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Crystal Structures of Some Niobium and Tantalum Oxides

IX. $K_3Nb_7O_{19}$: A New Potassium Niobium Oxide Tunnel Structure

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$K_3Nb_7O_{19}$ crystallizes in the triclinic system with unit cell dimensions (from single-crystal data) a = 14.143(3), b = 9.948(2), c = 6.463(2) Å, α = 106.45(2), β = 95.82(1), γ = 97.29(1)°, and space group $P\bar{1}$, z = 2. The structure was solved using the Patterson ("P1" method) and Fourier techniques. Of the 4974 unique reflections measured by counter techniques 2722 with $I \geq 3\sigma(I)$ were used in the least-squares refinement of the model to a conventional R of 0.049 (R_w 0.054). The structure of $K_3Nb_7O_{19}$ may be described as consisting of edge-shared pairs of octahedra that are corner shared to one another to form double strings seven pairs long. Each of these strings is corner shared to four other identical strings forming tunnels bounded by six octahedra. Two pairs of octahedra at each end of the strings of seven pairs are edge shared to adjacent strings forming a second series of tunnels approximately perpendicular to the first series. Potassium ions are located within both series of tunnels. The structure may also be described as one in which the oxygen ions are in approximately cubic close-packed layers perpendicular to [501] with potassium ions occupying anion sites in a regular manner.

Introduction

As part of a general study of compounds formed between alkali metal oxides and niobium and tantalum pentoxides a number of single-crystal structure determinations have been carried out ((*1*) and references therein). Of the stoichiometric compounds formed between potassium oxide and niobium pentoxide only two appear to have been structurally characterized. These are $KNbO_3$ (*2*) and KNb_3O_8 (*3*). The structure of $K_4Nb_6O_{17} \cdot 3H_2O$ has been inferred from that of $Rb_4Nb_6O_{17} \cdot 3H_2O$ (*4*) and the unit-cell dimensions of $K_8Nb_{18}O_{49}$ have been reported (*5*).

A sample from a preparation of the 4:9 $K_2O:Nb_2O_5$ phase was kindly supplied by Dr. R. S. Roth, National Bureau of Standards, Washington, D.C. During attempts to solve the structure of the 4:9 compound ($K_8Nb_{18}O_{49}$) a crystal selected from the above sample was found to have different unit-cell dimensions from the bulk sample. The crystal proved to be that of the compound $K_3Nb_7O_{19}$ (3:7, $K_2O:Nb_2O_5$). The only previous report of a compound with this composition was by Iyer and Smith (*11*), who refer to an earlier study not, apparently, widely published (*12*); the results of a single-crystal structure determination on this material are reported here.

Experimental Details

A colorless prismatic crystal with developed faces 010, 001, $2\bar{1}0$, $0\bar{1}0$, $00\bar{1}$, and $\bar{2}10$ and of dimensions 0.025 × 0.075 × 0.05 mm

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was selected from the sample and mounted on a silica capillary using Tyton 5 Minit Adhesive. Crystal data were obtained using a Philips PW1100 computer-controlled diffractometer. Lattice parameters were obtained from the average of 14 orientation matrices automatically determined at various stages of the data collection using 24 reflections in the range $2\theta = 20$ to 38°.

Crystal Data

$K_3Nb_7O_{19}$, $M = 1071.63$, triclinic, $a = 14.143(3)$, $b = 9.948(2)$, $c = 6.463(2)$ Å, $\alpha = 106.45(2)$, $\beta = 95.82(1)$, $\gamma = 97.29(1)°$; $U = 856.1$ Å^3, D_m not measured as insufficient sample available, $D_c = 4.16$ g cm^{-1}, $z = 2$, $F(000) = 991.3$, $\mu = 48.7$ cm^{-1} for Mo$K\alpha$ (0.7107 Å) radiation. Space group $P\bar{1}$ was confirmed by successful refinement.

Intensity Measurement

Intensity measurements were made with the crystal described above using the diffractometer and Mo$K\alpha$ radiation monochromated with a flat graphite monochromator crystal. A unique data set was collected out to 2θ (Mo$K\alpha$) = 60° using the $w - 2\theta$ scan technique with a symmetric scan range of $\pm(1.3 + 0.30 \tan\theta)°$ in 2θ from the calculated Bragg angle, at a scan rate of 0.04° sec^{-1}. No reflection was sufficiently intense to require the insertion of an attenuation filter. Of the 4974 unique reflections measured 2722 were considered to be significantly above the background ($I \geq 3\sigma(I)$) and only these were used in the refinement. Three standard reflections, monitored at 2-hr intervals, showed no significant variation in intensity.

The data were processed in a manner described previously (*6*). An absorption correction was applied on the basis of the indexed crystal faces and dimensions (see above)—the maximum and minimum values of the transmission factors were 0.8468 and 0.6852, respectively. No extinction correction was applied. The atomic scattering factors used were for neutral atoms and were corrected for anomalous dispersion (*7*). All calculations were carried out on the Monash University DEC VAX 11/780 computers; the major program used was SHELX (*8*).

Structure Solution and Refinement

The structure was solved using a method described by Abrahams (*9*) and referred to by this laboratory as the "P1" method (*10*). Following the location of the heavy atoms in the unit cell and determination of the center of symmetry a structure factor calculation gave a conventional $R = \Sigma||F_O| - |F_c||\Sigma|F_O| = 0.287$; parameters for the 19 oxygen atoms were taken from the subsequent difference Fourier synthesis. During refinement it became clear that two of the potassium ions should be considered to be disordered over two sites each; these are given as K(1) and K(1′) and K(2) and K(2′) in the tables that follow. Full-matrix least-squares refinement of all positional and isotropic thermal parameters resulted in $R = 0.14$; further refinement with anisotropic thermal parameters for niobium and potassium atoms and isotropic thermal parameters for oxygen resulted in convergence with $R = 0.049$ and $R_\omega = 0.054$. [$R_\omega = \Sigma\omega^{1/2}(||F_O| - |F_c||)/\Sigma\omega^{1/2}|F_O|$] and $\omega = (\sigma^2(F))^{-1}$. One hundred and eighty five parameters were varied in the final cycles and at convergence the biggest shift to esd ratio was for the x parameter of Nb(5) − 0.06. The largest feature in the final difference Fourier synthesis was between K(2) and K(2′) and was ~1.5 eÅ^3. Final parameters and their estimated standard deviations are given in Table I.[1]

[1] See NAPS document No. 04326 for 1 page of supplementary material. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10163. Remit in advance $4.00 for microfiche copy or for photocopy, $7.75 up to 20 pages plus $0.30 for each additional page. All

TABLE I

FINAL ATOMIC PARAMETERS WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES ($\times 10^4$)

	X	Y	Z	U (Å^2)
K(1)	957(3)	1762(4)	9921(9)	*a*
K(1′)	576(6)	2076(8)	1975(16)	*a*
K(2)	2512(3)	5604(5)	1965(9)	*a*
K(2′)	2094(5)	5928(8)	4133(15)	*a*
K(3)	6337(2)	238(3)	3581(5)	*a*
Nb(1)	5065(1)	6222(1)	3659(2)	*a*
Nb(2)	4193(1)	6845(1)	8267(2)	*a*
Nb(3)	1871(1)	8445(1)	9908(2)	*a*
Nb(4)	358(1)	4700(1)	7762(2)	*a*
Nb(5)	2583(1)	2929(1)	6186(2)	*a*
Nb(6)	3472(1)	2176(1)	1564(2)	*a*
Nb(7)	8891(1)	928(1)	5665(2)	*a*
O(1)	2231(5)	8335(8)	2879(13)	81(5)
O(2)	9707(6)	2765(8)	6739(13)	128(18)
O(3)	9323(5)	5494(8)	9115(13)	90(15)
O(4)	1209(5)	6598(8)	8761(13)	115(17)
O(5)	5463(5)	5849(7)	6911(12)	40(13)
O(6)	4058(5)	6911(8)	5192(13)	72(14)
O(7)	5237(5)	8353(8)	9057(13)	92(15)
O(8)	898(5)	9348(8)	1207(13)	98(15)
O(9)	7188(5)	9609(8)	9321(13)	84(15)
O(10)	4594(6)	6467(8)	1078(14)	123(16)
O(11)	3143(5)	7645(8)	8951(13)	103(16)
O(12)	1641(6)	3961(8)	7156(13)	147(18)
O(13)	7471(5)	6850(8)	6739(13)	89(15)
O(14)	0	0	$\frac{1}{2}$	159(25)
O(15)	0	$\frac{1}{2}$	$\frac{1}{2}$	179(26)
O(16)	1954(6)	1105(8)	5342(14)	125(17)
O(17)	6850(6)	7283(8)	918(13)	105(16)
O(18)	1593(6)	8867(9)	7022(14)	178(20)
O(19)	3748(5)	4751(7)	7140(12)	59(14)
O(20)	6073(6)	7842(8)	5031(13)	96(15)

[a] Anisotropic thermal parameters for potassium and niobium atoms are:

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
K(1)	124(21)	135(20)	393(32)	103(20)	−47(19)	−27(15)
K(1′)	203(41)	151(35)	374(54)	84(34)	−242(35)	−10(28)
K(2)	129(21)	154(20)	443(33)	96(20)	−122(20)	12(15)
K(2′)	107(34)	137(33)	359(49)	123(33)	−5(31)	−30(35)
K(3)	283(15)	131(12)	247(15)	82(11)	3(12)	34(11)
Nb(1)	32(4)	35(4)	39(4)	17(3)	−7(3)	−10(3)
Nb(2)	54(4)	43(4)	50(4)	23(3)	6(3)	15(3)
Nb(3)	83(5)	86(5)	162(6)	−32(4)	60(4)	−43(4)
Nb(4)	122(5)	152(5)	134(5)	−18(4)	47(4)	−68(4)
Nb(5)	47(4)	55(4)	68(5)	15(4)	9(3)	−10(3)
Nb(6)	67(4)	42(4)	33(4)	−5(3)	−5(3)	−20(3)
Nb(7)	170(5)	181(5)	91(5)	28(4)	−7(4)	−104(4)

and are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \cdots 2U_{12}hka^*b^* + \cdots)]$ ($\times 10^4$).

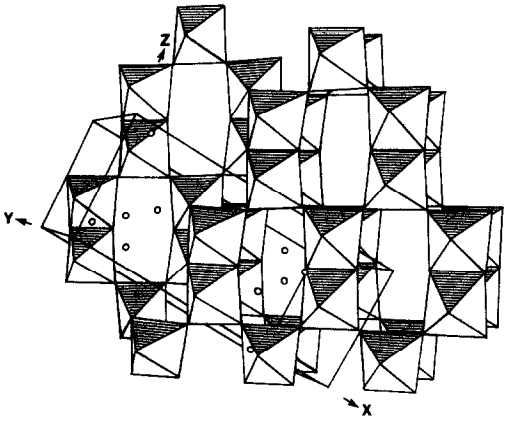

FIG. 1. A view of the structure of $K_3Nb_7O_{19}$ showing one of the sets of tunnels. Open circle represents K in the unit cell.

Description and Discussion of the Structure

The structure of $K_3Nb_7O_{19}$ may be described as consisting of edge-shared pairs of octahedra that are corner shared to one another to form double strings seven pairs long. Each of these strings is corner shared to four other identical strings forming tunnels bounded by six octahedra (Fig. 1). The two pairs of octahedra at each end of the strings of seven pairs are edge shared to adjacent strings (Fig. 2) forming a second series of tunnels—also bounded by six octahedra at their narrowest sections—approximately perpendicular to the first series. In Fig. 2 one set of tunnels is parallel to the plane of the paper and the other perpendicular to it. Overlapping of the strings of seven pairs of octahedra at both ends, by edge sharing, results in steps of one-half of an octahedron body diagonal in extent in both sets of tunnels and a highly condensed region of eight octahedra.

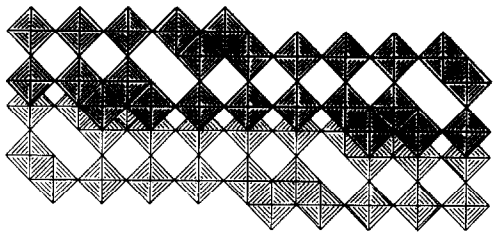

FIG. 2. An idealized diagram of $K_3Nb_7O_{19}$ showing the seven-octahedra chain and the highly condensed block of octahedra.

The structure may also be described as one in which the oxygen ions are cubic close packed in layers approximately perpendicular to [501] with niobium ions occupying octahedral sites in a regular manner (Fig. 3). The potassium ions occupy anion sites, each potassium ion having a vacant anion site adjacent to itself. K(1) and K(2) are unevenly distributed over their two anion sites with the occupancies being, K(1) 0.627(9), K(1′) 0.373(9); K(2) 0.634(9) and K(2′) 0.366(9). In the (010) projection of the structure shown in Fig. 3 the anion sites occur in pairs (smallest dots represent

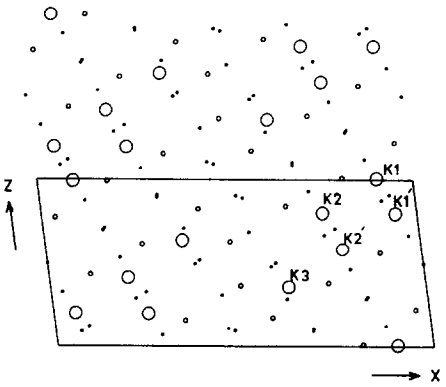

FIG. 3. A projection of the $K_3Nb_7O_{19}$ structure onto (010) with the smallest circles representing oxygen anions, small circles niobrium atoms, and large circles potassium ions. The anion layers, A, B, C, etc., are perpendicular to the page in the [501] direction.

TABLE II

SELECTED INTERATOMIC DISTANCES (Å) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Metal–oxygen			
Nb(1)–O(10)	1.825(9)	Nb(4)–O(15)	1.921(1)
–O(6)	1.905(9)	–O(3)[b]	1.921(8)
–O(20)	1.942(7)	–O(2)[b]	1.923(7)
–O(5)[a]	2.015(7)	–O(4)[b]	2.001(7)
–O(19)[a]	2.080(8)	–O(12)[b]	2.075(9)
–O(5)	2.264(8)	–O(3)[f]	2.090(9)
Nb(2)–O(11)	1.807(8)	Nb(5)–O(16)	1.820(8)
–O(7)	1.883(7)	–O(12)[b]	1.837(9)
–O(19)	1.996(7)	–O(13)[a]	1.960(9)
–O(6)	1.998(9)	–O(17)[a]	2.037(9)
–O(10)[b]	2.000(10)	–O(19)	2.187(7)
–O(5)	2.293(7)	–O(20)[a]	2.269(8)
Nb(3)–O(4)	1.859(7)	Nb(6)–O(9)[g]	1.803(7)
–O(8)	1.878(8)	–O(17)[g]	1.864(9)
–O(1)	1.974(9)	–O(13)[a]	1.986(8)
–O(18)[c]	2.036(10)	–O(7)[a]	2.011(8)
–O(9)[d]	2.105(5)	–O(5)[a]	2.225(6)
–O(11)[c]	2.137(8)	–O(20)[a]	2.235(9)
Nb(7)–O(18)[a]	1.877(10)		
–O(2)[j]	1.933(7)		
–O(14)[j]	1.943(1)		
–O(1)[a]	2.037(8)		
–O(16)[h]	2.104(7)		
–O(8)[a]	2.113(9)		
Metal–metal distances			
Edge-shared octahedra		**Corner-shared octahedra**	
Nb(1)–Nb(2)	3.267(1)	Nb(1)–Nb(2)	3.821(2)
–Nb(2)[a]	3.299(1)	–Nb(6)[c]	4.135(1)
–Nb(5)[a]	3.311(1)		
–Nb(1)[a]	3.359(2)	Nb(2)–Nb(3)[b]	3.940(2)
–Nb(6)[a]	3.382(1)	–Nb(5)	4.042(1)
Nb(2)–Nb(6)[a]	3.304(1)	Nb(3)–Nb(4)[c]	3.851(1)
		–Nb(7)[g]	3.896(2)
Nb(3)–Nb(7)[a]	3.086(2)	–Nb(6)[f]	3.896(1)
Nb(4)–Nb(4)[k]	3.085(3)	Nb(4)–Nb(4)[f]	3.847(3)
		–Nb(7)[m]	3.848(2)
Nb(5)–Nb(6)	3.286(2)	–Nb(5)	3.884(2)
		Nb(5)–Nb(6)[b]	3.879(2)
		–Nb(7)[n]	3.919(1)
Potassium contacts to oxygen out to 4.0 Å			
K(1)–O(8)[f]	2.655(8)	K(1′)–O(3)[s]	2.694(13)
–O(3)[f]	2.713(9)	–O(8)[s]	2.705(10)
–O(8)[o]	2.749(10)	–O(8)[q]	2.724(11)
–O(13)[o]	2.841(8)	–O(13)[o]	2.783(10)
–O(2)[b]	3.037(10)	–O(4)[s]	3.049(12)
–O(9)[o]	3.165(9)	–O(16)	3.206(13)
–O(14)	3.223(5)	–O(15)	3.263(8)
–O(18)[q]	3.250(9)	–O(18)[f]	3.275(12)
–O(17)[o]	3.272(9)	–O(14)	3.307(10)
–O(12)[b]	3.308(11)	–O(2)[b]	3.354(13)
–O(16)	3.341(11)	–O(12)[b]	3.421(11)
–O(4)[r]	3.713(9)	–O(2)	3.757(14)
–O(16)[b]	3.902(11)	–O(9)[g]	3.823(12)
K(2)–O(3)[s]	2.626(8)	K(2′)–O(3)[s]	2.679(10)
–O(1)	2.703(9)	–O(1)	2.728(12)
–O(6)	2.765(8)	–O(6)	2.773(10)

TABLE II—*Continued*

–O(13)[a]	2.798(10)	–O(13)[a]	2.820(11)
–O(4)	3.084(10)	–O(2)[s]	3.075(12)
–O(12)	3.112(9)	–O(15)	3.142(8)
–O(10)	3.118(10)	–O(12)[b]	3.187(14)
–O(17)	3.241(9)	–O(11)[m]	3.198(11)
–O(11)	3.294(11)	–O(18)	3.200(11)
–O(5)	3.470(9)	–O(4)[b]	3.286(13)
		–O(19)	3.419(12)
–O(19)[c]	3.672(10)		
–O(2)[s]	3.773(10)		
–O(19)	3.970(10)	–O(4)	3.835(13)
K(3)–O(20)[q]	2.794(10)		
–O(1)[a]	2.801(7)		
–O(6)[a]	2.864(8)		
–O(16)[n]	3.020(9)		
–O(18)[a]	3.047(9)		
–O(9)[q]	3.051(9)		
–O(11)[f]	3.075(10)		
–O(7)[u]	3.118(8)		
–O(17)[q]	3.172(8)		
–O(7)[a]	3.347(9)		

[a] $1-x, 1-y, 1-z$.
[b] $x, y, 1+z$.
[c] $x, y, -1+z$.
[d] $1-x, 2+y, -z$.
[e] $-1+x, y, -1+z$.
[f] $-x, 1-y, 1-z$.
[g] $1-x, 1-y, -z$.
[h] $1-x, -y, 1-z$.
[i] $1+x, y, z$.
[j] $1+x, y, 1+z$.
[k] $-x, 1-y, 2-z$.
[l] $x, 1+y, z$.
[m] $-1+x, y, z$.
[n] $1-x, y, 1-z$.
[o] $x, -1+y, 1+z$.
[p] $1-x, 1-y, 2-z$.
[q] $x, -1+y, z$.
[r] $x, 1-y, 1-z$.
[s] $-x, 1-y, -z$.
[t] $2-x, 1-y, 1-z$.
[u] $x, -1+y, -1+z$.

oxygen ions) and it can be seen that the pairs K(1) and K(1′), K(2) and K(2′) have moved off their sites towards the vacant site (they are never both present). In the

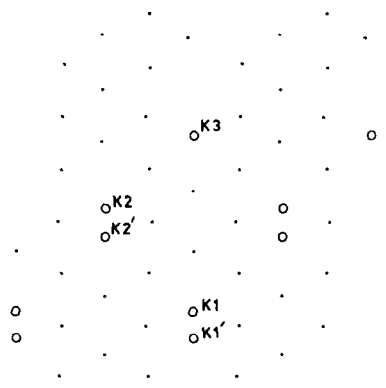

FIG. 4. One of the close-packed anion layers in $K_3Nb_7O_{19}$ in which oxygen atoms are represented by dots and potassium ions by circles; vacant anion sites are evident.

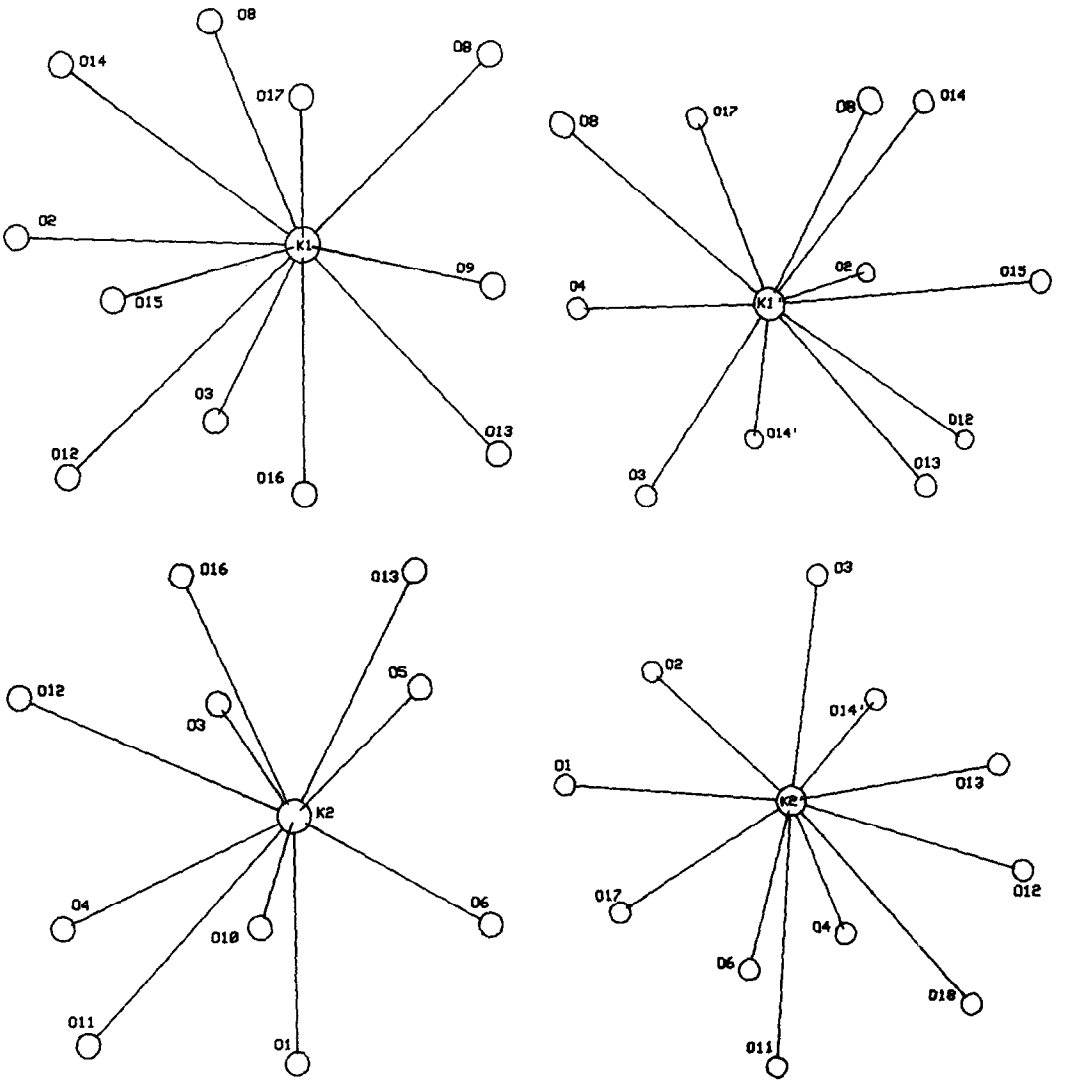

FIG. 5. The potassium ion coordination spheres in $K_3Nb_7O_{19}$.

case of K(3), which fully occupies a single site, it too has moved toward the adjacent vacant site. It appears that a distribution of K(3) over the two anion sites is prevented by its proximity to the highly condensed arrangement of niobium–oxygen octahedra. In Fig. 4 a single anion layer is drawn and the movement of potassium ions off the ideal anion sites can be more clearly seen, together with the vacancy adjacent to K(3).

Selected bond lengths are set out in Table II with estimated standard deviations. The niobium ions are octahedrally coordinated to oxygen with the Nb–O distances ranging from 1.803 to 2.293 Å (mean 2.004 Å). Nb(1) is edge shared to five other octahedra, Nb(2) and Nb(6) are each edge shared to three others, Nb(5) to two others, and Nb(3), Nb(4), and Nb(7) are edge shared to one other octahedron each. The edge- and

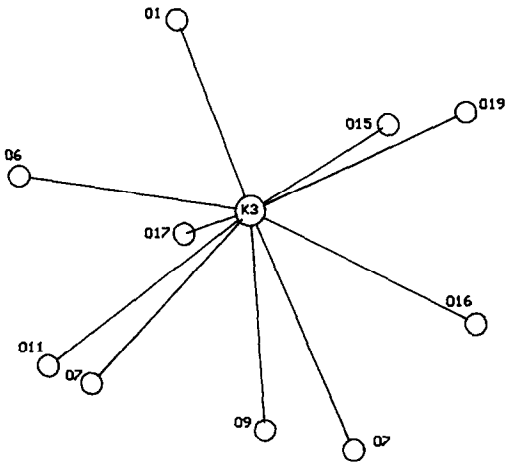

FIG. 5—*Continued.*

corner-shared distances between niobium atoms are given in Table II.

The potassium ion to oxygen distances are given in Table II out to 4.00 Å; however, it is considered that K(1), K(1′), and K(2′) are 11 coordinate (they are each adjacent to a vacant site); K(2) is 10 coordinate as the vacant site next to K(3) comes within its sphere. K(3) is also 10 coordinate since it has an adjacent vacant site, and that of another K(3) across a center of symmetry, within its sphere of coordination. The individual diagrams for the potassium ion coordination spheres are given in Fig. 5.

Several attempts have been made to solve the structure of the 4:9 compound, $K_8Nb_{18}O_{49}$ without success. A further attempt is in progress.

Acknowledgment

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