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The Crystal Structure of Sodium Molybdate Dihydrate, $Na_2MoO_4 \cdot 2H_2O$

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$Na_2MoO_4 \cdot 2H_2O$ is orthorhombic, with the space group of Pbca and with cell constants of $a=8.463(3)$, $b=10.552(3)$, and $c=13.827(6)$ Å; $U=1234.8$ Å^3; $Z=8$. The crystals are composed of alternate layers of MoO_4^{2-} tetrahedra and water molecules. The layers are connected by interlinking sodium cations and hydrogen bonds. The MoO_4^{2-} tetrahedron is slightly elongated in the direction of the hydrogen bonds.

Recent structure determinations of $Na_6Mo_5P_2O_{23} \cdot 13H_2O$,[1] $Na_4H_2Mo_5P_2O_{23} \cdot 10H_2O$,[2] and $Na_6Mo_7O_{24} \cdot 14H_2O$[3] have revealed the remarkable basic character of the oxygen atoms, which are octahedrally attached to the molybdenum atoms to form not only hydrogen bonds with water, but also coordination bonds with sodium ions.

Our main interest in the present structural study of $Na_2MoO_4 \cdot 2H_2O$ lies in the coordination of the oxygen atoms in the tetrahedral MoO_4^{2-} anion to Na^+ cations in comparison with those in octahedral MoO_6 groups in the heteropoly- and isopoly-anions.

About $Na_2MoO_4 \cdot 2H_2O$, the unit-cell dimensions and the space group,[4] the Raman spectra, and the infrared spectra data[5] have already been reported.

Experimental

Suitable crystals of $Na_2MoO_4 \cdot 2H_2O$ were selected from the reagent-grade chemicals commercially available from the KOSO Wako Company. Preliminary oscillation and Weissenberg photographs showed that the crystals were orthorhombic, with the space group Pbca; this confirmed the results of the preliminary measurements made by Poljak and Becka.[4]

The intensities of the reflections were measured on a Rigaku automated four-circle diffractometer. Graphite monochromatized Mo*Kα* radiation was used. The ω-2θ scan technique was employed. The scan range was calculated from this formula: $1.2+0.5 \tan\theta$; the scan speed was 0.5° per min in ω, and background counts of 10 s were taken at both limits of the scan. Three reference reflections, 220, 020, and 002, were measured for every 50 reflections. The net counts of these reflections altered only within 1% over the period of data collection. A total of 2104 independent intensities were measured up to $2\theta=60°$ ($0 \leq h \leq 11$, $0 \leq k \leq 14$, $0 \leq l \leq 19$); those reflections of which the $|F_o|$ value was less than 7.9 (absolutely scaled value) were regarded as unobserved in view of the accuracy of the measurement. The remaining 1497 reflections were adopted for the structure determination. The unit-cell dimensions and their standard deviations, as measured on the Rigaku diffractometer (Mo*Kα*, $\lambda=0.71069$ Å), were $a=8.463$ (3), $b=10.552$ (3), $c=13.827$ (6) Å; $U=1234.8$ Å^3 at 23 °C; $D_m=2.51$ and $D_x=2.60$ g cm^{-3} for $Z=8$; M.W.$=241.9$ and μ for Mo*Kα*$=23.2$ cm^{-1}. As the dimensions of the specimen used were approximately $0.15 \times 0.1 \times 0.2$ mm, the absorption correction was not made.

Structure Determination

The structure was solved by the heavy-atom technique and was refined by the least-squares method, the function minimized being $\sum\omega(|F_o|-k|F_o|)^2$. A weighting scheme, $w=0.2$ for $|F_o|<11.9$ and otherwise $w=1$, was employed. The refinements of the parameters of all the non-hydrogen atoms were carried out by the block-diagonal least-squares method. In the last cycle

TABLE 1. FINAL FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

	x	y	z
Mo	5149(1)	1982(1)	5233(0)
Na(1)	6565(4)	4952(3)	4145(2)
Na(2)	7424(4)	4492(3)	6482(2)
O(1)	5573(6)	3602(5)	5431(4)
O(2)	4505(7)	1759(5)	4013(4)
O(3)	6877(7)	1090(6)	5393(4)
O(4)	3716(6)	1486(5)	6097(4)
$H_2O(1)$	2288(7)	1416(6)	2011(4)
$H_2O(2)$	4617(8)	4077(6)	2996(4)

TABLE 2. FINAL TEMPERATURE FACTORS ($\times 10^4$) WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES
(The temperature factor is of the form:
$\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	31(1)	16(0)	13(0)	0(1)	1(1)	0(1)
Na(1)	40(4)	24(3)	18(2)	8(5)	−3(4)	−3(3)
Na(2)	43(4)	29(2)	16(1)	−9(5)	−5(5)	4(3)
O(1)	34(6)	12(4)	20(3)	−3(8)	−3(7)	−4(5)
O(2)	42(7)	26(4)	23(3)	26(10)	−3(7)	8(6)
O(3)	44(7)	25(4)	17(3)	−24(9)	11(7)	−2(6)
O(4)	40(7)	28(4)	14(3)	−4(9)	−7(7)	−7(5)
$H_2O(1)$	55(8)	33(5)	16(3)	0(10)	−10(8)	8(6)
$H_2O(2)$	71(8)	29(5)	21(3)	7(11)	−9(8)	−5(6)

of least-squares refinement with anisotropic temperature factors, the R index ($R=\Sigma||F_o|-|F_o||/\Sigma|F_o|$) converged to 0.037. A difference Fourier synthesis was calculated at this stage; some faint electron density peaks were detected, but their positions were inadequate for hydrogen atoms. The atomic scattering factors used were taken from the International Tables for X-ray Crystallography Vol. III.[19] Corrections for the anomalous dispersion were not made. The atomic coordinates and temperature factors are listed in Tables 1 and 2. The F_o-F_o table is kept at the office of this Bulletin as Document No. 7507.

Results and Discussion

Description of the Structure. The crystal structure

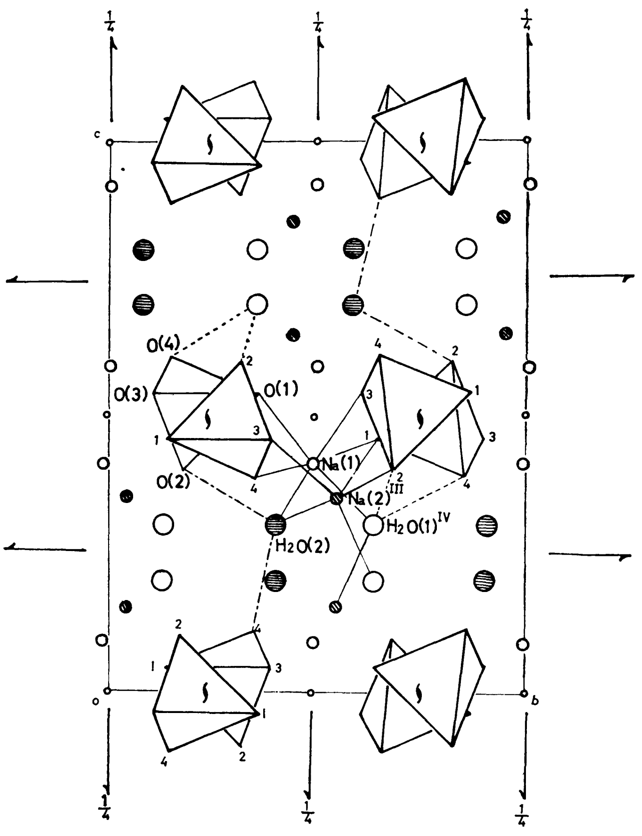

Fig. 1. The structure viewed along the a axis. Water layers and molybdate anion layers are seen alternately. Tetrahedra represent MoO_4^{2-} anions. The coordination bonds around Na^+ cations are shown with full lines. Dotted lines are $O(2)\cdots H_2O(1)\cdots O(4)$ hydrogen bonds between two MoO_4^{2-} anions in the same layer. Dot-dash lines are $O(2)$—·—$H_2O(2)$—·—$O(4)$ type hydrogen bonds bridging adjacent layers. The small letters 1, 2, 3, and 4 represent oxygen atoms equivalent to O(1), O(2), O(3), and O(4). The Na(2) atoms are shaded only in Fig. 1. Parameter transformations are as follows.

I	$1/2+x$	$1/2-y$	$-z$
II	$1/2-x$	$1/2+y$	z
III	$-x$	$-y$	$-z$
IV	$-x$	$1/2+y$	$1/2-z$
V	x	$1/2-y$	$1/2+z$
VI	$1/2+x$	y	$1/2-z$
VII	$1/2-x$	$-y$	$1/2+z$

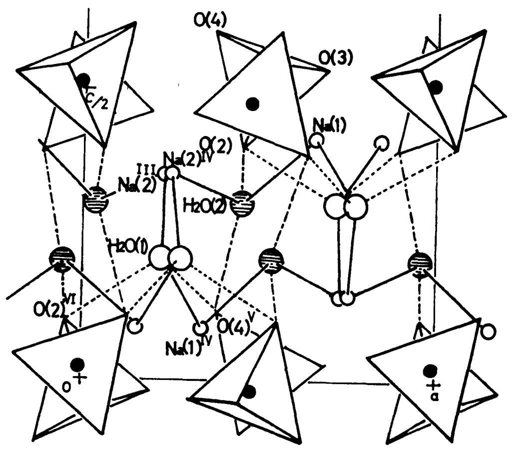

Fig. 2. The structure viewed along the b axis. Full lines represent Na–O(H_2O) bonds, Na–O(MoO_4) bondings are omitted. See the caption of Fig. 1.

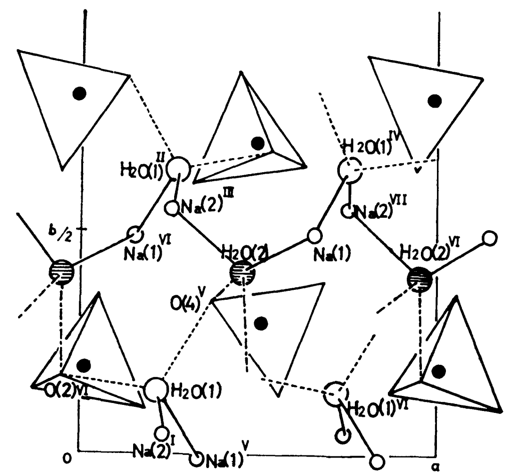

Fig. 3. The structure viewed along the c axis. Only the structure in the range of $0\leq z\leq 0.5$ is depicted. Bonds between Na^+ and MoO_4^{2-} are omitted. See the caption of Fig. 1.

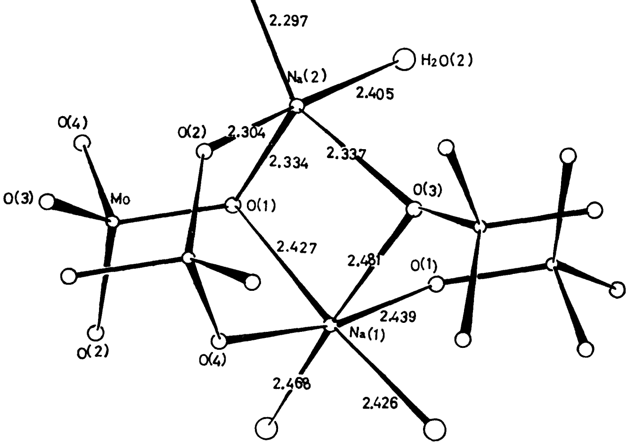

Fig. 4. Oxygen coordinations around the two sodium cations. Na(1) is hexacoordinated and Na(2) is pentacoordinated.

TABLE 3.

	The number of water oxygens coordinated to Na atom, with the range of Na–O distances in parentheses (Å)	The number of non-water oxygens coordinated to Na atom, with the range of Na–O distances in parentheses (Å)	Reference
$Na_2SO_4 \cdot 10H_2O$	6(2.39—2.47)	0	6)
$Na_2H_2P_2O_6 \cdot 6H_2O_6$	4(2.329—2.485)	2(2.325—2.459)	7)
$Na_2H_2P_2O_7 \cdot 6H_2O$	4(2.350—2.507)	2(2.332—2.434)	7)
$Na_2Zn(SO_4)_2 \cdot 4H_2O$	2(2.43—2.75)	4(2.32—2.38)	8)
$NaHC_2O_4 \cdot H_2O$	2(2.311—2.403)	4(2.328—2.475)	9)
$Na_2HAsO_4 \cdot 7H_2O$	6(2.365—2.509)	0	10)
$Na_2HPO_4 \cdot 7H_2O$	6(2.341—2.486)	0	10)
Na_2SiO_3	0	5(2.282—2.549)	11)
$Na_2H_2SiO_4 \cdot 4H_2O$	1(2.38)	4(2.31—2.40)	12)
$NaOH \cdot 4H_2O$	5(2.36—2.37)		13)

is considered to consist of alternate layers of MoO_4^{2-} tetrahedra parallel to (001) and of water molecules; it is shown in three projections in Figs. 1, 2, and 3. The MoO_4^{2-} tetrahedra within a layer are connected by interlinking Na(1) and Na(2), as well as by the hydrogen bonding, $O(2)\cdots H_2O(1)\cdots O(4)$. The adjacent layers are bridged by interlinking cations and hydrogen-bonding $O(2)$—·—$H_2O(2)$—·—$O(4)$ linkages, as is shown in Figs. 1 and 2.

Coordination around Sodium Ions. The oxygen coordinations around the two crystallographically-independent sodium atoms are remarkably different, as is shown in Fig. 4. The Na(1) ion is surrounded by two water oxygen atoms and four MoO_4^{2-} oxygen atoms, each of which belongs to a different MoO_4^{2-} group, thus form a distorted octahedron. The Na(2) ion is surrounded by two water oxygen atoms and three MoO_4^{2-} oxygen atoms in the form of a distorted trigonal bipyramid. The mean distance of Na(1)–O is 2.439 Å, while that of Na(2)–O is 2.335 Å; the difference is presumably attributable to the different coordination numbers, 6 and 5.

Table 3 gives the coordination numbers of the sodium atoms and the Na–O distances in some hydrated sodium salts of oxyacids. It shows that the most common coordination number of sodium atoms is six and that the pentacoordinated sodium ion as in $Na_2MoO_4 \cdot 2H_2O$ is rare.[12,13] Another example is found in Na_2SiO_3,[11] where the sodium ion is coordinated to form a distorted trigonal bipyramid and where the Na–O distances are 2.370, 2.303, 2.282, 2.549, and 2.404 Å. The Na(2)–$H_2O(1)$ distance, 2.297 Å, in $Na_2MoO_4 \cdot 2H_2O$ is, along with the Na–O distance in the above-mentioned Na_2SiO_3 and along with that of the hexacoordinated sodium ion in $Na_2OGeO_2 \cdot 6H_2O$, 2.28 Å,[14] one of the shortest Na–O distances reported thus far. Some of the compounds listed in Table 3 have sodium ions coordinated entirely by water oxygens. In hydrated sodium salts of oxyacids which contain elements of Group 4, 5, or 6 in the periodic table and which have sodium ions coordinated both by water and anion oxygens, the Na–O(H_2O) distance is generally a little longer than that of the Na–O(anion). However, in $Na_2MoO_4 \cdot 2H_2O$ there is no appreciable difference between the Na–O(H_2O) and Na–O(anion) distances.

TABLE 4. INTERATOMIC DISTANCES AND ANGLES IN HYDROGEN BONDING AND IN COORDINATION BONDING

$H_2O(1)\cdots\cdots O(2)^{VI}$	2.772(8) Å
$H_2O(1)\cdots\cdots O(4)^{V}$	2.821(8)
$H_2O(1)$——$Na(2)^{I}$	2.297(7)
$H_2O(1)$——$Na(1)^{V}$	2.426(7)
$O(2)^{VI}\cdots\cdots H_2O(1)\cdots\cdots O(4)^{V}$	91.9(2)°
$Na(1)^{V}$——$H_2O(1)$——$Na(2)^{I}$	108.2(3)
$H_2O(2)$—·—$O(2)$	2.824(8) Å
$H_2O(2)$—·—$O(4)^{V}$	2.798(8)
$H_2O(2)$——$Na(1)$	2.468(7)
$H_2O(2)$——$Na(2)^{III}$	2.405(7)
$O(2)$—·—$H_2O(2)$—·—$O(4)^{V}$	105.9(3)°
$Na(1)$——$H_2O(2)$——$Na(2)^{III}$	93.0(2)

TABLE 5. INTERATOMIC DISTANCES IN MoO_4^{2-} AND SODIUM-OXYGEN POLYHEDRA, WITH THEIR ESTIMATED STANDARD DEVIATIONS

Mo—O(1)	1.768(5) Å	$Na(2)^{III}$—$O(1)^{III}$	2.334(6) Å
Mo—O(2)	1.788(6)	$Na(2)^{III}$—$O(2)^{II}$	2.304(6)
Mo—O(3)	1.752(6)	$Na(2)^{III}$—$O(3)^{I}$	2.337(7)
Mo—O(4)	1.781(6)	$Na(2)^{III}$—$H_2O(1)^{II}$	2.297(7)
O(1)—O(2)	2.906(8)	$Na(2)^{III}$—$H_2O(2)$	2.405(7)
O(1)—O(3)	2.872(8)	Na(1)—O(1)	2.427(6)
O(1)—O(4)	2.882(8)	$Na(1)$—$O(4)^{I}$	2.393(7)
O(2)—O(3)	2.858(8)	$Na(1)$—$O(3)^{II}$	2.481(7)
O(2)—O(4)	2.972(8)	$Na(1)$—$O(1)^{III}$	2.439(6)
O(3)—O(4)	2.877(8)	$Na(1)$—$H_2O(1)^{IV}$	2.426(7)
		$Na(1)$—$H_2O(2)$	2.468(7)

TABLE 6. ANGLES IN MoO_4^{2-} AND SODIUM-OXYGEN POLYHEDRA, WITH THEIR ESTIMATED STANDARD DEVIATIONS

O(1)—Mo—O(2)	109.6(3)°	O(4)$^{\mathrm{I}}$—Na(1)—H_2O(2)	100.4(2)°
O(1)—Mo—O(3)	109.3(3)	O(3)$^{\mathrm{II}}$—Na(1)—O(1)$^{\mathrm{III}}$	85.7(2)
O(1)—Mo—O(4)	108.6(3)	O(3)$^{\mathrm{II}}$—Na(1)—H_2O(1)$^{\mathrm{IV}}$	86.4(2)
O(2)—Mo—O(3)	107.6(3)	O(1)$^{\mathrm{III}}$—Na(1)—H_2O(1)$^{\mathrm{IV}}$	93.2(2)
O(2)—Mo—O(4)	112.7(3)	O(1)$^{\mathrm{III}}$—Na(1)—H_2O(2)	83.9(2)
O(3)—Mo—O(4)	109.0(3)	H_2O(1)$^{\mathrm{IV}}$—Na(1)—H_2O(2)	94.7(2)
		O(4)$^{\mathrm{I}}$—Na(1)—O(1)$^{\mathrm{III}}$	174.2(2)
O(1)—Na(2)—O(2)$^{\mathrm{I}}$	95.6(2)	O(1)—Na(1)—H_2O(1)$^{\mathrm{IV}}$	174.0(2)
O(1)—Na(2)—O(3)$^{\mathrm{II}}$	93.4(2)	H_2O(2)—Na(1)—O(3)$^{\mathrm{II}}$	169.5(3)
O(1)—Na(2)—H_2O(1)$^{\mathrm{I}}$	111.3(2)	O(1)—Na(1)—O(4)$^{\mathrm{I}}$	89.6(2)
O(1)—Na(2)—H_2O(2)$^{\mathrm{III}}$	87.6(2)	O(1)—Na(1)—O(3)$^{\mathrm{II}}$	87.6(2)
O(2)$^{\mathrm{I}}$—Na(2)—O(3)$^{\mathrm{II}}$	91.6(2)	O(1)—Na(1)—H_2O(2)	91.2(2)
O(2)$^{\mathrm{I}}$—Na(2)—H_2O(1)$^{\mathrm{I}}$	94.0(2)	O(1)—Na(1)—O(1)$^{\mathrm{III}}$	86.3(2)
O(3)$^{\mathrm{I}}$—Na(2)—H_2O(2)$^{\mathrm{III}}$	175.9(3)	O(4)$^{\mathrm{I}}$—Na(1)—O(3)$^{\mathrm{II}}$	90.0(2)
O(3)$^{\mathrm{II}}$—Na(2)—H_2O(1)$^{\mathrm{I}}$	153.9(3)	O(4)$^{\mathrm{I}}$—Na(1)—H_2O(1)$^{\mathrm{IV}}$	90.4(2)
O(3)$^{\mathrm{II}}$—Na(2)—H_2O(2)$^{\mathrm{III}}$	85.5(2)		
H_2O(1)$^{\mathrm{I}}$—Na(2)—H_2O(2)$^{\mathrm{III}}$	87.3(2)		

Water of Crystallization. The hydrogen bondings and H_2O–Na coordinations are depicted in Figs. 2 and 3. Table 4 shows their distances and angles. Around H_2O(1) and H_2O(2), oxygen atoms from two MoO_4^{2-} anions and two sodium cations construct a distorted tetrahedron; this suggests that two lone pairs of a water oxygen atom point to the two sodium ions. The O(2)$^{\mathrm{vi}}$···H_2O(1)···O(4)$^{\mathrm{v}}$ angle differs noticeably from the water H-O-H angle in gas phase, 104.5°; this implies that the O-H···O hydrogen bonding is not linear. The O(2)-H_2O(2)-O(4)$^{\mathrm{v}}$ angle is near to 104.5°, and O-H···O in this case can be considered to be almost linear. Judging from the infrared spectra data, it would seem that the O-H···O distances of 2.78 and 2.87 Å can be predicted from the O-H stretching frequencies, 3250 and 3450 cm^{-1},[5] by the aid of the empirical relationships proposed by Nakamoto.[15] Actually, these values agree fairly well with the present structural data.

The Structure of the MoO_4^{2-} Anion. The Mo-O distances and O-Mo-O angles are listed in Tables 5 and 6. The shape of the anion is a slightly deformed tetrahedron, and the Mo-O distances in the MoO_4^{2-} anion are almost equal to those found in the anhydrous K_2MoO_4 crystals (1.74(1) and 1.78(1) Å).[16] The four oxygen atoms in MoO_4^{2-} are crystallographically unique. The O(2) atom which is coordinated to the Na(2) cation forms two hydrogen bonds with two water molecules, and O(4) also accepts two hydrogen bonds and is attached to Na(1); on the other hand, O(1) and O(3) form no hydrogen bonding, each oxygen atom being coordinated to Na(1) and to Na(2). The bond lengths, Mo-O(2) (1.788(6) Å) and Mo-O(4) (1.781(6) Å), appear to be significantly longer than Mo-O(1) (1.768(5) Å) and Mo-O(3) (1.752(6) Å). The O(2)-Mo-O(4) angle (112.74(26)°) is larger than any other O-Mo-O angle by 3.23—5.12(26)°. The MoO_4^{2-} tetrahedra appear to be elongated, as if pulled by the hydrogen bonds, on pushed by sodium cations. However, an example of the deformation of SO_4^{2-} anions in the opposite direction was found in the $CaSO_4 \cdot 2H_2O$ crystal,[17] containing two kinds of crystallographically independent sulfate oxygens, O_{I} and O_{II}, the former one with two hydrogen bonds to water molecules, and the later one with a close Ca^{2+} neighbor. Here elongation is observed in the direction of the Ca^{2+} cations, and the hydrogen bonds to the water molecules do not seem stretch the SO_{I} bond. Therefore, we need still more examples before we can undertake a general discussion of the effect of hydrogen-bond or coordination-bond formation on the shape of tetrahedral oxyanions.

Comparison with Octahedral MoO_6 Unit in Polymolybdates. In the present study, the Na-O (belonging to tetrahedral MoO_4^{2-}) bond lengths were found to lie between 2.29 and 2.48 Å, and in the literature those of the Na–O (belonging to MoO_6 unit) in the polymolybdates, $Na_6Mo_5P_2O_{23} \cdot 12H_2O$,[1] $Na_4H_2Mo_5P_2O_{23} \cdot 12H_2O$,[2] and $Na_6Mo_7O_{14} \cdot 14H_2O$,[3] range from 2.27 to 2.55 Å. These ranges agree with that of the Na–O(H_2O) bond lengths found in the above-mentioned four compounds. It seems that there is no distinct difference between the oxygen atoms in the MoO_4^{2-} anion and those of the MoO_6 unit in polymolybdate anions and water molecules in the coordination-bond distance to the Na^+ cation.

Crystal Structure of $Na_2WO_4 \cdot 2H_2O$. The structure determination of $Na_2WO_4 \cdot 2H_2O$ was also started at the same time in this laboratory; it was found that the crystals were exactly isostructural, with slightly larger unit-cell dimensions. However, it was impossible to find well-formed crystals for accurate experiments, and so further detailed computation was abandoned. Later the structure was reported by Okada, Morikawa, Iwai, and Marumo[18] independently.

The calculations were performed on a HITAC 8700/8800 computer at the Computer Centre of the University of Tokyo, using a local version of UNICS.[20]

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References

1) R. Strandberg, *Acta Chem. Scand.*, **27**, 1004 (1973).
2) B. Hedman, *ibid.*, **27**, 3335 (1973).
3) K. Sjoblom and B. Hedman, *ibid.*, **27**, 3673 (1973).
4) R. J. Poljak and L. N. Becka, *Ann. Asoc. Quim. Argent.*, **46**, 199 (1958).
5) R. H. Busey and O. L. Keller, *J. Chem. Phys.*, **41**, 215 (1964).
6) H. W. Ruben, D. H. Templeton, R. D. Rosenstein, and I. Olovsson, *J. Amer. Chem. Soc.*, **83**, 820 (1961).
7) L. Collin, M. Willis, *Acta Crystallogr.*, **B27**, 291 (1971).
8) M. Giglis, *ibid.*, **11**, 789 (1958).
9) R. Tellgren and I. Olovsson, *J. Chem. Phys.*, **54**, 127 (1971).
10) W. H. Baur and A. A. Khan, *Acta Crystallogr.*, **B26**, 1584 (1970).
11) W. S. McDonald and D. W. J. Cruickshank, *ibid.*, **22**, 37 (1967).
12) K. H. Jost and W. Hilmer, *ibid.*, **21**, 583 (1966).
13) G. Beurskens and G. A. Jeffrey, *J. Chem. Phys.*, **41**, 924 (1964).
14) P. B. Jamieson and L. S. D. Glasser, *Acta Crystallogr.*, **22**, 507 (1967).
15) K. Nakamoto, M. Margoshes, and R. E. Rundle, *J. Amer. Chem. Soc.*, **77**, 6480 (1955).
16) B. M. Getehouse and P. Leverett, *J. Chem. Soc., A*, **1969**, 849.
17) W. F. Cole and C. J. Laucucki, *Acta Crystallogr.*, **B30**, 921 (1974).
18) K. Okada, J. Morikawa, S. Iwai, and F. Marumo, *Bull. Tokyo Institute of Technology*, **7**, (1974).
19) "International Tables for X-ray Crystallography" Kynoch Press, Birmingham (1962), Vol. III.
20) "The Universal Crystallographic Computation Program System," Crystallographic Society of Japan (1967).