Acta Cryst. (1977). B**33**, 95–98

The Crystal Structure of Cadmium Potassium Orthovanadate, $KCd_4(VO_4)_3$

By E. Holt,* S. Drai, R. Olazcuaga and M. Vlasse

Laboratoire de Chimie du Solide du CNRS, Université de Bordeaux I, 351 *cours de la Libération,* 33405 *Talence, France*

(*Received* 5 *June* 1976; *accepted* 9 *July* 1976)

The structure of $KCd_4(VO_4)_3$ has been determined from Patterson and Fourier syntheses and refined by full-matrix least squares with 1130 diffractometer data to $R = 0{\cdot}061$. The space group is Cc with $a = 12{\cdot}89\ (1)$, $b = 13{\cdot}37\ (1)$, $c = 7{\cdot}092\ (5)$ Å, $\beta = 114{\cdot}84\ (5)°$, $Z = 4$. The structure is a three-dimensional framework based on a $Cd_2(VO_4)_3^{5-}$ unit. This framework leaves voids in which the K and remaining Cd atoms are inserted.

Introduction

The need for materials having attractive optical properties led to the study of a number of structures in which optically active ions can be introduced. For this reason several orthovanadates have been studied in recent years at this laboratory (Le Flem, Olazcuaga & Hagenmuller, 1967; Le Flem & Olazcuaga, 1968; Drai, Olazcuaga & Le Flem, 1974; Vlasse, Salmon & Parent, 1976; Salmon, Parent, Le Flem & Vlasse, 1976). The study of the system K_2O—CdO—V_2O_5 has produced two new phases $KCdVO_4$ and $KCd_4(VO_4)_3$. Both compounds crystallize with unknown structures. In order to further elucidate the crystal chemistry of these orthovanadates and to make easier the investigation of the optical properties of these host structures we decided to carry out a detailed crystallographic determination of the structure of $KCd_4(VO_4)_3$.

Experimental

Specimen preparation

$KCd_4(VO_4)_3$ was prepared by reacting a stoichiometric mixture of KVO_3, CdO and V_2O_5 in a sealed gold tube heated at 700 °C for 24 h.

Single crystals were prepared by heating to 950 °C a considerable amount of the powder sample with an excess of CdO in a gold boat sealed in a vicor tube and then cooling slowly, first at 40 °C h^{-1} down to 800 °C and then at 100 °C h^{-1} to 600 °C.

Yellow transparent single crystals were obtained. The powder diffraction spectrum of the single crystals was found to be identical to that of the powder sample.

Single-crystal diffraction data

The zero- and upper-layer Weissenberg and precession photographs indicate Laue symmetry $2/m$. The systematic extinctions (hkl: $h + k = 2n + 1$, $h0l$: $l = 2n + 1$) are consistent with $C2/c$ or Cc. The cell dimensions obtained and refined from powder diffraction data are $a = 12{\cdot}89\ (1)$, $b = 13{\cdot}37\ (1)$, $c = 7{\cdot}092\ (5)$ Å, $\beta = 114{\cdot}84\ (5)°$, where the reported errors represent the standard deviations. The cell contains four formula units [$d_x = 4{\cdot}93\ (3)$, $d_c = 4{\cdot}95$ g cm^{-3}].

A single crystal in the form of a parallelepiped $0{\cdot}05 \times 0{\cdot}05 \times 0{\cdot}08$ mm was mounted about **b**. The intensities were collected on an Enraf–Nonius CD-3 three-circle automatic diffractometer with Mo $K\alpha$ radiation ($\lambda = 0{\cdot}70942$ Å), a pyrolytic graphite monochromator (002), and a 4° take-off angle. A scintillation counter and a θ–2θ multiple scanning technique with a scan rate of 10° (2θ) min^{-1} were used. The background was taken at each end of the scanned range for a time equal to the actual scan time. Three control reflexions measured for every batch of 50 reflexions showed a random fluctuation of about 3%. 1250 independent reflexions were measured up to $2\theta_{\max} = 60°$; of these, 1130 had $I > 2\sigma(I)$, where $\sigma(I) = (\text{total counts} + \text{background counts})^{1/2}$, and were considered to be observed. These intensities were corrected for Lorentz and polarization effects, but not for absorption. For λ(Mo $K\alpha$) $\mu = 111$ cm^{-1} and $\mu r_{\max} = 0{\cdot}44$.

Determination and refinement of the structure

A Patterson synthesis was used to determine the positions of the heavy atoms from the Cd—Cd vectors based on the space group Cc. The one K, three V and twelve O atoms were located in a difference synthesis at an intermediate stage of the refinement. Full-matrix least-squares refinement (Busing, Martin & Levy, 1962) with anisotropic temperature factors reduced

---

* On leave from the University of Wyoming, Laramie, Wyoming, USA.

$R(=\Sigma|F_o| - |F_c|/\Sigma|F_o|)$ to 0·061, based on a data to parameter ratio of 10 with 107 independent parameters. A final $(F_o - F_c)$ synthesis confirmed the proposed solution and the assumed space group *Cc*.

The function $\Sigma\, w(|F_o| - |F_c|)^2$ was minimized with w taken as unity for all reflexions. An overall scale factor was used with a final value of 2·27 $(F_o = kF_c)$. The form factors for K^+, Cd^{2+}, V^{5+} and O^{2-} were taken from the tables of McMaster, Kerr del Grande, Mallet & Hubbel (1969), with real and imaginary anomalous dispersion terms given by Cromer (1965).

The final atomic and thermal parameters are given in Table 1. Table 2 contains the interatomic distances.

A table giving the calculated and observed structure amplitudes may be obtained on request from the last author.*

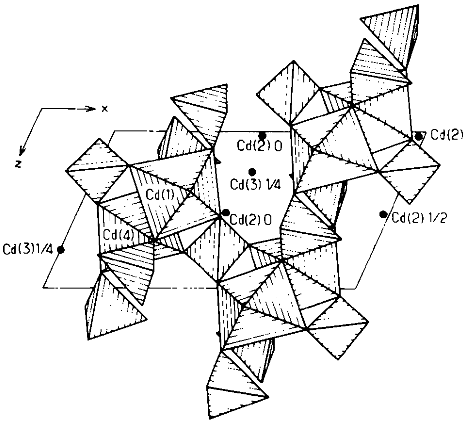


Fig. 1. Projection of a sheet of the $KCd_4(VO_4)_3$ structure on the (010) plane.

Results and discussion

Projections of a fragment of the structure on the (010) and the (001) planes are given in Figs. 1 and 2. The structure can be described as distorted scheelite-type, but with a significant rearrangement of the VO_4 tetrahedra to accommodate the extra inserted cations. The unit-cell relation between scheelite ($CaWO_4$) and $KCd_4(VO_4)_3$ is shown in Fig. 3. Scheelite has a tetragonal cell with $a_s = 5·24$, $c_s = 11·37$ Å, and its structure is made up of distorted WO_4 tetrahedra con-

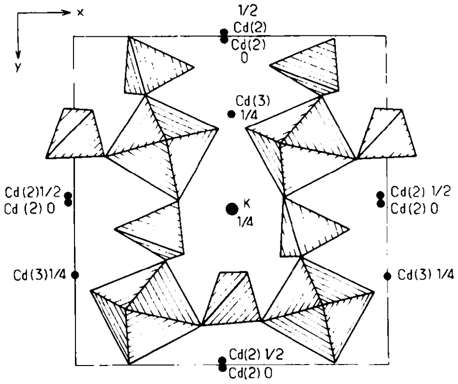


Fig. 2. Projection of a fragment of the $KCd_4(VO_4)_3$ structure on the (001) plane.

Table 1. *Atomic coordinates* $(\times 10^4$; *for* O $\times 10^3)$ *and isotropic and anisotropic temperature factors for* $KCd_4(VO_4)_3$ *with standard deviations in parentheses*

The anisotropic temperature factor T is given by: $\exp[-10^{-5}(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

	x	y	z	B (Å²)	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
K	18 (8)	311 (5)	2511 (10)	1·19 (7)	175 (37)	346 (35)	131 (50)	−20 (10)	25 (16)	28 (33)
Cd(1)	2781	3405 (3)	3524	0·92 (7)	234 (25)	120 (20)	255 (68)	18 (8)	75 (36)	44 (14)
Cd(2)	4793 (4)	36 (3)	232 (7)	2·11 (7)	590 (28)	191 (13)	972 (69)	29 (9)	28 (14)	77 (26)
Cd(3)	10 (5)	7328 (1)	2529 (9)	1·08 (4)	236 (13)	138 (9)	722 (42)	50 (23)	203 (19)	−60 (20)
Cd(4)	7211 (2)	6592 (3)	6483 (4)	0·86 (7)	209 (26)	147 (21)	605 (81)	−14 (8)	199 (41)	15 (8)
V(1)	2363 (8)	1103 (7)	1389 (10)	0·35 (6)	41 (25)	76 (43)	92 (37)	36 (11)	29 (8)	−43 (30)
V(2)	76 (9)	2959 (4)	2470 (9)	0·43 (8)	12 (8)	80 (19)	249 (95)	26 (17)	68 (21)	53 (33)
V(3)	7688 (9)	8909 (7)	8706 (8)	0·70 (8)	311 (58)	13 (26)	376 (90)	−37 (20)	86 (44)	45 (33)

	x	y	z	B (Å²)		x	y	z	B (Å²)
O(1)	53 (2)	223 (2)	475 (4)	0·87 (10)	O(7)	964 (2)	778 (2)	544 (4)	0·81 (10)
O(2)	96 (4)	369 (3)	222 (6)	2·39 (12)	O(8)	902 (2)	619 (2)	766 (4)	0·48 (9)
O(3)	169 (3)	−3 (4)	118 (5)	1·94 (12)	O(9)	828 (2)	−4 (3)	876 (4)	0·63 (10)
O(4)	384 (2)	92 (2)	197 (4)	0·69 (10)	O(10)	624 (3)	904 (3)	783 (6)	2·39 (14)
O(5)	224 (2)	176 (2)	333 (4)	0·63 (10)	O(11)	792 (2)	820 (2)	694 (4)	1·26 (12)
O(6)	161 (3)	174 (3)	−95 (6)	1·71 (13)	O(12)	844 (2)	833 (2)	106 (4)	0·42 (9)

---

* A list of structure factors has also been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32037 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Interatomic distances* (Å) *for* $KCd_4(VO_4)_3$ *with standard deviations in parentheses*

K–O(1a)	2·945 (8)	Cd(1)–O(2a)	2·150 (5)	Cd(2)–O(2j)	2·372 (5)
K–O(3c)	2·586 (9)	Cd(1)–O(5a)	2·295 (3)	Cd(2)–O(4a)	2·400 (3)
K–O(3i)	2·733 (9)	Cd(1)–O(7b)	2·337 (3)	Cd(2)–O(4r)	2·457 (3)
K–O(7p)	2·880 (8)	Cd(1)–O(9d)	2·260 (3)	Cd(2)–O(8n)	2·267 (3)
K–O(9l)	2·673 (8)	Cd(1)–O(11b)	2·362 (3)	Cd(2)–O(8s)	2·853 (3)
K–O(9p)	2·762 (8)	Cd(1)–O(12b)	2·252 (3)	Cd(2)–O(10c)	2·328 (4)
⟨K–O⟩	2·763 (8)	⟨Cd(1)–O⟩	2·276 (3)	⟨Cd(2)–O⟩	2·446 (3)
	Cd(3)–O(1g)	2·410 (3)	Cd(4)–O(1b)	2·154 (3)	
	Cd(3)–O(4m)	2·337 (3)	Cd(4)–O(3d)	2·174 (5)	
	Cd(3)–O(6c)	2·244 (4)	Cd(4)–O(5b)	2·267 (3)	
	Cd(3)–O(7k)	2·389 (3)	Cd(4)–O(6b)	2·272 (4)	
	Cd(3)–O(10d)	2·374 (4)	Cd(4)–O(8a)	2·177 (3)	
	Cd(3)–O(12k)	2·267 (3)	Cd(4)–O(11a)	2·303 (3)	
	⟨Cd(3)–O⟩	2·337 (3)	⟨Cd(4)–O⟩	2·224 (3)	
V(1)–O(3i)	1·727 (5)	V(2)–O(1a)	1·755 (3)	V(3)–O(9a)	1·598 (4)
V(1)–O(4a)	1·776 (3)	V(2)–O(2a)	1·576 (5)	V(3)–O(10a)	1·699 (4)
V(1)–O(5a)	1·692 (3)	V(2)–O(7p)	1·630 (3)	V(3)–O(11a)	1·703 (3)
V(1)–O(6h)	1·741 (4)	V(2)–O(8p)	1·818 (3)	V(3)–O(12e)	1·677 (3)
⟨V(1)–O⟩	1·734 (3)	⟨V(2)–O⟩	1·695 (3)	⟨V(3)–O⟩	1·677 (3)
O(1)–O(2a)	2·869 (5)	O(3)–O(5f)	2·759 (5)	O(7)–O(11a)	2·892 (5)
O(1)–O(5a)	2·872 (4)	O(3)–O(6g)	2·798 (6)	O(7)–O(12a)	2·900 (4)
O(1)–O(6a)	2·823 (5)	O(4)–O(5a)	2·847 (4)	O(8)–O(11a)	2·970 (4)
O(1)–O(7p)	2·761 (4)	O(4)–O(6h)	2·927 (5)	O(9)–O(10a)	2·714 (5)
O(1)–O(8p)	2·808 (4)	O(4)–O(8s)	2·863 (4)	O(9)–O(11a)	2·632 (5)
O(1)–O(11b)	3·073 (5)	O(4)–O(10c)	2·889 (5)	O(9)–O(12e)	2·679 (5)
O(2)–O(5a)	2·988 (5)	O(5)–O(6h)	2·779 (5)	O(9)–O(12o)	3·036 (5)
O(2)–O(7p)	2·552 (5)	O(5)–O(8b)	3·026 (4)	O(10)–O(11a)	2·753 (5)
O(2)–O(8p)	2·656 (5)	O(5)–O(11b)	3·014 (5)	O(10)–O(12e)	2·925 (5)
O(2)–O(10p)	3·054 (6)	O(7)–O(8a)	2·947 (4)	O(11)–O(12e)	2·710 (4)
O(3)–O(4f)	2·878 (5)	⟨O–O⟩	2·851 (4)		

Symmetry code

(a) x, y, z;
(b) $x+\frac{1}{2}, y+\frac{1}{2}, z$;
(c) $x, \bar{y}, z+\frac{1}{2}$;
(d) $x+\frac{1}{2}, y-\frac{1}{2}, z+\frac{1}{2}$;
(e) $x, y, z+1$;
(f) $x, y+1, z$;
(g) $x, y+1, z-1$;
(h) $x, y, z+1$;
(i) x, y, z;
(j) $x+\frac{1}{2}, y-\frac{1}{2}, z$;
(k) $x-1, y, z$;
(l) $x-1, y-1, z-1$;
(m) $x-\frac{1}{2}, y+\frac{1}{2}, z$;
(n) $x-\frac{1}{2}, y-\frac{1}{2}, z-1$;
(o) $x, y+1, z+1$;
(p) $x-1, \bar{y}, z-\frac{1}{2}$
(q) $x, 1-y, z-\frac{1}{2}$
(r) $x, \bar{y}, z-\frac{1}{2}$
(s) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$

nected by Ca^{2+} ions. Tetrahedra and Ca atoms alternate along **c** forming infinite chains. The Ca atoms are found in a distorted cubic coordination and their arrangement is shown in Fig. 3.

The unit-cell dimensions of $KCd_4(VO_4)_3$ can be derived in the following manner: $\mathbf{a} = -\mathbf{a}_s + 2\mathbf{b}_s$, $\mathbf{b} = \mathbf{c}_s$, $\mathbf{c} = -\mathbf{a}_s - \mathbf{b}_s$ and $V = 3V_s$. The scheelite unit cell taken in this orientation will have $a = 11{\cdot}72$, $b = 11{\cdot}37$, $c = 7{\cdot}41$ Å, $\beta = 109{\cdot}44°$, very close to the dimensions found for $KCd_4(VO_4)_3$. According to the volume relation the formula unit $Ca_3(WO_4)_3$ should correspond then to the unit $KCd_4(VO_4)_3$. In the distorted scheelite-like structure of $KCd_4(VO_4)_3$ the VO_4 tetrahedra should therefore replace the WO_4 tetrahedra and three of the cations should take the place of the Ca^{2+}. The remaining two cations act as inserted atoms.

The introduction of these two supplementary cations in the scheelite lattice of $KCd_4(VO_4)_3$ produces substantial distortions from the ideal scheelite structure and necessitates the clustering of a number of poly-

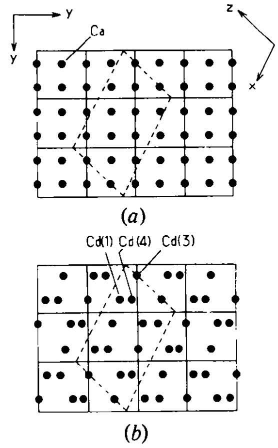
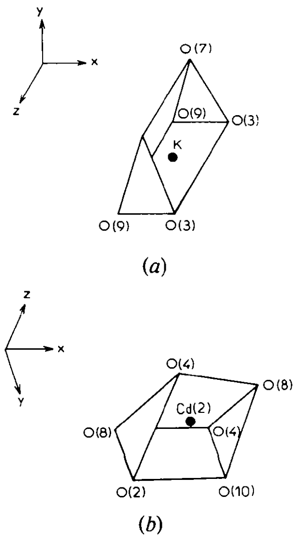


Fig. 3. Unit-cell relation between scheelite (solid lines) and $KCd_4(VO_4)_3$ (dotted lines): (a) projection of the Ca atoms on the (001) plane of $CaWO_4$, (b) projection of the Cd(1), Cd(3) and Cd(4) atoms on the (010) plane of $KCd_4(VO_4)_3$.

hedra. As can be seen in Fig. 1 the structure is a three-dimensional framework based on a polyhedral cluster $M_2(VO_4)_3$, where M represents the cations Cd(1) and Cd(4) in the two edge-sharing octahedra, and VO_4 the tetrahedra joined to these octahedra by common corners. These $M_2(VO_4)_3$ clusters are joined together in the [101] direction to form sheets parallel to the (010) plane. These sheets are in turn joined along the [010] direction to form a three-dimensional framework. This framework leaves a number of voids grouped together in the (200) plane as seen in Figs. 1 and 2. These voids accommodate the cations Cd(2), Cd(3) and K, giving the formulation $KCd_2[Cd_2(VO_4)_3]$. Cd(3) is found in a slightly distorted octahedral site, while Cd(2) and K occupy trigonal prismatic sites (Fig. 4).

A comparison of this structure with the ideal scheelite structure (Fig. 3) indicates that in fact Cd(1), Cd(3) and Cd(4) do replace the Ca atoms in scheelite, while Cd(2) and K are the two extra inserted atoms. This can be explained by the similarity of the ionic radii of Cd and Ca [$r(\mathrm{VI})_{\mathrm{Ca}} = 1{\cdot}00$, $r(\mathrm{IV})_{\mathrm{Cd}} = 0{\cdot}95$ Å] (Shannon & Prewitt, 1969). The polyhedra cluster $M_2(VO_4)_3$ is a rather strongly bound unit and may be found in a framework without any inserted ions, *cf.* $Eu_2(WO_4)_3$ also with a scheelite-like structure (Templeton & Zalkin, 1963).

The average V—O distances of 1·734, 1·695 and 1·677 Å found in the three V(1), V(2) and V(3) tetrahedra, respectively, are comparable to those found in $Na_3La(VO_4)_2$ (Vlasse, Salmon & Parent, 1976) ($\langle$V—O$\rangle$ = 1·673 to 1·726 Å).



(*a*)

(*b*)

Fig. 4. Coordination polyhedra (*a*) for K and (*b*) for Cd(2).

There are two types of average Cd—O distances: two short for Cd(1) and Cd(4), 2·276 and 2·224 Å, found in the polyhedral cluster $Cd_2(VO_4)_3^{5-}$, indicating a possible covalent character in the Cd—O bonds; and two longer for Cd(2) and Cd(3), 2·337 and 2·446 Å, found in the voids of the $[Cd_2(VO_4)_3^{5-}]_\infty$ framework. The $\langle$Cd(1)—O$\rangle$ and $\langle$Cd(4)—O$\rangle$ distances compare well with those found in $CdBa(PO_3)_4$ for Cd in a similar octahedral coordination and range from 2·245 to 2·321 Å (Averbuch-Pouchot, Durif & Guitel, 1975). The Cd—Cd distances range from 3·424 to 3·847 Å.

All O—O distances are normal with an average of 2·851 Å. The minimum, maximum and average O—V—O tetrahedral angles are 102·52, 118·94 and 109·43° respectively.

The framework character of this structure can be compared to the different types of structures found in the system $Na_{1+x}Zr_2P_{3-x}Si_xO_{12}$ (Goodenough, Hong & Kafalas, 1976), in which the Na ions are inserted in a similar framework of formula $(Zr_2P_{3-x}Si_xO_{12})^{(1+x)n}$, and are found to be good ionic conductors. This comparison suggests identical properties for $KCd_4(VO_4)_3$ which are presently under study.

References

Averbuch-Pouchot, M. T., Durif, A. & Guitel, J. C. (1975). *Acta Cryst.* **B31**, 2453–2456.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Oak Ridge National Laboratory Report ORNL-TM-305.

Cromer, D. T. (1965). *Acta Cryst.* **18**, 17–23.

Drai, S., Olazcuaga, R. & Le Flem, G. (1974). *J. Solid State Chem.* **10**, 95–101.

Goodenough, J. B., Hong, H. Y.-P. & Kafalas, A. (1976). *Mater. Res. Bull.* **11**, 203–220.

Le Flem, G. & Olazcuaga, R. (1968). *Bull. Soc. Chim. Fr.* pp. 2769–2780.

Le Flem, G., Olazcuaga, R. & Hagenmuller, P. (1967). *C.R. Acad. Sci. Paris, Sér. C*, **264**, 2138–2140.

McMaster, W. H., Kerr del Grande, N., Mallet, J. H. & Hubbel, J. H. (1969). *Compilation of X-ray Cross Sections*, Natl. Bur. Stand. UCRL-50174, Sec. II, Rev. I.

Salmon, R., Parent, C., Le Flem, G. & Vlasse, M. (1976). *Acta Cryst.* **B32**, 2799–2802.

Shannon, R. D. & Prewitt, C. T. (1969). *Acta Cryst.* **B25**, 925–946.

Templeton, D. H. & Zalkin, A. (1963). *Acta Cryst.* **16**, 762–766.

Vlasse, M., Salmon, R. & Parent, C. (1976). *Inorg. Chem.* **15**, 1440–1444.