Na—O(3)*C*1,*D*1	2.460 (1)	O(3)—O(3)—O(3)	173.74 (5)
Na—O(3)*C*2,*D*2	2.897 (1)		
Mean	2.565		

All calculations were performed using the *SDP* system of programs (B. A. Frenz & Associates, Inc., 1985).

Lists of structure factors and anisotropic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71625 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: OH1046]

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$CdV_2(P_2O_7)_2$

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Abstract

Cadmium vanadium diphosphate, $CdV_2(P_2O_7)_2$, is isotypic with $AV_2(P_2O_7)_2$ ($A = $ Ca, Sr) and $Na_xMoP_2O_7$ ($0.25 < x < 0.50$). Its structure consists of similar $[VP_4O_{14}]_\infty$ columns which are built up from VO_6 octahedra and P_2O_7 pyrophosphate groups, and linked together through VO_6 octahedra. This framework delimits tunnels in which the Cd ions are located with octahedral coordination. A comparison with $AV_2(P_2O_7)_2$ ($A = $ Ca, Sr) is given.

Comment

The studies performed over the past few years on diphosphates of transition elements with the formula $A_xMP_2O_7$ have allowed three diphosphates with very similar $[M_2P_4O_{14}]_\infty$ frameworks to be isolated: the vanadium diphosphates $AV_2(P_2O_7)_2$ ($A = $ Ca, Sr; Hwu & Willis, 1991) and the molybdenum diphosphate $Na_xMoP_2O_7$ ($0.25 \leq x \leq 0.50$; Leclaire, Borel, Grandin & Raveau, 1988). The stability of this structure type seems to be governed mainly by the size of the *A* cation since the vanadium diphosphate $BaV_2(P_2O_7)_2$ (Benhamada, Grandin, Borel, Leclaire & Raveau, 1991) exhibits a very different structure. In order to understand this behaviour, it is necessary to substitute the *A* cations with cadmium whose size is smaller than calcium and sodium. We report here the crystal structure of a new diphosphate, $CdV_2(P_2O_7)_2$, which is isotypic with $SrV_2(P_2O_7)_2$.

This new cadmium vanadium(III) phosphate exhibits the $SrV_2(P_2O_7)_2$-type structure. Its $[V_2P_4O_{14}]_\infty$ framework consists of similar VP_4O_{16} units built up from VO_6 octahedra linked in a *trans* configuration to two bidentate P_2O_7 groups. These VP_4O_{16} units are linked together forming $[VP_4O_{14}]_\infty$ columns, running along **a**, which are connected through VO_6 octahedra (Fig. 1). The $[V_2P_4O_{14}]_\infty$ framework delimits two types of tunnel: small empty tunnels and larger ones where Cd ions are located. In the series $AV_2(P_2O_7)_2$, the cell parameters decrease with the size of the *A* cation, *i.e.* $Sr^{2+} > Ca^{2+} > Cd^{2+}$. The PO_4 tetrahedra in $CdV_2(P_2O_7)_2$ exhibit a geometry and interatomic distances (Table 2) similar to those observed in $SrV_2(P_2O_7)_2$.

The VO_6 octahedra are significantly more distorted (Table 2) than those in the Sr diphosphate. Indeed, one observes V—O distances ranging from 1.94 to 2.149 Å for Cd, whereas they vary from 1.95 to 2.09 Å for Sr. In the same way, the O···O distances range from 2.643 to 3.130 Å in the Cd phase compared with 2.724 to 2.914 Å in the Sr phase, and the O—V—O angles extend from 81.0 to 99° for Cd as opposed to 86.94 to 92.27° for Sr.

An interesting structural feature concerns the Cd-ion coordination which can be described as slightly distorted octahedral with six Cd···O distances

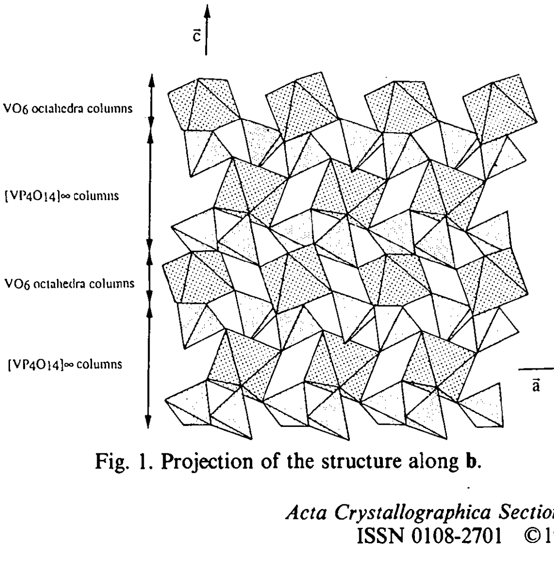

Fig. 1. Projection of the structure along **b**.

ranging from 2.307 to 2.586 Å (Table 2), compared with the octahedral coordination of Sr (Sr···O distances ranging from 2.48 to 2.76 Å). In the case of Sr, one observes four additional O atoms at distances ranging from 3.19 to 3.34 Å, forming a tetra-face-capped octahedron. In the case of Cd, these four O atoms are located at distances ranging from 3.308 to 3.399 Å, suggesting that they do not participate significantly in the coordination sphere of Cd, taking its much smaller size into consideration.

Experimental

Single crystals of this phase were extracted from a synthesis of $Cd_3V_3P_8O_{26}$ (nominal composition). The latter was prepared from a mixture of CdO, V_2O_5 and $H(NH_4)_2PO_4$, which was first heated in air at 673 K for 2 h. The resulting product (composition $Cd_3V_{1.2}P_8O_{26}$) was then added to 1.8 mol of metallic V, placed in an alumina crucible and heated in an evacuated silica ampoule at 1423 K for 48 h; the sample was then quenched. The composition of the $CdV_2(P_2O_7)_2$ crystal was confirmed by microprobe analysis.

Crystal data

$CdV_2(P_2O_7)_2$
$M_r = 562.2$
Triclinic
$P\bar{1}$
$a = 4.7833$ (6) Å
$b = 6.9698$ (8) Å
$c = 7.7644$ (8) Å
$\alpha = 89.41$ (1)°
$\beta = 87.77$ (1)°
$\gamma = 73.16$ (1)°
$V = 247.6$ (7) Å^3
$Z = 1$

$D_x = 3.770$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 18–22°$
$\mu = 4.64$ mm^{-1}
$T = 294$ K
Needle
0.103 × 0.051 × 0.051 mm
Green

Data collection

Enraf-Nonius CAD-4 diffractometer
Bisect scans [width $(1 + 0.35\tan\theta)°$]
Absorption correction: none
4275 measured reflections
4275 independent reflections
2674 observed reflections $[I > 3\sigma(I)]$

$\theta_{max} = 45°$
$h = -9 \rightarrow 9$
$k = -13 \rightarrow 13$
$l = 0 \rightarrow 15$
3 standard reflections frequency: 60 min intensity variation: −1.5%

Refinement

Refinement on F
$R = 0.021$
$wR = 0.022$
$S = 1.001$
2674 reflections
101 parameters
$w = f[\sin(\theta/\lambda)]$
$(\Delta/\sigma)_{max} < 0.004$
$\Delta\rho_{max} = 1.0$ e Å^{-3}
$\Delta\rho_{min} = -0.9$ e Å^{-3}

Extinction correction: Zachariasen (1967)
Extinction coefficient: 1.95×10^{-6}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Cd	0	0	0	1.090 (2)
V(1)	0	0	1/2	0.412 (4)
V(2)	1/2	1/2	0	0.404 (4)
P(1)	0.61504 (7)	0.78903 (5)	0.28111 (5)	0.435 (4)
P(2)	0.03341 (7)	0.38306 (5)	0.24804 (5)	0.377 (4)
O(1)	0.3861 (2)	−0.1585 (2)	0.4226 (2)	0.78 (1)
O(2)	0.1789 (2)	0.0779 (2)	0.7297 (1)	0.66 (1)
O(3)	0.0792 (3)	0.2191 (2)	0.3769 (2)	0.83 (1)
O(4)	0.3091 (2)	0.4396 (2)	0.2072 (2)	0.79 (1)
O(5)	0.4959 (2)	0.7742 (2)	0.1019 (2)	0.73 (1)
O(6)	0.8945 (2)	0.3303 (2)	0.0852 (1)	0.64 (1)
O(7)	0.8019 (3)	0.5693 (2)	0.3332 (2)	0.77 (1)

Table 2. *Distances* (Å) *and angles* (°) *in the* VO_6 *and* PO_4 *polyhedra and the main* Cd···O *distances* (Å)

The M—O distances are on the diagonal; above it are the O···O distances and below it are the O—M—O angles.

V(1)	O(1^i)	O(1)	O(2^i)	O(2)	O(3^i)	O(3)
O(1^i)	1.933 (1)	3.866 (2)	2.887 (2)	2.893 (2)	2.643 (2)	2.796 (2)
O(1)	180.00	1.933 (1)	2.893 (2)	2.887 (2)	2.796 (2)	2.643 (2)
O(2^i)	89.86 (5)	90.14 (5)	2.148 (1)	4.297 (2)	2.911 (2)	2.844 (2)
O(2)	90.14 (5)	89.86 (5)	180.00	2.148 (1)	2.844 (2)	2.911 (2)
O(3^i)	86.79 (5)	93.21 (5)	91.33 (5)	88.67 (5)	1.914 (1)	3.829 (2)
O(3)	93.21 (5)	86.79 (5)	88.67 (5)	91.33 (5)	180.00	1.914 (1)

V(2)	O(4^{ii})	O(4)	O(5^{ii})	O(5)	O(6^{ii})	O(6)
O(4^{ii})	1.922 (1)	3.843 (2)	2.831 (2)	2.818 (2)	2.809 (2)	2.804 (2)
O(4)	180.00	1.922 (1)	2.818 (2)	2.831 (2)	2.804 (2)	2.809 (2)
O(5^{ii})	90.27 (5)	89.73 (5)	2.070 (1)	4.141 (2)	3.130 (2)	2.673 (2)
O(5)	89.73 (5)	90.27 (5)	180.00	2.070 (1)	2.673 (2)	3.130 (2)
O(6^{ii})	90.09 (5)	89.91 (5)	99.00 (4)	81.00 (4)	2.046 (1)	4.091 (2)
O(6)	89.91 (5)	90.09 (5)	81.00 (4)	99.00 (4)	180.00	2.046 (1)

P(1)	O(1^{iii})	O(2^{iv})	O(5)	O(7)
O(1^{iii})	1.491 (2)	2.552 (2)	2.545 (2)	2.402 (2)
O(2^{iv})	114.95 (7)	1.536 (1)	2.512 (2)	2.529 (2)
O(5)	114.22 (7)	109.47 (7)	1.540 (1)	2.520 (2)
O(7)	102.39 (7)	107.94 (7)	107.19 (6)	1.591 (1)

P(2)	O(3)	O(4)	O(6^v)	O(7^v)
O(3)	1.485 (1)	2.477 (2)	2.497 (2)	2.444 (2)
O(4)	111.94 (7)	1.504 (1)	2.540 (2)	2.495 (2)
O(6^v)	110.90 (7)	112.69 (7)	1.547 (1)	2.501 (2)
O(7^v)	106.07 (7)	108.31 (7)	106.52 (6)	1.574 (1)

Cd···O(2^i)	2.353 (1)	Cd···O(6^v)	2.307 (1)
Cd···O(2^{vi})	2.353 (1)	Cd···O(6^{ix})	2.307 (1)
Cd···O(5^{vii})	2.586 (1)	P(1)···P(2^x)	2.962 (2)
Cd···O(5^{viii})	2.586 (1)	P(1)—O(7)—P(2^x)	138.74 (8)

Symmetry codes: (i) $-x, -y, 1-z$; (ii) $1-x, 1-y, -z$; (iii) $x, 1+y, z$; (iv) $1-x, 1-y, 1-z$; (v) $x-1, y, z$; (vi) $x, y, z-1$; (vii) $-x, 1-y, -z$; (viii) $x, y-1, z$; (ix) $1-x, -y, -z$; (x) $1+x, y, z$.

Calculations were performed using the *SDP* system (B. A. Frenz & Associates, Inc., 1982) on a MicroVAX II computer.

Lists of structure factors and anisotropic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71763 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU1063]

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Hydrazinium(1+) Hexafluorotitanate(IV), $2N_2H_5^+.TiF_6^{2-}$

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Abstract

The crystals exhibit racemic twinning. The structure consists of hydrazinium(1+), $N_2H_5^+$, cations and usual octahedral hexafluorotitanate(IV) anions. They are linked together *via* hydrogen bonds of the types N—H···F and N—H···N.

Comment

The current characterization of $2N_2H_5.TiF_6$ is one in a series of investigations of hydrazinium(1+) and hydrazinium(2+) fluorometallates. Examples of the crystal structures of $N_2H_5^+$ fluorometallates are few: $[N_2H_5][BF_4]$ and $[N_2H_5][ClO_4]$ (Conant & Roof, 1970), $[N_2H_5]_2[BeF_4]$ (Tedenac, Vilminot, Cot, Norbert & Maurin, 1971), $[N_2H_5]_3[CrF_6]$ (Kojić-Prodić, Šćavničar, Liminga & Šljukić, 1972), $Li[N_2H_5][BeF_4]$ (Anderson, Brown & Vilminot, 1973), $[N_2H_5][InF_4H_2O]$ (Bukovec & Golič, 1976), $[N_2H_5]_2[GeF_6]$ (Gantar, Golič, Leban & Rahten, 1985) and $[N_2H_5][Sn_3F_7]$ (Granier & Vilminot, 1988).

The crystal structure determination revealed two formula units in the asymmetric unit related by a pseudocentre of symmetry. Subsequently, refinement was performed for racemic twinning and Flack's absolute structure parameter x was refined to 0.50 (3) (Flack, 1983). All H atoms were located in the difference map and included in the refinement. Restraints were imposed only on the lengths of the N—H bonds. A common isotropic displacement parameter U refined to 0.043 (3) Å^2. An extended network of hydrogen bonds of the types N—H···F and N—H···N exists. The distances and angles are generally as expected.

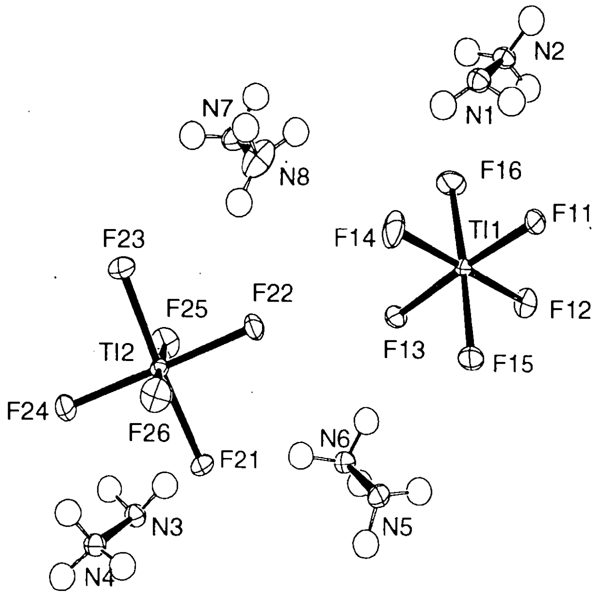

Fig. 1. *ORTEP* (Johnson, 1965) view of the asymmetric unit of the structure with atomic numbering.

Experimental

Crystals of the title compound were prepared in the Laboratory for Fluorine Chemistry at the Institute J. Stefan, Ljubljana.

Crystal data

$2(N_2H_5)[TiF_6]$
M_r = 228.02
Monoclinic
$P2_1$
a = 7.815 (1) Å
b = 10.019 (1) Å
c = 9.338 (1) Å
β = 93.58 (1)°
V = 729.72 (14) Å^3
Z = 4
D_x = 2.076 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 10–15°
μ = 1.235 mm^{-1}
T = 293 (2) K
Transparent prisms
0.42 × 0.26 × 0.18 mm
Colourless

Data collection

Enraf-Nonius CAD-4 diffractometer
Variable rate $\omega/2\theta$ scans
Absorption correction: none
4505 measured reflections
4228 independent reflections
3212 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int}$ = 0.0188

$\theta_{\rm max}$ = 30.00°
$h = 0 \rightarrow 10$
$k = -14 \rightarrow 14$
$l = -13 \rightarrow 13$
3 standard reflections monitored every 500 reflections
frequency: 40 min
intensity variation: 3.2%