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# The Crystal Structure of Potassium Dimolybdate Hydrate

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$K_2Mo_2O_7 \cdot H_2O$ crystallizes in the triclinic system with unit-cell dimensions $a = 7.640(1)$, $b = 8.909(1)$, $c = 7.654(1)$ Å, $\alpha = 109.42(1)$, $\beta = 95.75(1)$, $\gamma = 119.19(2)°$, and space group $P\bar{1}$ with $Z = 2$. The structure was solved by Patterson and Fourier methods. Of the 2361 unique reflections measured by counter techniques, 2229 with $I \geq 3\sigma(I)$ were used in the least-squares refinement of the model to a conventional $R$ of 0.032 ($R_w = 0.036$). The structure of $K_2Mo_2O_7 \cdot H_2O$ consists of infinite chains of edge-shared $MoO_6$ octahedra and $MoO_5$ trigonal bipyramids parallel to the crystallographic $a$ axis. The chains are separated by potassium ions and water molecules. This compound appears to be the third example of an isopolymolybdate that crystallizes from aqueous solution with an infinite chain structure; the previous two are $(NH_4)_2Mo_2O_7$ and $(NH_4)_6Mo_8O_{27} \cdot 4H_2O$. © 1987 Academic Press, Inc.

## Introduction

In the general area of alkali metal or silver molybdates and tungstates, the dimolybdates and ditungstates have been widely studied. The structural types involved can be divided into two groups: (a) structures with $MO_6$ octahedra and $MO_4$ tetrahedra—among these are $K_2Mo_2O_7$ (*1*), $Na_2Mo_2O_7$ (*2, 3*), and $Na_2W_2O_7$ (*4, 5*)—and (b) structures with $MO_6$ octahedra only—these are $Li_2W_2O_7$ (*6, 7*) and $Ag_2Mo_2O_7$ and $Ag_2W_2O_7$ (*8*). All of the above compounds were prepared by crystallization from melts and are, therefore, anhydrous materials. $(NH_4)_2Mo_2O_7$, prepared from aqueous solution, was shown (*9*) to have an anion isomorphous with that of $K_2Mo_2O_7$ (above).

The crystals used in the current study were prepared during an attempt to crystallize potassium heptamolybdate $K_6Mo_7O_{24} \cdot 4H_2O$, the detailed structure of which was reported together with that of the ammonium salt (*10*), and were thought at the time to be those of a hydrated potassium tetramolybdate, perhaps containing the unknown $[Mo_4O_{13}]^{2-}$ anion. All such isopolyanions crystallized from aqueous solution up to the time of the preparation contained discrete rather than infinite chain anions. Two infinite-chain isopolymolybdates crystallized from aqueous solution are now known—they are $(NH_4)_6Mo_8O_{27} \cdot 4H_2O$ (*11*) and $(NH_4)_2Mo_2O_7$ (*9*) above.

We report here the structure determination of $K_2Mo_2O_7 \cdot H_2O$. A preliminary report was published elsewhere (*12*).

## Experimental

A clear tabular crystal (0.28 × 0.27 × 0.08 mm) was selected from a batch of

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material prepared during attempts to grow crystals of potassium heptamolybdate hydrate (*10*). Thermogravimetric analysis of the bulk material showed it to lose 4.3% of its mass at 160°C. The theoretical mass loss corresponding to one water molecule as in $K_2Mo_2O_7 \cdot H_2O$ would be 4.5%. The crystal was mounted on a silica capillary using clear epoxy resin ("TYTON 5 MINIT" adhesive) and the crystal data were obtained using a Philips PW1100 computer-controlled diffractometer in a manner described earlier (*13*).

*Crystal data.* $K_2Mo_2O_7 \cdot H_2O$, $M$ = 400.09, $a$ = 7.640(1), $b$ = 8.909(1), $c$ = 7.654(1) Å, $\alpha$ = 109.42(1), $\beta$ = 95.75(1), $\gamma$ = 119.19(2)°, $U$ = 406.58(13) Å$^3$, $D_c$ = 3.27 g cm$^{-3}$ for $Z$ = 2, $D_m$ (flotation in diiodomethane/dichloromethane) = 3.24(3) g cm$^{-3}$. $F(000)$ = 376. $\mu(\mathrm{Mo}K_\alpha$ radiation ($\lambda$ = 0.7107 Å)) = 39.7 cm$^{-1}$. Space group $P1$ or $P\bar{1}$; $P\bar{1}$ confirmed by successful refinement.

## Intensity Measurements

Intensity measurements were made with the crystal described above using the diffractometer and $\mathrm{Mo}K_\alpha$ radiation monochromated with a flat graphite monochromator crystal. A unique data set was collected out to $2\theta(\mathrm{Mo}K_\alpha) = 60°$ using the $w - 2\theta$ scan technique with a symmetric scan range of $\pm(1.5 + 0.30 \tan \theta)°$ in $2\theta$ from the calculated Bragg angle, at a scan rate of 0.05° sec$^{-1}$. Twenty reflections were sufficiently intense to require the insertion of the attenuation filter. Of the 2524 reflections measured, 2361 were unique, and of these 2229 were considered to be significantly above the background ($I \geq 3\sigma(I)$) and only these were used during the refinement. Ten reflections considered to be extinction affected were omitted in the final cycles of refinement. Three standard reflections, measured at 3-hr intervals, showed no significant variation in intensity.

The data were processed in a manner described previously (*13*). An absorption correction was applied to the data based on the indexed crystal faces 100, $\bar{1}00$, 010, $0\bar{1}0$, 001, and $00\bar{1}$. The atomic scattering factors used were for neutral atoms and were corrected for anomalous dispersion (*14*). All calculations were carried out on the Monash University VAX 11/780 computer system; the major program used was SHELX76 (*15*).

## Structure Solution and Refinement

The structure was solved by conventional Patterson methods for the two molybdenum atoms ($R$ = 0.34) and the remaining nonhydrogen atoms located in subsequent difference Fourier syntheses. Using anisotropic thermal parameters for molybdenum and potassium and isotropic

TABLE I

FINAL ATOMIC PARAMETERS (Å) WITH THEIR ESTIMATED STANDARD DEVIATIONS (Mo × $10^5$, OTHERS × $10^4$)

| Atom type[a] | $x$ | $y$ | $z$ | $U$ |
|---|---|---|---|---|
| Mo(1) | 18,814(4) | 70,615(4) | 50,318(4) | 98(2)[b] |
| Mo(2) | 28,745(4) | 38,022(4) | 31,675(4) | 107(2)[b] |
| K(1) | 2,367(1) | 8,928(1) | 840(1) | 254(2)[b] |
| K(2) | 7,409(1) | 8,276(1) | 2,955(1) | 201(2)[b] |
| O(1) C | 581(4) | 4,171(4) | 3,993(3) | 153(5) |
| O(2) B | 5,659(4) | 4,718(4) | 3,552(3) | 152(5) |
| O(3) B | 3,729(4) | 6,775(4) | 3,914(4) | 166(5) |
| O(4) A | 1,709(4) | 1,602(4) | 3,228(4) | 201(5) |
| O(5) A | 6,555(4) | 1,044(4) | 2,656(4) | 215(5) |
| O(6) A | 1,967(4) | 3,171(4) | 695(4) | 208(5) |
| O(7) A | 888(4) | 7,880(4) | 3,733(4) | 215(5) |
| *AQ* (water molecule) | 6,506(5) | 3,565(5) | 152(5) | 300(7) |

| | $U_{11}$[c] | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| Mo(1) | 91(2) | 88(2) | 120(2) | 51(1) | 35(1) | 49(1) |
| Mo(2) | 113(2) | 106(2) | 102(2) | 33(1) | 42(1) | 68(1) |
| K(1) | 190(4) | 284(4) | 252(4) | 75(3) | 84(3) | 113(4) |
| K(2) | 212(4) | 215(4) | 212(4) | 103(3) | 93(3) | 132(3) |

[a] See text.

[b] $U_{eq}$, Å$^2$ × $10^4$.

[c] The anisotropic thermal parameters are of the form

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)].$$

thermal parameters for oxygen resulted in a conventional $R = \Sigma| |F_o| - |F_c| |/\Sigma|F_o| = 0.032$ and $R_w = \Sigma(w^{1/2}| |F_o| - |F_c| |)/\Sigma w^{1/2}|F_o| = 0.036$, where $w = \sigma^2(F_o)^{-1}$, the weight of each reflection. There was no evidence for anisotropy of the oxygen atoms.

The final cycles of refinement involved 2219 reflections and 69 parameters were varied; the function minimized in the full-matrix least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$; the maximum shift to e.s.d. ratio in the final cycle was 0.002. The final difference synthesis had its maximum density in the vicinity of atom *AQ* (water molecule oxygen atom) and was $\sim$1 *e* Å$^3$.

Final parameters and their estimated standard deviations are presented in Table I[1] and selected interatomic distances and angles in Table II.

TABLE II

SELECTED BOND LENGTHS (Å) WITH THEIR ESTIMATED STANDARD DEVIATIONS IN $K_2Mo_2O_7 \cdot H_2O$

| Trigonal-bipyramid | | | Octahedron | |
|---|---|---|---|---|
| Mo(1)–O(7) | 1.723(4) | | Mo(2)–O(4) | 1.733(3) |
| O(5$^{1}$) | 1.741(2) | | O(6) | 1.740(3) |
| O(3) | 1.800(3) | | O(2) | 1.817(3) |
| O(1$^{1}$)$^{b}$ | 2.028(3) | | O(1) | 2.055(3) |
| O(1) | 2.058(3) | | O(3) | 2.236(3) |
| | | | O(2$^{1}$) | 2.257(2) |
| K(1)–(*AQ*$^{1*}$)$^{c}$ | 2.670(5) | | K(2)–O(3) | 2.763(3) |
| O(5)$^{d}$ | 2.684(3) | | O(6$^{1}$)$^{c}$ | 2.857(3) |
| O(6$^{1}$)$^{d}$ | 2.750(3) | | O(7)$^{a}$ | 2.877(4) |
| O(4)$^{d}$ | 2.779(4) | | O(4$^{1}$) | 2.885(3) |
| O(7) | 2.811(4) | | O(5)$^{d}$ | 2.911(4) |
| O(5$^{1}$)$^{c}$ | 2.882(3) | | (*AQ*$^{1}$)$^{c}$ | 2.913(3) |
| O(1$^{1}$)$^{d}$ | 3.443(2) | | O(2) | 2.999(3) |
| | | | O(7$^{1}$)$^{d}$ | 3.011(3) |
| | | | O(4)$^{e}$ | 3.094(3) |
| | | | *AQ* | 3.685(4) |
| Mo(1)–Mo(2) | 3.264(1) | edge-shared | *AQ*–K(1$^{1}$)$^{e}$ | 2.670(5) |
| Mo(1)–Mo(1$^{1}$)$^{b}$ | 3.363(1) | edge-shared | O(2) | 2.730(5) |
| Mo(1)–Mo(2$^{1}$)$^{b}$ | 3.831(1) | corner-shared | O(6$^{1}$)$^{e}$ | 2.886(6) |
| Mo(2)–Mo(2$^{1}$) | 3.226(1) | edge-shared | K(2$^{1}$)$^{e}$ | 2.913(3) |
| Mo(1)–K(2$^{1}$)$^{d}$ | 3.648(1) | | O(3$^{1}$)$^{e}$ | 3.002(5) |
| Mo(2)–K(1$^{1}$)$^{f}$ | 3.800(1) | | O(5$^{1}$)$^{e}$ | 3.272(4) |
| | | | O(6) | 3.394(6) |
| | | | O(5) | 3.414(6) |
| | | | O(7)$^{a}$ | 3.479(3) |
| | | | K(2) | 3.685(4) |
| | | | O(1) | 3.755(5) |

TABLE II—*Continued*

| Angles (°) in the $Mo_2O_7^{2-}$ chain | | |
|---|---|---|
| O(1)–Mo(1)–O(1$^{1}$)$^{b}$ | 69.2(2) | CC |
| O(1)–Mo(1)–O(3) | 77.4(1) | BC |
| O(1)–Mo(1)–O(5$^{1}$) | 131.8(2) | AC |
| O(1)–Mo(1)–O(7) | 119.6(1) | AC |
| O(3)–Mo(1)–O(5$^{1}$) | 104.6(1) | AB |
| O(3)–Mo(1)–O(7) | 105.1(2) | AB |
| O(5$^{1}$)–Mo(1)–O(7) | 106.5(2) | AA |
| O(5$^{1}$)–Mo(1)–O(1$^{1}$)$^{b}$ | 92.0(1) | AC |
| O(7)–Mo(1)–O(1$^{1}$)$^{b}$ | 98.7(2) | AC |
| O(3)–Mo(1)–O(1$^{1}$)$^{b}$ | 145.5(1) | BC pole–pole |
| O(1)–Mo(2)–O(2$^{1}$) | 79.8(1) | BC |
| O(1)–Mo(2)–O(3) | 68.5(1) | BC |
| O(1)–Mo(2)–O(6) | 98.0(1) | AC |
| O(1)–Mo(2)–O(4) | 91.9(1) | AC |
| O(2)–Mo(2)–O(2′) | 75.8(1) | BB |
| O(2)–Mo(2)–O(3) | 87.8(1) | BB |
| O(2)–Mo(2)–O(4) | 106.5(2) | AB |
| O(2)–Mo(2)–O(6) | 101.7(1) | AB |
| O(4)–Mo(2)–O(2$^{1}$) | 89.8(1) | AB |
| O(4)–Mo(2)–O(6) | 102.8(1) | AA |
| O(3)–Mo(2)–O(6) | 90.1(1) | AB |
| O(3)–Mo(2)–O(2$^{1}$) | 77.4(1) | BB |
| O(1)–Mo(2)–O(2) | 149.1(1) | BC pole–pole |
| O(2$^{1}$)–Mo(2)–O(6) | 167.3(1) | AB pole–pole |
| O(3)–Mo(2)–O(4) | 158.0(1) | AB pole–pole |
| O(2)–*AQ*–O(6) | 102.9(2) | |
| O(2)–*AQ*–O(5) | 114.2(1) | |

*Note.* Superscript 1 indicates atom in $1 - x$, $1 - y$, $1 - z$ position.
* *AQ* = Water molecule oxygen atom.
[a] (+, 0, 0).
[b] (−, 0, 0).
[c] (0, 0, −).
[d] (0, +, 0).
[e] (+, +, 0).
[f] (−, 0, −).

## Description and Discussion of the Structure

The potassium dimolybdate hydrate structure consists of chains of edge-shared

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[1] For a table of observed and calculated structure factors see NAPS document No. 04486 for 13 pages of supplementary material. Order from ASIS/NAPS. Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance $4.00 for microfiche copy or for photocopy, $7.75 up to 20 pages plus $.30 for each additional page. All orders must be prepaid. Institutions and Organizations may order by purchase order. However, there is a billing and handling charge for this service of $15. Foreign orders add $4.50 for postage and handling, for the first 20 pages, and $1.00 for additional 10 pages of material, $1.50 for postage of any microfiche orders.

pairs of $MoO_6$ octahedra sharing edges with edge-shared pairs of $MoO_5$ trigonal bipyramids parallel to the crystallographic *a* axis. The edge-shared Mo–Mo distances (Table II) have a mean value of 3.284 Å and lie within the range normal for edge-shared octahedra; the edge-shared trigonal bipyramids have a Mo–Mo distance of 3.363 Å. The corner-shared distance of Mo(1)–Mo(2′)$^b$ (3.831 Å) is typical of corner-shared octahedra. Adjacent chains have no oxygen atoms in common, the chains being separated by potassium ions and water molecules. The anion chains are illustrated in Fig. 1a together with the polyhedra detail and numbering in Fig. 1b. Five-coordinate molybdenum(VI) is not widely known; previous reports include the chain structures of mixed octahedra and square pyramids (or trigonal bipyramids) in the trimolybdate series, $M_2Mo_3O_{10}$ ($M$ = K, Rb, Cs) (*16, 17*), and the chains of octahedra and square pyramids in $Na_6Mo_{10}O_{33}$ (*18*). The edge-shared pairs of square pyramids (trigonal bipyramids) in the trimolybdates have only a single $MoO_6$ octahedron separating them. In the decamolybdate there are two different chains, one consisting of octahedra only and the other of pairs of edge-shared square pyramids separated by corner-shared pairs of octahedra.

The molybdenum to oxygen distances give an indication of the distortions present in the two molybdenum–oxygen polyhedra. These distances can be correlated with the type of oxygen atom involved, where the oxygen atoms are classified as type A, those with one bond to a molybdenum atom, type B, those with two bonds to molybdenum, and type C, those with three bonds to molybdenum atoms. The oxygen atoms are classified as A, B, or C in Table I. A summary of Mo–O distances and oxygen type and O–Mo–O angles and oxygen type is given in Table III. Clearly the bond distance increases with increasing sharing of the oxygen atom between molybdenum atoms.

The average Mo–O distances for the $Mo–O_5$ and $Mo–O_6$ polyhedra are 1.870(3) and 1.973(3) Å, respectively, and compare favorably with the analogous distances of 1.86(4) and 1.95(4) Å in $K_2Mo_3O_{10}$ (*16*). The O–Mo–O angles also reflect, in general, the high distortions of the polyhedra from the ideal. These angles deviate further from the

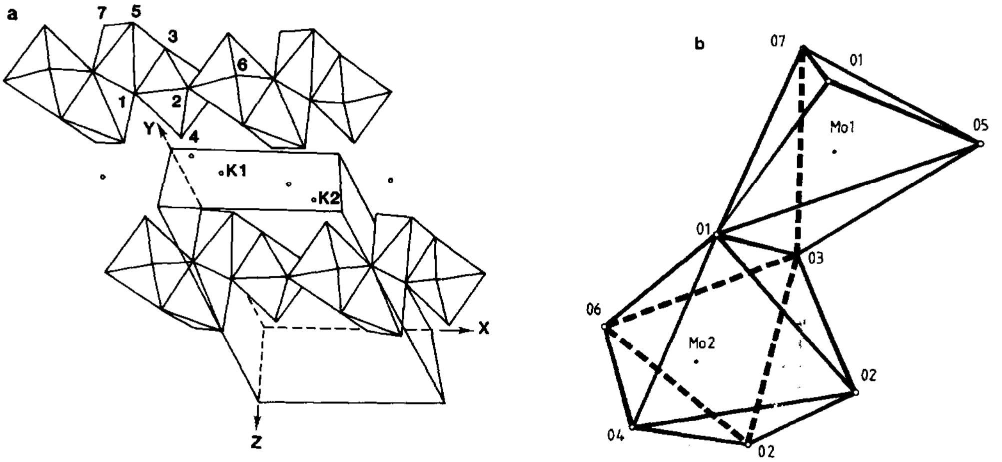

FIG. 1. (a) The infinite anion chains $[Mo_2O_7]^{2-}$ are shown together with the unit-cell outline for $K_2Mo_2O_7 \cdot H_2O$. (b) The Mo(1) (trigonal bipyramidal) and Mo(2) (octahedral) edge-shared polyhedra are shown together with the numbering scheme used for $K_2Mo_2O_7 \cdot H_2O$.

TABLE III

SUMMARY OF (a) Mo–O DISTANCE VERSUS OXYGEN TYPE AND (b) O–Mo–O ANGLE VERSUS OXYGEN TYPE IN $K_2Mo_2O_7 \cdot H_2O$

| | Type of oxygen | No. per asymmetric unit | Range | Average |
|---|---|---|---|---|
| (a) | A | 4 | 1.723–1.741 Å | 1.734 Å |
| | B | 4 | 1.800–2.257 | 2.028 |
| | C | 3 | 2.028–2.058 | 2.047 |
| (b) | AC | 6 | 91.9–131.8° | 105.3° |
| | AA | 2 | 102.8–106.5 | 104.7 |
| | AB | 6 | 89.8–106.5 | 99.6 |
| | BB | 3 | 75.8– 87.8 | 80.3 |
| | BC | 3 | 68.5– 79.8 | 75.2 |
| | CC | 1 | — | 69.2 |
| | Pole–pole | 4 | 145.5–167.3 | 155.0 |

TABLE IV

EQUATIONS OF LEAST-SQUARES PLANES AND DISTANCES (Å) OF ATOMS FROM THE PLANES[a]

(a) Plane through O(7′), O(1′), and O(5)—central plane of the trigonal bipyramid

Plane equation: $0.8555X + 0.3689Y - 0.3635Z - 3.0329 = 0$

| | | | |
|---|---|---|---|
| Mo(1′) | −0.1504(3) | O(1) | 1.781(3) |
| O(3′) | −1.872(3) | | |

(b) Plane through O(7′), O(1′), O(3′), and O(1)—base plane of the square pyramid

Plane equation: $-0.3055X - 0.2602Y - 0.9159Z + 5.2168 = 0$

| | | | | | |
|---|---|---|---|---|---|
| O(7′) | −0.293(3) | O(3′) | 0.386(6) | O(1′) | −0.489(3) |
| O(1) | 0.395(3) | O(5) | 2.243(3) | Mo(1′) | 0.5524(3) |

[a] *X*, *Y*, *Z* are the orthogonal coordinates related to the fractional coordinates *x*, *y*, *z* in the crystal systems by the matrix equations.

ideal as the number of bonds to molybdenum per oxygen atom increases, with the largest deviation being 20.8(1)° for the oxygens defining the edge shared between the two five-coordinate molybdenum atoms.

A mean planes analysis of the $MoO_5$ polyhedron (Table IV) shows it to be closer to a trigonal bipyramid than to a square pyramid. The molybdenum atom is only 0.150(1) Å out of the central plane of the trigonal pyramid, and the two apical oxygen atoms, 0(1′) and 0(3), are both ca. 1.8 Å from the plane. The three oxygen atoms forming this plane show considerable deviation from an equilateral triangle as one oxygen, 0(1), is shared by two other molybdenum atoms, Mo(1′) and Mo(2), and hence is pulled away from Mo(1).

Potassium to oxygen distances <3.8 Å are given in Table II. Since there is an ~0.6-Å gap after 2.882 Å for K(1) and a similar gap following 3.094 Å for K(2), these gaps were chosen as cut-off points to establish the potassium–oxygen coordination polyhedra in this compound. K(1) is six-coordinate and approximately octahedral, and K(2) has an irregular nine-coordination. The polyhedra are shown in Fig. 2, from which it can be seen that they are edge-shared to one another. A calculation of bond valences for K(1) and K(2), using the method of Brown and Wu (*19*), resulted in values of 1.06 and 0.97, respectively, supporting the suggested coordination numbers.

Nearest-neighbor distances <3.8 Å are given for the oxygen of the water molecule (Table II) and confirm its assignment. A careful examination of the final difference Fourier synthesis failed to show any reasonable hydrogen atom positions. Consideration of angles to other oxygen atoms about *AQ* produced two (Table II) that suggested the possibility of hydrogen bonding—again no reasonable peaks were present in the difference Fourier along these directions.

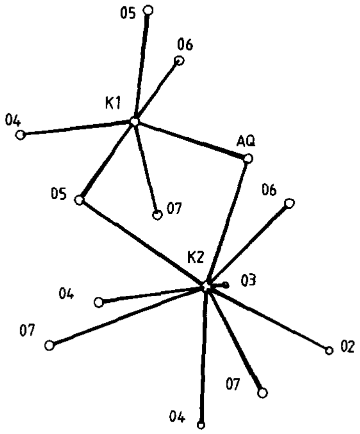

FIG. 2. The edge-shared potassium–oxygen polyhedra in $K_2Mo_2O_7 \cdot H_2O$.

$K_2Mo_2O_7 \cdot H_2O$, described here, is the first hydrated dimolybdate reported and is of a new structural type for the infinite-chain $[Mo_2O_7]^{2-}$ anion. The infinite chain dimolybdate anion can thus adopt a number of structures—exclusively $MoO_6$ octahedra ($Ag_2Mo_2O_7$), $MoO_6$ octahedra, and $MoO_4$ tetrahedra ($Na^+$, $K^+$, and $NH_4^+$ salts of $Mo_2O_7^{2-}$) and now $MoO_6$ octahedra and $MoO_5$ trigonal bipyramids ($K_2Mo_2O_7 \cdot H_2O$). Further variations are observed within the second of these groups in that in $Na_2Mo_2O_7$ the polyhedra linkages are corner-sharing whereas in $K_2Mo_2O_7$ edge-shared octahedra and corner-shared tetrahedra occur.

Finally, it is noted that the discrete $[Mo_2O_7]^{2-}$ ion, analogous to the $[Cr_2O_7]^{2-}$ ion that consists of a pair of corner-shared tetrahedra, was reported in a solution-prepared species $[(\eta\text{-}C_4H_9)_4N]_2Mo_2O_7$ (*20*). Several dimolybdates prepared from melts contain discrete $[Mo_2O_7]^{2-}$ units, for example, $MgMo_2O_7$ (*21*) and $Ce_6(MoO_4)_8(Mo_2O_7)$ (*22*). The latter consists of eight isolated $MoO_4$ tetrahedra and an isolated (two tetrahedra sharing a corner) $[Mo_2O_7]^{2-}$ unit.

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