

distortions are now more precisely described, are quite clearly real and cannot be suspected to be artifacts of refinement.

In both the Ti(1) and the Ti(2) coordination octahedra in BaTi_4O_9 , the Ti atoms are displaced away from the centers of the octahedra as already observed by Templeton & Dauben (1960). Such distortions have been described and compared with similar observations in other compounds by Shirane, Pepinsky & Frazer (1956) in PbTiO_3 , by Baur (1961) in brookite and by Tillmanns (1974) in BaTi_2O_5 . In BaTi_4O_9 , in $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ and in BaTi_2O_5 these octahedral distortions can be correlated with the bond-strength deviations at the O atoms (Baur, 1970).

The b cell edge of about 4.0 Å in the Wadsley/Andersson type phases corresponds to the corner-to-corner distance of the coordination octahedra or to twice the Ti—O distance in a titanate. In the barium titanates which adopt this structural type this means that the b edges are about 3.9 Å long. However, the b constant of BaTi_4O_9 measures only 3.794 Å and is thus the shortest on record for any barium titanate. This shortness is connected to the above-mentioned off-centering of the Ti atoms and results in angles O—Ti—O

parallel to [010] of 151 and 156° instead of the expected 180° (see Table 2).

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Structures of Phase IV Rubidium Nitrate, RbNO_3 , and Phase II Caesium Nitrate, CsNO_3

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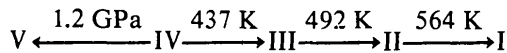
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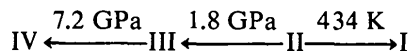
Abstract. RbNO_3 : $M_r = 147.47$, trigonal, $P3_2$, $a = 10.502$ (1), $c = 7.473$ (1) Å, $V = 713.8$ (1) Å³, $Z = 9$, $D_x = 3.106$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 152.5$ cm⁻¹, $F(000) = 612$, $T = 299.5$ K, final $R = 3.3\%$ for 797 unique observed reflections. CsNO_3 : $M_r = 194.91$, trigonal, $P3_1$, $a = 10.931$ (2), $c = 7.763$ (3) Å, $V = 803.1$ (4) Å³, $Z = 9$, $D_x = 3.626$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 100.96$ cm⁻¹, $F(000) = 774$, $T = 299.5$ K, final $R = 4.7\%$ for 760 unique observed reflections. The structures were found to be isomorphous and similar to that of $\text{TlNO}_3(\text{III})$. The three unique nitrates have site symmetries of C_1 but the symmetry of two of them is close to C_s or C_2 . Large nitrate-ion reorientations are

proposed for transformation to the high-pressure phases.

Introduction. The known polymorphs of RbNO_3 are related as follows:



and CsNO_3 undergoes the polymorphic transformations:



(Kalliomäki & Meisalo, 1979; Adams & Tan, 1981). A comprehensive review of the above thermal-phase transformations is given by Pistorius (1976). It has been suggested (Brooker, 1973; DeLacy & Kennard, 1971) that the room-temperature phases $\text{RbNO}_3(\text{IV})$

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and $\text{CsNO}_3(\text{II})$ are isomorphous and it was the object of this series of experiments to determine these two structures in order to allow correlation with the transformation properties. The structures of $\text{RbNO}_3(\text{IV})$ and $\text{CsNO}_3(\text{II})$ have recently been solved by neutron diffraction [Shamsuzzoha & Lucas (1982) and Lucas (1983) respectively].

Experimental. Source, E. Merck. Enraf-Nonius CAD-4 diffractometer. Crystals cut from *c*-axis needles with $\{2\bar{1}0\}$ and $\{001\}$ form faces.

RbNO₃: Recrystallized from aqueous solution by ethanol vapour diffusion, crystal 0.1 mm across \times 0.13 mm long. Cell parameters from setting angles of 25 reflections, $24 < \theta < 28^\circ$, transmission values from absorption corrections: min. = 0.15, max. = 0.23. For intensity measurements max. $\sin(\theta)/\lambda = 0.595 \text{ \AA}^{-1}$, index ranges ($0 \leq h \leq 12$, $0 \leq k \leq 12$, $-8 \leq l \leq 8$) and ($-12 \leq h \leq 0$, $0 \leq k \leq 12$, $0 \leq l \leq 8$), standard reflections $\bar{3}00$, $\bar{2}11$ and 111 with no variation, 1259 reflections measured, all unique and 465 unobserved ($F < 5\sigma_F$), $R_{\text{int}} = 0.0104$. Structure solved by Patterson and successive Fourier synthesis, $\sum w(\Delta F)^2$ minimized. Atomic coordinates, anisotropic thermal parameters, scale factor, weighting scheme and secondary extinction refined. Final $R = 3.3\%$, $R_w = 3.5\%$, $w = k(\sigma_F^2 + |g|F^2)$, $k = 2.62$, $g = -0.00037$, max. $(\Delta/\sigma) = 0.286$, max. and min. heights 1.15 and 0.677 e \AA^{-3} , secondary extinction coefficient = 0.0016 mm^{-1} .

CsNO₃: Recrystallized from aqueous solution by evaporation, crystal 0.1 mm across \times 0.19 mm long. Cell parameters from setting angles of 25 reflections, $5 < \theta < 21^\circ$, transmission values from absorption corrections: min. = 0.03, max. = 0.21. For intensity measurements max. $\sin(\theta)/\lambda = 0.571 \text{ \AA}^{-1}$, index ranges ($0 \leq h \leq 12$, $0 \leq k \leq 12$, $-12 \leq l \leq 12$), standard reflections $22\bar{2}$, 242 and $\bar{1}2\bar{1}$ with no variation, 1055 reflections measured, 940 unique and 180 unobserved ($F < 5\sigma_F$), $R_{\text{int}} = 0.0245$. Structure solved by Patterson and successive Fourier synthesis, $\sum w(\Delta F)^2$ minimized. Atomic coordinates, anisotropic thermal parameters, scale factor, weighting scheme and secondary extinction correction refined. Final $R = 4.7\%$, $R_w = 5.5\%$, $w = k(\sigma_F^2 + |g|F^2)$, $k = 19.8$, $g = 0.00033$, max. $(\Delta/\sigma) = 0.381$, max. and min. heights 1.64 and -1.66 e \AA^{-3} , secondary extinction coefficient = 0.0012 mm^{-1} .

The absolute configurations were affirmed (Hamilton, 1965) to below the $\frac{1}{2}\%$ significance level by changing the sign of the imaginary anomalous-scattering factor f'' for the metal atoms.

Scattering factors for Rb and Cs from *International Tables for X-ray Crystallography* (1974), for N and O from *SHELX76* (Sheldrick, 1976). Computer programs: *SUSCAD* (Guss, 1979) for data reduction and *Lp* corrections, *ABSORB* (Guss, 1980) for absorption corrections, *SHELX76* for structure solution and

refinement, and *ORTEPII* (Johnson, 1976) for structure drawings.

Discussion. The structures of RbNO_3 and CsNO_3 are the same and in general agreement with those determined by Shamsuzzoha & Lucas (1982) and Lucas (1983) respectively. Atoms are numbered accordingly in the tables. Rotation of the unit-cell basis of RbNO_3 by 180° around the line $[\frac{1}{3}, y, \frac{1}{2}]$ will bring it into coincidence with the basis chosen by Shamsuzzoha & Lucas (1982). The CsNO_3 cell basis coincides with that of Lucas (1983) after rotation by 180° around the line $[\frac{1}{2}, \frac{1}{2}, z]$ with a further 180° around the line $[x, x + \frac{1}{3}, \frac{1}{2}]$.

The coordinates in Table 1 refer to the basis of Shamsuzzoha & Lucas (1982) and Lucas (1983). The standard deviations of the *x* coordinates for RbNO_3 are a complex function of the original *x* and *y* standard deviations and were not determined. Coordinates and anisotropic thermal parameters referred to the original unit-cell bases of RbNO_3 and CsNO_3 are deposited.* Distances and angles are in Table 2.

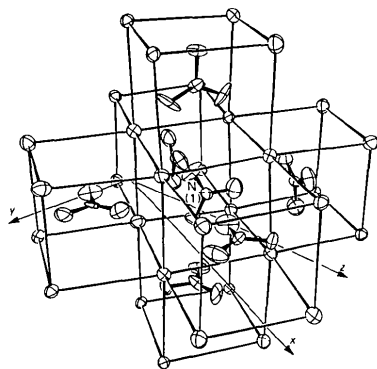
Comparison of coordinates and bonding geometry with the neutron-data results of Shamsuzzoha & Lucas (1982) and Lucas (1983) yielded some discrepancies above three standard deviations, the most significant of which are given in Table 3. The cell constants from this X-ray study have errors about one tenth of those of the previous work and have been used with the latter fractional coordinates in the comparison. Discrepancies in the coordinates (with $\sum\sigma$ in brackets) for RbNO_3 are: $\text{Rb}(3)z$ 0.20 (1) and $\text{N}(2)z$ 0.13 (1) \AA . This leads to a difference of 0.13 (2) \AA in the $\text{N}(2)\text{--O}(4)$ bond length and of $8 (1)^\circ$ in the $\text{O}(5)\text{--N}(2)\text{--O}(6)$ angle. Discrepancies in the coordinates for CsNO_3 are: $\text{N}(1)y$ 0.23 (2), $\text{N}(2)y$ 0.20 (2), $\text{N}(3)x$ 0.23 (2) and $\text{O}(8)y$ 0.22 (2) \AA . The differences in bonding geometry are: $\text{N}(2)\text{--O}(4)$ 0.18 (3), $\text{N}(3)\text{--O}(8)$ 0.16 (3), $\text{N}(3)\text{--O}(9)$ 0.18 (3) \AA , $\text{O}(3)\text{--N}(1)\text{--O}(1)$ $8 (2)$, $\text{O}(9)\text{--N}(3)\text{--O}(7)$ $14 (2)^\circ$. The discrepancies in the N positions are associated with those in the $\text{O}\text{--N}\text{--O}$ bond angles and $\text{N}\text{--O}$ bond lengths. The N in the nitrates is strongly bonded to the O atoms and as there is inequality between $\text{O}\text{--N}\text{--O}$ angles within any one nitrate ion the electron distribution (on which the present work depends) cannot wholly represent the position of the nucleus. The larger nitrate discrepancies for CsNO_3 (compared with RbNO_3) can be attributed to masking of the fine detail by the more highly scattering Cs atom. No explanation can be found for the difference between the two $\text{Rb}(3)z$ coordinates.

* Lists of structure factors and anisotropic thermal parameters and Figs. 1(b) and (c) showing nearest-neighbour nitrate and Rb^+ ions for $\text{N}(2)$ and $\text{N}(3)$ respectively have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39513 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Positional and equivalent isotropic thermal parameters

$$B_{eq} = \frac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
(a) RbNO₃(IV)				
Rb(1)	0.4557	0.5679 (1)	0.6267 (2)	2.9
Rb(2)	0.1190	0.2215 (2)	0.0000	2.4
Rb(3)	-0.2243	0.2206 (2)	0.6115 (5)	3.8
N(1)	0.4347	0.5659 (9)	0.1009 (13)	2.6
N(2)	0.1057	0.2097 (9)	-0.4850 (13)	3.1
N(3)	-0.2554	0.2101 (10)	0.1079 (11)	2.3
O(1)	0.3379	0.5586 (10)	-0.0011 (11)	5.8
O(2)	0.3980	0.4755 (10)	0.2205 (12)	5.1
O(3)	0.5618	0.6513 (8)	0.0573 (12)	4.3
O(4)	-0.0031	0.1086 (8)	-0.3822 (10)	4.2
O(5)	0.2309	0.2534 (9)	-0.4430 (13)	6.8
O(6)	0.0570	0.2450 (10)	-0.6132 (10)	4.1
O(7)	-0.3129	0.1184 (10)	0.2445 (11)	4.9
O(8)	-0.1288	0.2798 (10)	0.0851 (11)	5.8
O(9)	-0.3368	0.2186 (10)	0.0064 (11)	6.0
(b) CsNO₃(II)				
Cs(1)	0.4488 (2)	0.5610 (2)	0.6328 (6)	3.6
Cs(2)	0.1079 (2)	0.2249 (2)	0.0000	3.1
Cs(3)	-0.2289 (1)	0.2133 (1)	0.6488 (6)	3.0
N(1)	0.4365 (15)	0.5528 (15)	0.1048 (22)	2.1
N(2)	0.0906 (14)	0.1856 (18)	-0.4679 (22)	3.2
N(3)	-0.2369 (14)	0.2112 (17)	0.1299 (23)	4.0
O(1)	0.3458 (17)	0.5583 (20)	0.0243 (21)	7.5
O(2)	0.4071 (18)	0.4993 (17)	0.2403 (19)	6.0
O(3)	0.5611 (17)	0.6575 (16)	0.0549 (19)	6.6
O(4)	0.0090 (17)	0.1153 (14)	-0.3803 (17)	4.4
O(5)	0.2110 (20)	0.2337 (16)	-0.4119 (22)	7.0
O(6)	0.0696 (21)	0.2490 (25)	-0.5950 (20)	17.0
O(7)	-0.3186 (20)	0.1138 (15)	0.2461 (20)	7.9
O(8)	-0.1310 (16)	0.2926 (19)	0.1387 (27)	11.0
O(9)	-0.3349 (20)	0.2272 (16)	0.0312 (16)	7.4

Fig. 1. (a) Nearest-neighbour nitrate and Rb⁺ ions for N(1). Axes directions are $x//a, y//b, z//c$.

As shown in Figs. 1 (a)–(c) (b and c are deposited) the nitrate planes are nearly parallel to the pseudocube faces with the N near the cube centre and one N–O bond nearly parallel to a cube edge. It can be seen that nitrates occupy sites of C_1 symmetry which is in agreement with Karpov & Shultin (1970). The figures also show that nitrates 2 and 3 occupy more symmetrical sites than nitrate 1. Their symmetry is close to C_s or C_2 which conforms with the conclusions of Brooker (1973).

Table 2. Nitrate-ion interatomic distances (\AA) and angles ($^\circ$)

(a) RbNO₃(IV)			
O(1)–N(1)	1.237 (11)	O(2)–N(1)	1.221 (11)
O(3)–N(1)	1.217 (10)	O(4)–N(2)	1.343 (12)
O(5)–N(2)	1.200 (11)	O(6)–N(2)	1.220 (11)
O(7)–N(3)	1.322 (11)	O(8)–N(3)	1.162 (12)
O(9)–N(3)	1.179 (11)		
O(2)–N(1)–O(1)	118.1 (9)	O(3)–N(1)–O(1)	116.7 (10)
O(3)–N(1)–O(2)	124.6 (10)	O(5)–N(2)–O(4)	119.0 (9)
O(6)–N(2)–O(4)	111.7 (9)	O(6)–N(2)–O(5)	129.3 (10)
O(8)–N(3)–O(7)	122.2 (9)	O(9)–N(3)–O(7)	117.5 (10)
O(9)–N(3)–O(8)	120.2 (10)		
(b) CsNO₃(II)			
O(1)–N(1)	1.198 (23)	O(2)–N(1)	1.168 (20)
O(3)–N(1)	1.325 (18)	O(4)–N(2)	1.079 (20)
O(5)–N(2)	1.226 (20)	O(6)–N(2)	1.291 (20)
O(7)–N(3)	1.340 (20)	O(8)–N(3)	1.052 (17)
O(9)–N(3)	1.398 (22)		
O(2)–N(1)–O(1)	117.9 (17)	O(3)–N(1)–O(1)	108.8 (16)
O(3)–N(1)–O(2)	127.0 (17)	O(5)–N(2)–O(4)	114.2 (18)
O(6)–N(2)–O(4)	123.9 (18)	O(6)–N(2)–O(5)	118.8 (19)
O(8)–N(3)–O(7)	130.0 (21)	O(9)–N(3)–O(7)	102.7 (14)
O(9)–N(3)–O(8)	121.2 (21)		

Table 3. Discrepancies in structural results between this work and that of Shamsuzzoha & Lucas (1982) and Lucas (1983)

Discrepancies (in \AA) between coordinates

RbNO ₃		CsNO ₃	
Entity	Difference	Entity	Difference
Rb(3) _y	0.20 (1)	Cs(1) _x	0.046 (4)
N(2) _y	0.06 (1)	Cs(1) _y	0.04 (1)
N(2) _z	0.13 (1)	Cs(2) _x	0.11 (1)
N(3) _y	0.05 (1)	Cs(2) _y	0.22 (4)
N(3) _z	0.07 (1)	Cs(3) _x	0.075 (3)
O(1) _z	0.08 (1)	Cs(3) _y	0.070 (4)
O(3) _z	0.07 (2)	N(1) _y	0.23 (2)
O(4) _z	0.05 (1)	N(2) _x	0.16 (2)
O(6) _z	0.06 (1)	N(2) _y	0.20 (2)
O(9) _z	0.06 (1)	N(3) _x	0.23 (2)
		O(1) _x	0.09 (2)
		O(2) _z	0.13 (2)
		O(4) _x	0.08 (2)
		O(5) _x	0.15 (2)
		O(6) _x	0.17 (3)
		O(7) _z	0.07 (2)
		O(8) _y	0.22 (2)
		O(8) _z	0.13 (3)

Discrepancies in bonding geometry

RbNO ₃		CsNO ₃	
Entity	Difference	Entity	Difference
N(2)–O(4)(\AA)	0.13 (2)	N(1)–O(1)(\AA)	0.10 (3)
N(2)–O(5)(\AA)	0.07 (2)	N(1)–O(3)(\AA)	0.10 (3)
N(3)–O(9)(\AA)	0.08 (1)	N(2)–O(4)(\AA)	0.18 (3)
O(1)–N(1)–O(2)($^\circ$)	4 (1)	N(3)–O(8)(\AA)	0.16 (3)
O(4)–N(2)–O(6)($^\circ$)	6 (1)	N(3)–O(9)(\AA)	0.18 (3)
O(5)–N(2)–O(6)($^\circ$)	8 (1)	O(3)–N(1)–O(1)($^\circ$)	8 (2)
		O(9)–N(3)–O(7)($^\circ$)	14 (2)

The structure is most similar to that of phase III of TiNO_3 (Fraser, Kennedy & Snow, 1975) which has a pseudo primitive tetragonal array of cations. Phase III of TiNO_3 transforms on heating to phase II which is isomorphous with $\text{RbNO}_3(\text{IV})$ (Kennedy & Patterson, 1961). From Fig. 2 in the TiNO_3 structure report it is

evident that the ratio of nitrate groups in each of the three perpendicular planes is 2:1:1 and some nitrates within each plane are oriented at 60° to each other. However, in RbNO₃ the corresponding ratio is 1:1:1 and there are two orientations at 30° to each other for nitrates in any one plane. Consequently during the transformation TiNO₃(III) → TiNO₃(II) at least four nitrate groups in three unit cells must rotate by 90° about a line in their plane and some nitrates must rotate by 30° about their plane normals. In RbNO₃ and CsNO₃ similar nitrate rotations must occur when the crystals transform to and from the high-pressure structures.

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Acta Cryst. (1984). **C40**, 1515–1520

Reaction between Dibenzo-30-crown-10* and Potassium Thiocyanate; Structures of the 1:1 Complexes, Anhydrous and Monohydrated, $[K(C_{28}H_{40}O_{10})]^+ \cdot SCN^-$ and $[K(C_{28}H_{40}O_{10})]^+ \cdot SCN^- \cdot H_2O$

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Abstract. Monohydrate: $M_r = 651.8$, monoclinic, $P2_1/n$, $a = 13.335$ (2), $b = 12.386$ (1), $c = 20.584$ (2) Å, $\beta = 102.67$ (1)°, $U = 3317.0$ (6) Å³, $Z = 4$, $D_x = 1.305$ Mg m⁻³, $Mo K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.272$ mm⁻¹, $F(000) = 1384$, room temperature, $R = 0.129$ for 3081 reflexions. The conditions required to obtain reproducibly the anhydrous and monohydrate forms of dibenzo-30-crown-10–potassium thiocyanate (1:1) complex have been established. The crystal structure of the anhydrous form has been re-refined and some anomalies in the published structure [Hašek,

Hlavatá & Huml (1980). *Acta Cryst.* **B36**, 1782–1785] resolved by choice of a different space group, $C2/c$. The complex cation $[K(C_{28}H_{40}O_{10})]^+$ lies on a twofold axis; the ligand has the same conformation as in the corresponding potassium iodide complex, but the packing is different, the thiocyanate ions occupying (with disorder) centres of symmetry. The X-ray crystal structure of the monohydrate has been determined. The $[K(C_{28}H_{40}O_{10})]^+$ cations are without symmetry and have four torsion angles differing by more than 20° from those of the anhydrous form. There is some disorder in the aliphatic chains of the ligand, similar to that in the isomorphous rubidium complex, and the K–O distances are significantly longer than in the anhydrous complex. Thiocyanate anions and water molecules are hydrogen bonded, with some disorder of nitrogen, but not sulphur, in positions to give chains along the b axis.

* Systematic name: 6,7,9,10,12,13,15,16,23,24,26,27,29,30,32,33-hexadecahydrodibenzol[b,q][1,4,7,10,13,16,19,22,25,28]-decaoxacyclotriacontin.

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