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.

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Structure of Condensed Cadmium(II) Silicate Phosphate

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Abstract. $Cd_2SiP_4O_{14}$, $M_r = 600·7$, monoclinic, $C2/c$, $a = 17·191 (3)$, $b = 5·136 (1)$, $c = 12·486 (2)$ Å, $\beta = 103·39 (1)°$, $V = 1072·5 (3)$ Å^3, $Z = 4$, $D_m = 3·69 (1)$ (flotation method), $D_x = 3·72$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 6·37$ mm^{-1}, $F(000) = 1128$, room temperature, final $R = 0·036$ 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 $r = 0·24$ 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 ($7·31 < \theta < 27·85°$) centred on the diffractometer. The ω–2θ scan technique was used to measure all independent reflections with $(\sin\theta)/\lambda < 0·63877$ 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 [$I < 1·96\sigma(I)$], 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 ($A_{\rm max} = 7·783$ and $A_{\rm min} = 6·644$).

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

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thermal parameters of all atoms, scale factor and isotropic extinction parameter) were refined by the full-matrix least-squares method, function minimized $\sum w(|F_o|-|F_c|)^2$, with $w^{-1}=\sigma^2(|F|)+(0{\cdot}03|F|)^2$ and $\sigma(|F|)$ based on counting statistics. The refinement converged to $S=1{\cdot}47$ with $\Delta/\sigma<0{\cdot}01$ and R factors $wR=0{\cdot}053$ and 0·052, $R=0{\cdot}036$ and 0·036 for all and observed reflections, respectively. Extreme residual electron densities determined from final difference Fourier maps $\Delta\rho=2{\cdot}0$ and $-1{\cdot}0$ e Å^{-3}. The isotropic secondary-extinction correction was made after Becker & Coppens (1974), type I, Lorentz distribution with the refined $g=1{\cdot}10\,(4)\times10^{-4}$. Scattering factors and corrections for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974). The calculations were carried out by a local system of crystallographic programs (Petříček & Malý, 1987) on a Siemens 7536 computer.*

Discussion. The final atomic parameters are given in Table 1 and bond distances and angles of interest are in Table 2. The compound studied (Fig. 1) is the first example of condensed silicate–phosphate chains built of PO_4 and SiO_4 tetrahedra. For this reason we made an additional analysis on the JEOL JXA 733 electron microprobe which showed that the content of Cd, P and Si atoms is in good accordance with the formula given in the *Abstract*.

The tetrahedrally coordinated Si atoms occupy special positions on the twofold axes. Four PO_4 and two SiO_4 corner-sharing tetrahedra form a ring about the centre of symmetry. SiO_4 tetrahedra are shared with adjacent rings so that a chain-like structure parallel to **c** is formed. However, because of the proximity of the atomic numbers of Si and P there is only indirect evidence for the ordered occupancy of the tetrahedral positions as stated above: (i) the insertion of a P atom instead of Si leads to a less satisfactory temperature factor for this atom; (ii) PO_4 tetrahedra usually do not share all corners in condensed compounds (see *e.g.* Corbridge, 1971); and (iii) Si—O bonds are usually slightly longer than most P—O bonds (Leclaire, Monier & Raveau, 1984, 1985).

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Table 1. *Fractional atomic coordinates and* B_{eq} *values* (*Hamilton,* 1959) *with e.s.d.'s in parentheses*

	x	y	z	B_{eq}(Å^2)
Cd	0·25529 (2)	0·34408 (5)	0·36807 (2)	0·82 (1)
Si	0·5	0·3594 (3)	0·75	0·60 (4)
P(1)	0·36893 (7)	0·6739 (2)	0·58593 (10)	0·70 (3)
P(2)	0·38207 (7)	0·8550 (2)	0·37060 (9)	0·70 (3)
O(1)	0·4368 (2)	0·5396 (6)	0·6708 (3)	1·42 (7)
O(2)	0·4107 (2)	0·7134 (6)	0·4860 (2)	1·01 (6)
O(3)	0·4585 (2)	0·8223 (5)	0·3244 (3)	1·04 (7)
O(4)	0·3517 (2)	0·9272 (6)	0·6297 (2)	1·28 (7)
O(5)	0·3003 (2)	0·4892 (5)	0·5495 (2)	1·00 (6)
O(6)	0·3136 (2)	0·7010 (6)	0·3025 (3)	1·23 (7)
O(7)	0·3674 (2)	1·1335 (5)	0·3852 (3)	1·19 (8)

Table 2. *Bond distances* (Å) *and angles* (°)

Cd—O(4^{iv})	2·188 (3)	P(1)—O(1)	1·545 (3)
Cd—O(5)	2·339 (3)	P(1)—O(2)	1·590 (3)
Cd—O(5^{v})	2·315 (3)	P(1)—O(4)	1·468 (3)
Cd—O(6)	2·328 (3)	P(1)—O(5)	1·500 (3)
Cd—O(6^{vi})	2·304 (3)	P(2)—O(2)	1·588 (3)
Cd—O(7^{vii})	2·177 (3)	P(2)—O(3)	1·562 (4)
Si—O(1)	1·587 (3)	P(2)—O(6)	1·506 (3)
Si—O(3^{ii})	1·597 (3)	P(2)—O(7)	1·471 (3)
O(4^{iv})—Cd—O(5)	84·7 (1)	O(1)—Si—O(1^{i})	108·6 (2)
O(4^{iv})—Cd—O(5^{v})	87·5 (1)	O(1)—Si—O(3^{ii})	108·2 (2)
O(4^{iv})—Cd—O(6)	90·8 (1)	O(1)—Si—O(3^{iii})	111·7 (2)
O(4^{iv})—Cd—O(6^{vi})	85·9 (1)	O(3^{ii})—Si—O(3^{iii})	108·5 (2)
O(4^{iv})—Cd—O(7^{vii})	173·3 (1)	O(1)—P(1)—O(2)	100·9 (2)
O(5)—Cd—O(5^{v})	83·3 (1)	O(1)—P(1)—O(4)	109·0 (2)
O(5)—Cd—O(6)	91·0 (1)	O(1)—P(1)—O(5)	110·0 (2)
O(5)—Cd—O(6^{vi})	168·6 (1)	O(2)—P(1)—O(4)	110·2 (2)
O(5)—Cd—O(7^{vii})	88·6 (1)	O(2)—P(1)—O(5)	108·0 (2)
O(5^{v})—Cd—O(6)	174·1 (1)	O(4)—P(1)—O(5)	117·5 (2)
O(5^{v})—Cd—O(6^{vi})	89·9 (1)	O(2)—P(2)—O(3)	100·1 (2)
O(5^{v})—Cd—O(7^{vii})	92·1 (1)	O(2)—P(2)—O(6)	108·0 (2)
O(6)—Cd—O(6^{vi})	95·6 (1)	O(2)—P(2)—O(7)	111·0 (2)
O(6)—Cd—O(7^{vii})	89·0 (1)	O(3)—P(2)—O(6)	110·4 (2)
O(6^{vi})—Cd—O(7^{vii})	100·8 (1)	O(3)—P(2)—O(7)	109·5 (2)
		O(6)—P(2)—O(7)	116·5 (2)

Symmetry code: (i) $1-x, y, \frac{3}{2}-z$; (ii) $1-x, 1-y, 1-z$; (iii) $x, 1-y, \frac{1}{2}+z$; (iv) $\frac{1}{2}-x, \frac{3}{2}-y, 1-z$; (v) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$; (vi) $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (vii) $x, -1+y, z$.

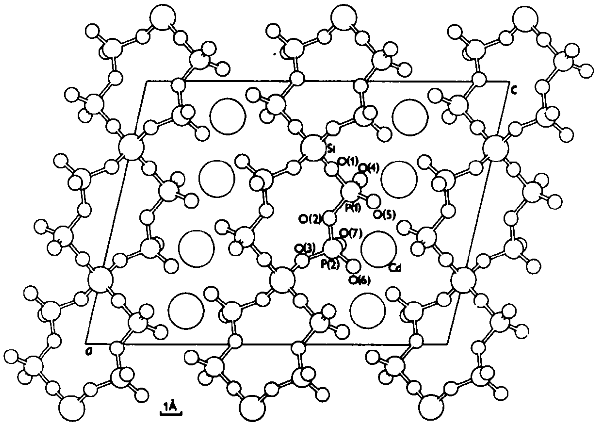

Fig. 1. The projection of the structure along **b**. The chains at $x=0$ and $x=1$ are raised about **b**/2 with respect to those at $x=\frac{1}{2}$ because of the C centring.

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* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44159 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Die Struktur des Trikaliumvanadathydrats

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Abstract. Tripotassium vanadate monohydrate, $K_3VO_4.H_2O$, $M_r = 250{\cdot}25$, orthorhombic, *Pbca*, $a = 10{\cdot}2136\,(8)$, $b = 10{\cdot}4447\,(8)$, $c = 12{\cdot}4878\,(6)$ Å, $V = 1332{\cdot}2\,(2)$ Å^3, $Z = 8$, $D_x = 2{\cdot}495$ Mg m^{-3}, Cu $K\alpha_{1,2}$, $\lambda = 1{\cdot}540562$, $1{\cdot}544390$ Å for lattice parameters, Mo $K\bar{\alpha}$, $\lambda = 0{\cdot}71073$ Å for intensity measurement, $\mu = 3{\cdot}27$ mm^{-1}, $F(000) = 976$, $T = 298$ K, final $R = 0{\cdot}050$ for 2137 unique observed reflections. The coordination polyhedra of the three K ions are connected through a common edge to form a cation group. This group and the VO_4 group are arranged like Na and Cl in the NaCl structure. The water molecule is coordinated to the K ions and hydrogen bonded to the VO_4 groups.

Einleitung. Im Rahmen unserer Untersuchungen über Vanadate der Alkalimetalle haben wir bereits die Strukturen einiger Divanadate bzw. Divanadathydrate (Kato & Takayama, 1983; Kato & Takayama-Muromachi, 1985*a*, 1987*a*) sowie diejenigen der Orthovanadathydrate, $Rb_3VO_4.4H_2O$ (Kato & Takayama-Muromachi, 1985*b*) und $Na_3VO_4.3H_2O$ (Kato & Takayama-Muromachi, 1987*b*) bestimmt. In der vorliegenden Arbeit ist nun die Struktur des $K_3VO_4.H_2O$ untersucht worden, das Lux & Brändl (1965) als einen Bodenkörper im System K_3VO_4–KOH–H_2O beschrieben. Die untersuchten Einkristalle wurden durch Verdampfung einer wässerigen Lösung bei 373 K hergestellt. Zu den Alkalimetall-Orthovanadathydraten mit bekannten Strukturen zählt noch das Pseudo-$Na_3VO_4.12H_2O$ (Tillmanns & Baur, 1971).

Experimentelles. Kristallgestalt unregelmäßig, Größe 0,35 × 0,33 × 0,33 mm, stark hygroskopisch, eingeschlossen in Glasröhrchen von 0,01 mm Wandstärke. Gitterkonstanten aus 2θ-Werten (> 90°) von 19 $0kl$- und 26 $h0l$-Reflexen gemessen auf Rückstrahl-Weissenberg-Aufnahmen von 57,3 mm Filmradius. Intensitäten von 2952 Reflexen mit $0 \le h \le 16$, $0 \le k \le 16$, $0 \le l \le 20$ und bis zu $(\sin\theta)/\lambda = 0{,}807$ Å^{-1} gemessen auf Einkristalldiffraktometer AFC-3 von Fa. Rigaku, ω-Scan für $2\theta < 30°$, $\omega/2\theta$-Scan für $2\theta \ge 30°$, Scan-Breite und -geschwindigkeit $1{,}1° + 0{,}5°\tan\theta$ bzw. 2° min^{-1} für ω-Kreis. Vier Standardreflexe 60mal gemessen mit Standardweichungen von 0,41 bis 0,47%. 2137 Reflexe mit $I > \sigma(I)$ als beobachtet betrachtet, 815 Reflexe unbeobachtet. Auf Absorptionskorrektur verzichtet. Struktur gelöst mit Hilfe der Pattersonfunktion, H-Atome nicht lokalisiert. Verfeinerung nach der Methode der kleinsten Quadrate bezüglich *F*, gewichtet nach $\sigma(F)$. Atomformfaktoren nach Cromer & Mann (1968), Dispersionskorrekturen nach Cromer & Liberman (1970), anisotrope Temperaturfaktoren[†] für alle experimentell bestimmten Atome. Extinktionskorrektur nach Zachariasen (1967, 1968) unter Verwendung einer vereinfachten Formel

$$F_c = sF[1 + (g/\sin 2\theta)(1 + \cos^4 2\theta \cos^2 2\theta_M) \times (1 + \cos^2 2\theta \cos^2 2\theta_M)^{-1} F^2]^{-1/4},$$

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[†] Die Liste der Strukturamplituden und die Tabelle der anisotropen Temperaturfaktoren sind bei der British Library Document Supply Centre (Supplementary Publication No. SUP 44253: 22 pp.) hinterlegt. Kopien sind erhältlich durch: The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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