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# Two Molybdenum Diphosphates with a Tunnel Structure Involving Mo(III): $KMoP_2O_7$ and $K_{0.17}MoP_2O_7$

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The structure of two novel molybdenum diphosphates $KMoP_2O_7$ and $K_{0.17}MoP_2O_7$ has been determined. The trivalent molybdenum diphosphate $KMoP_2O_7$ is monoclinic with $a = 7.375(1)$ Å, $b = 10.348(1)$ Å, $c = 8.351(2)$ Å, $\beta = 106.88(1)°$, space group $P2_1/c$, whereas the mixed valence Mo(III)–Mo(IV) diphosphate $K_{0.17}MoP_2O_7$ crystallizes in the tetragonal system with $a = b = 21.278(2)$ Å, $c = 4.921(6)$ Å, space group $I4_1/a$. Both oxides have their mixed framework built up from $[MoP_2O_{11}]$ units in which a $P_2O_7$ group shares two of its corners with the same octahedron. $KMoP_2O_7$ is isostructural with $KFeP_2O_7$ and $CsMoP_2O_7$ whereas $K_{0.17}MoP_2O_7$ exhibits an original structure. Both oxides have a tunnel structure: heptagonal tunnels and smaller hexagonal running along [001] and [110], respectively, are observed in $KMoP_2O_7$, whereas very large tunnels formed of rings of eight polyhedra and running along [001] are present in $K_{0.17}MoP_2O_7$.

## Introduction

Phosphates and silicophosphates of molybdenum form a large family of structures characterized by mixed frameworks of $MoO_6$ octahedra and $PO_4$ tetrahedra and by various oxidation states of molybdenum. Among these oxides, the Mo(III) phosphates have only been recently synthesized. Trivalent molybdenum indeed appears as a rare species especially in oxides. The presence of trivalent molybdenum was observed in the oxide $KMo_3P_6Si_2O_{25}$ (*3*) in the form of a mixed-valence Mo(III)–Mo(IV) and in the phase $MoP_3SiO_{11}$ (*4*). This stabilization of Mo(III), and the existence of the trivalent iron diphosphate $KFeP_2O_7$ (*1*), has encouraged the investigation of diphosphates of general formulation $A_xMoP_2O_7$ where $A$ is a univalent cation. Two sodium diphosphates $NaMoP_2O_7$ (*5*) and $Na_{0.3}MoP_2O_7$ (*6*) were recently isolated and characterized by original structures different from that of $KFeP_2O_7$ (*1*), whereas $RbMoP_2O_7$ (*7*) and $CsMoP_2O_7$ (*2*) were found to be isostructural to $KFeP_2O_7$. The present work deals with the structural study of two novel potassium diphosphates $KMoP_2O_7$ and $K_{0.17}MoP_2O_7$, in which molybdenum presents the valence III and the mixed-valence III–IV, respectively.

## Experimental

### Synthesis

The synthesis of $KMoP_2O_7$ was performed in two steps. First $(NH_4)_2HPO_4$, $MoO_3$, and $K_2CO_3$ were mixed in an agate mortar in the molecular ratio 4 : 1 : 1 and heated

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at 600 K in a platinum crucible to decompose the potassium carbonate and the ammonium phosphate. The resulting mixture was then added to the required amount of metallic molybdenum and heated in an evacuated silica ampoule for several days at 1373 K. Thus green-yellow crystals were obtained.

Some $K_{0.17}MoP_2O_7$ black needles were obtained in one of the preparations but we never obtained those crystals later, even with an adequate mixture of oxides when the crystal structure was known and the composition was confirmed by microprobe analysis.

### *Structure Determinations*

A green-yellow crystal of $KMoP_2O_7$ with dimension 0.120 × 0.096 × 0.096 mm was selected for the structure determination. The Laue patterns showed monoclinic symmetry ($2/m$). The cell parameters, initially measured on precession films and later refined by diffractometric techniques at 294 K, with a least-squares refinement based on 25 reflections are: $a = 7.3758(7)$, $b = 10.348(1)$, $c = 8.351(2)$ Å, $\beta = 106.88(1)$, with $Z = 4$ formula units of $KMoP_2O_7$. The systematic absences led to the $P2_1/c$ space group. The data were collected on a CAD-4 Enraf–Nonius diffractometer with Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å). The intensities were measured out to $\theta = 45°$ with a $\omega - 2/3\theta$ scan of $(1.50 + 0.35 \tan \theta)°$ and a counterslit aperture of $(1.40 + \tan \theta)$ mm, all determined after a study of some reflections in the $\omega \cdot \theta$ plane. The background intensities were measured on both sides of each reflection. A periodic measurement of three reflections verified the stability of the sample. The 2803 reflections with $I \geq 3\sigma(I)$ were corrected for Lorentz and polarization effect; no absorption corrections were performed.

Atomic coordinates of the molybdenum atom and of the oxygen atoms bounded to it were deduced from the Patterson function and the other atoms were located by subsequent Fourier series. Refinement of the atomic coordinates and their anisotropic thermal parameters led to $R = 0.039$, $R_w = 0.047$ and to the atomic parameters of Table I.[1]

TABLE I

ATOMIC PARAMETERS OF $KMoP_2O_7$

| Atom | $x$ | $y$ | $z$ | $B$ (Å$^2$) |
|---|---|---|---|---|
| Mo | 0.23374(4) | 0.60021(2) | 0.76012(3) | 0.692(4) |
| K | 0.1774(1) | 0.3234(1) | 0.0570(1) | 1.91(2) |
| P(1) | 0.4447(1) | 0.63969(8) | 0.1942(1) | 0.81(1) |
| P(2) | 0.1329(1) | 0.90101(8) | 0.8261(1) | 0.80(1) |
| O(1) | 0.3442(3) | 0.5701(3) | 0.3192(3) | 1.12(4) |
| O(2) | 0.0758(3) | 0.7314(2) | 0.2471(3) | 1.15(4) |
| O(3) | 0.6420(4) | 0.5838(2) | 0.2362(4) | 1.24(5) |
| O(4) | 0.1345(4) | 0.5946(3) | 0.5046(3) | 1.54(5) |
| O(5) | 0.3214(4) | 0.6076(3) | 0.0217(3) | 1.60(5) |
| O(6) | 0.0087(4) | 0.4967(3) | 0.2177(3) | 1.09(4) |
| O(7) | 0.4594(3) | 0.7824(2) | 0.2386(3) | 1.13(4) |

For the study of $K_{0.17}MoP_2O_7$ a dark needle with dimensions 0.144 × 0.022 × 0.024 mm was used. The Laue patterns showed tetragonal symmetry ($4/m$). The cell parameters are $a = b = 21.278(2)$ Å, $c = 4.9209(6)$ Å, with $Z = 16$ formula units.

The systematic absences led to the $I4_1/a$ space group. The data collection conditions were similar to those of $KMoP_2O_7$ but with a $\omega - \theta$ scan of $(0.90 + 0.35 \tan \theta)°$ and a counterslit aperture of $(1. + \tan \theta)$ mm. The 772 reflections with $I > 3\sigma(I)$ were corrected for Lorentz and polarization effect; no absorption corrections were performed.

The coordinates of the atoms which form the $MoP_2O_7$ frameworks were deduced from the Patterson function and subsequent Fourier series. The refinement of these coordinates led to $R = 0.081$ and $R_w = 0.095$. Then a difference synthesis showed a peak at 0. 0.25 − 0.30 and its equivalent at 0. 0.25 −0.45. The short distance between these

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[1] Lists of structure factors and of anisotropic thermal motion parameters are available on request from the authors.

TABLE II

ATOMIC PARAMETERS OF $K_{0.17}MoP_2O_7$

| Atom | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| Mo | 0.14319(6) | 0.13582(6) | 0.44610(29) | 0.51(2) |
| K | 0.00000(0) | 0.25000(0) | −0.29271(677) | 3.75(120) |
| P(1) | 0.24790(17) | 0.14298(17) | −0.06027(100) | 0.65(7) |
| P(2) | 0.14599(17) | 0.29314(17) | 0.32871(88) | 0.61(7) |
| O(1) | 0.07789(51) | 0.10227(53) | 0.18103(274) | 1.08(23) |
| O(2) | 0.20690(51) | 0.16774(53) | 0.71963(264) | 1.16(24) |
| O(3) | 0.15571(49) | 0.04520(49) | 0.59595(270) | 1.13(25) |
| O(4) | 0.13098(58) | 0.22445(53) | 0.29148(302) | 1.56(27) |
| O(5) | 0.21145(55) | 0.11480(54) | 0.17383(290) | 1.39(25) |
| O(6) | 0.28481(45) | 0.20258(54) | 0.04863(282) | 1.02(22) |
| O(7) | 0.07359(61) | 0.14914(53) | 0.71896(272) | 1.41(26) |

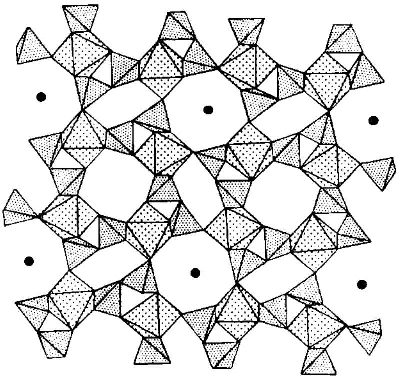

FIG. 2. Projection of the structure of $K_{0.17}MoP_2O_7$ along $c$ on the $ab$ plane.

two peaks involves a half occupancy of this position giving the upper limit formula $K_{0.25}MoP_2O_7$ and, on the other hand, the microprobe analysis showed an amount of potassium of about 0.18. The refinement of the coordinates and anisotropic thermal factors of all the atoms and of the occupancy factor of the potassium atom led to $R = 0.063$, $R_w = 0.063$, to the atomic parameters of Table II and to the formula $K_{0.17}MoP_2O_7$.

### *Description of the Structures and Discussion*

Both structures are built up from corner-sharing $MoO_6$ octahedra and diphosphate groups $P_2O_7$ (Figs. 1 and 2). $KMoP_2O_7$ is isostructural with $KFeP_2O_7$ (*1*), i.e., with $RbMoP_2O_7$ (*7*) and $CsMoP_2O_7$ (*2*), whereas $K_{0.17}MoP_2O_7$ exhibits an original structure.

In both diphosphates, the $PO_4$ tetrahedra present the features usually observed in the other diphosphates: one long P–O distance corresponding to the bridging oxygen of the $P_2O_7$ group and three shorter P–O bonds corresponding to the oxygen atoms which are shared with the $MoO_6$ octahedra (Tables III and IV). The diphosphate groups present a staggered configuration in $KMoP_2O_7$ as in the isostructural diphosphates in-

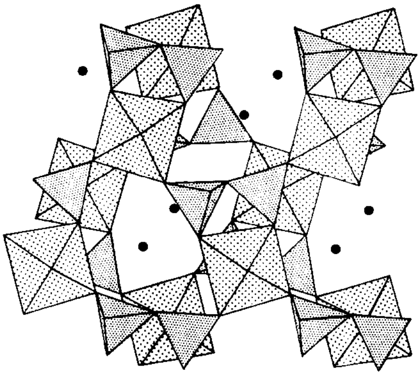

FIG. 1. Projection of the structure of $KMoP_2O_7$ onto the (010) plane.

TABLE III

DISTANCES (Å) AND ANGLES (°) IN THE $PO_4$ TETRAHEDRA IN $KMoP_2O_7$

| P(1) | O(1) | O(3) | O(5) | O(7) |
|---|---|---|---|---|
| O(1) | 1.615(3) | 2.492(4) | 2.471(4) | 2.518(4) |
| O(3) | 105.8(2) | 1.510(3) | 2.530(3) | 2.460(4) |
| O(5) | 105.0(2) | 114.4(2) | 1.500(3) | 2.553(4) |
| O(7) | 106.9(2) | 108.6(1) | 115.5(2) | 1.519(3) |
| P(2) | O(1$^{viii}$) | O(2$^{viii}$) | O(4$^{viii}$) | O(6$^{viii}$) |
| O(1$^{viii}$) | 1.605(3) | 2.526(3) | 2.499(4) | 2.490(3) |
| O(2$^{viii}$) | 107.5(2) | 1.526(3) | 2.505(4) | 2.477(4) |
| O(4$^{viii}$) | 107.8(2) | 112.4(2) | 1.488(3) | 2.517(4) |
| O(6$^{viii}$) | 105.9(2) | 109.0(1) | 113.9(2) | 1.516(3) |

*Note*. The P–O lengths are on the diagonal through P, the O . . . O distances are above it, and the O–P–O angles are below it.

TABLE IV

DISTANCES (Å) AND ANGLES (°) IN THE $PO_4$ TETRAHEDRA OF $K_{0.17}MoP_2O_7$

| P(1) | $O(2^{i})$ | $O(3^{ii})$ | O(5) | O(6) |
|---|---|---|---|---|
| $O(2^{i})$ | 1.49(1) | 2.52(2) | 2.51(2) | 2.43(2) |
| $O(3^{ii})$ | 114.2(7) | 1.52(1) | 2.44(2) | 2.52(2) |
| O(5) | 113.2(7) | 107.5(7) | 1.51(1) | 2.51(2) |
| O(6) | 104.7(7) | 108.7(6) | 108.3(7) | 1.59(1) |
| **P(2)** | $O(1^{iii})$ | O(4) | $O(6^{iv})$ | O(7) |
| $O(1^{iii})$ | 1.48(1) | 2.48(2) | 2.45(2) | 2.49(2) |
| O(4) | 112.7(7) | 1.51(1) | 2.50(2) | 2.50(2) |
| $O(6^{iv})$ | 106.0(7) | 107.3(7) | 1.59(1) | 2.53(2) |
| O(7) | 111.6(7) | 110.9(7) | 108.0(7) | 1.53(1) |

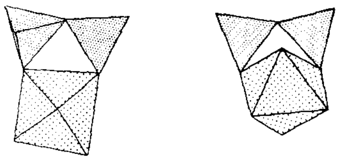

FIG. 3. The $MoP_2O_{11}$ unit in (A) $KMoP_2O_7$ and (B) $NaMoP_2O_7$.

volving rubidium and cesium (*2–7*). In contrast, an almost eclipsed configuration as in $NaMoP_2O_7$ (*5*) and $Na_{0.30}MoP_2O_7$ (*6*) is observed for $K_{0.17}MoP_2O_7$.

The $Mo^{III}O_6$ octahedra are characterized by three short Mo–O distances (2.046 to 2.092 Å) and three longer ones (2.105 to 2.11 Å) in $KMoP_2O_7$ (Table V) to be compared to the three Mo(III) diphosphates $AMoP_2O_7$ ($A$ = Na, Rb, Cs) (*2, 5, 7*). On the other hand, $K_{0.17}MoP_2O_7$ exhibit smaller Mo–O distances (Table VI), close to those of $AMo_2P_3O_{12}$ (*8, 9*) and of $Na_{0.30}MoP_2O_7$ (*6*) in agreement with its mean oxidation state of 3.83.

A common feature to these two diphosphates concerns the existence of $MoP_2O_{11}$ units (Fig. 3) which are formed of a diphosphate group sharing two of its corners with the same $MoO_6$ octahedron. It is worth pointing out that such units are also observed in $NaMoP_2O_7$ (*5*) and $Na_{0.30}MoP_2O_7$ (*6*). The only difference between these units deals with the configuration of the $P_2O_7$ group which can be either staggered or almost eclipsed as described above.

In $KMoP_2O_7$, the $MoP_2O_{11}$ units (Fig. 3a) share the corner of their polyhedra forming $[MoP_2O_7]_\infty$ layers parallel to the (001) plane (Fig. 4a). In those layers, one can distinguish strings of corner-sharing $MoO_6$ octahedra and diphosphate groups running along [100] (Fig. 4b); these chains exhibit some similarity with those observed for $NaMoP_2O_7$ and $Na_{0.30}MoP_2O_7$ (Fig. 4c); but they differ mainly from the latter by the staggered configuration of the $P_2O_7$ groups. Consequently the structure of $KMoP_2O_7$ results from alternative stacking of $[MoP_2O_7]_\infty$ layers and of the enantiomorphic ones

TABLE V

DISTANCES (Å) AND ANGLES (°) IN THE $MoO_6$ OCTAHEDRA IN $KMoP_2O_7$

| Mo | $O(2^{viii})$ | $O(3^{ix})$ | O(4) | $O(5^{x})$ | $O(6^{xi})$ | $O(7^{viii})$ |
|---|---|---|---|---|---|---|
| $O(2^{viii})$ | 2.081(2) | 4.181(3) | 2.836(4) | 2.984(4) | 2.849(4) | 2.900(4) |
| $O(3^{ix})$ | 172.2(1) | 2.110(2) | 2.956(4) | 2.996(4) | 2.897(4) | 3.228(4) |
| O(4) | 86.8(1) | 90.7(1) | 2.046(3) | 4.137(4) | 2.968(4) | 2.909(3) |
| $O(5^{x})$ | 91.3(1) | 90.9(1) | 177.2(1) | 2.092(3) | 2.875(3) | 3.053(4) |
| $O(6^{xi})$ | 85.8(1) | 86.9(1) | 91.3(1) | 86.5(1) | 2.105(3) | 4.208(4) |
| $O(7^{viii})$ | 87.6(1) | 99.8(1) | 88.8(1) | 93.2(1) | 173.3(1) | 2.110(3) |

*Note*. The Mo–O lengths are on the diagonal through Mo, the O . . . O distances are above it, and the O–Mo–O angles below it.

TABLE VI

Distances (Å) and Angles (°) of $MoO_6$ Octahedron in $K_{0.17}MoP_2O_7$

| Mo | O(1) | O(2) | O(3) | O(4) | O(5) | O(7) |
|---|---|---|---|---|---|---|
| O(1) | 2.04(1) | 4.06(2) | 2.90(2) | 2.89(2) | 2.85(2) | 2.83(2) |
| O(2) | 178.2(6) | 2.03(1) | 2.89(2) | 2.92(2) | 2.91(2) | 2.86(2) |
| O(3) | 89.4(5) | 89.4(5) | 2.08(1) | 4.13(3) | 2.81(2) | 2.88(2) |
| O(4) | 89.9(5) | 91.3(5) | 179.(1) | 2.05(1) | 2.95(2) | 2.91(2) |
| O(5) | 89.3(5) | 91.9(5) | 86.4(5) | 92.8(5) | 2.03(1) | 4.04(2) |
| O(7) | 88.6(5) | 90.1(5) | 89.3(5) | 91.4(5) | 175.3(5) | 2.02(1) |

*Note.* The Mo–O lengths are on the diagonal, the O . . . O distances are above it, and the O–Mo–O angles below it.

in such a way that one octahedron of one layer shares its corner with one tetrahedron of the adjacent layer (Fig. 5). These layers of polyhedra delimit large heptagonal windows (Fig. 4a) formed of four $PO_4$ tetrahedra and three $MoO_6$ octahedra. The stacking along *c* of those crowns of polyhedra leads to tunnels running along [001] where the potassium ions are located, realizing a 10-fold coordination with K–O distances ranging from 2.740 to 3.355 Å (Table VII). Along [110] one also observes hexagonal tunnels formed of two $P_2O_7$ groups and two $MoO_6$ octahedra, whose size is smaller than that of the heptagonal tunnels.

The structure of $K_{0.17}MoP_2O_7$ is very different from those of the sodium, potassium, rubidium, and cesium diphosphates, except for the existence of the $MoP_2O_{11}$ units. The stacking of the $MoP_2O_{11}$ units form infinite columns running along *c* (Fig. 6) in such a way that along this direction one $MoO_6$ oc-

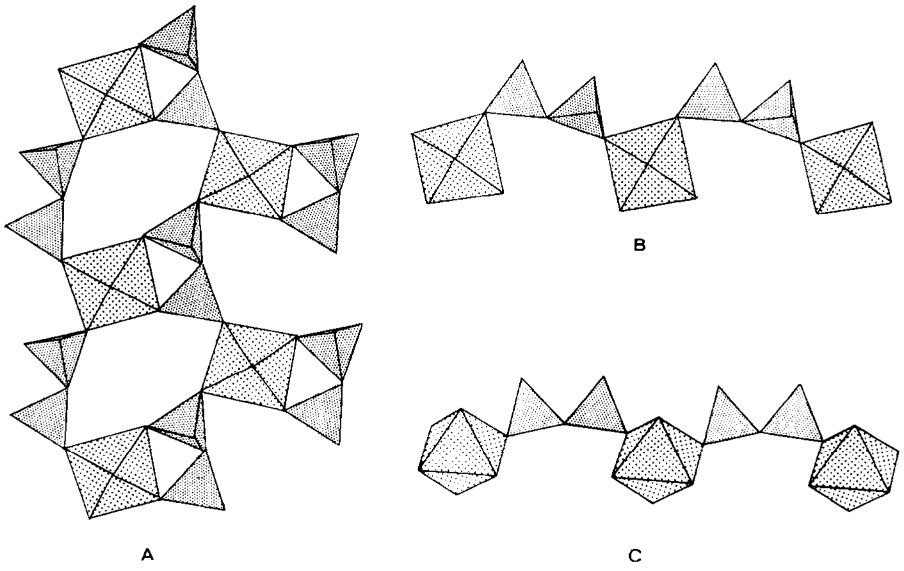

Fig. 4. (A) "$MoP_2O_7$" layer showing heptagonal windows. (B) String of corner-sharing octahedra and diphosphate group in $KMoP_2O_7$. (C) Similar string in $NaMoP_2O_7$ and $Na_xMoP_2O_7$.

TABLE VII

K–O BOND LENGTH IN $KMoP_2O_7$

| | |
|---|---|
| K–O($2^{xii}$) | = 2.740(3) Å |
| K–O(6) | = 2.745(3) |
| K–O($7^{xiii}$) | = 2.759(2) |
| K–O($6^{xii}$) | = 2.964(3) |
| K–O($2^{viii}$) | = 2.973(3) |
| K–O($3^{xiii}$) | = 3.093(3) |
| K–O(5) | = 3.170(3) |
| K–O($4^{viii}$) | = 3.237(3) |
| K–O($3^{xiv}$) | = 3.254(3) |
| K–O(1) | = 3.355(3) |

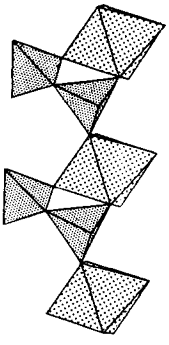

FIG. 6. Columns of corner-sharing $MoP_2O_7$ units in $K_{0.17}MoP_2O_7$.

tahedron alternates with one $PO_4$ tetrahedron. Laterally in the (001) plane, these columns share the corners of their polyhedron forming very small rectangular and very large tunnels running along *c*. Those latter tunnels are formed of rings of eight polyhedra (four $PO_4$ tetrahedra + four Mo $O_6$ octahedra) so that these windows should allow a great mobility of the potassium ions in the structure. The latter exhibit an eightfold coordination with K–O distances ranging from 2.66 to 3.50 Å (Table VIII); their high thermal factor ($B = 3.8$ Å$^2$) is in agreement with the large size of the cavities.

These results and those previously observed for different diphosphates of molybdenum show that the $MoP_2O_{11}$ unit is a common feature to several diphosphates involving Mo(III) or the mixed-valence Mo(III)–Mo(IV). The flexibility of the diphosphate group in these units is remarkable: it allows us by a small change of configuration to induce different frameworks such as those observed in $NaMoP_2O_7$ (*5*) and $Na_{0.3}MoP_2O_7$ (*6*) or in the present work with $KMoP_2O_7$ and $K_{0.17}MoP_2O_7$.

TABLE VIII

K–O BOND LENGTH IN $K_{0.17}MoP_2O_7$

| | |
|---|---|
| K–O($7^{i}$) | = 2.66(1) Å |
| K–O($7^{vi}$) | = 2.66(1) |
| K–O($7^{vii}$) | = 2.80(2) |
| K–O($7^{iii}$) | = 2.80(2) |
| K–O($4^{iii}$) | = 3.10(2) |
| K–O($4^{vii}$) | = 3.10(2) |
| K–O($4^{vi}$) | = 3.50(2) |
| K–O($4^{i}$) | = 3.50(2) |

*Note*. Symmetry code: i, $x, y, z - 1$; ii, $0.25 + y, 0.25 - x, z - 0.75$; iii, $0.25 - y, 0.25 + x, 0.25 - z$; iv, $0.50 - x, 0.50 - y, 0.50 - z$; v, $0.25 - y, 0.25 + x, 1.25 - z$; vi, $-x, 0.50 - y, z - 1$; vii, $y - 0.25, 0.25 - x, 0.25 - z$; viii, $x, 1.50 - y, 0.50 + z$; ix, $1 - x, 1 - y, 1 - z$; x, $x, y, 1 + z$; xi, $-x, 1 - y, 1 - z$; xii, $-x, 1 - y, -z$; xiii, $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; xiv, $1 - x, 1 - y, -z$.

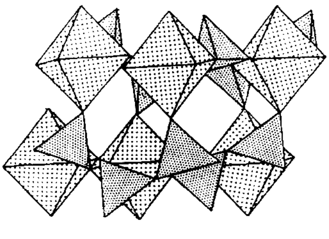

FIG. 5. Stacking of two "$MoP_2O_7$" layers.

## References

*1.* D. Riou, Ph. Labbe, and M. Goreaud, *Eur. J. Solid State Inorg. Chem.*, in press (1988).

*2.* K. H. Lii and R. C. Haushalter, *Acta Crystallogr. Sect. C* **43,** 2036 (1987).

*3.* A. Leclaire, M. M. Borel, A. Grandin, and B. Raveau, *Mater. Chem. Phys.* **12,** 537 (1985).

*4.* A. Leclaire and B. Raveau, *J. Solid State Chem.* **71,** 283 (1987).

*5.* A. Leclaire, M. M. Borel, A. Grandin, and B. Raveau, *J. Solid State Chem.* **76,** 131 (1988).

*6.* A. Leclaire, M. M. Borel, A. Grandin, and B. Raveau, *Z. Kristallogr.*, in press (1988).

*7.* D. Riou, A. Leclaire, A. Grandin, and B. Raveau, *Acta Crystallogr.*, in press (1988).

*8.* A. Leclaire, J. C. Monier, and B. Raveau, *J. Solid State Chem.* **59,** 301 (1985).

*9.* A. Leclaire and B. Raveau, *Acta Crystallogr. Sect. C* **44,** 226 (1988).