Y—O = 2.389 Å, $D_x = 2.570$ Mg m^{-3} (Ribár, Radivojević, Argay & Kálmán, 1990)], indicates the decrease of the average length of the Y—O bonds with the increase of the crystal density, which is directly related to the decrease of the number of water molecules.

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Caesium Nitrate (II) at 296 K

By Dieter Pohl and Torsten Gross

Mineralogisch-Petrographisches Institut der Universität, Grindelallee 48, *W*-2000 *Hamburg* 13, *Germany*

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Abstract. $CsNO_3$(II), $M_r = 194.91$, trigonal, $P3_1$ (or its enantiomorph $P3_2$), $a = 10.902$ (2), $c = 7.740$ (2) Å, $V = 796.7$ (4) Å^3, $Z = 9$, $D_x = 3.656$ (2) g cm^{-3}, λ(Ag $K\alpha$) = 0.56087 Å, $\mu = 102.04$ cm^{-1}, $F(000) = 774$, $R = 0.019$ and $wR = 0.027$ for 1036 unique data with $I > 3\sigma(I)$. The structure is isomorphous to that of $RbNO_3$(IV). Regarding the Cs and N atoms alone, the structure is of a slightly distorted CsCl type with nine pseudocubes per unit cell. The nitrate groups form almost planar equilateral triangles. Each nitrate plane is essentially parallel to a pair of pseudocube faces and one of the N—O bonds is nearly parallel to a pseudocube cell edge.

Experimental. Single crystals of $CsNO_3$ were grown, by slow evaporation of an aqueous solution at 292 K, as hexagonal-shaped *c*-axis needles. A single crystal 0.18 mm across and 31 mm long was mounted on a glass fiber. An Enraf–Nonius CAD-4 diffractometer controlled by a PDP 11/34 computer under Enraf–Nonius software (Frenz, 1983), with graphite monochromator, was used to measure both unit-cell dimensions and integrated intensities. The former were determined from accurate measurement of the Bragg angles of 25 reflections with $10 < \theta < 20°$. Data were collected by an ω–2θ scan technique, for $\Delta\omega = 0.6° + 0.45°\tan\theta$. The maximum measurement time was 300 s. The integrated intensity of each reflection was measured for $2 < \theta < 22°$ (max. $\sin\theta/\lambda = 0.668$ Å^{-1}) with indices in the range $-14 \leq h \leq 14$, $-14 \leq k \leq 6$, $0 \leq l \leq 10$. Two standard reflections (060, 600) measured every 2 h showed no systematic variation of the intensities. Three other standard reflections ($10,\bar{8},\bar{1}$, 090, 900) measured every 300 reflections were used to control the orientation. 3353 reflections measured included 613 reflections which were considered unobserved, $I < 3\sigma_c(I)$, σ_c from counting statistics. The shape and dimensions of the crystal were used to calculate absorption corrections with maximum and minimum transmission values of 0.60 and 0.51, respectively. Lorentz and polarization corrections were made. Merging equivalent reflections [$R_{\rm int}(F_o) = 0.027$ for observed reflections and $R_{\rm int}(F_o) = 0.041$ for all reflections] resulted in 1036 reflections which were used to refine the structure. The room-temperature structure of $RbNO_3$(IV) (Pohl, Pohl & Adiwidjaja, 1992) with space group $P3_1$ was used as the initial model structure. The refinement converged rapidly using the programs *SHELX76* (Sheldrick, 1976) and *ORXFLS3* (Busing *et al.*, 1971). The origin was fixed by the Cs(2) atom. Scattering factors for Cs$^+$, N and O atoms and anomalous-dispersion terms for all atoms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). In the final cycle all atoms were refined with anisotropic temperature factors and an isotropic extinction parameter ($q = 0.03 \times 10^4$) was included. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where weights $w = 1/\sigma^2(F)$ were

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Table 1. *Fractional positional coordinates* (× 10^4) *and* B_{eq} *values* (Å^2) *for* $CsNO_3$(II) *with e.s.d.'s in parentheses*

$$B_{eq} = (4/3)\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Cs(1)	4481 (1)	5557 (1)	6527 (3)	2.43 (2)
Cs(2)	1205 (1)	2220 (1)	0	2.32 (3)
Cs(3)	−2161 (1)	2282 (1)	6333 (1)	2.36 (3)
N(1)	4629 (7)	5933 (7)	1604 (16)	2.7 (3)
N(2)	1085 (7)	2034 (7)	−4692 (12)	2.0 (3)
N(3)	−2290 (9)	2345 (7)	1093 (20)	3.2 (3)
O(1)	4417 (7)	6650 (8)	2670 (10)	4.2 (3)
O(2)	4004 (10)	4650 (7)	1673 (15)	7.8 (4)
O(3)	5510 (7)	6605 (8)	452 (11)	4.1 (3)
O(4)	45 (6)	1134 (6)	−3876 (11)	3.3 (2)
O(5)	2265 (5)	2314 (7)	−4274 (12)	4.8 (3)
O(6)	828 (10)	2565 (8)	−5985 (11)	6.3 (5)
O(7)	−2484 (13)	1638 (9)	2304 (11)	7.4 (6)
O(8)	−1073 (6)	3216 (7)	481 (13)	4.8 (3)
O(9)	−3311 (6)	2231 (6)	210 (11)	3.4 (2)

Table 2. *Interatomic distances* (Å) *and angles* (°) *in* $CsNO_3$(II) *with e.s.d.'s in parentheses*

Cs(1)—O(1)	3.228 (8)	Cs(2)—O(8)	3.191 (6)
Cs(1)—O(1^{v})	3.235 (6)	Cs(3)—O(2^{ii})	3.154 (7)
Cs(1)—O(1^{xi})	3.288 (8)	Cs(3)—O(3^{xi})	3.197 (6)
Cs(1)—O(2)	3.856 (12)	Cs(3)—O(4^{i})	3.223 (5)
Cs(1)—O(2^{v})	3.936 (11)	Cs(3)—O(5^{iv})	3.242 (7)
Cs(1)—O(3^{i})	3.242 (9)	Cs(3)—O(6^{i})	3.597 (9)
Cs(1)—O(3^{xi})	3.302 (7)	Cs(3)—O(7)	3.179 (9)
Cs(1)—O(5^{i})	3.196 (6)	Cs(3)—O(7^{iii})	3.707 (10)
Cs(1)—O(6^{vi})	3.160 (8)	Cs(3)—O(8^{i})	3.398 (9)
Cs(1)—O(7^{ix})	3.692 (11)	Cs(3)—O(8^{vii})	3.466 (7)
Cs(1)—O(8^{v})	3.211 (8)	Cs(3)—O(9^{i})	3.241 (8)
Cs(1)—O(9^{ix})	3.199 (5)	Cs(3)—O(9^{iii})	3.237 (6)
Cs(2)—O(1^{x})	3.295 (7)	Cs(3)—O(9^{vii})	3.243 (8)
Cs(2)—O(2)	3.147 (8)	N(1)—O(1)	1.23 (1)
Cs(2)—O(3^{x})	3.379 (8)	N(1)—O(2)	1.21 (1)
Cs(2)—O(4)	3.241 (8)	N(1)—O(3)	1.25 (1)
Cs(2)—O(4^{ii})	3.238 (5)	N(2)—O(4)	1.24 (1)
Cs(2)—O(4^{ix})	3.234 (7)	N(2)—O(5)	1.21 (1)
Cs(2)—O(5)	3.489 (9)	N(2)—O(6)	1.25 (1)
Cs(2)—O(5^{ii})	3.446 (7)	N(3)—O(7)	1.16 (2)
Cs(2)—O(6^{i})	3.181 (9)	N(3)—O(8)	1.28 (1)
Cs(2)—O(6^{ix})	3.684 (8)	N(3)—O(9)	1.26 (1)
Cs(2)—O(7^{viii})	3.149 (8)		

O(1)—N(1)—O(2)	122 (1)	O(5)—N(2)—O(6)	124 (1)
O(1)—N(1)—O(3)	116 (1)	O(7)—N(3)—O(8)	125 (1)
O(2)—N(1)—O(3)	122 (1)	O(7)—N(3)—O(9)	121 (1)
O(4)—N(2)—O(5)	120 (1)	O(8)—N(3)—O(9)	114 (1)
O(4)—N(2)—O(6)	116 (1)		

Symmetry code: (i) $x, y, 1+z$; (ii) $-y, x-y, \frac{1}{3}+z$; (iii) $-y, 1+x-y, \frac{1}{3}+z$; (iv) $-y, x-y, \frac{4}{3}+z$; (v) $1-y, 1+x-y, \frac{1}{3}+z$; (vi) $1-y, 1+x-y, \frac{4}{3}+z$; (vii) $-1+y-x, -x, \frac{2}{3}+z$; (viii) $y-x, -x, -\frac{1}{3}+z$; (ix) $y-x, -x, \frac{2}{3}+z$; (x) $y-x, 1-x, -\frac{1}{3}+z$; (xi) $y-x, 1-x, \frac{2}{3}+z$.

from counting statistics. Final agreement factors were $R = 0.0187$, $wR = 0.0273$ and $S = 1.680$. All shifts were less than σ. The maximum positive and negative features in the final difference electron density were $(\Delta\rho)_{max} = 0.71$, $(\Delta\rho)_{min} = -0.56$ e Å^{-3}. Large correlation coefficients occur between several parameters.

The final positional and equivalent isotropic thermal parameters are given in Table 1.* The interatomic distances and angles are collected in Table 2. The NO_3 groups are closely planar. Deviations of the N atom from the plane of the O atoms are within the limits of error: 0.004 (10), 0.020 (9) and 0.026 (11) Å for N(1), N(2) and N(3), respectively. Two of the Cs atoms, Cs(2) and Cs(3), are each coordinated to twelve O atoms with Cs—O distances in the range 3.147 (8) to 3.707 (10) Å, whereas the third Cs atom, Cs(1), has only ten neighbouring O atoms in this range.

Related literature. At atmospheric pressure, $CsNO_3$ has two stable phases (Gordon & Campbell, 1955; Plyuschev, Markina & Shklover, 1956; Cleaver, Rhodes & Ubbelohde, 1963; Kennedy, Taylor & Patterson, 1966); $CsNO_3(II) \rightarrow CsNO_3(I)$ at 427 K. The room-temperature structure, $CsNO_3$(II), has been determined previously by neutron (Lucas, 1983) and X-ray (Dean, Hambley & Snow, 1984) single-crystal diffraction methods. The solution of this structure, however, was based on its isotypism to $RbNO_3$(IV). Recently, Pohl, Pohl & Adiwidjaja (1992) reported a revised structure of $RbNO_3$(IV). Therefore, the possibility of a revised structure of $CsNO_3$(II) arose and was confirmed in the present paper. Comparison of coordinates with the results of Lucas (1983) and Dean, Hambley & Snow (1984) shows that the O(1) atom is located in a completely different position. This relocation is associated with a 90° flipping of the corresponding NO_3 group. All other atomic coordinates have only small discrepancies. However, most of these discrepancies are highly significant if the e.s.d.'s from the variance–covariance matrix are accepted. The data deposited by Dean, Hambley & Snow (1984) were used to refine both the structure determined by these authors and the structure given in Table 1. With the program *SHELX76* (Sheldrick, 1976), R values of 0.073 and 0.055 resulted, respectively. In both cases, however, several atoms showed non-positive-definite temperature factors resulting possibly from missing absorption-weighted mean path lengths, which are required to include an isotropic extinction factor in the refinement.

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* Lists of structure amplitudes and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55528 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SE0089]

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Structure of Tetrakis(dimethylammonium) Chloride Hexachlorobismuthate(III), $\{[(CH_3)_2NH_2]^+\}_4.Cl^-.[BiCl_6]^{3-}$ *

By Eberhardt Herdtweck† and Ursula Kreusel

Institut für Anorganische Chemie der Technischen Universität, Lichtenbergstraße 4,
D-8046 Garching bei München, Germany

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Abstract. $M_r = 641.5$, orthorhombic, $P2_12_12$, $a = 10.342$ (1), $b = 13.510$ (1), $c = 8.693$ (1) Å, $V = 1215$ Å^3, $Z = 2$, $D_x = 1.754$ g cm^{-3}, λ(Cu $K\alpha$) = 1.54184 Å, $\mu = 200.1$ cm^{-1}, $F(000) = 620$, $T = 293$ K, $R = 0.059$, $wR = 0.068$, for 2059 observed reflections. The nearly perfect octahedral Cl coordination around the Bi atom shows crystallographic twofold symmetry. Both ionic interactions and strong hydrogen bridging including the N-bonded H atoms [H(11), H(12), H(21) and H(22)] and all covalent bonded Cl atoms [Cl(1), Cl(2), Cl(3)] together with an interstitial Cl atom [Cl(4)] build up a three-dimensional network with distances N—H···Cl in the range 3.02 (2)–3.57 (2) Å. The relatively high thermal parameters for Cl(4) are typical for non-coordinated atoms involved in strong hydrogen bonds. Although the site-specific symmetry allows distortion of the $[BiCl_6]^{3-}$ octahedron, no stereochemical activity of the lone pair is observed.

Experimental. The title compound was prepared by heating a mixture of 1.3 mmol bismuth subsalicylate and 5 ml dimethylformamide at 358 K for 0.5 h. After adding aqueous hydrochloric acid (0.1 ml; 1 n) the stirred suspension rapidly cleared. Cooling to 263 K over night yielded colourless crystals suitable for X-ray structure analysis. Elemental analysis:

Calculated C 14.98, H 5.03, N 8.73, Bi 32.58, Cl 38.68%;
Found C 15.55, H 5.29, N 8.92, Bi 30.9, Cl 38.5%.

A well shaped colourless prism (0.30 × 0.39 × 0.26 mm) was randomly mounted on a glass fibre. Preliminary examinations and data collection were carried out with Cu $K\alpha$ radiation on an Enraf–Nonius CAD-4 diffractometer equipped with a graphite monochromator. The observed extinctions ($h00$: $h = 2n + 1$; $0k0$: $k = 2n + 1$) together with the orthogonal crystal system confirmed the orthorhombic space group $P2_12_12$. Final cell constants were obtained by least-squares refinement of 25 automatically centred high-angle reflections ($80.7 < 2\theta < 85.5°$). Data were collected using $\theta/2\theta$ scans. Each reflection in the hemisphere h 12, k 15, l ±10 and $\theta_{\max} \leq 65.0°$ was measured twice ($\psi \pm 1.5°$, check for Renninger effects). Three orientation control reflections were monitored every 200 reflections. A loss of 30.3% of intensity, indicated by three standards checked every 3600 s during the data collection, was corrected. Lorentz and polarization corrections (Müller, Schmidt, Massa & Herdtweck, 1986) together with a numerical absorption correction based on six indexed faces were applied. The transmission factors ranged from 0.0202 to 0.1645. 28 systematically absent data were rejected from the original data set of 4559 measured reflections. 89 reflections with negative measured intensities were assigned a positive value of $I = 1/100\sigma(I)$. After averaging ($R_{\rm merge} = 0.023$), 2059 ($I > 0.01$) out of 2060 unique reflections were used in the refinement. The structure was solved by Patterson methods and subsequent difference Fourier maps. Full-matrix least-squares refinement was carried out by minimizing $\sum w(||F_o| - |F_c||)^2$, where $w = 1/\sigma^2(F_o)$.

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* Main Principles in Solid State Coordination Chemistry of Sb and Bi Compounds. Part I.

† To whom correspondence should be addressed.

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