Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
Preiss, H. (1971). *Z. Anorg. Allg. Chem.* **380**, 56–64.
Prout, K., Cameron, T. S., Forder, R. A., Critchley, S. R., Denton, B. & Rees, G. V. (1974). *Acta Cryst.* **B30**, 2290–2304.
Prout, K. & Daran, J. C. (1979). *Acta Cryst.* **B35**, 2882–2888.

---

*Acta Cryst.* (1987). C**43**, 2036–2038

# $CsMoP_2O_7$: a Molybdenopyrophosphate Containing Isolated $Mo^{3+}$ Cations

By Kwang-Hwa Lii* and Robert C. Haushalter

*Exxon Research and Engineering Company, Route* 22 *East, Annandale, New Jersey* 08801, *USA*

(*Received* 29 *December* 1986; *accepted* 26 *June* 1987)

**Abstract.** $CsMoP_2O_7$, $M_r = 402{\cdot}793$, monoclinic, $P2_1/c$, $a = 7{\cdot}7239\,(22)$, $b = 10{\cdot}304\,(10)$, $c = 8{\cdot}4881\,(15)$ Å, $\beta = 104{\cdot}772\,(17)°$, $V = 653\,(1)$ Å$^3$, $Z = 4$, $D_x = 4{\cdot}10$ g cm$^{-3}$, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 80{\cdot}22$ cm$^{-1}$, $F(000) = 732$, $T = 296$ K, $R = 0{\cdot}041$ for 915 independent reflections. The title compound is isostructural with $KAlP_2O_7$ and contains unusual isolated $Mo^{3+}$ cations in the oxygen array. The pyrophosphate groups form sheets linked by Mo atoms. The $MoO_6$ octahedra are slightly distorted. The Cs ions are located in tunnels formed by the polyhedra and are coordinated by ten O atoms.

**Introduction.** The investigations of the system $M$–$Mo^{V}$–P–O ($M$ = metal cation) have shown the formation of $K_4Mo_8P_{12}O_{52}$ (Leclaire, Monier & Raveau, 1983), $Cs_2Mo_4P_6O_{26}$ (Lii & Haushalter, 1987), $Cs_4Mo_8P_{12}O_{52}$ (Lii & Haushalter, 1987) and $AgMo_5P_8O_{33}$ (Lii, Johnston, Goshorn & Haushalter, 1987). A phosphate containing $Mo^{IV}$ has been observed in $TlMo_2P_3O_{12}$ (Leclaire, Monier & Raveau, 1985). In contrast to the $Mo^{V}$-containing compounds, which exhibit isolated $MoO_6$ octahedra linked only to $PO_4$ tetrahedra, $TlMo_2P_3O_{12}$ contains corner-sharing $Mo_2O_{11}$ units and $PO_4$ groups. As the formal oxidation state of the Mo atom is further reduced, one might expect the formation of metal–metal bonds which were found in the cubane-like $Mo_4O_4$ cluster unit in the compounds $Cs_3Mo_5P_6O_{25}$ (Lii, Haushalter & O'Connor, 1987) and $Cs_3Mo_4P_3O_{16}$ (Haushalter, 1987). The interconnection between the building units is governed by several factors such as the nature of the counter cation, the oxidation state of the Mo atom, and the nonmetal-to-metal ratio. Therefore, one might be able to prepare a caesium molybdenophosphate containing isolated highly reduced Mo cations by adjusting the nonmetal-to-metal ratio. Hence, we prepared $CsMoP_2O_7$ which contains unusual isolated $Mo^{3+}$ cations in the oxygen array. This compound was found to be isostructural with $KAlP_2O_7$ (Ng & Calvo, 1973). To convert the $KAlP_2O_7$ coordinates to those of $CsMoP_2O_7$, one must shift the origin in $KAlP_2O_7$ by $-\frac{1}{2}$ in $y$, then apply the values $1-x$, $y-\frac{1}{2}$, $1{\cdot}5-z$ to all coordinates.

**Experimental.** Yellow needle crystals of $CsMoP_2O_7$ were discovered in the reaction products formed by heating a mixture of $Cs_2MoO_4$, Mo and $P_2O_5$ (mole ratio of 1:1:2) at 1270 K in an evacuated quartz ampule for 32 h. Although reactions to prepare a pure phase at several different temperatures have been performed, the X-ray powder patterns of the products always showed either a few unindexed reflections or reflections due to $Cs_3Mo_5P_6O_{25}$.

The intensity data were collected using an Enraf–Nonius CAD-4 diffractometer and graphite-monochromated Mo $K\alpha$ radiation. 25 independent reflections with $10{\cdot}6 < 2\theta < 50°$ were used for least-squares determination of cell constants. The intensities of three reflections were monitored and no significant decay was detected. The structure was solved by direct methods and refined by full-matrix least-squares refinement based on $F$ values. The Cs, Mo and P atoms were refined anisotropically. Attempts to refine the O atoms anisotropically resulted in negative temperature factors for some of these atoms so they were refined isotropically. A refinement of the occupancy factors for the Cs and Mo atoms resulted in a value of 0·97 (1) for both atoms, indicating full occupancy. All calculations were performed on a VAX-based TEXRAY system. Scattering factors and anomalous-dispersion terms were taken from *International Tables for X-ray Crystallography* (1974). Data-collection and refinement parameters are collected in Table 1.† Final

---

* Present address: Institute of Chemistry, Academia Sinica, Nankang, Taipei, Taiwan.

† Lists of structure factors, anisotropic thermal parameters and a full list of intramolecular distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44194 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/87/112036-03$01.50 © 1987 International Union of Crystallography

Table 1. *Summary of data-collection and processing parameters*

| | |
|---|---|
| Crystal dimensions (mm) | 0·30 × 0·20 × 0·10 |
| Data collection range (°) | $3 < 2\theta < 50$ |
| Scan width (°) | $0{\cdot}70 + 0{\cdot}35\tan\theta$ |
| Scan type | $\omega$–$2\theta$ |
| Scan rate (° min $^{-1}$) in $\omega$ | 4 |
| Corrections | Lorentz–polarization<br>Empirical absorption (relative transmission factors: 0·81–1·00) |
| Range of $h, k, l$ | $0 < h < 9; 0 < k < 12; -10 < l < 9$ |
| Total data collected | 1214 |
| Unique data with $I > 3{\cdot}0\sigma(I)$ | 915 |
| Total variables | 66 |
| Quantity minimized | $\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$<br>$w = 4F_o^2/\sigma^2(F_o^2)$ |
| $R$; $wR$ | 0·041; 0·051 |
| $S$ | 3·96 |
| $(\Delta/\sigma)_{\max}$ | <0·01 |
| $(\Delta\rho)_{\max}$; $(\Delta\rho)_{\min}$(e Å $^{-3}$) | 2·24; −2·02 |

Table 2. *Positional parameters and equivalent isotropic thermal parameters*

$$B_{eq} = \tfrac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $B_{eq}$*(Å$^2$) |
|---|---|---|---|---|
| Cs | 0·8033 (1) | 0·1958 (1) | 0·9546 (1) | 1·27 (4) |
| Mo | 0·7617 (2) | −0·3992 (1) | 0·7414 (1) | 0·35 (5) |
| P(1) | 0·8704 (5) | −0·0965 (4) | 0·6707 (5) | 0·5 (1) |
| O(1) | 0·914 (1) | −0·234 (1) | 0·738 (1) | 0·7 (2) |
| O(4) | 0·853 (2) | −0·412 (1) | 0·990 (1) | 1·1 (2) |
| O(6) | 0·995 (1) | −0·502 (1) | 0·728 (1) | 0·7 (2) |
| O(7) | 0·679 (1) | −0·443 (1) | 0·199 (1) | 0·8 (2) |
| P(2) | 0·5714 (5) | −0·3699 (4) | 0·3142 (4) | 0·5 (1) |
| O(2) | 0·678 (1) | −0·394 (1) | 0·488 (1) | 1·3 (2) |
| O(3) | 0·614 (1) | −0·572 (1) | 0·732 (1) | 0·9 (2) |
| O(5) | 0·560 (1) | −0·271 (1) | 0·769 (1) | 0·7 (2) |

* The values for all the O atoms are isotropic thermal parameters.

Table 3. *Selected interatomic distances* (Å)

| | | | |
|---|---|---|---|
| Mo—O(4) | 2·05 (1) | P(1)—O(4) | 1·50 (1) |
| Mo—O(1) | 2·07 (1) | P(1)—O(6) | 1·52 (1) |
| Mo—O(2) | 2·09 (1) | P(1)—O(1) | 1·54 (1) |
| Mo—O(5) | 2·10 (1) | P(1)—O(7) | 1·61 (1) |
| Mo—O(3) | 2·11 (1) | P(2)—O(5) | 1·50 (1) |
| Mo—O(6) | 2·12 (1) | P(2)—O(3) | 1·50 (1) |
| | | P(2)—O(2) | 1·51 (1) |
| | | P(2)—O(7) | 1·62 (1) |

positional and thermal parameters are listed in Table 2. Selected interatomic distances are given in Table 3.

**Discussion.** The structure of $CsMoP_2O_7$, viewed approximately parallel to the *c* axis, is shown in Fig. 1 and contains tunnels where the Cs atoms are located. As discussed by Ng & Calvo (1973), the pyrophosphate group is propagated in the *ab* plane by the screw axes to form a sheet and adjacent sheets are generated by the *c*-glide planes to form the framework of the structure. The Mo atom serves to link three pyrophosphate sheets and is coordinated by six O atoms at distances from 2·05 (1) to 2·12 (1) Å forming a slightly distorted octahedron [$d$(O···O) = 2·83 (1) to 3·13 (2) Å]. The closest distance between two neighboring Mo atoms is 5·24 Å indicative of negligible interaction. Each $MoO_6$ octahedron shares its six corners with five pyrophosphate groups and, therefore, each pyrophosphate group shares its six corners with five $MoO_6$ octahedra. Three pyrophosphate groups are in the same sheet while the other two are from adjacent sheets. One of the five $P_2O_7$ groups is coordinated to the Mo atom as a bidentate ligand. The oxidation state of Mo in $CsMoP_2O_7$ can be estimated by summing the bond strengths of Mo—O bonds which were calculated according to $s = (d/1{\cdot}882\ \text{Å})^{-6{\cdot}0}$ (Brown & Wu, 1976), where $s$ = bond strength of a particular Mo—O bond, $d$ = observed bond length, 1·882 Å = bond length of an Mo—O bond of unit valence, and −6·0 is a fitted constant. The oxidation state for Mo calculated by this method is +3·2 which is close to that based on its stoichiometry. The nearly staggered configuration of the $PO_4$ tetrahedra of the pyrophosphate group in $CsMoP_2O_7$ is similar to that in $KAlP_2O_7$ except that $CsMoP_2O_7$ has a larger dihedral angle (14 *vs* 9°) and a larger P—O—P bridge angle (127 *vs* 123°). Interestingly, the $P_2O_7$ groups in the molybdenum phosphates which were mentioned in the *Introduction* are in either eclipsed or semieclipsed configurations. However, a perfectly staggered pyrophosphate group was observed in $P_8W_{12}O_{52}$ (Domenges, Goreaud, Labbe & Raveau, 1982). Both of the $O_4$ tetrahedra in the pyrophosphate group in $CsMoP_2O_7$ are quite regular with O···O distances ranging from 2·48 (2) to 2·53 (2) Å for $P(1)O_4$ and from 2·47 (1) to 2·55 (2) Å for $P(2)O_4$. However, both of the atoms, P(1) and P(2), are displaced away from the bridging O(7) atom, as shown by the significantly longer P(1)—O(7) and P(2)—O(7) bond distances as compared to the other P—O bond distances. The Cs ions are located in the

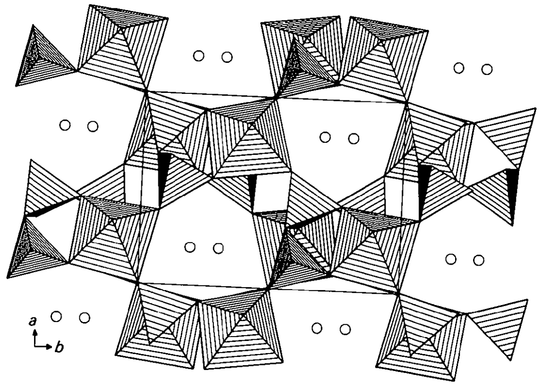

Fig. 1. *STRUPLO*84 drawing (Fischer, 1985) displaying the framework of $CsMoP_2O_7$ and the tunnels occupied by Cs ions. The *c* axis is approximately perpendicular to this plane. In this polyhedral representation of the structure, the corners of the octahedra and tetrahedra are $O^{2-}$ ions, the Mo and P ions are at the center of each octahedron and tetrahedron respectively, and the circles represent the $Cs^+$ ions.

tunnels and are each coordinated by ten O atoms at distances ranging from 2·97 (1) to 3·41 (1) Å. Each tunnel can be considered as resulting from the stacking of nearly planar elliptic rings along the $c$ axis, each of which is formed by the edges of three octahedra and four tetrahedra.

### References

Brown, I. D. & Wu, K. K. (1976). *Acta Cryst.* B**32**, 1957–1959.
Domenges, B., Goreaud, M., Labbe, Ph. & Raveau, B. (1982). *Acta Cryst.* B**38**, 1724–1728.
Fischer, R. X. (1985). *J. Appl. Cryst.* **18**, 258–262.
Haushalter, R. C. (1987). *Chem. Commun.* Submitted.
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
Leclair, A., Monier, J. C. & Raveau, B. (1983). *J. Solid State Chem.* **48**, 147–153.
Leclaire, A., Monier, J. C. & Raveau, B. (1985). *J. Solid State Chem.* **59**, 301–305.
Lii, K.-H. & Haushalter, R. C. (1987). *J. Solid State Chem.* In the press.
Lii, K.-H., Haushalter, R. C. & O'Connor, C. J. (1987). *Angew. Chem.* **26**, 549–551.
Lii, K.-H., Johnston, D. C., Goshorn, D. P. & Haushalter, R. C. (1987). *J. Solid State Chem.* In the press.
Ng, H. N. & Calvo, C. (1973). *Can. J. Chem.* **51**, 2613–2630.

*Acta Cryst.* (1987). C**43**, 2038–2040

# Structure of Condensed Cadmium(II) Silicate Phosphate

By M. Trojan and D. Brandová
*University of Chemical Technology, Leninovo náměstí* 565, 53 210 *Pardubice, Czechoslovakia*

and J. Fábry, J. Hybler,* K. Jurek and V. Petříček
*Institute of Physics, Czechoslovak Academy of Sciences,* 180 40 *Prague, Czechoslovakia*

(*Received* 25 *April* 1987; *accepted* 17 *June* 1987)

**Abstract.** $Cd_2SiP_4O_{14}$, $M_r = 600{\cdot}7$, monoclinic, $C2/c$, $a = 17{\cdot}191$ (3), $b = 5{\cdot}136$ (1), $c = 12{\cdot}486$ (2) Å, $\beta = 103{\cdot}39$ (1)°, $V = 1072{\cdot}5$ (3) Å$^3$, $Z = 4$, $D_m = 3{\cdot}69$ (1) (flotation method), $D_x = 3{\cdot}72$ Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71073 Å, $\mu = 6{\cdot}37$ mm$^{-1}$, $F(000) = 1128$, room temperature, final $R = 0{\cdot}036$ for 1176 reflections (including unobserved). The title compound consists of silicate–phosphate groups $(SiP_4O_{14})^{2-}$ condensed into polymeric chains and $Cd^{2+}$ cations octahedrally coordinated by terminal O atoms of the silicate–phosphate groups.

**Introduction.** The starting compound for reaction, dicadmium(II) cyclotetraphosphate $c$-$Cd_2P_4O_{12}$, was prepared by calcination of $Cd(H_2PO_4)_2.2H_2O$ (Trojan & Brandová, 1986) and purified by an acid extraction (Trojan & Brandová, 1984). It melts at 1073 K under vacuum conditions (<0·1 mPa) (Trojan & Seropegin, 1985). A mixture of $c$-$Cd_2P_4O_{12}$ and $SiO_2$ in the molecular ratio 1:1 was melted in a platinum crucible and very slowly cooled (0·1 K min$^{-1}$) in vacuum to give the crystalline product $Cd_2SiP_4O_{14}$ (Trojan, Brandová, Petříček, Hybler, Fábry & Jurek, 1987). Crystals are colourless, columnar along **b** or tabular along (100), stable in air, insoluble in water.

**Experimental.** Preliminary lattice constants and space group were obtained from precession photographs (Mo $K\alpha$, Zr filtered). A spherical crystal with $r = 0{\cdot}24$ mm was used for measurements on a Hilger & Watts four-circle diffractometer (Mo $K\alpha$, Nb filtered) controlled by an M7000 computer. Refined cell parameters were obtained by a least-squares method (Shoemaker, 1970) from 49 reflections ($7{\cdot}31 < \theta < 27{\cdot}85°$) centred on the diffractometer. The $\omega$–$2\theta$ scan technique was used to measure all independent reflections with $(\sin\theta)/\lambda < 0{\cdot}63877$ Å$^{-1}$ [$h \in (0,21), k \in (-6,0), l \in (-15, 15)$]. The learnt-profile method (Diamond, 1969; Clegg, 1981) was used for obtaining intensities and their e.s.d.'s. The scan speed varied from 1 to 8° min$^{-1}$ determined from a rapid prescan. The intensities of three standard reflections (10,0,0, 080 and 004) measured after every 30 reflections showed no significant variation. Of the 1176 independent reflections, 29 were classified as unobserved [$I < 1{\cdot}96\sigma(I)$], but these reflections were used in the refinement with $F_{\rm unobs} = \frac{1}{2}F_{\rm min}$ and $\sigma(F_{\rm unobs}) = 1/\sqrt{12} \times F_{\rm min}$ ($F_{\rm min}$ = the minimal observable value of $F$). The data were corrected for Lorentz and polarization effects and for absorption ($A_{\rm max} = 7{\cdot}783$ and $A_{\rm min} = 6{\cdot}644$).

The structure was solved by the heavy-atom method. 97 independent parameters (positional and anisotropic

---

* To whom correspondence should be addressed.

0108-2701/87/112038-03$01.50 © 1987 International Union of Crystallography