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Crystal Structure of $RbOsO_3N$: A New $CsReO_4$-Type Compound

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Crystals of $RbOsO_3N$ are orthorhombic, space group *Pnma*, with $z = 4$, $a = 5.571(1)$, $b = 5.794(1)$, $c = 13.735(3)$ Å. Intensities for 556 independent reflections collected on a four-circle diffractometer were used in the structure determination and the structure was refined to a final R value $= 0.046$ ($R_w = 0.056$). The structure consists of OsO_3N discrete tetrahedra linked together by 8-coordinated Rb ions. The oxygen and nitrogen atoms are distributed randomly. $RbOsO_3N$ is the first compound belonging to the $CsReO_4$-type family for which the complete structure has been determined. This structure can be related to scheelite type but appreciable differences occur in tetrahedra arrangement.

Introduction

The preparation of M^IOsO_3N compounds (M^I = K, Rb, NH_4, Tl, Cs) has been reported (*1*). The structure of $KOsO_3N$ previously described (*2*) consists of isolated OsO_3N tetrahedra linked together by the K ions. The arrangement is related to the scheelite-type structure (*3*). We have undertaken the determination of the crystal structure of $RbOsO_3N$, isotypic with the ammonium and thallium salts, in order to follow the evolution of the coordination of the M^I cation with increasing ionic radius.

Experimental

In order to prepare this compound, it is necessary to operate in several steps. The $KOsO_3N$ aqueous solution is treated with $AgNO_3$ and the Ag product which crystallizes is filtered off. After dissolution of this compound in water a solution of rubidium chloride is added. After separation of the AgCl precipitate, the crystals of $RbOsO_3N$ are obtained by slow evaporation in a desiccator.

The selected single crystal had a quasi-spherical shape with a mean radius of 0.09 mm. Cell dimensions were obtained by least squares from 25 values measured with the four-circle diffractometer NONIUS-CAD 4 used for the data collection (MoK_α radiation–graphite monochromator): $a = 5.571(1)$, $b = 5.794(1)$, $c = 13.735(3)$ Å, and $V = 443$ Å^3.

The systematic absences found ($0kl$: $k + l = 2n + 1$, and $hk0$: $h = 2n + 1$) agree with *Pnma* and $Pna2_1$ space groups. The centrosymmetric group *Pnma* (D_{2h}^{16}) was found to be correct during the structure determination. The intensities were collected in the $\omega - 2\theta$ scan mode ($2 < \theta < 30°$) and 556 independent reflections with $I \geq \sigma(I)$ (*4*) were used for the structure calculations. The intensities were corrected for Lorentz and polarization effects but no correction was made for absorption because no significant differences were observed at the

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TABLE I

ATOMIC AND THERMAL PARAMETERS WITH esd's IN PARENTHESES

Atom	x	y	z	B_{eqv}
Os	0.0356 (1)	0.250 (0)	0.37822 (4)	1.459 (9)
Rb	0.4710 (4)	0.250 (0)	0.6254 (1)	2.41 (3)
ON(1)	0.327 (3)	0.250 (0)	0.4185 (11)	3.3 (3)
ON(2)	−0.015 (2)	0.010 (2)	0.3097 (9)	4.1 (3)
ON(3)	−0.153 (4)	0.250 (0)	0.4758 (13)	4.4 (4)

Atom	$\beta(1,1)$	$\beta(2,2)$	$\beta(3,3)$	$\beta(1,2)$	$\beta(1,3)$	$\beta(2,3)$
Os	0.0100 (2)	0.0136 (2)	0.00166 (3)	0.0	0.0	0.0
Rb	0.0216 (6)	0.0211 (5)	0.00233 (8)	0.0	0.0	0.0

Note. The form of the anisotropic thermal parameter is $\exp[-(\beta(1,1)h^2 + \beta(2,2)k^2 + \beta(3,3)l^2 + \beta(1,2)hk + \beta(1,3)hl + \beta(2,3)kl)]$.

end of refinement using absorption-corrected data or uncorrected data. Structure factors were corrected for isotropic secondary extinction ($g = 1.0077\ 10^{-6}$).

Structure Determination and Refinement

The structure was solved by the heavy atom method. It was possible, from the Patterson map, to locate Os and Rb atoms in two 4*c* special positions. Then, a Fourier difference map showed the anions in two 4*c* and one 8*d* positions. In these positions it would be possible to order oxygen and nitrogen atoms but X-ray data do not allow one to distinguish between oxygen and nitrogen. Furthermore, no significant differences exist among the Os–anion bond lengths and we have distributed oxygen and nitrogen randomly over all the sites.

The refinement of positional parameters and anisotropic temperature factors for Os and Rb atoms and isotropic for O and N atoms gives a final R value equal to 0.046 ($R_w = 0.056$). The final atomic coordinates are listed in Table I. The calculations were performed with the SDP program system (*4*).[1]

Description of the Structure and Discussion

Jaeger and Zanstra (*1*) have assigned the space group of the Rb compounds $P2_12_12_1$ although the unit cell constants are comparable to $CsReO_4$. In our study we found the same space group *Pnma* as for $CsReO_4$-type phases. This structure has been described as an orthorhombic deformation of the scheelite-type structure. However, the positions of the light atoms have never been determined and therefore the structural filiation remained to be fully confirmed (*3*).

The structure of $RbOsO_3N$ is shown in Fig. 1 in comparison with $KOsO_3N$, which possesses a scheelite-type structure. The bond lengths and valence angles are given in Table II. The structure consists of OsO_3N discrete tetrahedra linked together by Rb ions. The mean distance of Os–O(N), 1.71 Å, is in good agreement with the values observed in $KOsO_3N$, 1.72 Å (*2*), and OsO_4, 1.74 Å (*5*). The substitution of potassium by rubidium leads to a distortion of the tetrahedra packing which can be described by two rotations of tetrahedra along the *b* and *c* axes. In our case, the rotation angles along **b** and **c** are equal to 16.3 and 24.4°, respectively. The result is that the coordination polyhedra around the K and

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[1] The list of observed and calculated structure factors can be obtained from the authors.

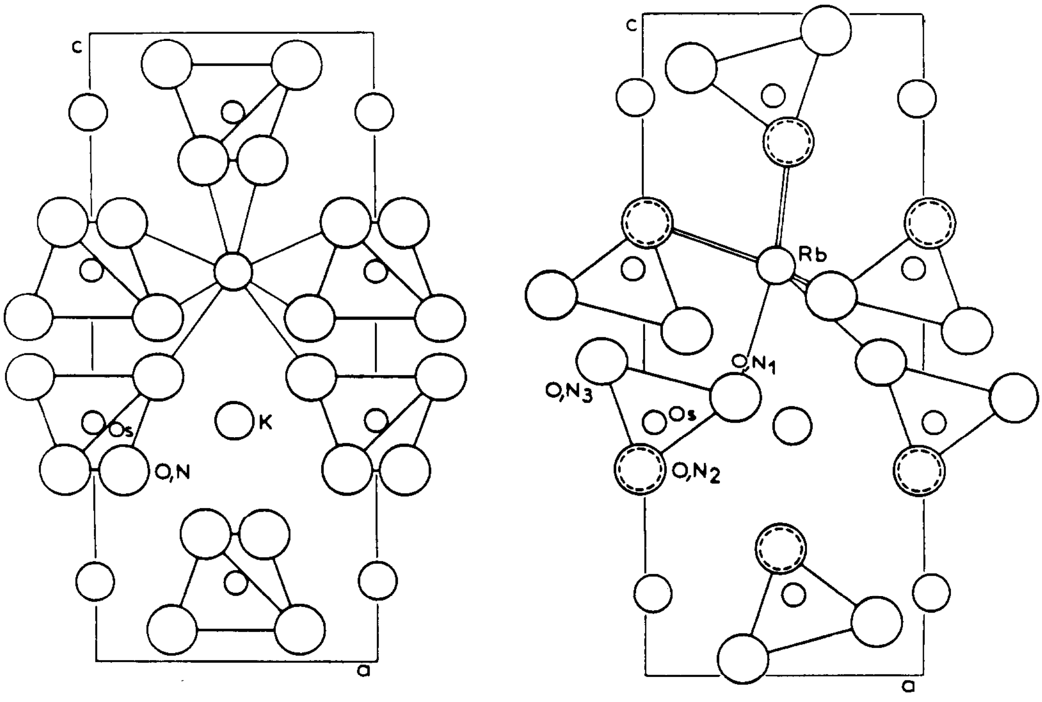

FIG. 1. Projection along the *b* axis of the $KOsO_3N$ and $RbOsO_3N$ structures.

Rb ions are quite different although the coordination number is equal to eight in both cases. As a consequence of this distortion, we observe a great dispersion of the Rb–O(N) distances which lie between 2.92 and 3.16 Å (in $KOsO_3N$, K–O(N) lengths are equal to 2.81 and 2.88 Å).

TABLE II

BOND LENGTHS (Å) AND ANGLES (°) IN Os AND Rb COORDINATION POLYHEDRA WITH esd's IN PARENTHESES

	Os coordination tetrahedron		
Os–ON(1^i)	1.717 (12)	ON(1^i)–Os–ON(2^i)	109.6 (3)
Os–ON(2^i)	1.705 (9)	ON(1^i)–Os–ON(2^{ii})	109.6 (3)
Os–ON(2^{ii})	1.705 (9)	ON(1^i)–Os–ON(3^i)	109.3 (5)
Os–ON(3^i)	1.704 (12)	ON(2^i)–Os–ON(2^{ii})	109.6 (5)
		ON(2^i)–Os–ON(3^i)	109.3 (3)
		ON(2^{ii})–Os–ON(3^i)	109.3 (3)
	Rb coordination polyhydron		
Rb–ON(1^i)	2.952 (10)	Rb–ON(2^v)	3.082 (9)
Rb–ON(1^{iii})	3.165 (5)	Rb–ON(2^{vi})	3.082 (9)
Rb–ON(1^{iv})	3.165 (5)	Rb–ON(2^{vii})	2.956 (8)
Rb–ON(3^i)	2.932 (12)	Rb–ON(2^{viii})	2.956 (8)

Symmetry code superscript

i x, y, z	v $-x, -y, 1-z$
ii $x, \frac{1}{2}-y, z$	vi $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$
iii $1-x, -y, 1-z$	vii $-x, \frac{1}{2}+y, 1-z$
iv $1-x, 1-y, 1-z$	viii $\frac{1}{2}-x, -y, \frac{1}{2}+z$

$RbOsO_3N$ and the $CsMe^{VII}O_4$ compounds (Me^{VII} = I, Re, Tc) (*6*) belong to an isostructural family for which we have determined the complete structure. From a general point of view, Jeitschko *et al.* (*7*) have shown the filiations in the scheelite-related structures and their space group relationships. Although there are no orthorhombic distortions of the scheelite structure, we can compare the tetrahedra packing in $RbOsO_3N$ and $CaWO_4$ compounds. Both $CsReO_4$ and scheelite structures can be related to the zircon structure.

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