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A New Vanadium III Potassium Phosphate with a Cage Structure: $K_6V_2P_4O_{16}$

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A new vanadium III phosphate, $K_6V_2P_4O_{16}$, with a cage structure has been isolated. Its structure was solved by single crystal X-ray diffraction. It crystallizes in the monoclinic system with the space group $P2_1/c$. The cell parameters are $a = 9.578(1)$ Å, $b = 11.097(1)$ Å, $c = 18.127(2)$ Å, and $\beta = 121.67°(1)$. The $[V_2P_4O_{16}]_\infty$ host lattice is rather complex and very original. It consists of corner and edge-sharing PO_4 tetrahedral and VO_6 octahedra. This ability of the PO_4 tetrahedron to share one edge with an octahedron has been observed in other M(III) compounds: α $CrPO_4$ and $NaV_3P_3O_{12}$. The small number of links between the $[V_2P_4O_{18}]_\infty$ chains makes the $[V_2P_4O_{16}]_\infty$ framework very flexible, so that its cohesion is in fact ensured by a great number of K^+ ions. © 1991 Academic Press, Inc.

Introduction

The different studies of the V–P–O system have shown the extraordinary ability of VO_6 octahedra and PO_4 tetrahedra to form mixed frameworks whatever the oxidation state of vanadium may be. One indeed observes five different forms for the pentavalent vanadium phosphate VPO_5 (*1–5*), two tetravalent vanadium phosphates VP_2O_7 (*6*) and $V_2P_2O_9$ (*7, 8*) and two trivalent vanadium phosphates VPO_4 (*9*) and VP_3O_9 (*6*). Mixed valent vanadium phosphates $V_3P_4O_{15}$ (*10*) and $V_{12}P_3O_{34}$ (*11*) have also been isolated. This suggests that it should be possible to create new tunnel or cage or layered structures in which the mixed framework of VO_6 octahedra and PO_4 tetrahedra would allow large cations such as potassium to be interpolated. A limited number of investigations with V(IV) and V(III) compounds have been performed in the K–V–P–O system. Only one tetravalent vanadium phosphate $K_2V_3P_4O_{17}$ (*12*) and one trivalent phosphate KVP_2O_7 (*13*) were known until now. We report here on the crystal structure of a new vanadium(III) phosphate $K_6V_2P_4O_{16}$ characterized by a high potassium content.

Synthesis

Single crystals of the phase $K_6V_2P_4O_{16}$ have been isolated from samples of nominal composition "$K_5V_4P_3O_{15}$." The preparation was performed in two steps. First K_2CO_3, $H(NH_4)_2PO_4$, and V_2O_5 were heated up to 673 K in air in order to eliminate CO_2, H_2O, and NH_3. In the second step the finely ground product was mixed with an appropriate amount of vanadium and sealed in an evacuated silica ampoule. This sample was then heated up at 972 K for about a week.

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TABLE I

SUMMARY OF CRYSTAL DATA, INTENSITY MEASUREMENTS AND STRUCTURE REFINEMENT PARAMETERS FOR $K_6V_2P_4O_{16}$

1. Crystal data	
Space group	$P2_1/c$
Cell dimensions	$a = 9.578(1)$ Å
	$b = 11.097(1)$ $\beta = 121.67°$ (1)
	$c = 18.127(2)$
Volume	$V = 1640(9)$ Å^3
z	4
2. Intensity measurement	
λ (Mo$K\alpha$)	0.71073 Å
Scan mode	$\omega - 2/3\ \theta$
Scan width (°)	$0.9 + 0.35 \tan\theta$
Slit aperture (mm)	$1. + \tan\theta$
Max θ (°)	45
Standard reflections	3 measured every 2000s (no decay)
Reflections with $I > 3\sigma$	1229
3. Structure solution and refinement	
Parameters refined	173
Agreement factors	$R = 0.041$, $R_w = 0.045$
Weighting scheme	$W = f(\sin\theta/\lambda)$
$\Delta/\sigma_{\max}$	0.005

Under this condition, from the mixture one could isolate green crystals, the composition of which deduced from the structural determination $K_6V_2P_4O_{16}$ was confirmed by microprobe analysis. Subsequent attempts to prepare a pure phase were unsuccessful; it was always obtained as a mixture with other compounds.

Structure Determination

A green crystal with dimensions 0.072 × 0.072 × 0.036 mm was selected for the structure determination. The cell parameters reported in Table I were determined and refined by diffractometric techniques at 294 K with a least squares refinement based upon 25 reflections with $18 < \theta < 22°$. The data were collected on a CAD-4 Enraf–Non-

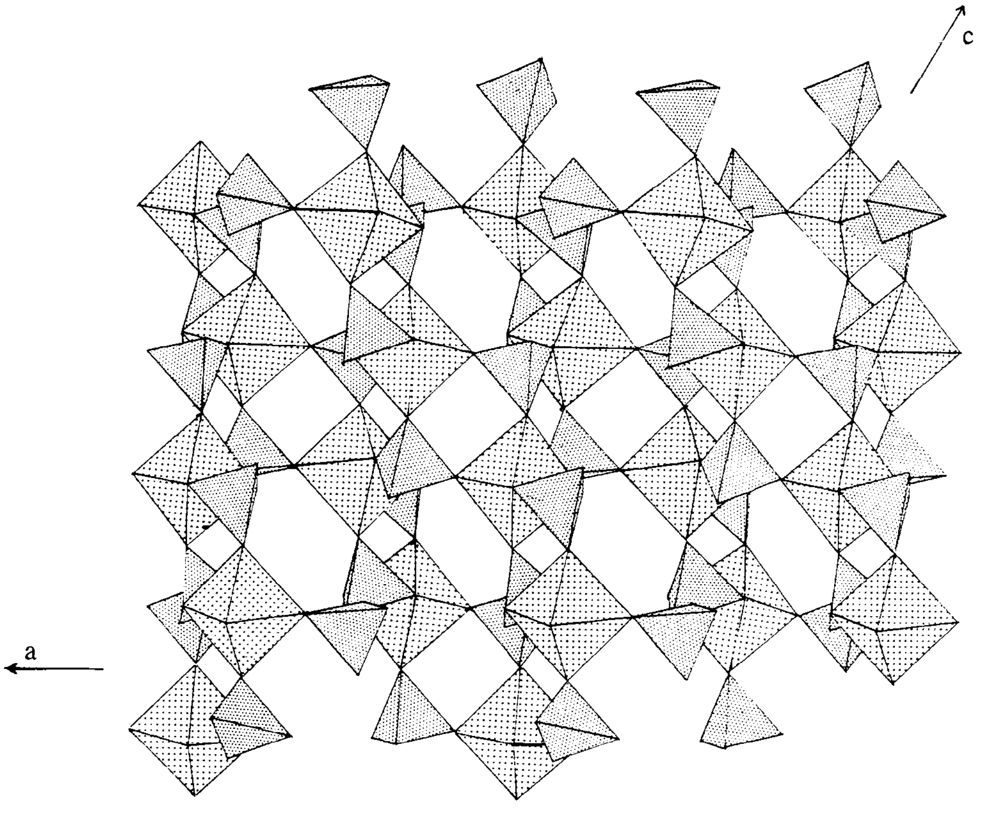

FIG. 1. Projection of the structure onto the 010 plane.

TABLE II

Positional Parameters and Their Estimated Standard Deviations

Atom	x	y	z	B(Å^2)
V(1)	0.5541(2)	0.1308(2)	0.1316(1)	0.46(3)
V(2)	0.0394(2)	0.6560(2)	0.6140(1)	0.34(3)
K(1)	0.2896(3)	0.1185(3)	0.4940(2)	1.27(5)
K(2)	0.7416(3)	0.1006(3)	0.0015(2)	1.12(5)
K(3)	0.4336(4)	0.0766(3)	0.3178(2)	1.86(6)
K(4)	0.4466(3)	0.3612(3)	0.2596(2)	1.66(6)
K(5)	0.0409(3)	0.0973(3)	0.2468(2)	1.39(6)
K(6)	0.9808(3)	0.3812(3)	0.0800(2)	1.62(6)
P(1)	0.2107(3)	0.8617(3)	0.6464(2)	0.52(5)
P(2)	0.3272(3)	0.3613(3)	0.4080(2)	0.49(5)
P(3)	0.1770(3)	0.1234(3)	0.1000(2)	0.38(5)
P(4)	0.7215(4)	0.3362(3)	0.1644(2)	0.57(6)
O(1)	0.446(1)	0.1538(9)	0.0069(5)	1.6(2)★
O(2)	0.5437(9)	0.3142(8)	0.1467(5)	0.7(1)★
O(3)	0.3462(9)	0.0730(9)	0.1217(5)	1.2(2)★
O(4)	0.6549(9)	0.1071(9)	0.2594(5)	1.3(2)★
O(5)	0.7658(9)	0.2092(8)	0.1477(5)	0.9(1)★
O(6)	0.603(1)	−0.0419(8)	0.1238(5)	1.1(2)★
O(7)	0.1668(9)	0.6244(9)	0.7417(5)	1.3(1)★
O(8)	0.0399(9)	0.8452(8)	0.6342(5)	1.1(1)★
O(9)	−0.088(1)	0.6940(9)	0.4877(5)	1.1(2)★
O(10)	0.0699(9)	0.4851(8)	0.5927(5)	0.8(1)★
O(11)	−0.1591(9)	0.5976(8)	0.6104(5)	1.0(2)★
O(12)	0.2437(9)	0.7337(8)	0.6223(5)	0.8(1)★
O(13)	0.216(1)	0.9594(9)	0.5879(5)	1.3(2)★
O(14)	0.3178(9)	0.2440(9)	0.3655(5)	1.2(2)★
O(15)	0.1968(9)	0.2086(8)	0.1704(5)	0.8(1)★
O(16)	0.722(1)	0.4353(9)	0.1051(5)	1.4(2)★

Note. Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $B = (4/3) \sum_i \sum_j \beta ij \cdot \vec{di} \cdot \vec{aj}$.

ius diffractometer with the data collection parameters reported in Table I. The reflections were corrected for Lorentz and polarization effects; no absorption corrections were performed. The atoms were located by the heavy atom method. The small number of reflections (1229) did not allow the anisotropic thermal factors to be refined for all the atoms. Anisotropic factors were only attributed to V, K, and P atoms whereas the O atoms were refined with isotropic thermal factors. The atomic parameters of Table II were obtained for $R = 0.041$ and $R_w = 0.045$.

Description of the Structure and Discussion

The $[V_2P_4O_{16}]_\infty$ host lattice is rather complex and very original. It consists of corner and edge-sharing PO_4 tetrahedra and VO_6 octahedra as shown from the projection of the structure onto the (010) plane (Fig. 1). The original feature of this structure deals with the existence of binuclear $[VPO_8]$ units (Fig. 2a) built up from one PO_4 tetrahedron (P(1) or P(4)) sharing one edge with one VO_6 octahedron (V(2) or V(1)); such units can be considered as clusters since they are characterized by very short P–V distances of 2.669 and 2.690 Å. This ability of PO_4 tetrahedra to share one edge with an octahedron has already been observed in other *M*(III) compounds, α $CrPO_4$ *(14)* and $NaV_3P_3O_{12}$ *(15)*. Along [201], two [VPO_8] units share the corners of their polyhedra in such a way that one P(1) (or P(4)) tetrahedron is linked to one V(1) (or V(2)) octahedron, leading to [$V_2P_2O_{14}$] units (Fig. 2b). These latter units are connected along [201] through single PO_4 tetahedra (P(2) and P(3)) forming $[V_2P_4O_{18}]_\infty$ chains (Fig. 2c). It is worth pointing out that two P(1) and P(3) tetrahedra and two V(1) and V(2) octahedra form four-sided rings similar to those observed in several other phosphates involving MO_6 octahedra.

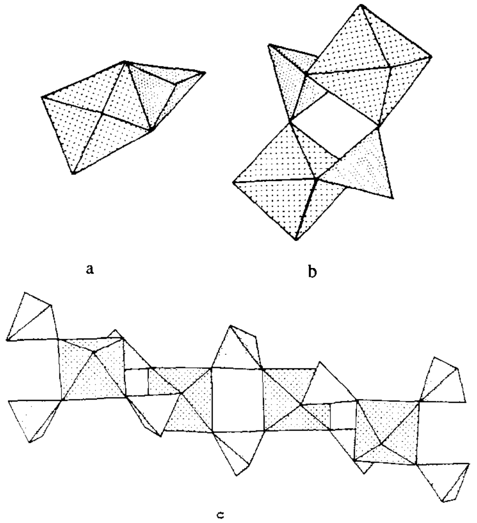

FIG. 2. (a) Binuclear [VPO_8] units. (b) The $V_2P_2O_{14}$ units. (c) $[V_2P_4O_{18}]_\infty$ chains.

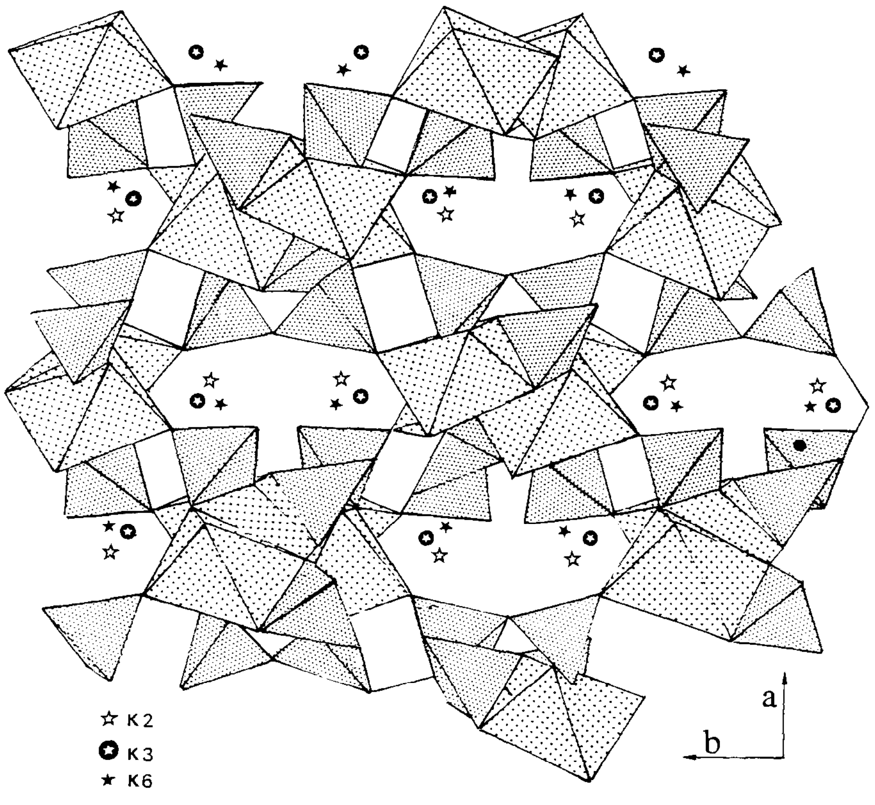

FIG. 3. Projection of the structure along [201] showing that two successive $[V_2P_4O_{18}]_\infty$ chains located at the same level in the 010 plane are not connected. The connections are observed in the $\bar{1}12$ or $11\bar{2}$ plane.

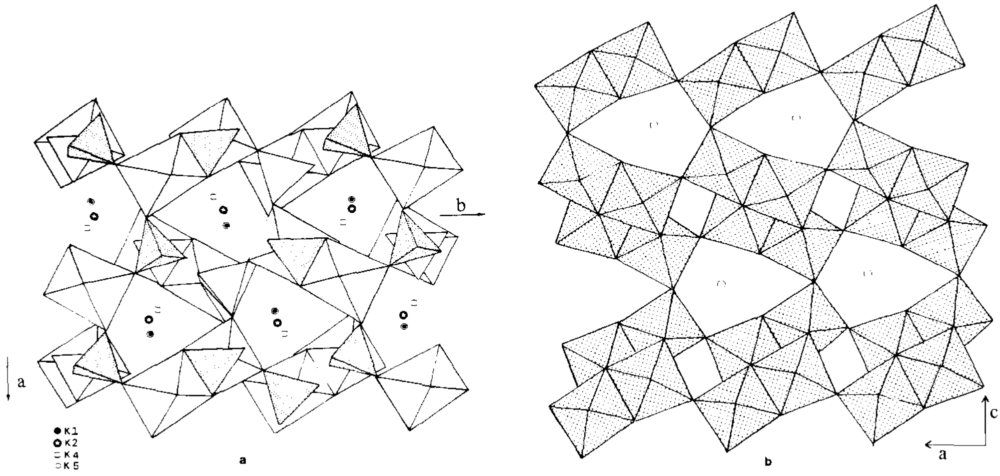

FIG. 4. (a) Projection of the structure along 101 direction; (b) projection of KTi_3NbO_9 along **b**.

The $[V_2P_4O_{16}]_\infty$ framework can then be described by the association of those $[V_2P_4O_{18}]_\infty$ chains through the corners of their polyhedra. However, it is remarkable that the number of connections is limited compared to many three-dimensional frameworks. Two successive $[V_2P_4O_{18}]_\infty$ chains located at the same level in the (010) plane are not connected (Fig. 3). Consequently each of the PO_4 tetrahedra (P(1), P(2), P(3), and P(4)) exhibits one free apex. In fact the connection between the different chains takes place between the P(2) (or P(3)) tetrahedra of one chain and the (V(1) (or V(2)) octahedra of the next chain in the (11$\bar{2}$) plane (Fig. 3). Similar connections are also observed between the successive chains in the ($\bar{1}$12) plane. This smaller num-

TABLE III

DISTANCES (Å) AND ANGLES (°) IN THE VO_6 OCTAHEDRA

V(1)	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)
O(1)	1.95(1)	2.83(1)	2.86(1)	3.95(1)	2.84(1)	2.85(1)
O(2)	89.5(4)	2.06(1)	3.17(1)	2.88(1)	2.42(1)	4.04(1)
O(3)	92.4(4)	102.4(4)	2.01(1)	2.71(1)	4.08(1)	2.75(1)
O(4)	177.5(5)	90.3(4)	85.3(4)	2.00(1)	2.96(1)	2.78(1)
O(5)	89.3(3)	71.3(4)	173.5(4)	93.0(4)	2.08(1)	3.11(1)
O(6)	92.4(4)	170.4(4)	86.9(4)	88.1(4)	99.3(4)	2.00(1)

V(2)	O(7)	O(8)	O(9)	O(10)	O(11)	O(12)
O(7)	2.00(1)	2.96(1)	3.99(1)	2.81(1)	2.77(1)	2.89(1)
O(8)	91.5(4)	2.13(1)	2.82(1)	4.10(1)	3.24(1)	2.41(1)
O(9)	177.7(5)	86.2(4)	1.99(1)	2.87(1)	2.85(1)	2.84(1)
O(10)	89.8(4)	170.6(4)	92.4(4)	1.98(1)	2.68(1)	3.12(1)
O(11)	88.3(4)	104.0(4)	91.9(4)	85.3(4)	1.98(1)	4.04(1)
O(12)	90.6(4)	70.1(1)	88.9(4)	100.6(4)	174.0(4)	2.07(1)

Note. The V–O(i) distances are on the diagonal, above it are the O(*i*)–O(*j*) distances and under it are the O(*i*)–V–O(*j*) angles.

TABLE IV

DISTANCES (Å) AND ANGLES (°) IN THE PO_4 TETRAHEDRA

P(1)	O(4^{i})	O(8)	O(12)	O(13)
O(4^{i})	1.54(1)	2.57(1)	2.55(1)	2.47(1)
O(8)	112.9(5)	1.54(1)	2.41(1)	2.57(1)
O(12)	109.9(5)	101.9(5)	1.57(1)	2.56(1)
O(13)	107.1(6)	113.6(6)	111.4(6)	1.53(1)

P(2)	O(1^{ii})	O(6^{iii})	O(11^{iv})	O(14)
O(1^{ii})	1.54(1)	2.48(1)	2.52(1)	2.46(1)
O(6^{iii})	108.0(6)	1.53(1)	2.49(1)	2.47(1)
O(11^{iv})	109.7(6)	109.0(5)	1.53(1)	2.51(1)
O(14)	108.2(6)	109.7(6)	112.1(5)	1.49(1)

P(3)	O(3)	O(9^{v})	O(10^{vi})	O(15)
O(3)	1.56(1)	2.59(1)	2.50(1)	2.54(1)
O(9^{v})	112.0(6)	1.57(1)	2.52(1)	2.50(1)
O(10^{vi})	107.3(6)	108.6(5)	1.54(1)	2.51(1)
O(15)	111.0(6)	107.8(6)	110.0(5)	1.52(1)

P(4)	O(2)	O(5)	O(7^{i})	O(16)
O(2)	1.58(1)	2.42(1)	2.52(1)	2.57(1)
O(5)	101.4(5)	1.55(1)	2.55(1)	2.59(1)
O(7^{i})	108.7(5)	112.2(6)	1.53(1)	2.49(1)
O(16)	111.6(6)	114.3(6)	108.5(6)	1.54(1)

ber of links between the $[V_2P_4O_{18}]_\infty$ chains makes the $[V_2P_4O_{16}]_\infty$ framework very flexible, so that its cohesion is in fact ensured by a great number of K^+ cations. Two of them are surrounded by seven oxygen atoms, two others by eight oxygen atoms, the distances of which are ≤ 3.35 Å. The number of independant K^+ with a 9-fold or a 6-fold coordination involves the formulation $K_6V_2P_4O_{16}$ instead of $K_3VP_2O_8$.

The view of this structure along the (101) direction is also interesting since it shows (Fig. 4a) tunnels similar to those observed in the pure octahedral framework of the oxide KTi_3NbO_9 *(16)* (Fig. 4b). The interatomic distances are close to those observed in other phosphates. The PO_4 tetrahedra are almost regular with P–O distances ranging from 1.49 to 1.57 Å (Table IV); nevertheless it is worth pointing out that for each of them the smallest P–O distance corresponds to the free corner of the PO_4 tetrahedron. The VO_6 octahedra, which exhibit distances ranging from 1.95 to 2.08 Å for V(1) and from 1.98 to 2.13 Å (Table III) for V(2) are characterized by a strong distortion. One can observe very short O(2)–O(5) and O(8)–O(12) distances of 2.42 Å and 2.41 Å, respectively, corresponding to the common edge between a PO_4 tetrahedron and a VO_6 octahedron. In the same way the two largest V–O distances observed in each octahedron correspond to the two oxygen atoms forming this common edge. The K–O distances (Table V) are close to those usually observed, the shortest ones corrsponding to the free oxygen of the PO_4 tetrahedra. It is also worth pointing out that the three K^+ ions (K_3–K_4–K_5), which are located in the same large cage, exhibit rather short K–K distances of 3.35 Å.

TABLE V

MAIN DISTANCES K–O (Å)

K(1)–O(1$^{\mathrm{ii}}$)	=	2.89(1)
K(1)–O(2$^{\mathrm{ii}}$)	=	2.66(1)
K(1)–O(8$^{\mathrm{iv}}$)	=	2.80(1)
K(1)–O(9$^{\mathrm{iv}}$)	=	2.97(1)
K(1)–O(13$^{\mathrm{vii}}$)	=	2.79(1)
K(1)–O(14)	=	2.84(1)
K(1)–O(16$^{\mathrm{ix}}$)	=	2.67(1)
K(2)–O(1$^{\mathrm{viii}}$)	=	3.31(1)
K(2)–O(1)	=	2.94(1)
K(2)–O(3$^{\mathrm{viii}}$)	=	2.73(1)
K(2)–O(5)	=	2.81(1)
K(2)–O(6$^{\mathrm{viii}}$)	=	2.93(1)
K(2)–O(10$^{\mathrm{ix}}$)	=	3.32(1)
K(2)–O(10$^{\mathrm{x}}$)	=	2.84(1)
K(2)–O(11$^{\mathrm{x}}$)	=	2.77(1)
K(2)–O(12$^{\mathrm{ix}}$)	=	2.75(1)
K(3)–O(2$^{\mathrm{ix}}$)	=	2.96(1)
K(3)–O(3)	=	3.20(1)
K(3)–O(4)	=	2.84(1)
K(3)–O(7$^{\mathrm{vi}}$)	=	3.11(1)
K(3)–O(13$^{\mathrm{i}}$)	=	2.87(1)
K(3)–O(14)	=	2.54(1)
K(3)–O(15)	=	2.84(1)
K(3)–O(16$^{\mathrm{ix}}$)	=	2.97(1)
K(4)–O(2)	=	2.71(1)
K(4)–O(3$^{\mathrm{iii}}$)	=	3.10(1)
K(4)–O(4$^{\mathrm{iii}}$)	=	2.85(1)
K(4)–O(6$^{\mathrm{iii}}$)	=	2.63(1)
K(4)–O(12$^{\mathrm{i}}$)	=	2.80(1)
K(4)–O(14)	=	3.06(1)
K(4)–O(15)	=	2.67(1)
K(5)–O(5$^{\mathrm{xi}}$)	=	2.59(1)
K(5)–O(7$^{\mathrm{vi}}$)	=	2.76(1)
K(5)–O(8$^{\mathrm{iv}}$)	=	2.72(1)
K(5)–(10$^{\mathrm{vi}}$)	=	3.09(1)
K(5)–O(11$^{\mathrm{vi}}$)	=	3.08(1)
K(5)–O(14)	=	2.88(1)
K(5)–O(15)	=	2.80(1)
K(5)–O(16$^{\mathrm{ix}}$)	=	3.03(1)
K(6)–O(8$^{\mathrm{xii}}$)	=	3.15(1)
K(6)–O(9$^{\mathrm{ix}}$)	=	2.86(1)
K(6)–O(13$^{\mathrm{ix}}$)	=	2.75(1)
K(6)–O(13$^{\mathrm{xii}}$)	=	2.81(1)
K(6)–O(15$^{\mathrm{xiii}}$)	=	2.66(1)
K(6)–O(16)	=	2.81 (1)

Note. Symmetry codes. i: $1 - x$; $1 - y$; $1 - z$. ii: x; $1/2 - y$; $1/2 + z$. iii: $1 - x$; $1/2 + y$; $1/2 - z$. iv: $-x$; $1 - y$; $1 - z$. v: $-x$; $-1/2 + y$; $1/2 - z$. vi: $+x$; $1/2 - y$; $-1/2 + z$. vii: x; $y - 1$; z. viii: $1 - x$; $-y$; $-z$. ix: $1 - x$; $-1/2 + y$; $1/2 - z$. x: $1 + x$; $1/2 - y$; $-1/2 + z$. xi: $-1 + x$; y; z. xii: $1 + x$; $3/2 - y$; $-1/2 + z$. xiii: $1 + x$; y; z.

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