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Studies in Heavy-Metal Molybdates. I. Crystal Structure of a Basic Zinc Molybdate, $NaZn_2OH(H_2O)(MoO_4)_2$[1a]

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The reaction between Zn(II) solutions and sodium molybdate yields a basic sodium zinc molybdate. The crystals, grown hydrothermally, are monoclinic with $a = 9.436$ (2) Å, $b = 6.338$ (1) Å, $c = 7.679$ (1) Å, $\beta = 115.8$ (1)°. Based upon an empirical formula $Na_{0.5}H_{0.5}Zn(OH)MoO_4$ and $Z = 4$, the calculated density is 4.089 g cm^{-3}. This compares to an observed value, determined by flotation of a single crystal in a thallous formate–thallous malonate solution, of 3.9 g cm^{-3}. The systematic absences indicated a *C*-centered space group which was confirmed as the centrosymmetric one $C2/m$ by the refinement procedure. Intensity data were collected by counter diffractometer methods (θ–2θ scan) and the structure was solved by Patterson and Fourier methods. Refinement of 789 reflections by block-diagonal methods led to a final $R_F = 0.043$ and $R_{wF} = 0.041$. Zinc atoms lie on inversion centers in the *xy* plane and are linked to each other through double oxygen bridges. The zinc atoms are octahedrally coordinated by oxygens. The octahedra share edges thus forming chains of zinc–oxygen octahedra parallel to the *b* axis. The chains are connected to each other through tetrahedral molybdate groups forming zinc–molybdate layers parallel to the *xy* plane. The layers are linked together by sodium ions lying halfway between them. Only one of the two unique hydrogens could be located with certainty. Placement of the other hydrogen atom was made using Baur's electrostatic bond strength criteria. This placement results in the formula $NaZn_2(OH)(H_2O)(MoO_4)_2$.

Introduction

A large number of zinc molybdates have been reported to form in aqueous solution.[2,3] Little structural information is available for these compounds and, indeed, for many of them their very existence has not been substantiated. In contrast single crystals of α-$ZnMoO_4$ have been prepared at high temperatures from the oxides and the structure of this compound has been determined.[4]

One of the several contradictions in the literature concerns the preparation of $ZnMoO_4 \cdot H_2O$. This compound is reported to form by a metathesis reaction between a soluble zinc salt and sodium molybdate.[3,5] On the other hand, Pezerat and his coworkers[6–8] showed that the reactions are much more complicated. They found instead that three types of compounds, which have the ideal formulas $ZnMoO_4 \cdot H_2O$, $NaHZn_2O(MoO_4)_2 \cdot H_2O$, and $Na_{2-x}(H_3O)_xZn_2O(MoO_4)_2$, can form. These preparations were designated as phases Φ_c, Φ_x, and Φ_y, respectively.[6] Similar compounds of nickel and cobalt and isomorphs with other alkali metals were also prepared. In the main the solids obtained by Pezerat and claimed to be single phases exhibited variable and nonstoichiometric compositions. Subsequently, Pezerat determined the crystal structures of phases Φ_x and Φ_y from very small single crystals of potassium cobalt molybdate (isomorphous with the zinc and nickel compounds) and ammonium zinc molybdate, respectively.[9] Based on these structures, he proposed a theory of nonstoichiometry which involves cationic and anionic vacancies with resultant charge imbalances compensated by the presence of protons.[9,10]

The studies by Pezerat left many questions unanswered. For example, the crystal structures were determined from a limited amount of data (122 and 147 reflections for the Φ_x and Φ_y crystals, respectively). Thus, accurate bond distances and angles were not obtained and therefore the nature of the hydrogen-bonding scheme in these compounds could not be deduced. Furthermore, the effects of nonstoichiometry upon the x-ray intensities could not be ascertained. For these reasons we undertook a fundamental study of the preparation and structure of these compounds. It is further our intent to examine the changes which these phases undergo at elevated temperature so as to ascertain their possible relationship to compounds prepared at elevated temperatures from oxide mixtures. In this paper the crystal structure of phase Φ_x redetermined from a sodium zinc molybdate crystal is described.

Experimental Section

Preparation. One molar solutions of zinc sulfate or zinc chloride and sodium molybdate were prepared from reagent grade solids (Fisher Chemical Co.). The solutions were filtered to remove insoluble material and 100 ml of the sodium molybdate solution placed into a three-neck round-bottom flask. The flask was fitted with a mechanical stirrer, a reflux condensor, and separatory funnel. The sodium molybdate solution was brought to a boil and then the zinc solution (100 ml) was added dropwise with stirring. When the addition was complete, boiling under reflux was continued for 24 h. A white, crystalline solid was obtained. Changing the order of addition of the reagents or the time of reflux (1–48 h) did not alter the end-point product obtained. The white crystals were washed thoroughly with distilled water until free of chloride or sulfate ion and dried to constant weight in a desiccator.

Analytical Work. Roughly 0.25 g of the white solid was dissolved in concentrated sulfuric acid and diluted to 400–500 ml with distilled water. Molybdenum was precipitated with α-benzoin oxime from an aliquot of this solution and the resultant complex calcined at 500–525°. Zinc was determined on a separate aliquot of the solution by precipitation with $K_2Hg(CNS)_4$. The precipitated $ZnHg(CNS)_4$ was washed with a dilute $K_2Hg(CNS)_4$ solution followed by water, then dried at 110°, and weighed. Sodium determinations were carried out using flame photometry (Jarrel-Ash atomic absorption spectrometer, Model No. 82-536, with flame attachment). Anal. Calcd for $NaH_3Zn_2O_2(MoO_4)_2$: Na, 4.52; Zn, 25.71; Mo, 37.73; loss on ignition 5.31%. Found: Na, 3.7; Zn, 25.38; Mo, 37.54; loss on ignition at 670°C 6.4%.

Dehydration Behavior. Weight losses at elevated temperatures were determined by heating samples to constant weight in a Stabil-Therm constant-temperature oven (up to 300°, ±2%) or in a Lindberg furnace (from 300 to 700°, ±3%). The results were as follows: 0.0% at 91°C, 0.4% at 170°C, 1.0% at 200°C, 6.4% at 405°C, and 6.4% at 670°C.

Preparation of Single Crystals. About 1 g of the white sodium zinc molybdate powder was sealed in a thick-walled Pyrex tube together with 10 ml of 1 M sodium molybdate solution. The tube was kept at 160 ± 10° for about 5 weeks during which time very small, clear, colorless crystals formed. Comparison of the powder patterns of the crystals and the starting material showed that they were the same compound.

Crystal Data. A crystal of dimensions approximately 0.07 × 0.04 × 0.04 mm was used for the entire study. Because of its small size no morphological features could be discerned microscopically. Therefore, a random search of reciprocal space was carried out by the precession method. A triclinic cell was found and reduced by the use of Buerger's algorithm.[11] This cell was subjected to a reduced cell calculation which showed that the true unit cell was monoclinic.

Accurate unit cell dimensions were obtained with a CAD-4 four-circle counter diffractometer (Enraf-Nonius) at 24 ± 2°C. Subroutines SEARCH, INDEX, and DETCELL[12] were used to collect 25

Table I. Final Positional and Anisotropic Thermal Parameters[a–c]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	$2\beta_{12}$	$2\beta_{13}$	$2\beta_{23}$
Zn	$^1/_4$	$^1/_4$	0	29 (1)	65 (2)	49 (2)	8 (4)	29 (2)	−7 (3)
Mo	0.0812 (1)	0	0.2879 (1)	198 (7)	53 (1)	33 (1)	0	19 (1)	0
Na	0	$^1/_2$	$^1/_2$	62 (9)	79 (14)	66 (11)	0	62 (15)	0
O(1)	0.2335 (9)	0	0.5198 (11)	85 (11)	241 (26)	118 (16)	0	75 (22)	0
O(2)	0.4647 (6)	0.2744 (9)	0.2602 (6)	88 (6)	157 (14)	78 (8)	54 (17)	81 (12)	57 (19)
O(3)	0.1695 (9)	0	0.1164 (11)	77 (9)	66 (15)	151 (17)	0	114 (21)	0
O(4)	0.6480 (8)	0	0.0820 (9)	72 (9)	148 (19)	78 (13)	0	72 (18)	0

[a] Standard deviations in parentheses are right adjusted to the last digits of the preceding number and are derived from the inverse of the final least-squares matrix. [b] Thermal parameters in units of Å^2 are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)] \times 10^4$. [c] For atoms Mo, Na, O(1), O(3), and O(4) symmetry requires $\beta_{12} = \beta_{23} = 0$.

reflections at high and moderate 2θ angles. The reflections were scanned at both $+2\theta$ and -2θ by the θ–2θ scan technique using a graphite–monochromated beam of Mo Kα radiation (λ 0.7107 Å) at a takeoff angle of 4°. The Bragg angles were accurately determined by the program DETCELL which automatically centers reflections while compensating for wavelength dispersion. Then the cell dimensions were obtained from a least-squares calculation using the θ_1 values and $\lambda_{K\alpha_1}$ 0.70926 Å. The cell dimensions so derived were $a = 9.436$ (2) Å, $b = 6.338$ (1) Å, $c = 7.679$ (1) Å, $\beta = 115.8$ (1)°, $V = 413.4$ Å^3. The density was determined by flotation in a thallous formate–thallous malonate solution and found to be ~3.9 ± 0.1 g cm^{-3}. This compares to a calculated density of 4.089 g cm^{-3} based upon $Z = 4$ for an ideal empirical formula of $Na_{0.5}H_{0.5}Zn(OH)MoO_4$.

Systematic absences found on the reindexed precession photographs and confirmed by data collection on the automated diffractometer were $0k0$ with $k = 2n + 1$, hkl with $h + k = 2n + 1$, $h0l$ with $h = 2n + 1$. Thus, the space group is not uniquely determined since these absences are common to space groups Cm, $C2$, and $C2/m$.

Intensity data were collected under the following conditions. The crystal to counter distance was 208 mm and the crystal to aperture distance 173 mm. The θ–2θ scan method was used at a variable scan rate ranging from about 0.25°/min for the weakest reflections to 10°/min for the strongest ones. The angular scan width was also variable and amounted to $3[(0.7 + 0.2 \tan\theta)°]$. The right and left backgrounds were each scanned for 25% of the total scan time. During data collection two standard reflections were recorded every 24 reflections and these were used to place all the reflections on a common scale. The change in intensities of the standards was small and random, with maximum fluctuation about the mean of ±4%. Several sets of equivalent reflections also agreed in their intensity values to ±5%. A total of 1632 reflections were scanned out to $2\theta = 80°$. Of these, 789 had intensities with $I \geq 3\sigma(I)$, where $\sigma(I) = (\text{TOT CTS} + \text{BKGD CTS})^{1/2}$, and thus were considered to be observed. The total scan count (T_0) and the background counts were combined to yield a set of intensities given by the equation

$$I = T_0 - 2(B_L + B_R)$$

These data were corrected for Lorentz and double-polarization effects[29] but not for absorption or extinction. The absorption error was expected to be small since the size of the crystal was such that μr ranged from 0.18 to 0.32 ($\mu = 89.81$ cm^{-1}).

Solution and Refinement of the Structure

A three-dimensional Patterson map was prepared from which it was deduced that one of the heavy-metal atoms was at $^1/_4$, $^1/_4$, 0 and the other one at approximately 0.1, 0, $^1/_4$. Two ambiguities had now to be resolved: the choice of the space group and which of the heavy atoms was in the special position $^1/_4$, $^1/_4$, 0. E statistics[13] slightly favored a noncentric space group. However, no clear-cut decision could be made so that refinement was carried out in all three space groups. Only the trial structure with zinc at $^1/_4$, $^1/_4$, 0 refined (in all space groups) to give a reasonable final structure. The metal atom parameters were refined by block-diagonal methods using an overall temperature and scale factor determined by Wilson's method.[14] After two cycles the reliability index

$$R_F = \frac{\Sigma \| F_o | - | F_c \|}{\Sigma | F_o |}$$

was ~0.23 (for each of the space groups). The positional parameters of the remaining atoms were determined from successive Fourier and difference maps on the assumption that the correct space group is $C2/m$. Refinement in this space group proceeded smoothly to $R_F = 0.061$. A difference synthesis revealed slight anisotropic thermal motion. Therefore, refinement was continued with assignment of anisotropic thermal parameters which further reduced R_F to 0.045. A second difference map revealed several maxima ranging in value from 0.9 to 1.0 e/Å^3 in the vicinity of possible hydrogen atom positions. The hydrogen atoms were then placed as described later and assigned temperature factors one unit higher than the atoms to which they are bonded. Refinement was then continued until the changes in the positional and thermal parameters for all nonhydrogen atoms were less than one-tenth of their standard deviations. The final value of R_F was 0.0428 and of the weighted residual

$$R_{wF} = \left[\frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma w |F_o|^2}\right]^{1/2}$$

was 0.041.

Refinement was also carried out in the noncentric space groups. Equal values of the residual were attained but some of the temperature factors were non positive definite and some of the Zn–O bonds were inordinately long. Therefore, it was concluded that $C2/m$ is the correct space group.

The function minimized was $\sum w(|F_o| - |F_c|)^2$ with weights assigned according to the expression[15]

$$w = 1/\left\{1 + [(|F_o| - P_2)/P_1]^2\right\}$$

where $P_1 = 30$ and $P_2 = 120$.

Ionic scattering factors were assigned as follows: Na^+, F^-, from the compilation in ref 16; Zn^{2+}, Mo^{6+}, from Cromer and Waber.[17] Neutral atom scattering factors were used for hydrogen as given by Stewart, Davidson, and Simpson.[18] The heavy-metal atom scattering factors were corrected for the real part of the anomalous dispersion effect.[19] The scattering factors as used produced better results during refinement, such as reasonable positive definite temperature factors, than other combinations of scattering factors, particularly neutral atom scattering factors.

The final positional and thermal parameters are given in Table I. A table of observed and calculated structure factors is available.[20] Unobserved reflections were assigned a threshold value which was slightly less than the value of the weakest observed reflection in the same angular range. About 6% of the calculated values for the unobserved reflections were slightly higher than the assigned threshold values. Comparison of the F_c and F_o values for the low-angle reflections indicated no systematic lowering of the intensities due to extinction. A final difference synthesis revealed the following features: a series of ripples around the heavy-metal atoms with the highest electron density being 1.6 e/Å^2 and several other regions of positive electron density ranging from 0.5 to 0.9 e/Å^3 were observed and randomly distributed. Refinement of the occupancy factors for the several atoms did not improve the difference map nor change these factors significantly. It is therefore concluded that the compound is stoichiometric within the accuracy of the x-ray data.

Description of the Structure

Zinc atoms lie on centers of inversion in the *ab* face. The coordination of oxygens about the zinc atoms is octahedral with the bond distances and angles shown in Tables II and III, respectively. The zinc atoms are linked to each other through double oxygen bridges. Thus the octahedra share edges and this creates infinite chains of octahedra running parallel to the

Table II. Interatomic Distances (Å)

A. Zinc-Oxygen (Each Twice)	
Zn-O(2)	2.143 (5)
Zn-O(3)	2.117 (6)
Zn-O(4)	2.088 (5)
B. Molybdenum-Oxygen	
Mo-O(3)	1.839 (8)
Mo-O(2)	1.758 (6) (twice)
Mo-O(1)	1.737 (8)
C. Sodium-Oxygen	
Axial Na-O(1)	2.583 (9) (twice)
Equatorial Na-O(2)	2.448 (5) (four times)
D. Other Distances of Interest	
Zn-Zn	3.169
Zn-Mo	3.606, 3.308
Zn-Na	3.864
Mo-Mo	3.999
Mo-Na	3.791

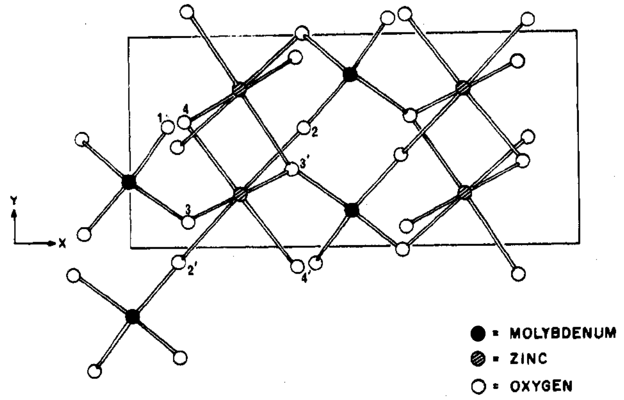

Figure 1. A portion of the zinc molybdate layer in $NaZn_2OH(H_2O)(MoO_4)_2$ centered in the *ab* face.

b axis and centered at $^1/_4a$ and $^3/_4a$. Adjacent chains are connected to each other through tetrahedral molybdate groups. These tetrahedra are centered at $y = 0$ and $^1/_2$ and lie roughly halfway between the Zn–O chains at approximately $-^1/_4z$ and $+^1/_4z$, respectively. The tetrahedra share two of their corners with the zinc–oxygen octahedra at O(2) and O(3). Since there are two O(2) and O(3) atoms in each octahedron, four octahedral corners are shared with four different molybdate tetrahedra. This arrangement produces a layered structure with the zinc–molybdate layers lying parallel to and centered in the *ab* plane as shown in Figure 1.

Sodium ions are located at 0, $^1/_2$, $^1/_2$ and $^1/_2$, 0, $^1/_2$. They serve to connect the array of layers in the [00*l*] direction by sharing oxygen atoms between layers as shown in Figure 2. There are four oxygen atoms of type O(2) and two of type O(1) forming a distorted octahedral arrangement about each sodium. The interatomic distances and angles for the sodium–oxygen octahedron are given in Tables II and III.

Table III. Interatomic Angles[a]

Atoms	Angle, deg	O–O contact, Å
A. Zinc–Oxygen Octahedra (Each Twice)		
O(4)(2)–Zn–O(3)(1)	98.2 (2)	3.179
O(4)(2)–Zn–O(3)(4)	81.8 (2)	2.752
O(4)(2)–Zn–O(2)(1)	92.2 (2)	3.049
O(4)(2)–Zn–O(2)(4)	87.8 (2)	2.934
O(3)(1)–Zn–O(2)(1)	91.6 (2)	3.054
O(3)(1)–Zn–O(2)(4)	88.4 (2)	2.970
B. Molybdenum–Oxygen Tetrahedra		
O(2)(2)–Mo–O(2)(8)	108.8 (2)	2.861
O(2)(2)–Mo–O(3)(1)	111.6 (3)	2.975
O(2)(8)–Mo–O(3)(1)	111.6 (3)	2.975
O(2)(2)–Mo–O(1)(1)	108.6 (3)	2.839
O(2)(8)–Mo–O(1)(1)	108.6 (3)	2.839
O(3)(1)–Mo–O(1)(1)	107.7 (3)	2.887
C. Sodium–Oxygen Octahedra		
O(2)(2)–Na–O(2)(6)	89.5 (2)	3.446
O(2)(2)–Na–O(2)(8)	90.5 (2)	3.477
O(2)(2)–Na–O(1)(2)	103.0 (2)	3.938
O(2)(8)–Na–O(1)(2)	103.0 (2)	3.938
O(2)(2)–Na–O(1)(4)	76.8 (2)	3.128
O(2)(8)–Na–O(1)(4)	76.8 (2)	3.128
O(2)(2)–Na–O(2)(4)	180.0	
D. Other Bond Angles of Interest		
Zn–O(3)–Zn′	97.0 (3)	
Zn–O(4)–Zn′	98.7 (2)	
Zn–O(3)–Mo	131.3 (3)	
Zn–O(2)–Na	114.2 (3)	
Mo–O(2)–Na	127.9 (3)	
Mo–O(1)–Na	109.4 (3)	
Mo–O(2)–Zn	117.3 (3)	

[a] Atoms are identified by two parenthesized numbers next to the atomic symbol. The first refers to the positional coordinates given in Table I. The second refers to the symmetry operation number (8j for space group *C*2/*m*).

Assignment of Hydrogen Atoms. There are six hydrogens to be placed in the unit cell. The difference Fourier map contained more than a sufficient number of regions of positive electron density. Therefore, placement of the hydrogen atoms was made from indirect considerations.

Each O(2) atom is three-coordinate having as near neighbors molybdenum, zinc, and sodium. The O(3) atoms are also three-coordinate since they form oxo bridges between zinc atoms and are also bonded to molybdenum. The other two oxygen atoms have only two metal atom near neighbors. O(4) bridges two zinc atoms while O(1) is bonded to a molybdenum atom and is in the coordination sphere of the sodium ion. These two oxygen atoms approach each other closely. In particular the O(1)–O(4) distance is 2.762 Å and the O(4)–O(4) distance, where the oxygen atoms are related

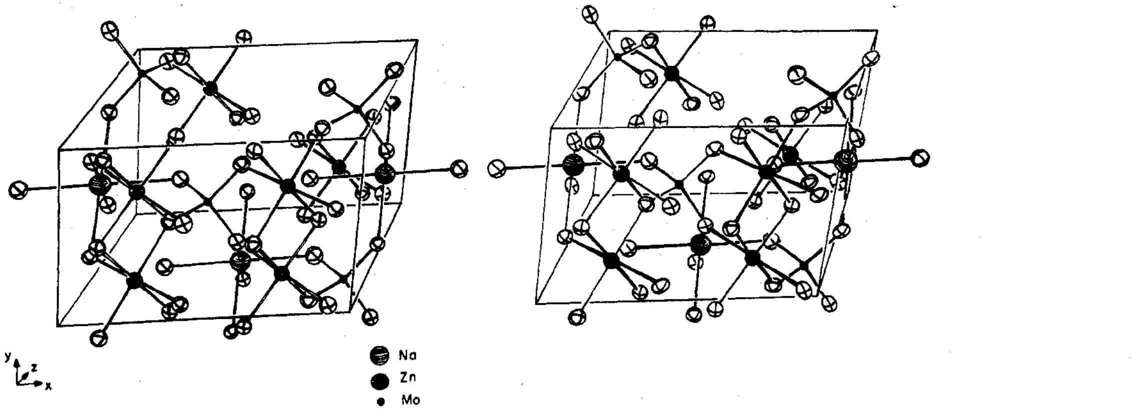

Figure 2. A portion of the unit cell of $NaZn_2OH(H_2O)(MoO_4)_2$.

through the centers of symmetry at $^1/_2$, 0, 0 and 0, $^1/_2$, 0, is 2.510 Å. A search of the regions around these oxygen atoms in the final difference map showed a split peak about the inversion centers. When a hydrogen atom was placed on the center of symmetry and refined without restraints, the electron density divided equally and moved toward the O(4) atoms. This behavior indicates a disordered hydrogen statistically divided between the two oxygens.

The space between O(1) and O(4) did indeed contain a broad region of positive electron density on the difference map. However, it was not possible to make a choice as to which atom was the donor and which the acceptor. If O(1) is considered to be the donor, then the structural formula becomes $NaZn_2OHO(MoO_3OH)_2$. However, if the hydrogen atom is closer to O(4), the structural formula is $NaZn_2OH(H_2O)(MoO_4)_2$.

Baur has shown that for a variety of compounds the lengths of hydrogen bonds formed between pairs of anions vary inversely as the difference in the electrostatic bond strengths of the donor and acceptor.[21] Pauling[22] defined the electrostatic bond strength received by an anion from a cation as Z/CN, where Z is the formal charge of the cation and CN is its coordination number. If the anion is bonded to more than one cation, the bond strengths are additive. The strengths of the bonds from metal to oxygen are $^3/_2$ for Mo(VI), $^1/_3$ for Zn(II), and $^1/_6$ for Na^+. In addition Baur has shown that for each hydrogen bond $^5/_6$ of the bond strength should go to the donor and $^1/_6$ to the acceptor.[23] On this basis the electrostatic bond strength difference considering O(1) as donor is $+^5/_3$ which would require an extremely short O(1)–O(4) distance. Considering the reverse case where O(4) is the donor, the difference is $^1/_6$. The predicted O–O distance for this difference is 2.8 Å which is very close to the observed value. Thus, the formula $NaZn_2OH(H_2O)(MoO_4)_2$ is chosen as the correct one.

Discussion

The zinc–oxygen bond lengths observed in the present study are in excellent agreement with expectations. The sum of the radii for Zn^{2+} and O^{2-} with coordination numbers 6 and 3, respectively, according to Prewitt and Shannon,[24] is 2.105 Å. This value compares to our average value of 2.116 (28) Å.[25] Abrahams found Zn–O distances ranging from 1.977 (11) to 2.243 (10) Å (2.078 Å average) in the zinc–oxygen octahedra of α-$ZnMoO_4$ and slightly shorter bond distances in the five-coordinate polyhedron.[4] Values very close to those reported in this study were also found for the zinc–oxygen octahedra in the compound $Zn_2Mo_3O_8$.[26]

In all metal molybdates for which reliable data are available, the molybdenum–oxygen bonds are found to be very short when the molybdenum coordination is tetrahedral.[4,27,28] Abrahams et al.[27] have reported an average Mo–O distance of 1.765 Å for six such structures. The individual values range from 1.70 to 1.86 Å with, in general, one bond significantly longer than the other three. In the present structure the average Mo–O bond distance is 1.773 (45) Å so that the range and average are in good agreement with previous results. The tetrahedra are fairly regular since the bond angles are close to the ideal tetrahedral value and the oxygen–oxygen contacts all fall within a very narrow range.

The sharing of coordination polyhedra are in agreement with expectations from the electrostatic valence rule. Molybdate tetrahedra share corners and deviate from the expected bond angles only slightly. No distortion is necessary since the metal–metal distances are large enough without it to make the repulsion effect small. On the other hand, the zinc–oxygen octahedra share edges. Zinc–zinc repulsions are reduced by distorting the octahedron such that the shared edge is the shortest in the octahedron and the O(4)(2)–Zn–O(3)(4) bond angles show the largest negative deviation from 90°.

The structure described in this study is essentially the same as that given earlier by Pezerat.[9] However, no evidence for nonstoichiometry of the crystal was forthcoming from the present x-ray results whereas Pezerat's analytical data showed large deviations from rationality. In this connection it should be remembered that our crystals were grown hydrothermally (160°C) in excess sodium molybdate while the solid analyzed was prepared at reflux temperature from a 1:1 ratio of reactants. Our analysis showed low sodium and high water values. Such would be the case if hydronium ion replaced sodium ion in the crystal lattice. Since the proposed formula contains water coordinated to the zinc atom, the OH stretching and bending modes should be observed in the infrared spectrum. This has been observed by us and Pezerat.[7] However, both spectra were taken on solids having a deficiency of sodium ion. Thus, in any case hydronium ion would be present. In order to eliminate conclusively the alternative formulation $NaZnOHO(MoO_3OH)_2$, spectra should be taken on the stoichiometric solid. These points are under investigation.

Registry No. $NaZn_2(OH)(H_2O)(MoO_4)_2$, 57606-42-5.

Supplementary Material Available: Listing of structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Portions of this paper were taken from the Ph.D. thesis of M.J.S., submitted to the Department of Chemistry, Sept 1971. (b) NDEA Title IV Fellow, 1967–1970.
(2) "Gmelin's Handbuch der anorganischen Chemie", Vol. XVII, System No. 53, Verlag Chemie, Berlin, 1935.
(3) H. O. Schoen and B. G. Brand, "Molybdate Pigments: New Corrosion Inhibitors", Battelle Memorial Institute Official Digest, 1960.
(4) S. C. Abrahams, *J. Chem. Phys.*, **46**, 2052 (1967).
(5) A. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. XI, Longmans, Green and Co., New York, N.Y., 1931, p 596.
(6) H. Pezerat, *C. R. Hebd. Seances Acad. Sci.*, **261**, 5490 (1965).
(7) H. Pezerat, I. Mantin, and S. Kovacevic, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **262**, 95 (1966).
(8) H. Pezerat, I. Mantin, and S. Kovacevic, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **263**, 60 (1966).
(9) H. Pezerat, *Bull. Soc. Fr. Mineral. Cristallogr.*, **90**, 549 (1967).
(10) H. Pezerat, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **265**, 368 (1967).
(11) R. J. Davis, *Mineral. Mag.*, **32**, 817 (1961).
(12) Enraf-Nonius, "Instruction Manual for CAD-4 System", Delft, Holland, 1972.
(13) I. L. Karle, K. S. Dragonette, and S. A. Brenner, *Acta Crystallogr.*, **19**, 713 (1965).
(14) A. J. C. Wilson, *Nature (London)*, **150**, 151 (1942).
(15) The programs used in this work were those of F. R. Ahmed, S. R. Hall, M. E. Pippy, and C. P. Huber, "NRC Crystallographic Programs for the IBM/360", National Research Council, Ottawa, Canada, 1968.
(16) "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1962.
(17) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).
(18) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **53**, 1891 (1970).
(19) D. T. Cromer and B. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
(20) Supplementary material.
(21) W. H. Baur, *Trans. Am. Crystallogr. Assoc.*, **6**, 129 (1970).
(22) L. Pauling, "The Nature of the Chemical Bond", 3rd ed, Cornell University Press, Ithaca, N.Y., 1960, p 547.
(23) W. H. Baur, *Acta Crystallogr.*, **15**, 815 (1962).
(24) C. T. Prewitt and R. D. Shannon, *Trans. Am. Crystallogr. Assoc.*, **5**, 51 (1969).
(25) The standard deviation of the mean was determined as $\sigma = [\sum(X_i - \bar{X})/(n-1)]^{1/2}$ where $\bar{X}$ is the mean of n values.
(26) G. B. Ansell and L. Katz, *Acta Crystallogr.*, **21**, 482 (1966).
(27) S. C. Abrahams, J. L. Bernstein, and P. B. Jamieson, *J. Chem. Phys.*, **48**, 2619 (1968).
(28) L. Kihlborg, R. Norrestam, and B. Olivecrona, *Acta Crystallogr., Sect. B*, **27**, 2066 (1971).
(29) U. W. Arndt and B. T. Willis, "Single Crystal Diffractometry", Cambridge University Press, London, 1966, pp 284–291.