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Structure of $CsMo_3P_{5.8}Si_2O_{25}$

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Abstract. $M_r = 1056{\cdot}53$, trigonal, $P\bar{3}1c$, $a = b = 8{\cdot}2642$ (5), $c = 17{\cdot}559$ (2) Å, $V = 1038{\cdot}5$ (2) Å^3, $Z = 2$, $D_x = 3{\cdot}778$ Mg m^{-3}, $\lambda(\text{Mo }K\bar{\alpha}) = 0{\cdot}71069$ Å, $\mu = 4{\cdot}28$ mm^{-1}, $F(000) = 992$, $T = 293$ K. $R = 0{\cdot}028$ for 715 independent observed reflections. The three-dimensional framework, built up from corner-sharing octahedra and tetrahedra delimiting wide tunnels, has the same shape and size as those of the Tl, Rb or K compounds. It is observed that the thermal motion of the *A* ion in the tunnel decreases drastically as the size of the *A* ion increases.

Introduction. The investigation of the system *A*—P—Si—Mo—O has shown the formation of molybdosilicophosphates $AMo_3P_{5.8}Si_2O_{25}$ (Leclaire, Monier & Raveau, 1984; Leclaire, Borel, Grandin & Raveau, 1985) with an original intersecting tunnel structure whose host lattice is built up from corner-sharing MoO_6 octahedra, PO_4 tetrahedra and Si_2O_7 groups. From the single-crystal studies, it appears that the tunnels are much greater in size than expected from the size of the *A* ions (K, Rb, Tl). As a result, the observed *A*—O distances are much greater than the sum of the ionic radii (Shannon, 1976). As a consequence very high thermal factors were observed for *A* ions in agreement with their mobility in the structure. Thus it appears that the insertion of a bigger cation such as Cs^+ should be possible and this cation would fit into this size of tunnel. The structure of the molybdosilicophosphate $CsMo_3P_{5.8}Si_2O_{2.5}$ is reported here.

Experimental. Hexagonal needle ($0{\cdot}048 \times 0{\cdot}03 \times 0{\cdot}072$ mm) obtained from appropriate amount of $(NH_4)_2HPO_4$, Cs_2CO_3, MoO_3 and SiO_2 first heated in air up to 873 K and then mixed with appropriate amount of metallic Mo and heated in evacuated silica ampoules for several days. Trigonal symmetry ($\bar{3}m$), systematic absences in $hh\overline{2h}l$ for $l = 2n + 1$ led to $P31c$ or $P\bar{3}1c$, structure solved and refined in $P\bar{3}1c$. Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\bar{\alpha}$. Unit-cell dimensions refined from 25 reflections ($2 < \theta < 37°$). Data measured up to $\theta = 45°$ ($-16 < h < 0$, $0 < k < 16$, $0 < l < 34$) with ω–$\frac{4}{3}\theta$ scan of $(1 + 0{\cdot}35\ \text{tg}\theta)°$ and $(1 + \text{tg}\theta)$ mm counter slit aperture. Three check reflections ($\bar{3}00$, 030, 008) stable throughout data collection. 715 reflections with $I > 3\sigma(I)$, Lp correction, absorption correction applied using *AGNOSTC* (Coppens, Leiserowitz & Rabinovich, 1965; de Meulenaer & Tompa, 1965). Atomic coordinates deduced from Rb and Tl compounds. Atomic parameters (xyz,β_{ij}) and an isotropic extinction parameter (Coppens & Hamilton, 1970) refined by full-matrix least-squares methods on *F* with a weighting scheme $w = f(\sin\theta/\lambda)$ adjusted by the program *POND* (Leclaire, unpublished). Atomic scattering factors and anomalous-dispersion factors from *International Tables for X-ray Crystallography* (1974). Last refinement cycle gave $R = 0{\cdot}028$, $wR = 0{\cdot}029$,* $S = 0{\cdot}9446$, $g = 11$ (2) (Coppens & Hamilton, 1970), $\Delta/\sigma < 0{\cdot}1$, $\Delta\rho < 1$ e Å^{-3} and the atomic parameters of Table 1.

Discussion. The host lattice of this oxide (Fig. 1) built up from corner-sharing MoO_6 octahedra and PO_4 and SiO_4 tetrahedra is quite similar to those observed for the Tl, Rb and K oxides (Leclaire *et al.*, 1984, 1985). The different polyhedra of the structure are almost regular and the interatomic distances are very close to those previously observed for other *A* ions (Tables 2 and 3). Curiously it appears that the size of the tunnels does not depend on the size of the *A* ion. Even for the Cs compound, the Cs—O distances [3·197 (5) Å] are slightly greater than the sum of the ionic radii (3·07 Å) (Shannon, 1976); correlatively the thermal motion of Cs^+ ($B = 2{\cdot}5$ Å^2) is not negligible. Nevertheless comparison of the observed *A*—O distances with the theoretical distances shows that the difference between these two values increases drastically as the size of the *A* ion decreases: a difference of 0·12 Å is observed in the case of Cs^+, against 0·22 Å [3·142 (4) → 2·92 Å] for Rb^+, 0·25 Å [3·147 (9) → 2·90 Å] for Tl^+, and 0·34 Å [3·112 (6) → 2·77 Å] for K^+. The linear but drastic evolution of the thermal factor *versus* ionic radius, from 2·5 Å^2 for Cs^+ to 7·2 Å^2 for K^+ (Fig. 2), is in agreement with the evolution of the *A*—O distance. Thus, it appears that the size of the tunnel is mainly imposed by the framework '$Mo_3P_{5.8}Si_2O_{25}$' and is not influenced by the size of the *A* ions.

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* Lists of observed and calculated structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42388 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atomic coordinates and equivalent isotropic thermal parameters*

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

	x	y	z	$B_{\rm eq}$(Å^2)
Mo(1)	$\frac{1}{3}$	$-\frac{1}{3}$	0·02137 (4)	0·38 (2)
Mo(2)	$-\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{4}$	0·41 (2)
Cs	$\frac{1}{3}$	$-\frac{1}{3}$	$\frac{1}{4}$	2·43 (3)
P	0·37931 (20)	0·32974 (27)	0·11024 (7)	0·49 (4)
Si	0	0	0·09030 (15)	0·69 (5)
O(1)	0·11095 (65)	−0·41158 (58)	0·09285 (24)	1·06 (13)
O(2)	−0·19291 (65)	0·24313 (65)	0·45308 (22)	1·01 (13)
O(3)	0·46617 (68)	0·33466 (92)	0·18691 (20)	1·36 (15)
O(4)	0	0	0	1·56 (26)
O(5)	0·03544 (61)	−0·16229 (57)	0·12292 (24)	0·97 (12)

Table 2. *Principal bond lengths* (Å) *in* $A\mathrm{Mo_3P_{5.8}Si_2O_{25}}$ (A = K, Rb, Tl, Cs)

		K	Rb	Tl	Cs
Mo(1)–O(1)	×3	2·040 (5)	2·044 (4)	2·043 (9)	2·045 (5)
Mo(1)–O(2)	×3	2·049 (6)	2·059 (4)	2·046 (12)	2·051 (6)
Mo(2)–O(3)	×6	1·983 (6)	1·986 (5)	1·970 (10)	1·998 (6)
P–O(1)		1·508 (7)	1·509 (5)	1·502 (12)	1·509 (7)
P–O(2)		1·514 (5)	1·509 (5)	1·511 (9)	1·518 (5)
P–O(3)		1·509 (5)	1·513 (4)	1·526 (9)	1·516 (5)
P–O(5)		1·571 (4)	1·579 (3)	1·564 (9)	1·581 (5)
Si–O(4)	×3	1·581 (3)	1·583 (2)	1·587 (4)	1·585 (3)
Si–O(5)		1·621 (5)	1·614 (4)	1·621 (10)	1·614 (6)
A–O	×6	3·112 (6)	3·142 (4)	3·147 (9)	3·197 (5)

Table 3. *Geometry of the polyhedra forming the framework*

The diagonal through the cation indicates the cation–O bond length (Å). The values above the diagonal are the O–O lengths (Å) and the values below are the O–X–O angles (°).

Mo(1)	O(1)	O(1$^{\rm i}$)	O(1$^{\rm ii}$)	O(2$^{\rm iii}$)	O(2$^{\rm iv}$)	O(2$^{\rm v}$)
O(1)	2·045 (5)	2·797 (8)	2·797 (8)	2·917 (6)	2·987 (7)	4·095 (8)
O(1$^{\rm i}$)	86·3 (2)	2·045 (5)	2·797 (8)	4·095 (8)	2·917 (6)	2·987 (7)
O(1$^{\rm ii}$)	86·3 (2)	86·3 (2)	2·045 (5)	2·987 (7)	4·095 (8)	2·917 (6)
O(2$^{\rm iii}$)	90·8 (2)	177·1 (2)	93·6 (2)	2·051 (6)	2·881 (9)	2·881 (9)
O(2$^{\rm iv}$)	93·6 (2)	90·8 (2)	177·1 (2)	89·3 (2)	2·051 (6)	2·881 (9)
O(2$^{\rm v}$)	177·1 (2)	93·6 (2)	90·8 (2)	89·3 (2)	89·3 (2)	2·051 (6)

Mo(2)	O(3$^{\rm vi}$)	O(3$^{\rm vii}$)	O(3$^{\rm viii}$)	O(3$^{\rm ix}$)	O(3$^{\rm x}$)	O(3$^{\rm xi}$)
O(3$^{\rm vi}$)	1·998 (3)	2·88 (1)	2·88 (1)	2·760 (6)	2·780 (8)	3·995 (9)
O(3$^{\rm vii}$)	92·2 (2)	1·998 (3)	2·88 (1)	3·995 (9)	2·760 (6)	2·780 (8)
O(3$^{\rm viii}$)	92·2 (2)	92·2 (2)	1·998 (3)	2·780 (8)	3·995 (9)	2·760 (6)
O(3$^{\rm ix}$)	87·4 (3)	179·5 (5)	88·2 (2)	1·998 (3)	2·88 (1)	2·88 (1)
O(3$^{\rm x}$)	88·2 (2)	87·4 (3)	179·5 (5)	92·2 (2)	1·998 (3)	2·88 (1)
O(3$^{\rm xi}$)	179·5 (5)	88·2 (2)	87·4 (3)	92·2 (2)	92·2 (2)	1·998 (3)

P	O(1$^{\rm vii}$)	O(2$^{\rm xi}$)	O(3)	O(5$^{\rm vii}$)
O(1$^{\rm vii}$)	1·509 (7)	2·548 (7)	2·458 (8)	2·490 (9)
O(2$^{\rm xi}$)	114·6 (2)	1·518 (5)	2·547 (6)	2·488 (7)
O(3)	108·7 (3)	114·2 (4)	1·516 (5)	2·451 (6)
O(5$^{\rm vii}$)	107·3 (3)	106·8 (3)	104·6 (2)	1·581 (2)

Si	O(4)	O(5)	O(5$^{\rm vii}$)	O(5$^{\rm xii}$)
O(4)	1·585 (3)	2·634 (5)	2·634 (5)	2·634 (5)
O(5)	110·8 (2)	1·614 (6)	2·614 (8)	2·614 (8)
O(5$^{\rm vii}$)	110·8 (2)	108·1 (2)	1·614 (6)	2·614 (8)
O(5$^{\rm xii}$)	110·8 (2)	108·1 (2)	108·1 (2)	1·614 (6)

Symmetry code: (i) $-y, x-y-1, z$; (ii) $1-x+y, -x, z$; (iii) $y, x, z-0·5$; (iv) $-x, y-x-1, z-0·5$; (v) $1+x-y, -y, z-0·5$; (vi) $x-1, y, z$; (vii) $-y, x-y, z$; (viii) $y-x, 1-x, z$; (ix) $-y, 1-x, 0·5-z$; (x) $x-1, x-y, 0·5-z$; (xi) $y-x, y, 0·5-z$; (xii) $y-x, -x, z$.

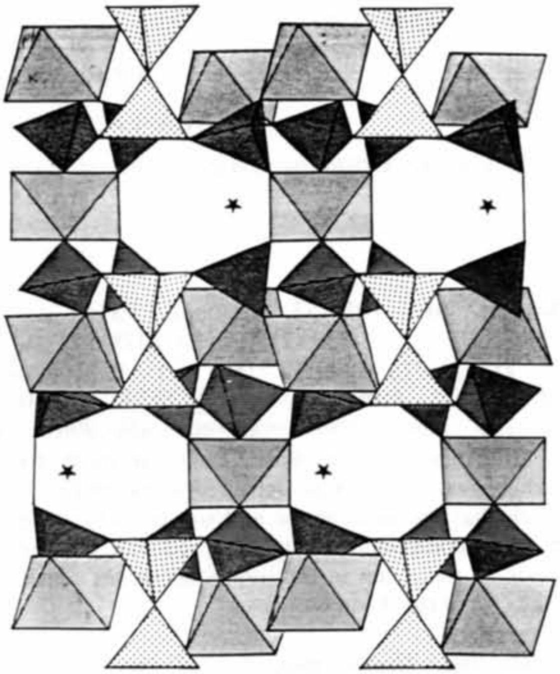

Fig. 1. Projection of the structure along **a** showing the tunnels.

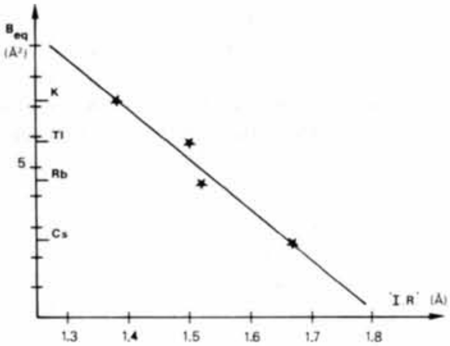

Fig. 2. Plot of $B_{\rm eq}$ *versus* 'ionic radii' of Shannon (1976).

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