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A Vanadium (III) Phosphate with V_2O_{10} Octahedral Units: $KV_4P_7O_{24}$

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A new vanadium III phosphate, $KV_4P_7O_{24}$, was isolated and its structure was determined from single crystal X-ray diffraction data. This phase crystallizes in the triclinic space group $P\bar{1}$ with a = 10.0846 (7); b = 10.2309 (6); c = 10.8283 (9) Å; α = 112.757 (5); β = 109.226 (7); γ = 104.675 (5)°. The $[V_4P_7O_{24}]_\infty$ host lattice is built-up from corner-sharing PO_4 tetrahedra, P_2O_7 groups, P_4O_{13} units, and pairs of edge-sharing VO_6 octahedra forming V_2O_{10} units. This mixed framework delimits cages where the potassium cations are located. The relationships between this structure and the V(IV) phosphate $(VO)_2P_2O_7$ are discussed.

Introduction

Recent studies of the vanadium phosphates have confirmed the extraordinarily rich crystal chemistry of these compounds. This great ability to form original mixed frameworks comes from the great ability of vanadium to adapt various coordinations ranging from strongly distorted octahedral to pyramidal and even to tetrahedral. This great flexibility of the vanadium polyhedra is especially encountered in V(IV) and V(V) phosphates and mixed valence oxides V(IV)–V(V). In the case of trivalent vanadium, the coordination remains octahedral, but the VO_6 octahedra can be significantly distorted. For this reason the creation of tunnel structures involving large cavities should also be considered for V(III) phosphates, by introducing large univalent cations, such as potassium, rubidium, and cesium into such mixed frameworks. Up to now the number of compounds isolated in the A–V(III)–P–O systems remain rather limited since only six phosphates—Cs(Rb)VP_2O_7 (*1*), Cs(Rb)VP_4O_{12} (*2*), $CsV_2P_5O_{16}$ (*3*), and $Cs_3V_3P_{12}O_{36}$ (*4*)—were isolated in the cases of cesium and rubidium. We have investigated recently the system K–V–P–O, for which three V(III) phosphates—KVP_2O_7 (*5*), $K_6V_2P_4O_{16}$ (*6*), and $K_{11}V_{15}P_{18}O_{73}$ (*7*)—have been isolated. We report here on the crystal structure of a new vanadium (III) phosphate, $KV_4P_7O_{24}$, involving V_2O_{10} octahedral units, which exhibits structural similarities with $(VO)_2P_2O_7$ (*8*).

Synthesis

Green crystals of $KV_4P_7O_{24}$ were crystallized as a minor product in a mixture of nominal composition $K_{0.25}VP_2O_7$ in the following way. First an adequate mixture of K_2CO_3, V_2O_5, and $H(NH_4)_2PO_4$ was heated

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TABLE I

Summary of Crystal Data, Intensity Measurements, and Structure Refinement Parameters for $KV_4P_7O_{24}$

Crystal data	
Space group	$P\bar{1}$
Cell dimensions	a = 10.0846(7) Å; α = 112.757(5) b = 10.2309(6) Å; β = 109.226(7) c = 10.8283(9) Å; γ = 104.675(5)
Volume	875(5) $Å^3$
Z	2
Intensity measurements	
λ (Mo$K\alpha$)	0.71073 Å
Scan mode	$\omega - \frac{2}{3}\theta$
Scan width (°)	$1 + 0.35 \tan\theta$
Slit aperture (mm)	$1.09 + \tan\theta$
max θ (°)	38°
Standard reflections	three measured every 3000 sec
Reflections with $I > 3\sigma$	6727
$\mu(\mathrm{mm}^{-1})$	2.986 mm^{-1}
Structure solution and refinement	
Parameters refined	325
Agreement factors	$R = 0.023$ $R_w = 0.027$
Weighting scheme	$w = f(\sin\theta/\lambda)$

to 653 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 at 1273 K for two weeks. Some green crystals were then isolated from the resulting mixture. The composition deduced from the structural determination $KV_4P_7O_{24}$ was confirmed by microprobe analysis.

Structure Determination

A green crystal with dimensions 0.179 × 0.128 × 0.154 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 space group is $P\bar{1}$. The data were collected on a CAD-4 Enraf–Nonius diffractometer with the data collection parameters reported in Table I. The reflections were corrected for Lorentz and polarization effects; no correction was made for extinction and absorption.

Atomic coordinates of the vanadium atom were deduced by the heavy atom method, and the other atoms were located by subsequent Fourier series. Refinement of the atomic coordinates and their anisotropic thermal parameters led to $R = 0.023$ and $R_w = 0.027$ and to the atomic parameters reported in Table II.

Description of the Structure and Discussion

As shown on the projection of the structure of this phosphate along **c** (Fig. 1), the host lattice $[V_4P_7O_{24}]_\infty$ is very original. It consists of monophosphate PO_4, diphosphate P_2O_7, and tetraphosphate P_4O_{13} groups sharing their corners with octahedral V_2O_{10} units. The V_2O_{10} units, which are built up from two edge-sharing VO_6 octahedra, are observed for the first time in V(III) phos-

TABLE II

TABLE OF POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS

Atom	x	y	z	B(A2)
V(1)	0.75498(2)	0.14970(2)	0.25561(2)	0.316(3)
V(2)	0.37412(2)	0.22301(2)	−0.11396(2)	0.325(3)
V(3)	0.07363(2)	0.68772(2)	0.07401(2)	0.309(3)
V(4)	0.42673(3)	0.58143(2)	0.41113(2)	0.310(3)
P(1)	0.38321(4)	−0.06258(4)	0.11691(4)	0.311(5)
P(2)	0.50103(4)	0.27387(4)	0.24211(4)	0.333(5)
P(3)	0.24365(4)	0.81280(4)	0.43424(4)	0.348(5)
P(4)	0.30263(4)	0.51073(4)	0.05170(4)	0.321(5)
P(5)	−0.00160(4)	0.00662(4)	0.22450(4)	0.344(5)
P(6)	0.06493(4)	0.32096(4)	0.26257(4)	0.341(5)
P(7)	0.27241(4)	0.13098(4)	0.52037(4)	0.340(5)
K	0.86440(6)	0.57356(6)	0.32447(6)	2.087(9)
O(1)	0.9650(1)	0.3223(1)	0.3413(1)	0.67(2)
O(2)	0.5537(1)	−0.0451(1)	0.1739(1)	0.50(2)
O(3)	0.6906(1)	0.1085(1)	0.0473(1)	0.80(2)
O(4)	0.6707(1)	0.3016(1)	0.2972(1)	0.66(2)
O(5)	0.8275(1)	0.1810(1)	0.4606(1)	0.65(2)
O(6)	0.8330(1)	−0.0211(1)	0.1979(1)	0.52(2)
O(7)	0.2677(1)	0.3530(1)	−0.0790(1)	0.65(2)
O(8)	0.4323(2)	0.2682(1)	0.0949(1)	0.96(2)
O(9)	0.5868(1)	0.3615(1)	−0.0465(1)	0.90(2)
O(10)	0.2770(1)	0.1781(1)	−0.3299(1)	0.82(2)
O(11)	0.1106(1)	0.7126(1)	0.2713(1)	0.72(2)
O(12)	0.2904(1)	0.8387(1)	0.1580(1)	0.59(2)
O(13)	0.0022(2)	0.6650(1)	−0.1254(1)	0.84(2)
O(14)	−0.1380(1)	0.4885(1)	−0.0102(1)	0.51(2)
O(15)	0.0154(1)	0.8714(1)	0.1277(1)	0.85(2)
O(16)	0.2299(1)	0.4409(1)	0.3745(1)	0.78(2)
O(17)	0.4898(1)	0.3945(1)	0.3726(1)	0.46(2)
O(18)	0.3749(1)	0.7671(1)	0.4623(1)	0.76(2)
O(19)	0.6400(1)	0.7391(1)	0.4934(1)	0.71(2)
O(20)	0.3682(2)	0.5274(1)	0.2067(1)	0.95(2)
O(21)	0.4020(1)	0.1099(1)	0.2180(1)	0.63(2)
O(22)	0.3177(1)	0.9912(1)	0.4671(1)	0.64(2)
O(23)	0.0668(1)	0.1482(1)	0.2040(1)	0.67(2)
O(24)	0.0922(1)	0.0635(1)	0.4002(1)	0.71(2)

Note. Anisotropically refined atoms are given in the isotropic equivalent displacement parameter defined as $B = \frac{4}{3}[\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}\,ab\cos\gamma + \beta_{13}\,ac\cos\beta + \beta_{23}\,bc\cos\alpha]$.

phates. Indeed, most of the V(III) phosphates are characterized by single VO_6 octahedra sharing their corners with PO_4 tetrahedra as shown for AVP_2O_7 with A = Li (*9*), K (*5*), Rb (*1*), and Cs (*10*), $AV_2(P_2O_7)_2$ with A = Ba (*11*) and Sr (*12*), $CsV_2P_5O_{16}$ (*3*), $V(PO_3)_3$ (*13*), $Cs_3V_3P_{12}O_{36}$ (*4*), whereas only one oxide—VPO_4—exhibits infinite chains of edge-sharing octahedra (*14*), and two phosphates—$V_4(P_2O_7)_3$ (*15*) and $V_3P_5SiO_{19}$ (*16*)—present V_2O_9 octahedral clusters of two face-sharing octahedra. In this respect this new structure is to be compared to the mixed-valent vanadium phosphate $KV_3P_4O_{16}$ (*17*) and the tetravalent vanadium phosphate $(VO)_2P_2O_7$ (*8*) in which pairs of

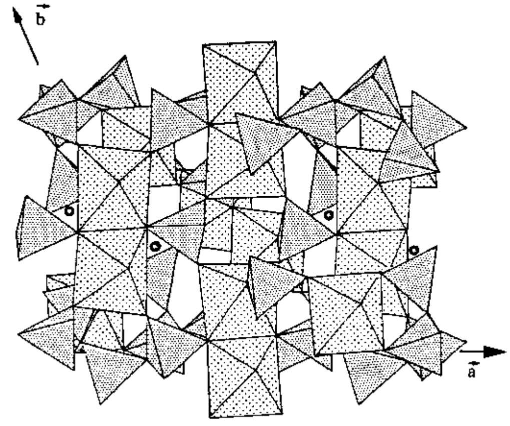

FIG. 1. Projection of the structure along **c**.

edge-sharing VO_6 octahedra can be recognized. Nevertheless, in both latter structures the V_2O_{10} units share the corners of their octahedra, forming infinite octahedral chains. This is not the case for $KV_4P_7O_{24}$, whose V_2O_{10} units are isolated, i.e., share their corners with PO_4 tetrahedra only.

In fact the $[V_4P_7O_{24}]_\infty$ framework exhibits rather close relationships with the tetravalent vanadium phosphate $(VO)_2P_2O_7$. The consideration of layers parallel to the (001) plane, shows that they form ribbons (Fig. 2a) whose disposition of PO_4 tetrahedra and V_2O_{10} units is very similar to that encountered for $(VO)_2P_2O_7$ (hatched polyhedra in Fig. 2b).One remarkable feature common to these structures is that the oxygen atoms common at the two edge-sharing octahedra are also shared by PO_4 tetrahedron, leading to a significant distortion of the VO_6 octahedra. These $(VO)_2P_2O_7$-like ribbons which extend indefinitely along **a** are interrupted in the **b** direction by a connection with V_2O_{10} units (labelled V_4 in Fig. 2a) oriented differently with respect to the layer, and forming with the other P_2O_7 groups rather large holes where the K^+ atoms are located. Thus the $[V_4P_7O_{24}]_\infty$ framework can be described as the stacking along **c** of such similar layers. Each layer shares the corners of its P_2O_7 groups either with P_2O_7 groups of the next one, forming P_4O_{13} units, or with V_2O_{10} units. Thus the orientation of the P_2O_7 groups with respect to the V_2O_{10} units is completely different from that observed for $(VO)_2P_2O_7$; the P–P directions are respectively parallel and perpendicular to the V · · · V direction, as shown for the comparison of Fig. 2a and b.

One observes three kinds of V_2O_{10} units; two of these—V(1)–V(2) and V(3)–V(3)—belong to the $(VO)_2P_2O_7$-like ribbons (Fig. 2a), whereas the third one, V(4)–V(4), is shared between two (001) layers. The V–V distances are respectively of 3.199 (5), 3.211 (5), and 3.143 (5) Å. The V(1)–V(2) unit is linked (Fig. 3a) to two P_2O_7 groups, two P_4O_{13} units, and two PO_4 monophosphate groups. It is remarkable that each P_2O_7 group and each P_4O_{13} group shares two of its apices with the same V_2O_{10} unit, whereas the oxygen atoms O(2) and O(6) are shared by three polyhedra, V(1), V(2), and P(1) or P(5), belonging to one P_2O_7 or one P_4O_{13} unit respectively. As a result the four V–O distances—V(1)–O(2), V(1)–O(6), V(2)–O(2), and V(2)–O(6)—exhibit the largest values (Table III) in the V(1) and V(2) octahedra (2.06 to 2.13 Å), in agreement with the fact that the O(2) and O(6) atoms are linked to three polyhedra. The O(7) and O(9) atoms which are shared between a V(2) octahedron and a monophosphate group P(4) exhibit much shorter V–O distances (1.91 to 1.94 Å); in the same way the O(8), O(4), and O(3), which are shared between one VO_6 octahedron and one P_2O_7 group, exhibit rather short distances, ranging from 1.93 to 1.96 Å (Table III). The O(5), and especially the O(1) and O(10) atoms which are shared between one VO_6 octahedron and one P_4O_{13} group tend to present intermediate V–O distances ranging from 1.95 to 2.02 Å. It is also worth pointing out that the V(1) octahedron is significantly less distorted than the V(2) octahedron as shown by the range of the O–V–O angles in Table III.

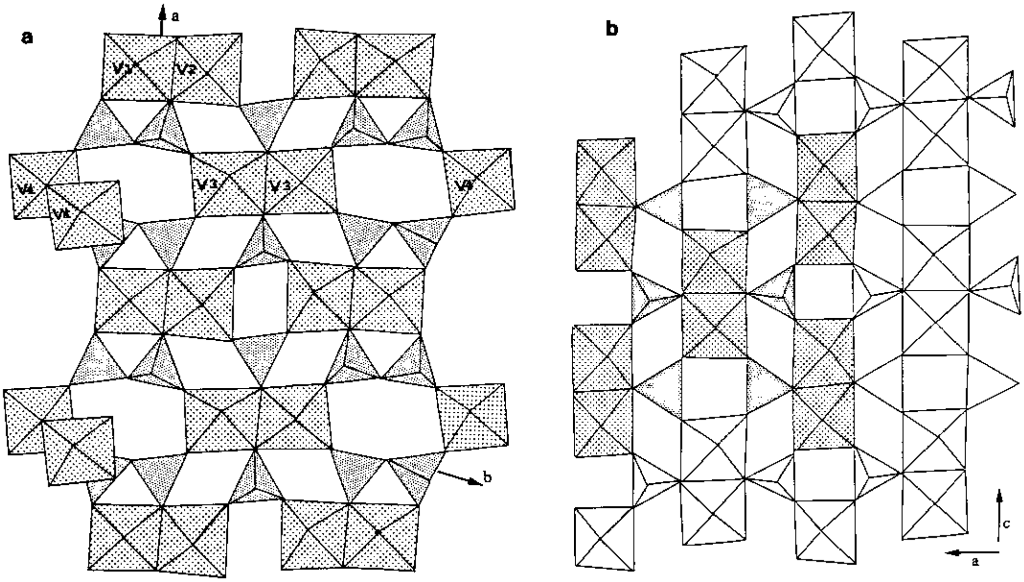

FIG. 2. (a) A layer parallel to the 001 plane in the $[V_4P_7O_{24}]_\infty$ framework. (b) A layer of $(VO)_2P_2O_7$ structure.

The V(3)–V(3) unit (Fig. 3b) is linked to two P_2O_7 groups, four P_4O_{13} groups, and two PO_4 single tetrahedra. In this case each tetrahedral unit P_2O_7 shares only one apex with the same V_2O_{10} unit; i.e., each V(3) octahedron is linked to one P_2O_7 group (bond V(3)–O(12)–P(1)). One of the two P_4O_{13} shares two of its corners with the same octahedron (bond V(3)–O(11)–P(3) or V(3)–O(15)–P(5)); the other one P_4O_{13} unit shares one corner with the same V(3) octahedron (bond V(3)–O(13)–P(6)). As for the V(1)–V(2) units, the two oxygen atoms O(14) common to the two octahedra are also shared by a third polyhedron, the monophosphate group P(4). Consequently the V(3) octahedron is also strongly distorted (Table III), with two significantly longer V–O distances corresponding to the threefold linked O(14) atom (2.02 to 2.14 Å), whereas the other V–O distances which correspond to oxygen atoms shared by two polyhedra range from 1.93 to 2.03 Å.

The V(4)–V(4) unit (Fig. 3c) is also linked to two P_2O_7 groups, four P_4O_{13} units, and two PO_4 tetrahedra, but in a very different way. In this case, for two P_4O_{13} groups, each unit shares two of its apices with two different octahedra of the same V_2O_{10} unit (bonds V(1)–O(16)–P(6) and V(4)–O(19)–P(7)), whereas for the two other P_4O_{13} groups each unit shares only one apex with one V(4) octahedron (bonds V(4)–O(18)–P(3)). Each P_2O_7 group shares only one apex with each V_2O_{10} unit, but at the junction of two V(4) octahedra, so that the O(17) atom is triply bonded (bond P(2)–O(17)–V(4)). Each monophosphate group P(4) shares one oxygen with each V(4) octahedron of the V_2O_{10} units (bond V(4)–O(20)–P(4)). The V–O distances, and especially the larger values obtained for V(4)–O(17) bonds (Table III) are in agreement with the fact that O(17) is shared by three polyhedra whereas other oxygens are shared by two polyhedra.

The seven independent PO_4 tetrahedra exhibit an almost regular "O_4" tetrahedral geometry (Table IV) but are characterized

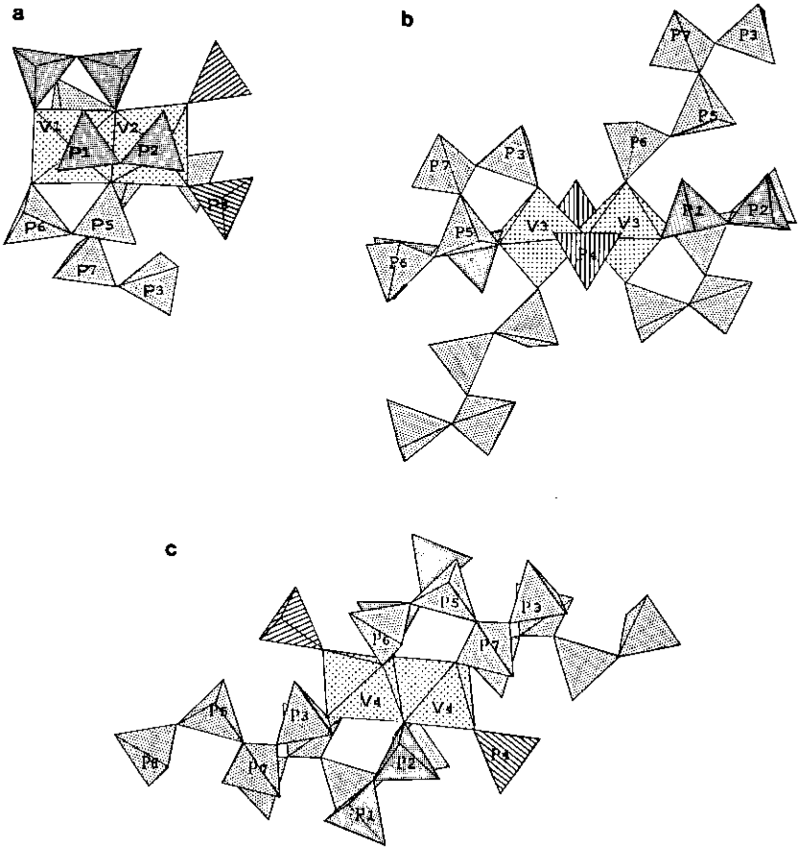

FIG. 3. (a) Neighborhood of the $[(V(1)-V(2))O_{10}]$ unit. (b) Neighborhood of the $[(V(3)-V(3))O_{10}]$ unit. (c) Neighborhood of the $[(V(4)-V(4))O_{10}]$ unit.

by a significant variation of the P–O distances. In the monophosphate groups P(4), the longer distance (1.57 Å) corresponds to the triply linked oxygen atom O(14), whereas the three other distances, ranging from 1.508 to 1.533 Å, are close to those observed in monophosphates.

The P(1) and P(2) tetrahedra which form the P_2O_7 groups exhibit one longer P–O bond (1.59 Å) characteristic of the P–O–P bridging bonds, whereas intermediate P–O distances (1.536 to 1.558 Å) correspond to the oxygen atoms O(2) and O(17) which are triply bonded. In each tetrahedron the two other P–O distances ranging from 1.497 to 1.521 Å are close to those encountered in regular PO_4 tetrahedra.

The P(3), P(5), P(6), and P(7) tetrahedra which form the P_4O_{13} units exhibit P–O distances similar to those observed in the tetraphosphates $Mo_2P_4O_{15}$ (*18*) and $Nb_2P_4O_{15}$ (*19*). The two terminal P(3) and P(6) tetrahedra exhibit only one longer P–O distance (1.628 to 1.638 Å), characteristic of the bridging oxygen of the P_2O_7 group, whereas the three other distances, ranging from 1.49 to 1.52 Å, are in agreement with the existence of V–O–P bonds. The two intermediate P(5) and P(7) tetrahedra, exhibit for each of them two longer P–O distances, ranging

TABLE III

DISTANCES (Å) AND ANGLES IN VO_6 OCTAHEDRA

V(1)	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)
O(1)	2.002(1)	4.062)	2.884(2)	2.784(2)	2.700(2)	2.928(2)
O(2)	172.46(5)	2.069(1)	2.841(2)	2.989(2)	2.860(2)	2.679(2)
O(3)	93.36(6)	89.59(6)	1.962(1)	2.773(2)	3.916(6)	2.752(2)
O(4)	90.17(5)	96.73(5)	90.91(6)	1.929(1)	2.826(2)	3.985(6)
O(5)	86.02(6)	90.51(5)	175.70(6)	93.35(6)	1.956(1)	2.825(2)
O(6)	92.29(5)	80.96(5)	86.35(6)	176.42(6)	89.42(5)	2.059(1)

V(2)	O(2^{i})	O(6^{ii})	O(7)	O(8)	O(9)	O(10)
O(2^{i})	2.081(1)	2.679(2)	3.976(6)	2.999(2)	2.706(2)	2.945(2)
O(6^{ii})	78.85(5)	2.137(1)	2.869(2)	2.896(2)	4.035(6)	2.788(2)
O(7)	168.70(5)	89.99(5)	1.914(1)	2.644(2)	3.094(2)	2.662(2)
O(8)	95.68(6)	89.76(6)	85.96(6)	1.963(1)	2.763(2)	3.963(6)
O(9)	84.47(5)	163.21(5)	106.74(6)	90.07(7)	1.942(1)	2.993(2)
O(10)	91.87(5)	84.25(5)	85.17(6)	169.29(6)	98.22(6)	2.017(1)

V(3)	O(11)	O(12)	O(13)	O(14)	O(14^{ii})	O(15)
O(11)	1.943(1)	2.822(2)	3.861(6)	2.735(2)	2.933(2)	2.783(2)
O(12)	92.26(6)	1.971(1)	2.883(2)	4.092(6)	2.785(2)	2.805(2)
O(13)	169.72(6)	95.18(6)	1.934(1)	2.903(2)	2.836(2)	2.670(2)
O(14)	83.74(5)	166.70(5)	90.51(6)	2.149(1)	2.659(2)	3.295(2)
O(14^{ii})	95.55(6)	88.56(5)	91.72(6)	79.24(5)	2.018(1)	4.052(6)
O(15)	88.65(6)	88.78(6)	84.43(6)	103.77(5)	175.10(6)	2.038(1)

V(4)	O(16)	O(17)	O(17^{iii})	O(18)	O(19)	O(20)
O(16)	1.938(1)	2.784(2)	2.692(2)	2.887(2)	3.889(6)	2.883(2)
O(17)	87.09(5)	2.099(1)	2.666(2)	4.115(6)	2.976(2)	2.804(2)
O(17^{iii})	83.56(5)	78.83(5)	2.099(1)	3.101(2)	2.751(2)	3.969(6)
O(18)	93.73(6)	176.39(6)	97.76(5)	2.017(1)	2.686(2)	2.868(2)
O(19)	168.07(6)	93.86(5)	84.95(5)	84.61(6)	1.972(1)	2.833(2)
O(20)	97.64(6)	89.08(6)	167.79(6)	94.29(6)	94.27(6)	1.893(1)

Note. The V(O) distances are on the diagonal. Above it are the O(*i*) · · · O(*j*) distances and below it are the O(*i*)–V–O(*j*) angles.

from 1.57 to 1.60 Å, characteristic of the bridging P–O–P bonds; in each of these tetrahedra the two other P–O distances range from 1.47 to 1.52 Å in agreement with the formation of V–O–P bonds.

The K^+ ions which are located in the cages are surrounded by seven oxygen atoms, at distances ranging from 2.81 to 3.20 Å (Table V); in fact one can consider for potassium a 3 + 3 coordination, forming a strongly distorted antiprism with three short K–O distances (2.8 to 2.88 Å) and three longer ones (3.02 to 3.04 Å) (Fig. 4).

Concluding Remarks

These results confirm the extraordinary flexibility of the VO_6 octahedra involving trivalent vanadium. The existence of really isolated V_2O_{10} units has been obtained for

TABLE IV

Distances (Å) and Angles in PO_4 Tetrahedra

P(1)	O(2)	O(3$^{\mathrm{i}}$)	O(12$^{\mathrm{iv}}$)	O(21)
O(2)	1.558(1)	2.516(2)	2.536(2)	2.491(2)
O(3$^{\mathrm{i}}$)	110.84(8)	1.497(1)	2.535(2)	2.515(2)
O(12$^{\mathrm{iv}}$)	112.29(7)	115.79(8)	1.496(1)	2.434(2)
O(21)	104.34(7)	108.77(8)	103.86(7)	1.596(1)

P(2)	O(4)	O(8)	O(17)	O(21)
O(4)	1.521(1)	2.496(2)	2.482(2)	2.530(2)
O(8)	112.27(8)	1.485(1)	2.552(2)	2.486(2)
O(17)	108.50(7)	115.28(8)	1.536(1)	2.452(2)
O(21)	108.89(7)	107.96(8)	103.42(7)	1.588(1)

P(3)	O(5$^{\mathrm{iii}}$)	O(11)	O(18)	O(22)
O(5$^{\mathrm{iii}}$)	1.523(1)	2.453(2)	2.544(2)	2.526(2)
O(11)	107.47(7)	1.520(1)	2.533(2)	2.525(2)
O(18)	115.15(8)	114.64(8)	1.490(1)	2.488(2)
O(22)	106.52(7)	106.65(8)	105.79(7)	1.628(1)

P(4)	O(7)	O(9$^{\mathrm{v}}$)	O(14$^{\mathrm{ii}}$)	O(20)
O(7)	1.532(1)	2.444(2)	2.444(2)	2.555(2)
O(9$^{\mathrm{v}}$)	106.34(8)	1.522(1)	2.570(2)	2.508(2)
O(14$^{\mathrm{ii}}$)	103.74(7)	112.22(7)	1.574(1)	2.497(2)
O(20)	114.39(8)	111.77(9)	108.19(8)	1.508(1)

P(5)	O(6$^{\mathrm{vi}}$)	O(15$^{\mathrm{vii}}$)	O(23)	O(24)
O(6$^{\mathrm{vi}}$)	1.525(1)	2.543(2)	2.510(2)	2.449(2)
O(15$^{\mathrm{vii}}$)	116.29(8)	1.469(1)	2.476(2)	2.531(2)
O(23)	108.35(7)	109.10(8)	1.570(1)	2.551(2)
O(24)	103.56(7)	111.53(8)	107.59(7)	1.592(1)

P(6)	O(1$^{\mathrm{vi}}$)	O(13$^{\mathrm{ii}}$)	O(16)	O(23)
O(1$^{\mathrm{vi}}$)	1.518(1)	2.512(2)	2.475(2)	2.514(2)
O(13$^{\mathrm{ii}}$)	112.91(8)	1.496(1)	2.495(2)	2.530(2)
O(16)	110.54(8)	113.16(8)	1.493(1)	2.512(2)
O(23)	105.49(7)	107.60(8)	106.59(8)	1.638(1)

P(7)	O(10$^{\mathrm{viii}}$)	O(19$^{\mathrm{iii}}$)	O(22$^{\mathrm{vii}}$)	O(24)
O(10$^{\mathrm{viii}}$)	1.483(1)	2.516(2)	2.529(2)	2.459(2)
O(19$^{\mathrm{iii}}$)	115.75(8)	1.488(1)	2.519(2)	2.467(2)
O(22$^{\mathrm{vii}}$)	112.09(8)	111.12(7)	1.566(1)	2.535(2)
O(24)	105.36(8)	105.63(7)	106.00(7)	1.607(1)

Note. The P–O distances are on the diagonal. Above it are the O(i) · · · O(j) distances and below it are the O(i)–P–O(j) angles.

TABLE V

OXYGEN ATOMS SURROUNDING K^+ WITH K–O < 3.35 Å

K–O(1) = 3.038(2)
K–O(1^{ix}) = 3.030(2)
K–O(4) = 2.807(1)
K–O(5^{ix}) = 2.853(2)
K–O(7^{v}) = 3.021(2)
K–O(10^{v}) = 3.204(2)
K–O(11^{x}) = 2.882(2)

Symmetry code

(i):	$1 - x$	; $- y$	; $- z$
(ii):	$- x$	; $1 - y$	; $- z$
(iii):	$1 - x$	; $1 - y$	; $1 - z$
(iv):	$- x$	; $- 1 - y$	; $- z$
(v):	$1 - x$	; $1 - y$	; $- z$
(vi):	$- 1 + x$	; y	; z
(vii):	x	; $- 1 + y$	; z
(viii):	x	; y	; $1 + z$
(ix):	$2 - x$	; $1 - y$	; $1 - z$
(x):	$1 + x$	; y	; z

the first time in the V(III) phosphates. Such units can be considered as clusters which will be studied for their magnetic properties.

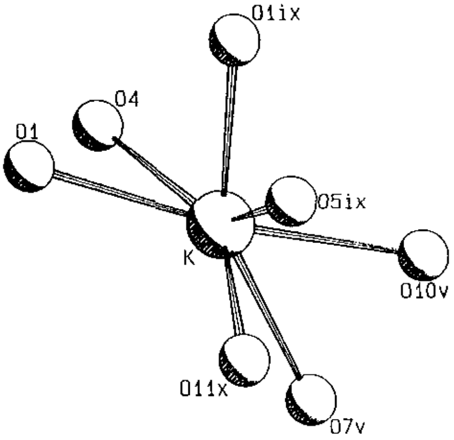

FIG. 4. The polyhedron of oxygen atoms around K^+ in $KV_4P_7O_{24}$.

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