370 *Inorg. Chem.* **1987**, *26*, 370-373

Contribution No. 4027 from the Central Research and Development Department,
E. I. du Pont de Nemours & Company, Experimental Station, Wilmington, Delaware 19898

Hexagonal Molybdates: Crystal Structure of $(Na{\cdot}2H_2O)Mo_{5.33}[H_{4.5}]_{0.67}O_{18}$

E. M. McCarron III,* D. M. Thomas, and J. C. Calabrese

Received July 30, 1986

Cation exchange in the hexagonal molybdate system $AH_{6x-1}Mo_{6-x}O_{18}$ (A = $Na{\cdot}2H_2O$, K, Rb, Cs, NH_4, $Ag{\cdot}2H_2O$) is found to be facile. Upon thermal decomposition, the measured water loss from these $AH_{6x-1}Mo_{6-x}O_{18}$ materials indicates that $x = {}^2/_3$. For the hexagonal sodium molybdate, the unit cell parameters are a = 10.595 (2) Å, c = 3.7224 (9) Å, V = 361.87 (23) Å^3, and Z = 1. The crystal structure of $(Na{\cdot}2H_2O)Mo_{5.33}[H_{4.5}]_{0.67}O_{18}$ was solved in space group $P6_3/m$ and refined to R = 0.070 from 473 independent reflections. The sodium-containing structure differs from that of the potassium analogue $KMo_5O_{15}OH{\cdot}2H_2O$ = $KMo_5[H_5]O_{18}$ in the location of the alkali-metal cation within the channel structure. The shift in the cation position allows, in the sodium case, two extra water molecules per unit cell to be accommodated within the channels. The increased volume of the channel contents ($Na{\cdot}2H_2O$ vs. K) accounts for the larger unit cell volume of the sodium molybdate. A simple relationship between the monovalent cation radius and its channel location is noted.

Introduction

Two polymorphs of molybdenum trioxide are known to exist; namely, α-MoO_3[1] and the recently reported metastable β phase.[2] α-MoO_3 has the unique layered structure shown in Figure 1. The basic structural unit of α-MoO_3 is the $MoO_{3/3}O_{2/2}O_{1/1}$[3] octahedron. The connectivity of these MoO_6 octahedra is such that edge sharing between octahedra results in the formation of zigzag chains, which propagate along the c axis (Figure 1a). Corner sharing between these chains of octahedra in the a-axis direction (Figure 1b) completes an MoO_3 layer. The layers stack in an *aba* sequence along the b axis as a result of concerted displacements of the molybdenum atoms away from the centers of the MoO_6 octahedra. These octahedral distortions also account for the orthorhombic symmetry of α-MoO_3. On the other hand, the structure of β-MoO_3, an analogue of WO_3, is related to the cubic ReO_3 structure, which is shown in Figure 2. The β-MoO_3 structure is a monoclinically distorted variant, consisting of corner-shared $MoO_{6/2}$[3] octahedra.

In addition to the orthorhombic and monoclinic phases mentioned above, a third form of molybdenum trioxide, a so-called "hexagonal phase", has been reported erroneously by a number of authors and continues to be a cause of confusion in the literature.[4-9] "Hexagonal MoO_3" would be constructed of the same zigzag chains of MoO_6 octahedra as those found in α-MoO_3 (Figure 1a); however, a different connectivity between chains (connecting through adjacent rather than through opposing oxygens) would give rise to the hexagonal symmetry. The hypothetical structure of "hexagonal MoO_3" is shown in Figure 3a. Although the structure of "hexagonal MoO_3" certainly appears plausible, it has never been synthesized.[10]

The so-called "hexagonal MoO_3" phase is, in fact, a hexagonal molybdate having the general composition $AH_{6x-1}Mo_{6-x}O_{18}$ (A = Na, K, NH_4). The structure was solved by Krebs and Paulat-Böschen[11] for the potassium molybdate $KMo_5O_{15}OH{\cdot}2H_2O$ (i.e. $KH_5Mo_5O_{18}$ for x = 1 above). The structure of this molybdate is shown in Figure 3b. The molybdenum vacancies (1 Mo[ ]/unit cell) in the ideal "hexagonal MoO_3" framework are charge-compensated by the potassiums (1 K/Mo[ ]) located in the channels and the hydrogens (5 H/Mo[ ]), which are presumed to be bonded to oxygens associated with the molybdenum vacancies. This defect structure is closely related to the previously determined $[A(I)]_x[B(V)]_xMo_{1-x}O_3$ structures,[12,13] which are free of framework vacancies.

Table I. Hexagonal Molybdates, $AH_{6x-1}Mo_{6-x}O_{18}$

A	a, Å	c, Å	radius,[a] Å	unit cell vol, Å^3	Mo/A
Li[b]					
$Na{\cdot}2H_2O$	10.595 (2)	3.722 (1)	1.02	361.87 (23)	5.31 (3)
K	10.520 (2)	3.725 (1)	1.38	356.97 (17)	5.35 (4)
Rb	10.573 (1)	3.720 (2)	1.52	360.14 (18)	5.55 (6)
Cs	10.604 (1)	3.721 (1)	1.67	362.35 (6)	5.23 (7)
NH_4	10.548 (3)	3.722 (1)	1.48	358.63 (18)	5.33 (4)
$Ag{\cdot}2H_2O$	10.585 (1)	3.726 (1)	1.15	361.54 (4)	5.30 (3)

[a] See ref 18. [b] Not stable. [c] Mo/N ratio.

Our interest in these materials stems from our studies on the relationship between catalytic activity and structure type. In particular, we have been interested in the selective oxidation of methanol to formaldehyde over molybdenum trioxide.[14] Therefore, we have been studying in detail the catalytic differences between the α and β phases of MoO_3.[15] In the hopes of extending this work, we viewed the thermal decomposition of the hexagonal ammonium molybdate as a possible route to the formation of a true hexagonal polymorph of molybdenum trioxide. Unfortunately, we find that this route does not result in a hexagonal modification of the molybdenum trioxide structure but instead produces α-MoO_3.

In the course of our investigations, we studied the cation-exchange properties of the hexagonal molybdate system. In this paper we report both our findings on the cation-exchange properties and the results of a single-crystal X-ray analysis of the sodium molybdate $(Na{\cdot}2H_2O)Mo_{5.33}[H_{4.5}]_{0.67}O_{18}$.[16]

Experimental Section

Preparation of the Hexagonal Alkali-Metal Molybdates. The sodium and potassium molybdates were prepared by first dissolving 50 g of the simple molybdate, either $Na_2MoO_4{\cdot}2H_2O$ or K_2MoO_4, in 100 mL of

---

(1) Andersson, G.; Magneli, A. *Acta Chem. Scand.* **1950**, *4*, 793.

(2) McCarron, E. M., III; *J. Chem. Soc., Chem. Commun.* **1986**, 336.

(3) This notation concisely describes the structure of the trioxides by listing the metal atom followed by the number of each type of coordinated oxygen divided by its coordination number. The sum of the oxygen numerators gives the coordination number about the metal atom.

(4) Sotani, N. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1820.

(5) Tatibouet, J. M.; Germain, J. E. *C. R. Seances Acad. Sci., Ser. C* **1980**, *290*, 321.

(6) Tatibouet, J. M.; Germain, J. E. *J. Catal.* **1981**, *72*, 375.

(7) Volta, J. C.; Portefaix, J. L. *Appl. Catal.* **1985**, *18*, 1.

(8) Germain, J. E. In *Adsorption and Catalysis on Oxide Surfaces*; Che, M., Bond, G. C. Eds.; Elsevier: Amsterdam, 1985; p 355.

(9) Garin, J. L.; Blanc, J. M. *J. Solid State Chem.* **1985**, *58*, 98.

(10) We are presently investigating the possibility of thermally decomposing $NH_4VMo_5O_{18}$ to give the open channel structure $VMO_5O_{17}OH$ (Figure 3b); the idea is that perhaps the instability of the framework is associated with the molybdenum vacancies and not simply with the removal of the channel ions.

(11) Krebs, B.; Paulat-Böschen, I. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1976**, *B32*, 1697.

(12) Darriet, B.; Galy, J. *J. Solid State Chem.* **1973**, *8*, 189.

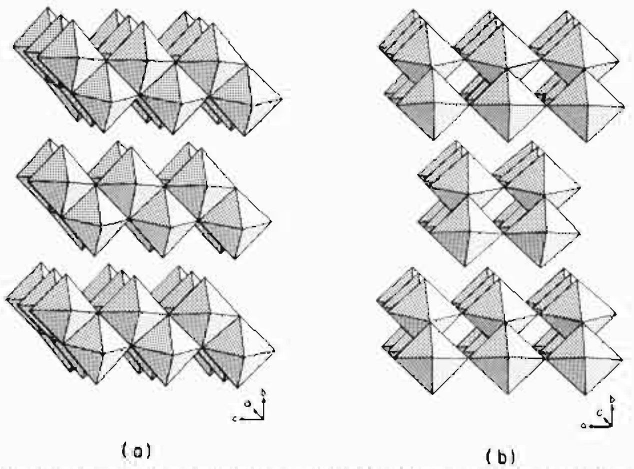
(13) Olenkova, I. P.; Plyasova, L. M.; Kirik, S. D. *React. Kinet. Catal. Lett.* **1981**, *16*, 81; *Zh. Strukt. Khim.* **1982**, *23*, 120.

(14) Cheng, W.-H.; Chowdhry, U.; Ferretti, A.; Firment, L. E.; Groff, R. P.; Machiels, C. J.; McCarron, E. M., III; Ohuchi, F.; Staley, R. H.; Sleight, A. W. In *Heterogeneous Catalysis, Proceedings of the 2nd Symposium of IUCCP of the Department of Chemistry, Texas A&M University*; Shapiro, B. L., Ed.; Texas A&M University Press: College Station, TX, 1984; p 165.

(15) Machiels, C. J.; Cheng, W.-H.; Chowdhry, U.; Farneth, W. E.; Hong, F.; McCarron, E. M., III; Sleight, A. W. *Appl. Catal.* **1986**, *25*, 249.

(16) The $[H_x]_y$ notation refers to x H/Mo[ ] ([ ] = vacancy) and y Mo[ ]/unit cell.

0020-1669/87/1326-0370$01.50/0 © 1987 American Chemical Society



(a) (b)

Figure 1. The α-MoO_3 structure emphasizing the (a) edge and (b) corner sharing between $MoO_{3/3}O_{2/2}O_{1/1}$ octahedra.

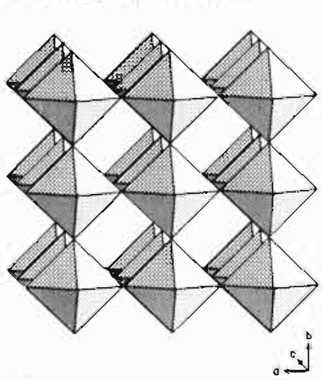


Figure 2. The ReO_3 structure.

Table II. Comparison of the Refined Lattice Parameters for the Sodium and Potassium Hexagonal Molybdates

	directly from soln	indirectly via cation exchange
	Sodium	
a, Å	10.595 (2)	10.593 (1)
c, Å	3.7224 (9)	3.7226 (3)
vol, Å^3	361.87 (23)	361.76 (9)
	Potassium	
a, Å	10.520 (2)	10.518 (1)
c, Å	3.7245 (4)	3.7246 (3)
vol, Å^3	356.97 (17)	356.84 (10)

distilled water and then adding this solution to 300 mL of 5 M HNO_3. The resulting acidified solution was heated to boiling and removed from the heat just as the white product began to precipitate out of the yellow solution. After the solution had cooled to room temperature, the crystalline product was isolated by suction filtration, washed with water, and then dried with acetone.

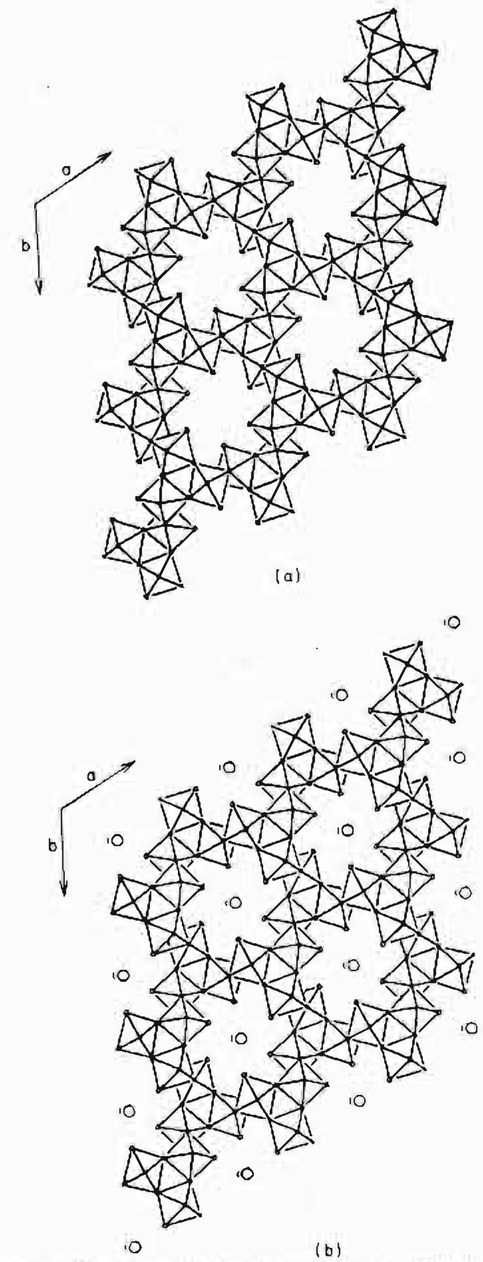
For the preparation of the rubidium and cesium analogues, the simple molybdates were generated in situ by the reaction

$$A_2CO_3 + MoO_3 \rightarrow A_2MoO_4 + CO_2 \qquad (1)$$

where A = Rb, Cs. For the rubidium compound, 3 g (0.0208 mol) of MoO_3 was added to 5 g (0.0216 mol) of Rb_2CO_3 dissolved in 10 mL of distilled water and the mixture gently heated until all the MoO_3 had reacted. This solution was then added to 30 mL of 5 M HNO_3 and boiled to precipitate the product. The product was washed and dried as mentioned above. Similarly, the hexagonal cesium molybdate was made by reacting 20 g (0.139 mol) of MoO_3 with 50 g (0.154 mol) of Cs_2CO_3 in 100 mL of distilled water and then adding 300 mL of 5 M HNO_3. Whereas the hexagonal Na, K, and Rb molybdates are white, the hexagonal Cs molybdate is yellow.

Cation Exchanges. The sodium ions of the hexagonal sodium molybdate were exchanged with monovalent metal cations as follows. Five grams of the hexagonal sodium molybdate was added to 50 mL of the appropriate 1 M metal chloride solution, and the mixture was stirred for 24 h. Silver nitrate was used for the silver exchange. The solution was changed three times. The product was recovered by suction filtration, washed with water, and acetone dried. The hexagonal molybdates produced via cation exchange are listed in Table I.

The hexagonal potassium molybdate synthesized directly from solution was also exchanged by sodium in order to determine whether or not the hexagonal molybdates produced via cation exchange were identical with those obtained directly from solution. The results are listed in Table II.



(a) (b)

Figure 3. (a) The hypothetical "hexagonal" MoO_3 structure. (b) The structure of $KMo_5O_{15}OH{\cdot}2H_2O$.

Table III. Comparison of the Measured Thermogravimetric (H_2O) Weight Loss with That Predicted on the Basis of the Molybdenum Defect Concentration, *x*, for $AH_{6x-1}Mo_{6-x}O_{18}$

	water loss, %		
A	obsd	predicted for $x = {}^2/_3$[a]	predicted for $x = 1$[b]
$Na{\cdot}2H_2O$	7.2	7.3	7.8
K	3.3	3.2	5.5
Rb	3.4	3.1	5.2
Cs	2.4	2.8	5.0
NH_4[c]	6.5	6.5	9.0
$Ag{\cdot}2H_2O$	6.8	6.6	8.8

[a] Present work. [b] K + P-B model. [c] Weight loss includes ammonia loss.

Analysis. Metals were determined by routine chemical analysis (Galbraith Laboratories). The results expressed as a ratio, Mo/A (where A = channel ion), are given in Table I.

Thermoanalysis. The water content of the hexagonal molybdates was determined by thermogravimetric analysis. TGA was carried out on a Du Pont 951-1090B instrument at a heating rate of 5 °C/min under an oxygen atmosphere. Table III lists the weight loss attributable to water for the hexagonal alkali-metal molybdates.

X-ray Powder Diffraction. X-ray powder diffraction patterns were obtained with a Guinier–Hägg type focusing camera (r = 40 mm). The radiation used was monochromatic Cu $K\alpha_1$, and the internal standard was silicon (a = 5.430 88(4) Å). An Optronics P-1700 photomation instrument was used to collect absorbance data from the film. Peak positions and relative intensities were determined with local computer programs. The lattice parameters were refined by a least-squares procedure. The refined lattice parameters for the hexagonal molybdates are listed in Tables I and II.

Structural Determination. Data were collected with an Enraf-Nonius CAD4 X-ray diffractometer equipped with a monochromatic Mo $K\alpha$ (λ = 0.710 69 Å) source using a colorless, hexagonal drum-shaped crystal with dimensions 0.055 × 0.055 × 0.150 mm sealed in a glass capillary. Twenty diffraction maxima were located and used to obtain a hexagonal cell with dimensions $a = b$ = 10.590 (5) Å and c = 3.722 (3) Å. The dimensions and Laue symmetry were verified by axial rotation photographs along each of the reciprocal axes. A total of 1104 reflections were collected (hkl: ±13,13,6) at ambient temperature with the θ–ω scan mode in the range 3° ≤ 2θ ≤ 50°, with a scan range determined by $\omega = 1.0 + 0.35 \tan \theta$ and speeds ranging from 0.3 to 0.5°/min. The slow scan speeds were necessitated by the small size of the crystal. There was no evidence of radiation damage to the crystal during data collection. The data were treated in the usual fashion for Lorentz–polarization, yielding 473 independent reflections with $I \geq 2\sigma(I)$. The effects of absorption (μ = 45.31 cm^{-1}) were neglected due to the small (<1.5%) intensity variation about a typical diffraction vector (ψ scan) and the size and isotropy of the crystal. The systematic absences ($00l$, $l = 2n + 1$) are consistent with space groups $P6_3$ (No. 173) and the centric equivalent $P6_3/m$ (No. 176).

Structure Solution. The structure of the MoO_3 framework was solved with direct methods (MULTAN)[17] in space group $P6_3/m$. The MoO_3 framework was identical with that reported by Krebs and Paulat-Böschen,[11] with double chains of corner-sharing MoO_6 octahedra forming linear columns and consequent channels along the short c axis. The Mo coordination shows the Mo–O distances grouped into long (~2.2 Å), intermediate (~1.9 Å), and short (~1.7 Å) values. The model was refined anisotropically with full-matrix least squares to R = 0.080 and R_w = 0.103, where $R_w = [\sum W(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ with w proportional to $[\sigma^2(I) + (0.03I)^2]^{-1/2}$ and neutral scattering factors from ref. 19. In addition, the Mo multiplicity was refined to yield an occupancy of 0.444 corresponding to a total of 5.33 molybdenum atoms/cell or a vacancy of 2 Mo for every three cells.

At this stage, a difference map revealed two broad peaks in the channel corresponding to peak densities of 5.3 and 3.8 e/Å^3. The larger peak was located along the channel axis on the $\bar{6}$ site at (0, 0, 0.25), while the second was located off the axis nearer the MoO_3 framework. Due to the similarity of the scattering powers of sodium ion and oxygen, all combinations of Na and O were investigated as potential models for an interpretation of the channel contents (i.e.: Na,Na; Na,O; etc.). The most reasonable combination, based on geometry and R value, was one in which the Na was located off the channel axis nearer the MoO_3 framework, with the second peak at the channel center modeled as an oxygen atom, presumably a water molecule. This resulted in an octahedral environment for the sodium ion (Figure 4a), with four of the Na–O bonds resulting from interactions with the MoO_3 framework oxygens and the remaining two from interactions with the channel H_2O molecules. Although the Na–O interactions are quite reasonable (distances of ~2.5 Å), the accuracy of these distances is undoubtedly affected by the size of the channel (diameter 5.74 Å), the thermal motion of the atoms, and the broad distribution of the electron density within the channel.

Table IV. Atomic Coordinates (×10 000) and Multiplicities of $(Na\cdot 2H_2O)Mo_{5.33}[H_{4.5}]_{0.67}O_{18}$

atom	mult	x	y	z	B_{eq},[a] Å^2
Mo	0.888	1050 (1)	4616 (1)	2500	0.8 (1)
Na	0.152	1181 (48)	1152 (53)	2500	2.2 (16)
O(1)	1.0	109 (13)	2765 (13)	2500	2.2 (4)
O(2)	1.0	−805 (10)	4993 (10)	2500	1.1 (3)
O(3)	1.0	2801 (11)	4966 (12)	2500	1.6 (3)
O(w)	0.294	0	0	1421 (196)	8.6 (24)

[a] $B_{eq} = {}^4/_3\sum_i\sum_j\beta_{ij}a_i\cdot a_j$.

Table V. Selected Bond Distances (Å) for $(Na\cdot 2H_2O)Mo_{5.33}[H_{4.5}]_{0.67}O_{18}$

Mo–O(1)	1.697 (12)	Mo–O(3)	2.37 (11)
Mo–O(2)	1.952 (3) (2×)	Mo–O(3)a	1.699 (10)
Mo–O(2)a	2.192 (9)		
Na–O(1)	2.478 (47)	Na–O(1)h	2.479 (31) (2×)
Na–O(1)i	2.513 (47)	Na–O(w)	2.578 (65)[a] (2×)

[a] See text.

An anisotropic refinement that included the two additional peaks (Na(1) and O(w)) resulted in a lowering of the agreement indices to the final values of R = 0.070 and R_w = 0.080. Due to the extreme elongation of the central H_2O oxygen, this atom was further refined isotropically as two half-atoms on either side of the $\bar{6}$ site since anisotropic refinement was precluded by the atom's proximity to the $\bar{6}$ site. This resulted in two Na–O(w) distances, 2.578 and 1.912 Å, with the longer appearing the more reasonable. The multiplicity of the oxygen O(w) refined to 0.149 while the Na peak refined to 0.075, yielding 2 H_2O/Na, for a formula of $(Na\cdot 2H_2O)Mo_{5.33}[H_{4.5}]_{0.67}O_{18}$. With Z = 1, the calculated density, 3.956 g/cm^3, is comparable to the value determined by Krebs and Paulat-Böschen.[11]

Refinement of the structure in the acentric space group $P6_3$ was attempted but ruled out on the basis of the expected least-squares instabilities (distorted molybdenum oxide framework and high correlations). No improvement in the agreement indices was noted. The statistical distribution of the channel contents and Mo multiplicity are consistent with the lack of higher diffraction reflections in the axial photos. The refinement was carried to completion with the maximum shift/error of 0.01 on the final cycle, and the estimated standard deviation of an observation of unit weight was 2.06. The highest peak on the final difference map is 3.1 e/Å^3 located near the Mo atom. An analysis of the structure factor amplitudes yields no evidence for extinction. The positional and thermal parameters and multiplicities from the final least-squares refinement cycle are listed in Table IV, and selected bond distances are given in Table V.

Results and Discussion

The analytical and X-ray diffraction results (listed in Tables I and II) for the sodium and potassium hexagonal molybdates produced either directly from solution or indirectly via cation exchange are virtually identical, indicating that both synthetic techniques produce chemically equivalent materials. The complete exchange of one cation for another at room temperature implies that cation exchange is very facile; the facility of the cation exchange reflects the open tunnel structure of these materials.

On the basis of a comparison of Guinier powder diffraction data, the hexagonal molybdates appear isomorphous. The hexagonal molybdate structure ($P6_3/m$) had previously been determined by Krebs and Paulat-Böschen (K & P-B) for the compound $KMo_5O_{15}OH\cdot 2H_2O$.[11] In the K & P-B structure (see Figure 3b), zigzag chains of edge-shared MoO_6 octahedra propagate along the c axis of the crystal. These chains are then corner-shared in such a way as to create a 1D hexagonal tunnel structure. If fully occupied by molybdenum, this molybdenum oxide framework would have the stoichiometry MoO_3. K & P-B found, however, that for every unit cell (there are 6 Mo sites/cell) there was one molybdenum vacancy. The molybdenum vacancy was charge-compensated for by one potassium located at the channel center and five hydrogens. Although not located, the five hydrogens were presumed, on the basis of chemical arguments, to reside in the vicinity of the molybdenum vacancy as two water molecules and an –OH group. Therefore, a full description of the structure is given by the formula $KMo_5[\,]O_{15}OH\cdot 2H_2O$, with [ ] denoting the molybdenum vacancy. Alternatively, in order to emphasize the defect MoO_3-framework structure, the hexagonal potassium

---

(17) Main, P.; Lessinger, L.; Woolfson, M. M.; Germain, G.; Declerq, J. P. "MULTAN 78"; University of York, York, England, and University of Louvain, Louvain-la-Neuve, Belgium, 1978. Additional programs were written by J.C.C.

(18) Shannon, R. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1976**, *A32*, 751.

(19) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

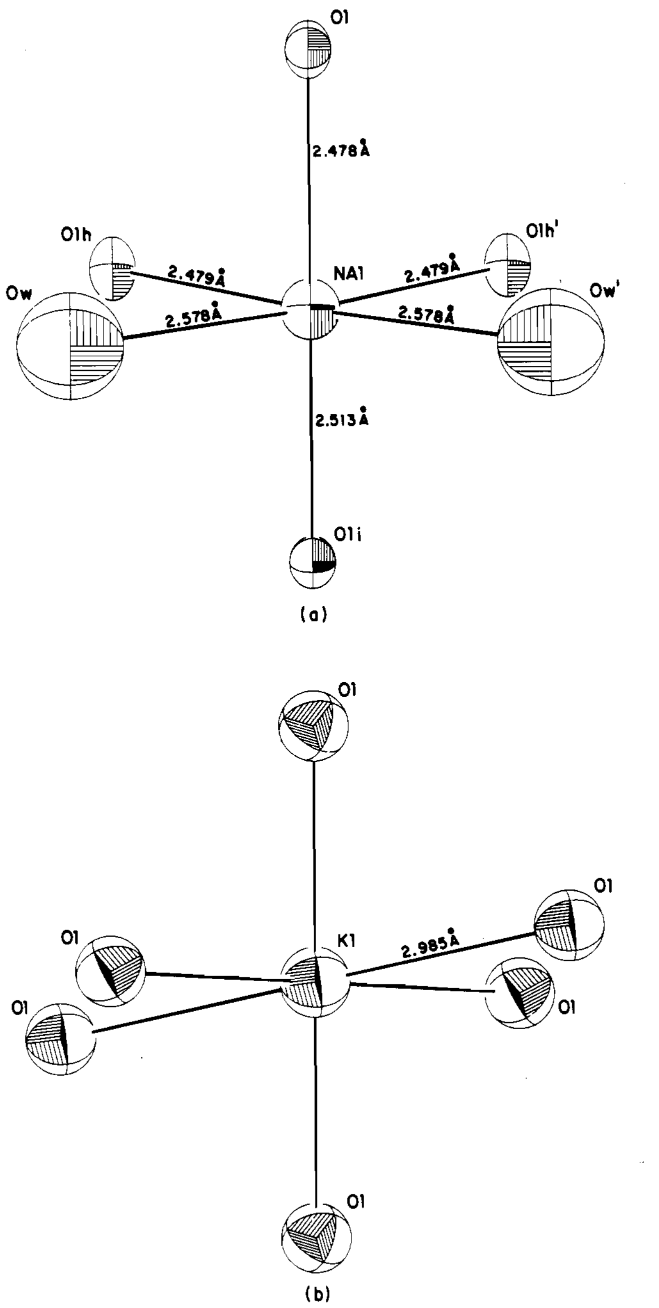


Figure 4. Comparison of the octahedral coordinations of the channel ions in the (a) Na and (b) K hexagonal molybdates.

molybdate structure can be written as $K(Mo_5[H_5]O_{18})$.[16]

The lattice parameters of the hexagonal molybdates synthesized in this study are given in Table I. In the case of the potassium, rubidium, and cesium molybdates, there appears to be a straighforward correlation between the unit cell volume and the ionic radius of the cation residing within the channels, as would be predicted on the basis of the K & P-B model. Even the apparent nonexistence of a hexagonal lithium molybdate can be rationalized in terms of the small size of the lithium cation being insufficient, relative to the free-channel diameter (roughly 3 Å), to stabilize this structure type. However, the anomalously large unit cell volume of the hexagonal sodium molybdate is not easily explained.

In an attempt to resolve this apparent anomaly, we grew single crystals of the hexagonal sodium molybdate and solved its crystal structure. Table IV lists the atomic coordinates and multiplicities for the sodium molybdate. While our structural solution generally agrees with K & P-B's earlier determination,[11] there are two important differences. First, the position of the sodium ion is shifted (x, y, $^1/_4$) relative to that of the potassium ion (0, 0, 0) so as to enhance the sodium–oxygen interactions. As a result of this shift, 2 water molecules/unit cell can also be accommodated within the channel. Therefore, the apparent unit cell volume anomaly is readily understood as being a consequence of the differing volumes of the channel contents: i.e., $Na^+{\cdot}2H_2O$ vs. K^+. Figure 4 details the differing coordinations of the channel ions for the Na and K molybdates.

It is interesting to note that the hexagonal ammonium molybdate also fits nicely into the radius/cell volume scheme outlined above; the radius of NH_4^+ is greater than that of K^+, implying that the NH_4^+ group also resides at (0, 0, 0). On the other hand, the silver analogue, with its anomalously large unit cell volume, presumably is isomorphous with the hexagonal sodium molybdate (Ag^+ at (x, y, $^1/_4$)). This suggests that the positioning of the channel ion is related to its radius and that the crossover point for the two possible locations lies between a radius of 1.15 (Ag^+) and 1.38 Å (K^+).

The second important difference between our model and that of K & P-B concerns the refined atomic multipliers. We find that there is an average of two molybdenum vacancies for every three unit cells, as opposed to K & P-B's determination of one Mo vacancy per unit cell.

The fact that the sodium and potassium hexagonal molybdates synthesized either directly from solution or indirectly via the cation exchange of one for the other are virtually identical (Table II) implies that the number of molybdenum vacancies per unit cell is most likely the same for both. This leads to two models for the structure of the hexagonal molybdates. On the basis of our model, $(Na{\cdot}2H_2O)Mo_{5.33}[H_{4.5}]_{0.67}O_{18}$, we would predict that the structure of the large-cation analogues (those having no water in the channels) would be $AMo_{5.33}[H_{4.5}]_{0.67}O_{18}$ vs. K & P-B's $AMo[H_5]O_{18}$. This inconsistency was resolved by measuring the amount of water liberated during the thermal decomposition of the hexagonal molybdates. The water loss data (Table III) clearly indicate that there is an average of $^2/_3$ Mo[ ]/unit cell (i.e., 3 H/unit cell). Moreover, the chemical analysis reported by K & P-B for $KMo_5O_{15}OH{\cdot}2H_2O$ (4.52% K; 59.48% Mo) gives an Mo/K ratio of 5.36 in agreement with our result.

Summary

Cation exchange in the hexagonal molybdate system is facile. The structure of the Na molybdate (and presumably the Ag molybdate) differs from that of the isostructural K, Cs, Rb, and NH_4 molybdates in the positioning of the alkali metal within the channel structure. For the larger cation molybdates, the cations (at 0, 0, 0)) occupy an octahedral site with bond distances, in the potassium case, of 2.985 Å. The change in the location of the smaller sodium ion (at (x, y, $^1/_4$)) allows for an octahedral coordination of the sodium ion via the formation of four $Na-O_{framework}$ bonds ($\sim$2.5 Å) and the incorporation of two additional water molecules ($Na-OH_2$ = 2.578 Å) into the channel. These materials are necessarily defect structures, the channel cations partially charge compensating the molybdenum vacancies in the molybdenum oxide framework. Attempts at retaining the hexagonal framework in the absence of channel ions have failed, indicating that the channel ions are necessary for the stability of this structure type.[10]

Acknowledgment. We wish to thank M. W. Sweeten for technical assistance and C. M. Foris for help in obtaining the powder diffraction data. We also wish to recognize many helpful discussions with Dr. A. W. Sleight.

Supplementary Material Available: Tables of anisotropic thermal parameters, intramolecular angles, intramolecular nonbonding distances, symmetry operation codes and powder X-ray diffraction data (2 pages); a table of structure factor amplitudes (2 pages). Ordering information is given on any current masthead page.