material synthesized in an analogous fashion in this laboratory, but the proposed formula was $BiMo_2O_5(OH)_5$.

Given the recent successes from this laboratory and others in solving unknown structures from powder diffraction data,[14] we decided to undertake an *ab initio* determination using high-resolution synchrotron X-ray techniques. We report the results of this study, show the true formula to be $BiMo_2O_7OH\cdot 2H_2O$, and discuss in detail the crystal chemistry.

Table I. Details of the Rietveld Refinement[a]

formula	$BiMo_2O_7OH\cdot 2H_2O$
fw	565.90
a, Å	6.343 21(3)
b, Å	11.597 03(5)
c, Å	5.792 44(3)
β, deg	113.329(1)
V, Å^3	391.27
space group	$P2_1/m$
Z	2
ρ_{calc}, g·cm^{-3}	4.80
λ, Å	1.198 80(3)
μ_{calc}, cm^{-1}	336.1
2θ range, deg	10–74.65
d space range	0.9885–6.877
no. of reflns	453
no. of structural variables	25
total no. of variables	34
R_{F^2}	0.0599
R_P	0.1267
R_{wP}	0.1692
R_E	0.0726
χ^2	5.44

[a] See ref 18 for a description of R factors.

Table II. Refined Fractional Coordinates and Temperature Factors

atom	x	y	z	$100U_{iso}$, Å^2
Bi(1)	0.2640(2)	0.2500	0.6584(2)	0.46(2)
Mo(1)	0.6550(2)	0.0956(1)	0.1930(2)	0.13(4)
O(1)	0.0740(19)	0.2500	0.8756(21)	0.58(10)
O(2)	0.5910(20)	0.2500	0.0336(20)	0.58(10)
O(3)	0.3643(14)	0.0669(7)	0.8381(16)	0.58(10)
O(4)	0.8257(13)	0.0708(7)	0.8989(15)	0.58(10)
O(5)	0.5117(14)	0.1148(6)	0.3867(15)	0.58(10)
O(6)	0.9426(13)	0.1195(6)	0.3936(15)	0.58(10)

Experimental Section

Synthesis. A 50-g sample of $Bi(NO_3)_3\cdot 5H_2O$ was dissolved in 2 L of 1.75 M nitric acid. To this was added, with stirring, a solution consisting of 20 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ dissolved in 50 mL of deionized water. The resulting clear, colorless solution was heated at 90 °C for 5 h. The resulting white precipitate was collected via filtration, washed twice with distilled water and twice with acetone, and then dried at 30–40 °C for several hours.

Chemical analysis established a Mo:Bi ratio of 2:1. TGA to 600 °C showed a rapid weight loss at 275 °C, with a total loss of 8% from 100 to 300 °C. Assuming oxidation states of 3+ for Bi and 6+ for Mo leads to a proposed formula of $BiMo_2O_5(OH)_5$ (which can be rewritten as $BiMo_2O_7OH\cdot 2H_2O$) and an expected weight loss of 7.96%. The density of the powder was estimated to be 4.91 g·cm^{-3} by volume displacement.

Laboratory X-ray Powder Diffraction. Standard laboratory powder diffraction data were collected with Cu Kα radiation on a flat plate

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Table III. Selected Distances (Å) and angles (deg) with Esd's

				Distances				
Bi(1)–O(1)		2.059(11)	Mo(1)–O(2)	1.981(5)	O(1)–O(3)	2×	2.875(11)	
Bi(1)–O(2)		2.336(11)	Mo(1)–O(3)	1.892(8)	O(1)–O(4)	2×	2.643(10)	
Bi(1)–O(3)	2×	2.340(8)	Mo(1)–O(3)′	2.176(9)	O(1)–O(6)	2×	2.989(12)	
Bi(1)–O(5)	2×	3.060(7)	Mo(1)–O(4)	2.370(8)	O(4)–O(2)		2.840(11)	
Bi(1)–O(6)	2×	2.514(8)	Mo(1)–O(5)	1.715(8)	O(4)–O(3)		2.806(11)	
			Mo(1)–O(6)	1.754(8)	O(4)–O(3)		2.789(11)	
					O(4)–O(4)		2.628(15)	
					O(4)–O(5)		2.889(12)	
					O(4)–O(6)		2.720(11)	

		Angles			
O(1)–Bi(1)–O(2)		87.1(4)	O(3)–Bi(1)–O(3)		130.4(4)
O(1)–Bi(1)–O(3)	2×	81.4(2)	O(3)–Bi(1)–O(6)	2×	74.8(3)
O(1)–Bi(1)–O(6)	2×	81.0(3)	O(3)–Bi(1)–O(6)	2×	146.0(3)
O(2)–Bi(1)–O(3)	2×	66.5(2)	O(6)–Bi(1)–O(6)		74.0(3)
O(2)–Bi(1)–O(6)	2×	140.8(2)			

O(2)–Mo(1)–O(3)	149.5(4)	O(3)–Mo(1)–O(3)′	76.0(4)	O(3)′–Mo(1)–O(5)	99.7(4)
O(2)–Mo(1)–O(3)′	76.0(4)	O(3)–Mo(1)–O(4)	80.9(3)	O(3)′–Mo(1)–O(6)	156.9(3)
O(2)–Mo(1)–O(5)	97.1(4)	O(3)–Mo(1)–O(5)	99.2(3)	O(4)–Mo(1)–O(5)	175.6(3)
O(2)–Mo(1)–O(6)	97.6(4)	O(3)–Mo(1)–O(6)	103.4(3)	O(4)–Mo(1)–O(6)	81.0(3)
O(2)–Mo(1)–O(4)	80.9(4)	O(3)′–Mo(1)–O(4)	76.1(3)	O(5)–Mo(1)–O(6)	103.2(4)

sample using a Philips APD 3600 diffractometer. The peak positions for the first 20 reflections were used as input into Visser's autoindexing program.[15] This indicated a monoclinic cell with $a = 6.326$ Å, $b = 11.560$ Å, $c = 5.779$ Å, and $\beta = 113.35°$, with a figure-of-merit (M_{20}[16]) of 23.6.

Diffraction data from a Guinier-Hägg focusing camera ($r = 40$ mm, $\lambda = 1.540\,56$ Å) were used to obtain refined cell parameters. Silicon powder ($a = 5.4305$ Å) was used as an internal standard. Lattice parameters for $BiMo_2O_7OH{\cdot}2H_2O$, calculated by a least-squares refinement of 103 reflections, are $a = 6.349(1)$ Å, $b = 11.594(1)$ Å, $c = 5.795(1)$ Å, and $\beta = 113.35(1)°$.

Synchrotron X-ray Powder Diffraction. A flat plate sample of the material was studied at beam line X7A of the National Synchrotron Light Source at Brookhaven.[17] A wavelength of 1.198 80(3) Å was chosen using a Si(111) channel-cut monochromator and the exact value determined by calibration with a silicon standard. The instrument was configured in the high-resolution mode with a Ge(220) analyzer crystal and Kevex Peltier-cooled solid-state detector. Sample averaging was increased by rocking the flat plate during the data collection. A step size of 0.005° was used, and data were collected from 4 to 75° in 2θ for a variable count time at ambient temperature. The incident intensity was monitored with an ion chamber before the sample, and the data were subsequently scaled to these values.

Structure Solution and Refinement. A locally modified version of the Rietveld–Hewat program[18,19] which implements the method developed by Le Bail and co-workers[20] was used to extract integrated intensities from the synchrotron X-ray powder diffraction data. A total of 387 reflection intensities were extracted and converted to F^2 values. The systematic absences ($0k0$ with k odd) were consistent with space groups $P2_1$ and $P2_1/m$. The centrosymmetric option was chosen and confirmed by the subsequent refinement. The first 371 integrated intensities, of which 360 were considered observed using a 3σ criteria, were input into SHELXS-86,[21] and the direct methods option was chosen. The E map for the top solution gave the correct placement of the bismuth and molybdenum atoms. These were used as input in the GSAS structure refinement code[22] which utilizes the Rietveld technique,[18] and subsequent alternation of least-squares refinements (only the unit cell, scale, and selected peak shape terms were varied) and difference Fourier syntheses led to the placement of the six oxygen atoms. Attempts to locate the hydrogen atoms were not successful.

An anisotropic peak broadening was observed such that those reflections which were nearly along the b axis were noticeably narrower than the rest. Several models to correct this were explored, and that which was the most successful entailed the use of a 010 "broadening" axis and allowing the anisotropic term to refine to a negative value. The overall peak shape was defined by a pseudo-Voigt function with three refinable variables: one Gaussian term (GW), one Lorentzian term (LY), and an asymmetry term. The background was estimated visually and fit via linear interpolation. Attempts were made to refine isotropic temperature factors for all of the atoms, but those of the oxygen atoms varied considerably and one became slightly negative. Therefore, in the final model all of the oxygen thermal parameters were constrained to be equal. The final refinement consisted of 34 variables: 25 structural, 4 peak shape, and 5 for the cell and zero-point correction. Neutral-atom scattering factors were taken from ref 23. Details of the refinement are presented in Table I, the atomic positions in Table II, and selected distances and angles in Table III. The observed, calculated, and difference profiles are shown in Figure 1. A listing of the first 31 lines as observed in the Guinier data set and those calculated using LAZY-PULVERIX[24] are presented in Table IV.

Results and Discussion

Synthesis. $BiMo_2O_7OH{\cdot}2H_2O$ can be synthesized by a variety of routes. Other soluble molybdate salts, such as $Na_2MoO_4{\cdot}2H_2O$ or Li_2MoO_4, can replace the ammonium molybdate. The source of bismuth can be the nitrate salt, as described above, or Bi_2O_3 dissolved in acid solution. Mo:Bi molar ratios of 1:1 and 3:2 in solution gave the same product. We have also replaced HNO_3 with $HClO_4$ in the synthesis, and although not tried, HCl would probably work as well. Acid concentrations can be in the range 1.5–2.0 M when the reaction is held at 90 °C. When the solution is heated at or close to boiling, a different product is obtained. This higher-temperature material has been characterized by chemical and TGA analysis and has a composition of $BiMo_2O_6(OH)_3$ or $BiMo_2O_7OH{\cdot}H_2O$. The X-ray powder diffraction pattern is clearly different from that of $BiMo_2O_7OH{\cdot}2H_2O$. We find that the title compound can be prepared at lower temperatures if the acid concentration is lowered. In fact, we have synthesized a fully deuterated analog of $BiMo_2O_7OH{\cdot}2H_2O$ for powder neutron diffraction studies by the reaction of Bi_2O_3 and Na_2MoO_4 in 0.85 M DNO_3 at room temperature.

***Ab Initio* Structure Solution.** This report is one of the many recent studies which include a structure solution based on powder diffraction data.[14] The increasing use of this alternative to standard single-crystal-based methods is due, in part, to both improved instrumentation and methodology. In particular, it is important to stress that the use of dedicated high-resolution powder

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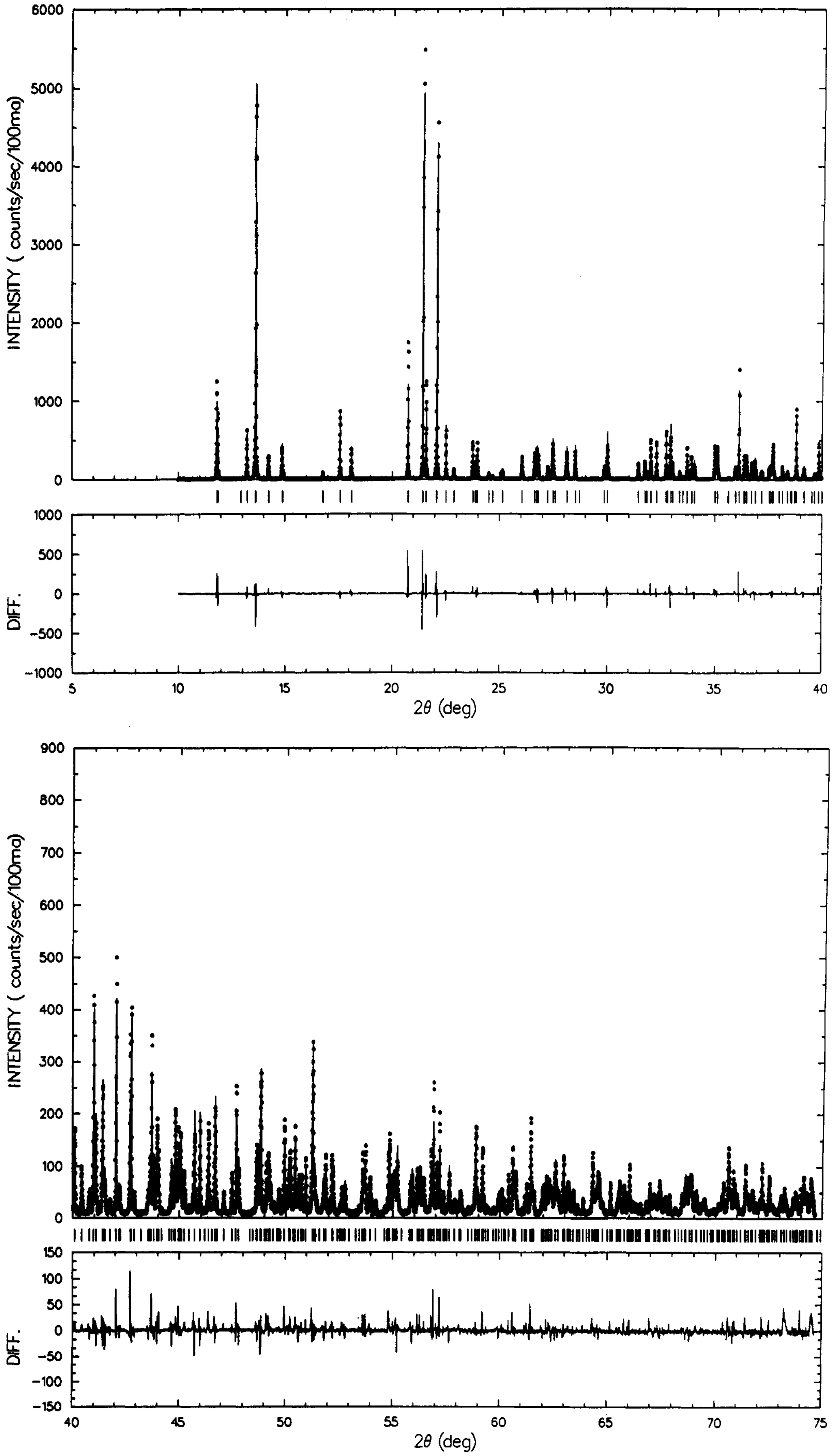

Figure 1. Synchrotron X-ray data for $BiMo_2O_7OH{\cdot}2H_2O$ showing the observed (dots), calculated (line), and difference (bottom) spectra from the Rietveld refinement. The vertical marks indicate the positions of allowed reflections.

diffractometers at synchrotron sources[17] greatly enhances the chances of success due to minimized peak overlap. This combines with novel intensity extraction methods[20] so that a powder problem can be easily and rapidly tacked using well-developed crystal-

Table IV. X-ray Powder Diffraction Data for $BiMo_2O_7OH\cdot 2H_2O$

h	*k*	*l*	d_{calc}, Å	d_{obs}, Å	$2\theta_{obs}$, deg	*I*(rel)
1	0	0	5.8285	5.8277	15.191	19.6
0	2	0	5.7971			10.3
1	1	0	5.2075	5.2133	16.994	10.8
−1	0	1	5.0499	5.0671	17.488	100.0
0	1	1	4.8350	4.8425	18.306	4.1
−1	1	1	4.6298	4.6362	19.128	7.8
0	2	1	3.9195	3.9250	22.636	12.4
−1	2	1	3.8078	3.8121	23.316	6.2
1	0	1	3.3271	3.3297	26.752	24.3
1	3	0	3.2210	3.2256	27.632	65.2
1	1	1	3.1981	3.2010	27.849	17.9
−2	0	1	3.1317			14.7[a]
0	3	1	3.1267			51.2[a]
−1	3	1	3.0691	3.0722	29.042	10.4
−2	1	1	3.0234	3.0257	29.498	2.4
2	0	0	2.9143	2.9146	30.649	8.2
−1	0	2	2.8908	2.8891	30.927	5.5
1	2	1	2.8856			6.1
0	4	0	2.8986			0.1
2	1	0	2.8264	2.8272	31.622	1.3
−1	1	2	2.8049			0.7
−2	2	1	2.7554	2.7564	32.456	1.8
0	0	2	2.6598	2.6618	33.643	6.1
2	2	0	2.6038	2.6032	34.424	5.4
0	1	2	2.5924	2.5932	34.560	7.9
1	4	0	2.5953			1.2
−1	2	2	2.5870			6.5
0	4	1	2.5452	2.5474	35.202	1.9
−2	0	2	2.5249	2.5254	35.519	11.4
1	3	1	2.5215			0.5
−1	4	1	2.5139			0.1
−2	1	2	2.4671	2.4677	36.378	8.4
−2	3	1	2.4332	2.4340	36.899	6.6
2	3	0	2.3269	2.3270	38.662	2.6
−2	2	2	2.3149	2.3161	38.851	0.5
−1	3	2	2.3148			8.9
2	0	1	2.2129	2.2127	40.746	3.3
0	3	2	2.1910	2.1919	41.149	4.0
1	4	1	2.1855			1.3
2	1	1	2.1737	2.1741	41.502	8.1
1	5	0	2.1546	2.1556	41.874	5.2
−2	4	1	2.1272	2.1268	42.470	1.1
0	5	1	2.1257			6.7
1	0	2	2.1228			0.1
−2	3	2	2.1138	2.1137	42.745	11.5
−3	0	1	2.1149			7.0

[a] These reflections were obscured by the Si standard.

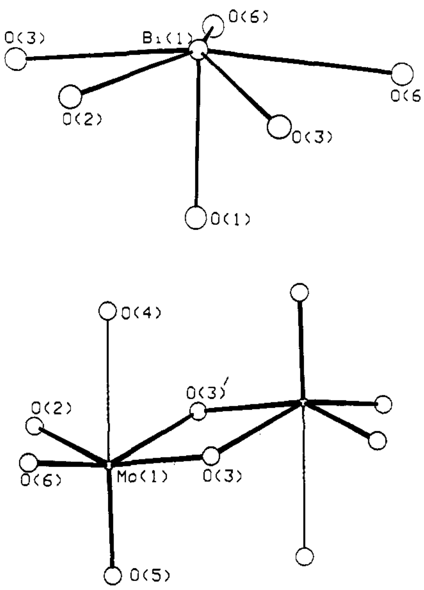

Figure 2. ORTEP[30] diagram showing the coordination of the bismuth and molybdenum atoms in $BiMo_2O_7OH\cdot 2H_2O$. The radii correspond to 50% probability spheres for the isotropically refined thermal parameters.

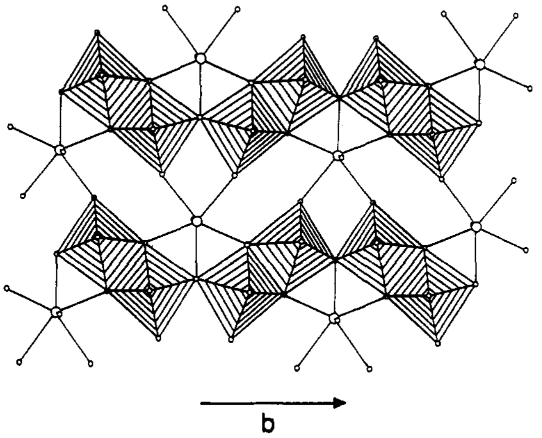

Figure 3. STRUPLO[31] representation of the structure of $BiMo_2O_7OH\cdot 2H_2O$ viewed approximately down [$\bar{1}$01] showing one of the layers. The molybdenum octahedra have been drawn, the bismuth atoms are the large circles, and the oxygen atoms are the small ones.

glographic tools such as Patterson or direct methods. The heavy atoms were readily located and the positions refined to a reasonable degree of accuracy from the X-ray data (Table II). As prior work from this laboratory has shown,[25,26] powder neutron diffraction data are a valuable complement and not only would be expected to provide more accurate locations of the oxygen atoms but should also allow the location of the hydrogen atoms. This experiment is planned for the near future now that we have successfully prepared the deuterated version, $BiMo_2O_7OD\cdot 2D_2O$.

Description of the Structure. The structure may be visualized as being composed of irregular six-coordinate bismuth units and distorted molybdenyl octahedra (Figure 2 and Table II). The bismuth coordination environment is best described as a monocapped pentagon, with the bismuth approximately in the center of the pentagonal plane and O(1) as the cap. Alternatively, if the two longest oxygen contacts to the O(6) atoms are ignored, then the coordination may be described as the more common sawhorse configuration. In addition, there are two oxygen atoms at a nonbonding distance of 3.06 Å which are opposite O(1). Thus, there appears to be a stereochemically active lone pair on the bismuth atom located *trans* to the O(1) atom. The molybdenum is in a distorted octahedron of oxygen atoms with two short bonds (*ca.* 1.72 Å) in a *cis* configuration, two normal bonds (*ca.* 1.94 Å), and two longer bonds (*ca.* 2.27 Å). The distortion from octahedral symmetry is such that the coordination is tending toward tetrahedral. This is the classical geometry for nearly all Mo^{VI} mononuclear compounds.[27] The three-dimensional structure is built from dimers of these MoO_6 units which are formed by sharing the edges defined by the O(3) atoms. These dimers are then corner-linked through O(2) atoms to form chains which run along [010]. The bismuth atoms hold these together via rather long bonds (2.34 and 2.51 Å) into sheets which are parallel to (101) (Figure 3), and the lone pairs project out from the planes. The layers appear to be held together by a hydrogen-bonding network as described below.

The overall formula of this material based on the crystallographic data (Table I) is $BiMo_2O_{10}$. The starting materials, mild aqueous synthesis conditions, lack of color, and coordination environments all suggest the formal valences are 3+ for bismuth and 6+ for molybdenum. This leaves an overall charge of 5− and suggests there are five hydrogen atoms per formula unit. This

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Table V. Bond Valence Sums

atom	valence	atom	valence	atom	valence	atom	valence
Mo	5.66+	O(1)	1.11−	O(3)	1.91−	O(5)	1.75−
Bi	3.27+	O(2)	1.99−	O(4)	0.25−	O(6)	1.85−

is also consistent with the observed 8% weight loss from TGA. The bond valence sums were calculated using the procedure of Brown and Altermatt[28] and the molybdenum parameters from Bart and Ragaini[29] (Table V). These are in close agreement with the proposed metal valences and also suggest O(1) is a hydroxide ion and O(4) a water molecule. This would then give the final formulation, $BiMo_2O_7OH{\cdot}2H_2O$. The first of these, O(1), is bonded solely to the bismuth atom and projects directly between the layers. The other, O(4), is only weakly bonded to the molybdenum atom and also points between the sheets. There are close contacts between these oxygen atoms (Table III), and therefore we propose that the layers are held together by a substantial hydrogen-bonding network (Figure 4). In addition, a third oxygen atom, O(5), projects out from the sheets into the interlayer region. However, this is strongly bonded to the molybdenum and is less likely to be part of the proposed network.

Comparison to Other Bismuth Molybdates. There are three other structurally well-characterized systems, the so-called α-($Bi_2Mo_3O_{12}$),[4,5] β-($Bi_2Mo_2O_9$),[6,7] and γ-(Bi_2MoO_6)[8,9] phases. The molybdenum coordinations are approximately five-coordinate, tetrahedral, and distorted octahedral, respectively. The title material is most like the γ phase in this regard. In all four cases the bismuth coordination is high and irregular. With the exception of Bi(3) in the β phase, the environment may be described as sawhorse with four longer contacts, and there appears to be a stereochemically active lone pair. In contrast to the pure oxides, $BiMo_2O_7OH{\cdot}2H_2O$ has a more open and two-dimensional structure, and the non-hydrogen atomic volume is 15.1 Å^3 compared to 14.0 (α), 14.8 (β), and 13.6 Å^3 (γ).

It has been suggested that the catalytic activity in these materials is bimetallic in nature,[1] and therefore the importance of a cleavage plane which contains both elements in close proximity has been noted.[5] Another important structural feature would appear to be the presence of a large number of defects to facilitate oxygen mobility.[2] The layered structure and the alternation of molybdenum and bismuth in the sheets of $BiMo_2O_7OH{\cdot}2H_2O$ clearly fulfill the first criteria. In addition, there are both loosely bound oxygen atoms on the bismuth and a water molecule on the molybdenum. These should lead to facile opening of the coordination environments and the possibility that oxygen mobility will be high. Therefore, if the thermal stability can be increased, this material may show interesting catalytic properties.

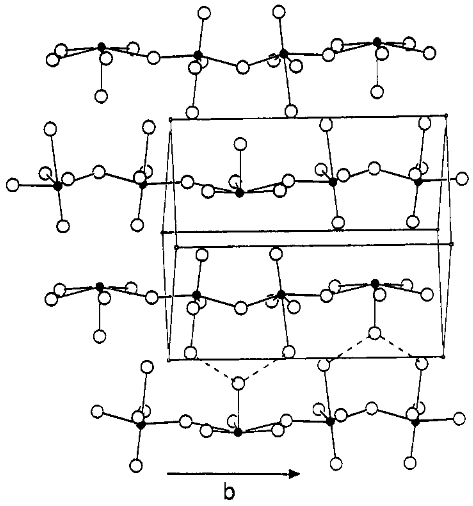

Figure 4. ORTEP[30] representation of the structure of $BiMo_2O_7OH{\cdot}2H_2O$ approximately down [101]. The metal atoms are the solid circles, and the oxygen atoms are the open circles. The proposed hydrogen bonding is shown by the dashed lines.

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