

Crystal Structures of Octacaesium and Octarubidium Docosaniobates

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Crystals of $\text{Cs}_8\text{Nb}_{22}\text{O}_{59}$ and $\text{Rb}_8\text{Nb}_{22}\text{O}_{59}$ are isomorphous. The structures of the two compounds have been determined by direct methods from 967 (Cs) and 791 (Rb) independent reflections, measured with a diffractometer, and refined by full-matrix least-squares methods to R 0.043 (Cs) and 0.102 (Rb). Crystals are rhombohedral (indexed on the hexagonal triple cell), space group $R\bar{3}m$, $a = 7.53(1)$ and $c = 43.02(6)$ Å (Cs), $a = 7.53(1)$ and $c = 43.39(6)$ Å (Rb). The structure consists of NbO_6 octahedra linked together through corners and edges, with the alkali-metal cations occupying positions which give an approximately close-packed array with the oxygen atoms.

THE niobium pentaoxide-alkali-metal oxide systems for rubidium and caesium have been extensively studied.¹⁻³ For compositions $\text{M}_2\text{O} : \text{Nb}_2\text{O}_5$ close to 1 : 3 there is some confusion. Reisman and Holtzberg report¹ a congruently melting compound (m.p. 1 319 °C) for the rubidium system with the ratio $4\text{Rb}_2\text{O} : 11\text{Nb}_2\text{O}_5$, but the isomorphous² caesium compound (m.p. 1 415 °C) is given the composition $5\text{Cs}_2\text{O} : 13\text{Nb}_2\text{O}_5$. Iyer and Smith³ starting from a mixture $4\text{Rb}_2[\text{CO}_3] : 11\text{Nb}_2\text{O}_5$, obtained pale yellow crystals with hexagonal symmetry, $a = 7.45$ and $c = 7.66$ Å, which they conclude have the composition RbNb_3O_8 .

We have obtained single crystals of excellent quality from the melt of the two isostructural compounds⁴ and have determined their crystal structures to show that their composition corresponds to $4\text{M}_2\text{O} : 11\text{Nb}_2\text{O}_5$. While this paper was in preparation, Gasperin reported⁵ the structure of a corresponding thallium(I) compound in which the Tl^+ cations were disordered, and showed that this was isostructural with the rubidium compound for which good single crystals were not obtained. Our results are very similar but we have had no problems of disorder for the univalent cations in the structure.

³ P. N. Iyer and A. J. Smith, *Acta Cryst.*, 1971, **B27**, 731.

¹ A. Reisman and F. Holtzberg, *J. Phys. Chem.*, 1960, **64**, 748.

⁴ G. R. Jones and D. S. Robertson, *J. Crystal Growth*, 1978, **43**, 115.

² A. Reisman and J. Mineo, *J. Phys. Chem.*, 1961, **65**, 966.

⁵ M. Gasperin, *Acta Cryst.*, 1977, **B33**, 398.

EXPERIMENTAL

The two compounds were prepared by the high-temperature melting of mixtures of alkali-metal carbonate and niobium pentaoxide. Large single crystals were obtained by the vertical-lift technique.⁴ Crystals of the caesium salt were ground to spheres but these were found to be too difficult to handle at radii small enough for absorption not to cause 'holes' in the spots. A thin needle crystal was obtained by crushing a large single-crystal chunk and was found to have the *a* axis parallel to the needle. Large single crystals of the rubidium compound obtained from the melt spontaneously fragmented on exposure to the normal laboratory atmosphere.⁴ Although the fragments were mainly too small for single-crystal use, one needle-shaped fragment was hand-picked from the powder and again found to be elongated parallel to the *a* axis. For both compounds, unit-cell and space-group data were obtained photographically and intensity data with a diffractometer.

Crystal Data (Values for the Rubidium Compound are in Square Brackets).—Refined as Cs₄Nb₁₁O₃₀ [Rb₄Nb₁₁O₃₀], *M* = 1 844 [2 034], Rhombohedral, *a* = 7.53(1) [7.53(1)], *c* = 43.02(6) [43.39(6)] Å, *U* = 2 131 [2 112] Å³, *D_m* = 4.83, *Z* = 3, *D_c* = 4.80 [4.31], *F*(000) = 2 733 [2 517]. Space group *R* $\bar{3}m$ (*D*_{3d}⁵, no. 166), *R* $\bar{3}$ (*C*_{3i}², no. 148), or *R*32 (*D*₃², no. 155) from systematic absence *hkl* when $-h + k + l \neq 3n$. The former space group was indicated by a negative Giebe-Schiebe test for piezoelectric activity, and the absence of a second harmonic signal from a 1.06- μ m Nd : YAG laser, and confirmed by the successful structure refinement. Mo-*K α* radiation λ 0.710 7 Å, μ = 88 [106] cm⁻¹.

Structure Determination.—Intensity data for both compounds were collected about the *a* axis (layers 0—5*kl*) with a Stoe two-circle computer-controlled diffractometer, by use of graphite-monochromated Mo-*K α* radiation. The stationary-counter-moving-crystal method was used, with an ω scan range of 1.2° on the lower levels, counting for 1 s at 0.01° intervals. For reflections on the third and higher layers ($\mu > 7^\circ$) a variable range was scanned, with $\Delta\omega$ defined by $[A + (B \sin\mu/\tan\mu)]$ where *A* = 1.0 and *B* = 0.5. Stationary-background counts were measured at the extremities of each scan for 10 s. Within the range $0.1 < (\sin\theta)/\lambda \leq 0.65$, 967 [791] independent reflections having *I* > 3 σ (*I*) were obtained and considered observed. Data were corrected for Lorentz and polarization factors but not for absorption.

Structure solution was initiated on the rubidium compound using the tangent-refinement direct-methods routine⁶ (TANGEN) of 'X-Ray '72' with all the settings at their default values and using the 233 reflections with *E* > 1.0. The (2,4,−5) reflection, with its phase fixed at 180°, was used for origin definition. From the *E* map produced after TANGEN, which was phased on 34 reflections having a computed phase of 0° and 33 reflections with a phase of 180°, as well as several subsequent difference-Fourier maps, the solution was eventually evolved by trial and error. [In a separate run through TANGEN with the phase of the (2,4,−5) reflection fixed at 0°, all the 67 phases were computed to be 0°.] Refinement of the structure of the

caesium compound was begun with the parameters of the rubidium compound as a starting point.

Scattering factors used were those for the neutral atoms,⁷ with corrections for the effects of anomalous dispersion⁸ ($\Delta f'$ and $\Delta f''$) applied to those for Rb, Cs, and Nb. Initial refinement was by full-matrix least-squares methods with layer scale factors refined separately, and all the atoms vibrating isotropically. Refinement was continued with layer scale factors held constant⁹ and with the introduction of anisotropic thermal parameters, for all the atoms, of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}h^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}hkb^*c^*)]$. In the final stages of refinement the weighting scheme¹⁰ $w = [\sigma^2(F_o) + (0.04|F_o|)^2]^{-1}$ was appropriate, giving a satisfactory analysis of the variation of $w\Delta^2$ with increasing $(\sin\theta)/\lambda$ and with increasing fractions of $|F_o|$. At convergence no parameter shift was > 0.001 σ and a final difference-Fourier map showed no significant features. The final *R* was 0.043 [0.102] and *R'* = 0.081 [0.147] {*R'* = $[\Sigma w(|F_o| - |F_c|)^2/\Sigma |F_o|^2]^{1/2}$ }. Most of the calculations were carried out on the CDC 7600 computer at the University of Manchester Regional Computer Centre using the 'X-Ray '72' system of programs.⁶ Observed and calculated structure factors and anisotropic thermal parameters are listed in Supplementary Publication No. 22257 (11 pp.),* final positional parameters with their estimated standard deviations in Table 1, and interatomic distances and angles in Table 2.

TABLE 1

Final atomic positional parameters with estimated standard deviations in parentheses. Values for the rubidium compound follow those for caesium

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Nb(1)	0.167 62(8)	0.335 25	0.028 88(2)
	0.167 7(1)	0.3354	0.028 80(4)
Nb(2)	0	0	0.099 71(4)
	0	0	0.099 56(7)
Nb(3)	1/3	1/6	1/6
	1/3	1/6	1/6
Cs(1)	2/3	1/3	0.072 20(5)
Rb(1)	2/3	1/3	0.066 4(2)
Cs(2)	1/3	2/3	0.115 10(5)
Rb(2)	1/3	2/3	0.118 7(4)
O(1)	0.124 4(8)	0.2487	0.069 6(2)
	0.124 2(10)	0.2484	0.069 8(3)
O(2)	0.249 8	0.124 9(8)	0.122 7(2)
	0.248 2	0.124 1(10)	0.122 8(3)
O(3)	0.285 1	0.142 5(7)	0.020 2(2)
	0.282 4	0.141 2(10)	0.019 1(3)
O(4)	0.449 4(8)	0.8989	0.031 3(2)
	0.448 0(10)	0.8960	0.031 6(3)
O(5)	0.129 8(10)	0.2596	0.174 7(3)
	0.125 2(10)	0.2504	0.175 2(3)

DISCUSSION

The crystal-structure analysis has established the stoichiometry of the compounds as A₈Nb₂₂O₅₉. The unit-cell contents that were refined corresponded to A₁₂Nb₃₃O₉₀, with A₄Nb₁₁O₃₀ in the primitive rhombohedral cell, and we assume that there is a disordered vacancy in one of the oxygen positions. Since this vacancy will only lower the site occupation factor to $\frac{1}{2}$ if only one oxygen atom is involved, we have not

⁷ D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

⁸ D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

⁹ E. C. Lingafelter and J. Donohue, *Acta Cryst.*, 1966, **20**, 321.

¹⁰ G. H. Stout and L. H. Jensen, 'X-Ray Structure Determination,' Macmillan, London, 1969, p. 456.

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

⁶ The 'X-Ray' system, Technical Report TR 192, the Computer Science Centre, University of Maryland, June 1972.

attempted to define it, and there is no evidence of any anomaly in the temperature factors for any of the oxygen atoms. A five-co-ordinate arrangement of oxygen

bridging to two other niobium atoms, and three oxygen atoms [O(1) and O(4)] bridging to one other

TABLE 2

Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses. Values for the rubidium compound follow those for caesium

(a) Distances			
Nb(1)—O(1)	1.842(8)	Nb(2)—O(1)	2.075(6)
	1.868(12)		2.072(8)
Nb(1)—O(3)	2.076(5)	Nb(2)—O(2)	1.906(8)
	2.080(7)		1.907(10)
Nb(1)—O(3 ^I)	2.138(9)	Nb(3)—O(2)	1.969(9)
	2.105(13)		1.982(12)
Nb(1)—O(4 ^{II})	1.924(6)	Nb(3)—O(5)	2.007(8)
	1.920(8)		1.994(8)
Cs(1) ··· O(3)	3.345(8)	Cs(2) ··· O(1)	3.355(6)
Rb(1) ··· O(3)	3.239(13)	Rb(2) ··· O(1)	3.456(13)
Cs(1) ··· O(4 ^{II})	3.334(8)	Cs(2) ··· O(5 ^{IV})	3.248(7)
Rb(1) ··· O(4 ^{II})	3.227(9)	Rb(2) ··· O(5 ^{IV})	3.209(12)
Cs(1) ··· O(2)	3.480(9)	Cs(2) ··· O(5)	3.691(9)
Rb(1) ··· O(2)	3.666(11)	Rb(2) ··· O(5)	3.658(15)
Cs(1) ··· O(1)	3.807(8)	Cs(2) ··· O(2)	3.818(8)
Rb(1) ··· O(1)	3.808(13)	Rb(2) ··· O(2)	3.810(14)
O(2) ··· O(1)	2.80(1)	O(3) ··· O(1)	2.76(1)
	2.81(2)		2.81(2)
O(1) ··· O(1 ^{III})	2.81(1)	O(1) ··· O(4 ^{II})	2.88(1)
	2.81(2)		2.89(2)
O(5) ··· O(2)	2.79(2)	O(2) ··· O(2 ^{III})	2.82(2)
	2.80(2)		2.80(2)
O(3) ··· O(4 ^{II})	2.72(1)	O(3) ··· O(3 ^I)	2.55(1)
	2.75(2)		2.48(2)
O(4) ··· O(4 ^{II})	2.62(1)	O(2) ··· O(5 ^{IV})	2.84(2)
	2.59(2)		2.83(2)
O(5) ··· O(5 ^{IV})	2.74(2)	O(5) ··· O(5 ^{III})	2.93(2)
	2.81(2)		2.83(2)
(b) Angles			
O(1)—Nb(1)—O(3)	89.2(3)	O(1)—Nb(1)—O(4 ^{II})	99.8(3)
	90.5(4)		99.5(4)
O(3)—Nb(1)—O(4 ^{II})	85.6(3)	O(3)—Nb(1)—O(3 ^{III})	101.7(2)
	86.7(3)		100.1(3)
O(3)—Nb(1)—O(3 ^I)	74.4(3)	O(4 ^{II})—Nb(1)—O(4 ^V)	85.9(2)
	72.5(4)		84.9(3)
O(4 ^{II})—Nb(1)—O(3 ^I)	99.6(3)	O(3)—Nb(1)—O(4 ^V)	168.6(2)
	100.5(5)		167.9(3)
O(1)—Nb(1)—O(3 ^I)	153.4(1)	O(1)—Nb(2)—O(2)	89.4(3)
	152.8(1)		89.9(4)
O(1)—Nb(2)—O(1 ^{III})	85.2(3)	O(2)—Nb(2)—O(2 ^{III})	95.5(3)
	85.2(4)		94.6(4)
O(1)—Nb(2)—O(2 ^{VIII})	172.7(3)	O(2)—Nb(3)—O(5)	89.0(3)
	173.4(4)		89.2(4)
O(2)—Nb(3)—O(5 ^{VI})	90.9(3)	O(5)—Nb(3)—O(5 ^{IV})	93.8(3)
	90.7(4)		90.3(3)
O(5)—Nb(3)—O(5 ^{IV})	86.2(3)	Nb(1)—O(1)—Nb(2)	146.4(3)
	89.7(3)		146.3(4)
Nb(2)—O(2)—Nb(3)	137.3(3)	Nb(1)—O(3)—Nb(1 ^{VII})	103.5(3)
	138.2(4)		105.0(4)
Nb(1)—O(3)—Nb(1 ^{VIII})	131.6(2)	Nb(1 ^V)—O(4)—Nb(1 ^{II})	153.2(1)
	131.2(3)		154.0(2)
Nb(3)—O(5)—Nb(3 ^{III})	139.4(3)		
	141.5(4)		

Roman numeral superscripts refer to atoms in the following positions:

I	$x - y, y, -z$	V	$1 - y, 1 + x - y, z$
II	$y - x, 1 - y, z$	VI	$\frac{2}{3} - x, \frac{1}{3} - y, \frac{1}{3} - z$
III	$-y, x - y, z$	VII	$y, y - x, -z$
IV	$\frac{2}{3} - y + x, \frac{1}{3} + x, \frac{1}{3} - z$	VIII	$y - x, -x, z$

atoms around a niobium atom, with a square-pyramidal configuration, has recently been found in the structure¹¹ of Cs₄[Nb₄O₁₂] and such an arrangement seems reasonable in the present case.

The composition A₄Nb₁₁O₃₀ corresponds to A₄[NbO₃]₁₅⁻[Nb₂O₅]₃. Nb(1) in an 18-fold position has an octa-

niobium atom, giving the stoichiometry Nb[O₄]₃-[O₄]₃ or NbO_{2.5}. Both Nb(2) in a six-fold position and Nb(3) in a nine-fold position are co-ordinated by singly bridging oxygen atoms, O(1) and O(2) for Nb(2) and

¹¹ G. Meyer, R. Hoppe, and M. Jansen, *Naturwiss.*, 1976, **63**, 386.

O(2) and O(5) for Nb(3), giving the composition $\text{Nb}(\text{O}_{\frac{1}{2}})_6$ or NbO_3 . Thus, overall, the cell contents are $[\text{Nb}(1)\text{O}_{2.5}]_{18} [\text{Nb}(2)\text{O}_3]_6 [\text{Nb}(3)\text{O}_3]_9 \text{M}(1)_6 \text{M}(2)_6$.

The atomic arrangement in the two compounds is almost identical, as shown by the excellent agreement of bond distances and angles in Table 2, and this discussion will refer only to the more accurate results for the caesium compound.

The octahedral co-ordination of the niobium atoms by oxygen is distorted, particularly for Nb(1) (Table 2). The Nb-O distances range from 1.842 to 2.138 Å, with each octahedron having the same average value of 1.99 Å, which is close to the value¹¹ of 1.95 Å in $\text{Cs}_4[\text{Nb}_4\text{O}_{12}]$. The angular distortion is also greater for the Nb(1) octahedron, presumably due to the presence of the triply bridging atoms O(3) and the doubly bridged system $\text{Nb}(1)[\text{O}(3)]_2\text{Nb}(1)$. These factors can also account for the different distances. Thus the longest distance is Nb(1)-O(3) of 2.138 Å, where O(3) is involved in the double bridge, with Nb(1)-O(3)-Nb(1) of 103.5° and a short Nb-Nb distance of 3.309 Å. The other two bonds to O(3) are of 2.076 Å where the angle Nb-O(3)-Nb is 131.6° and the niobium atoms are 3.79 Å apart. Both these distances are longer than the average Nb-O (1.99 Å), presumably due to the triply bridging role of O(3). These long distances in the Nb(1) octahedron are balanced by Nb(1)-O(1) (1.842 Å), where this shortest distance is *trans* to the longest Nb-O (2.138 Å).

The short Nb(1)-O(1) distance is balanced by a longer Nb(2)-O(1) distance (2.075 Å), with the Nb(2)-O(2) distance (1.906 Å) then being shorter than the average

value. The two distances in the Nb(3) octahedron are close to the mean value and this is the least distorted octahedron.

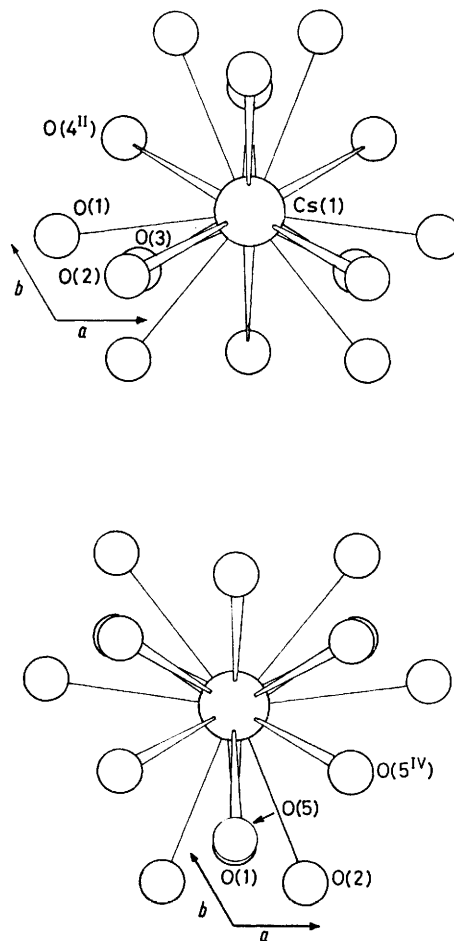


FIGURE 2 Projection of parts of the structure down [001] to show the co-ordination of the caesium ions

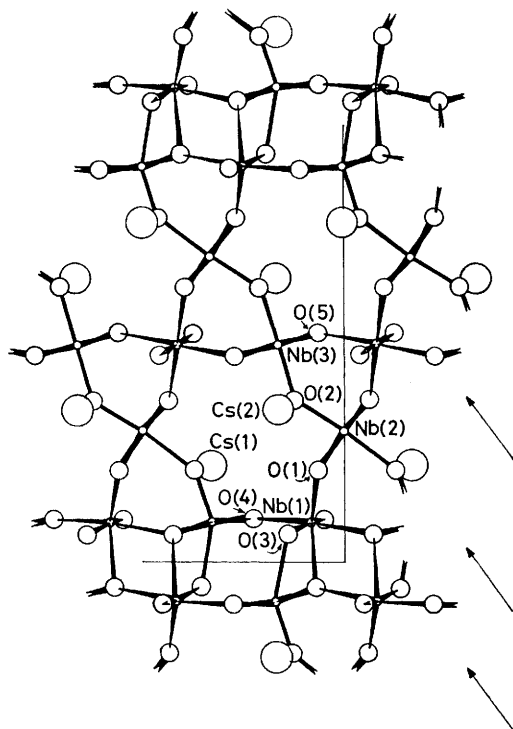


FIGURE 1 Projection of the structure down [010]. The arrows indicate planes of approximately close-packed atoms

The two caesium atoms have very similar environments to each other (Figure 2). Each has 15 oxygen atom neighbours with $\text{Cs}\cdots\text{O}$ distances within the range 3.248–3.818 Å. The co-ordination consists of six neighbours at approximately the same level on *c*, O(1) for Cs(1) and O(2) for Cs(2), six more [O(3) and O(4)] below for Cs(1) and above [O(5) and O(5'')] for Cs(2), and the three remaining [O(2) above for Cs(1) and O(1) below for Cs(2)]. Thus the caesium atoms fill holes in the oxygen lattice, and the caesium and oxygen atoms together form an approximately close-packed array. Planes of close-packed atoms are indicated in Figure 1, where the caesium atoms can be seen to be part of these planes. Although the close packing is distorted, the average volume per oxygen or caesium atom is 20.9 Å³, which is comparable with the 18 Å³ usually associated with a close-packed oxygen lattice. The type of packing cannot be distinguished, but the Nb-O-Nb angles between singly bridged octahedra are closer to the theoretical 132° for hexagonal than to the 180° for cubic

close packing. The Cs \cdots O distances are longer than those in $\text{Cs}_4[\text{Nb}_4\text{O}_{12}]$ where the range is from 2.94 to 3.10 Å. The interactions of the cations with the rigid lattice anion in the present structure may be weaker than those with the separate $[\text{Nb}_4\text{O}_{12}]^{4-}$ anions.

The two structures are very similar to that of the recently reported thallium compound.⁵ The alkali-metal atoms, however, appear to occupy definite sites in the lattice and there is no evidence for disorder or partial site occupation, as reported for the thallium atoms. The preparative treatment of the crystals was rather different, and replacement of some thallium ions with $[\text{H}_3\text{O}]^+$, as

suggested, when the crystals were treated with boiling water, seems likely. The temperature factors for the rubidium atoms were much higher than those for caesium, and it is possible that the larger caesium atom is more tightly held in the oxide framework. The Tl^+ ion is smaller than Rb^+ and would therefore be expected to be more easily replaced.

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