Fig. 1. The crystal structure of $Nb_5(Ge_x,Sn_{1-x})_2Ge$, $x = 0.25$, projected (a) along the c axis and (b) along the a axis; open circles Nb, filled circles Ge, shaded circles (Sn,Ge).

It is considered that the arrangement of Ge and Sn atoms in the structure is controlled by their atomic radii. The analysis shows that Sn was not accommodated in the $4(a)$ site, but this site is occupied by Ge. The atomic radii of the Sn atoms are relatively large compared with the small radius of Ge atoms. Thus, the $4(a)$ site with its restricted space is expected to be occupied by the smaller atoms. Sn atoms of other W_5Si_3-type intermetallic compounds, Ta_5SnGa_2 (Ye *et al.*, 1990), Nb_5Sn_2Ga (Ukei, Shishido & Fukuda, 1989) and Nb_5Sn_2Si (Horyn &

Lukaszewicz, 1970), show the same crystal chemical behavior as Sn in the present structure. That, in these compounds, Sn atoms are always accommodated in $8(h)$ sites. In binary systems of Va–Sn, such as Nb–Sn, Ta–Sn or V–Sn, compounds which have crystallized in a W_5Si_3-type structure have not been reported. This may be because W_5Si_3-type structures are unstable when containing large atoms.

The title compound has an interesting chemical composition, with Ge/Sn = 1. If Sn atoms occupy all the $8(h)$ sites, the chemical formula should be Nb_5Sn_2Ge for $Nb_5(Ge_x,Sn_{1-x})_2Ge$ with $x = 0$. However, the title compound never contains this amount of Sn atoms for the synthetic condition of the Sn self-flux method. This compound contains as many Sn atoms as the crystal structure allows. As a conclusion, the amount of Sn in the chemical composition seems to be governed by the space around the Nb atoms.

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Single-Crystal Structure of K3Nb8O21

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Abstract. Tripotassium 21-oxooctaniobate, $M_r = 1196.53$, hexagonal, $P6_3/mcm$, $a = 9.1584$ (5), $c = 12.0404$ (4) Å, $V = 874.6$ (1) Å^3, $Z = 2$, $D_x = 4.54$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 5.65$ mm^{-1}, $F(000) = 1106$, $T = 294$ K, $R = 0.044$, $wR = 0.047$ for 2540 reflections with $I > 3\sigma(I)$. The

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framework is built up from $[Nb_6O_{24}]$ units stacked along c giving $[Nb_6O_{21}]_\infty$ chains which are held together by single NbO_6 octahedra.

Introduction. During the investigation of the K–Nb–P–O system, single crystals of the compound $K_3Nb_8O_{21}$ were synthesized along with the new phosphate bronzes $KNb_3P_3O_{15}$ (Leclaire, Borel, Grandin & Raveau, 1989), $K_3Nb_6P_4O_{26}$ (Benabbas, Borel, Grandin, Leclaire & Raveau, 1990a), $K_7Nb_{14}P_9O_{60}$ (Leclaire, Benabbas, Borel, Grandin & Raveau, 1989), $K_4Nb_8P_5O_{34}$ (Benabbas, Borel, Grandin, Leclaire & Raveau, 1990b) and PNb_9O_{25} (Benabbas, Borel, Grandin, Leclaire & Raveau, 1991). This oxide was synthesized in the laboratory for the first time several years ago (Groult, Chailleux, Choisnet & Raveau, 1976). A structural model was established from X-ray powder diffraction data. We report here the structural determination from a single crystal, carried out in order to improve previous crystallographic results.

Experimental. Crystal: $0.216 \times 0.144 \times 0.036$ mm, $6/mmm$ symmetry with systematic absences $l = 2n + 1$ in $hh0l$, Enraf–Nonius diffractometer. Unit cell: least squares on 25 reflections $\pm 2\theta$, $18 \le \theta \le 22°$. Intensity measurement up to $\theta = 45°$ with an ω–$4/3\theta$ scan of width $(1 + 0.35\tan\theta)°$ and a counter slit aperture of $(1 + \tan\theta)$ mm, values determined by the study of reflections in the ω–θ plane. Scanning speed adjusted to obtain $\sigma(I)/I < 0.018$ or to approach it in a time limited to 60 s. Three standards for count (440, $\bar{4}80$, $\bar{8}40$) every 4000 s and orientation (080, 800, 0,4,10) every 600 reflections; no appreciable trends. 5257 reflections measured, 2540 with $I > 3\sigma(I)$ used to solve (heavy-atom method) and refine the structure on F. Positions and anisotropic thermal parameters refined. No correction made for extinction or absorption. The usual f's from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations carried out on a MicroVAX II with the *SDP* system (B. A. Frenz & Associates, Inc., 1982), $\Delta/\sigma_{max} = 0.005$, $\Delta\rho < 4$ e Å^{-3}, $R = 0.044$, $wR = 0.047$, $w = f(\sin\theta/\lambda)$, $S = 1.3$. Atomic parameters in Table 1*.

Discussion. This study confirms the powder diffraction results, *i.e.* that the octahedral framework $[Nb_8O_{21}]_\infty$ is, as described before, built up from edge- and corner-sharing NbO_6 octahedra (Fig. 1). Six octahedra [Nb(2) type] share edges in such a way

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Table 1. *Atomic coordinates and equivalent isotropic thermal parameters (Å²) for the title compound*

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

	x	y	z	B_{eq}
Nb(1)	0.667	0.333	0.000	0.875 (5)
Nb(2)	0.24888 (3)	0.249	0.09468 (2)	0.711 (2)
K	0.5938 (1)	0.594	0.250	1.57 (1)
O(1)	0.4818 (2)	0.3143 (2)	0.0958 (2)	0.84 (2)
O(2)	0.2006 (3)	0.000	0.0740 (2)	0.75 (3)
O(3)	0.2070 (4)	0.207	0.250	0.87 (3)

Table 2. *Main distances (Å) and angles (°) in the NbO_6 and KO_{12} polyhedra with the Nb—O distances on the diagonal, the O—O distances above and the O—Nb—O angles below*

Nb(1)	O(1)	O(1^i)	O(1^{ii})	O(1^{iii})	O(1^{iv})	O(1^v)
O(1)	1.983 (2)	2.794 (5)	2.794 (5)	2.969 (7)	2.969 (7)	3.955 (8)
O(1^i)	89.6 (2)	1.983 (2)	2.794 (5)	3.955 (8)	2.969 (7)	2.671 (6)
O(1^{ii})	89.6 (2)	89.6 (2)	1.983 (2)	2.671 (6)	3.955 (6)	2.969 (7)
O(1^{iii})	96.9 (2)	171.3 (2)	84.7 (2)	1.983 (2)	2.794 (5)	2.794 (5)
O(1^{iv})	84.7 (2)	96.9 (2)	171.3 (2)	89.6 (2)	1.983 (2)	2.794 (5)
O(1^v)	171.3 (2)	84.7 (2)	96.9 (2)	89.6 (2)	89.6 (2)	1.983 (2)

Nb(2)	O(1)	O(1^{vi})	O(2)	O(2^{vii})	O(2^{viii})	O(3)
O(1)	1.906 (3)	2.658 (6)	2.752 (4)	4.004 (8)	3.036 (6)	2.876 (6)
O(1^{vi})	88.4 (2)	1.906 (3)	4.004 (8)	2.752 (4)	3.036 (6)	2.876 (6)
O(2)	86.4 (2)	171.8 (2)	2.108 (2)	3.182 (9)	2.559 (3)	2.825 (3)
O(v^{ii})	171.8 (2)	86.4 (2)	98.0 (2)	2.108 (2)	2.559 (3)	2.825 (3)
O(2^{viii})	99.2 (2)	99.2 (2)	75.4 (2)	75.4 (2)	2.078 (5)	3.901 (9)
O(3)	97.9 (2)	97.9 (2)	89.2 (2)	89.2 (2)	156.1 (2)	1.909 (1)

K—O(2^{ii})	2.835 (5)	K—O(1^{ii})	3.196 (4)
K—O(2^{ix})	2.835 (5)	K—O(1^{xii})	3.196 (4)
K—O(1^x)	2.903 (4)	K—O(1^{ix})	3.196 (4)
K—O(1^{xi})	2.903 (4)	K—O(1^{xiii})	3.196 (4)
K—O(1^{vi})	2.903 (4)	K—O(3^{iv})	3.222 (6)
K—O(1)	2.903 (4)	K—O(3^{ii})	3.222 (6)

Symmetry code: (i) $1 - y$, $x - y$, z; (ii) $y - x$, $1 - x$, z; (iii) $1 - y$, $1 - x$, $-z$; (iv) x, $x - y$, $-z$; (v) $1 + x - y$, y, $-z$; (vi) y, x, z; (vii) $-y$, $x - y$, z; (viii) $x - y$, x, $-z$; (ix) $1 + y - x$, $1 - x$, $\frac{1}{2} - z$; (x) y, x, $\frac{1}{2} - z$; (xi) x, y, $\frac{1}{2} - z$; (xii) $1 - x$, $1 + y - x$, z; (xiii) $1 - x$, $1 + y - x$, $\frac{1}{2} - z$; (xiv) $1 - y$, $1 + x - y$, z.

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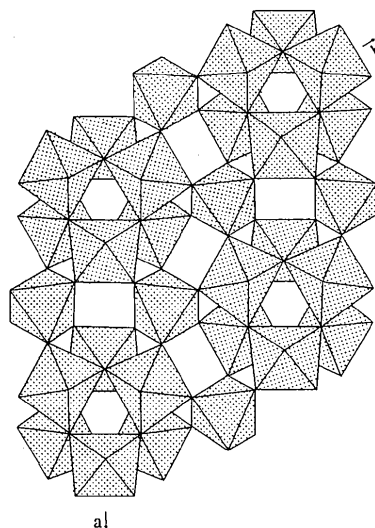
Fig. 1. Structure of $K_3Nb_8O_{21}$ projected along c.

that they form [Nb$_6$O$_{24}$] units. These units are stacked along the c axis and share corners in order to form [Nb$_6$O$_{21}$]$_\infty$ columns. The columns are linked together by sharing their vacant corners with single NbO$_6$ octahedra [Nb(1) type]. This framework delimits cages where the K ions are located. The structure may also be described as [Nb$_8$O$_{24}$]$_{2\infty}$ layers stacked along c and sharing their free corners.

The spread of the Nb(2)—O distances is half that observed from powder data but it is confirmed that the Nb(2)O$_6$ octahedron is strongly distorted as shown by the wide range of O—Nb(2)—O angles (75.4 to 99.2°) and O—O distances (2.559 to 3.182 Å) (Table 2). The Nb(1)O$_6$ octahedra are more regular. The mean valency of the Nb atoms deduced from the Zachariasen (1978) curve suggests that the Nb(1) sites are mainly occupied by Nb^V (mean valency 4.94), whereas the electrons would be preferentially delocalized in the Nb(2)O$_6$ octahedra (mean valency 4.86) in agreement with the size of these two types of sites. The mean valency deduced from this calcula-tion (4.88) is in agreement with the valency deduced from the charge balance according to the formula K$_3$Nb$_7^V$Nb^{IV}O$_{21}$ (4.875).

The K ions lie in cages between the [Nb$_8$O$_{24}$]$_{2\infty}$ layers. They are surrounded by 12 O atoms whose distances are smaller than 3.25 Å.

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Seven-Coordinate Manganese(II) Complexes of 2,6-Bis[1-(2-hydroxyethylimino)ethyl]pyridine

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Abstract. Diaqua{2,6-bis[1-(2-hydroxyethylimino)-ethyl]pyridine-N,N',N'',O,O'}manganese(II) diper-chlorate, [Mn(L)(H$_2$O)$_2$](ClO$_4$)$_2$ (L = C$_{13}$H$_{19}$N$_3$O$_2$) (I), M_r = 539.2, monoclinic, $C2/c$, a = 16.142 (3), b = 12.222 (3), c = 11.047 (3) Å, β = 94.41 (2)°, V = 2173 (1) Å^3, Z = 4, D_x = 1.648 Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, μ = 0.893 mm^{-1}, $F(000)$ = 1108, T = 293 K, final R = 0.064 for 1684 [$F > 6\sigma(F)$] indepen-dent observed reflections. {2,6-Bis[1-(2-hydroxyethyl-imino)ethyl]pyridine-N,N',N'',O,O'}bis(thiocyanato-N)manganese(II), [Mn(L)(NCS)$_2$] (II), M_r = 420, monoclinic, $I2/a$, a = 9.902 (2), b = 12.581 (2), c = 15.203 (3) Å, β = 101.46 (2)°, V = 1856.2 (6) Å^3, Z = 4, D_x = 1.504 Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, μ = 0.917 mm^{-1}, $F(000)$ = 868, T = 293 K, final R = 0.043 for 1505 [$F > 6\sigma(F)$] independent observed reflections. Bisazido{2,6-bis[1-(2-hydroxyethyl-imino)ethyl]pyridine-N,N',N'',O,O'}manganese(II), [Mn(L)(N$_3$)$_2$] (III), M_r = 388, orthorhombic, *Pbcn*, a = 18.643 (7), b = 12.616 (3), c = 7.127 (3) Å, V = 1676 (1) Å^3, Z = 4, D_x = 1.539 Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, μ = 0.783 mm^{-1}, $F(000)$ = 804, T = 173 K, final R = 0.041 for 818 [$F > 6\sigma(F)$] independent observed reflections. In each structure the Mn coordination geometry is approximately pen-tagonal bipyramidal with the five donors from the ligand L occupying the pentagonal plane. There is extensive hydrogen bonding in each structure.

Introduction. Many seven-coordinate complexes of first-row transition metals have been synthesized using macrocyclic ligands (Nelson, 1980; Drew, Othman & Nelson, 1976; Drew, Othman, McFall, McIlroy & Nelson, 1977) or rigid, resonance-stabilized planar systems (Capparelli, de Meester, Goodgame, Gunn & Skapski, 1985; Pelizzi, Pelizzi,

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