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$Ba(NO_3)_2 \cdot 2H_2O$: a Structure Stabilised by Anionic Impurities

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Abstract

An attempted preparation of barium cyanate yielded large crystals found to be cyanate-doped $Ba(NO_3)_2 \cdot 2H_2O$. Cubic, $a = 26.52(1)$ Å. Refinement to R 0.039 revealed a disordered cyanate group at the origin of a cell which also contains ordered and disordered nitrate ions and water molecules. Other anions are known to stabilise the otherwise unknown $Ba(NO_3)_2 \cdot 2H_2O$ in this way.

Introduction

$Ba(NO_3)_2 \cdot 2H_2O$ was reported as cubic crystals in 1854 [1]. This report has been rejected ever since and no pure barium nitrate hydrates are known, although mixed $Ba/Sr(NO_3)_2 \cdot 4H_2O$ is well characterised. In 1960 Garrini and Riganti [2] made '$Ba(ClO_2)_2 \cdot 5Ba(NO_3)_2 \cdot 12H_2O$' as 2 cm cubes with $a = 26.46$ Å in space group $F43c$ but no structure was reported.

Recently we attempted to make barium cyanate using barium nitrate as the source of barium ions. The product was colourless cubes up to 3 mm on edge which showed nitrate and a little cyanate in their infrared spectra. (The band at 2200 cm^{-1} is typical of CNO^-.) In the differential scanning calorimeter all the water is lost in a sharp endotherm at 63 °C, for which $\Delta H = 41.2 + 0.8$ kJ per mole of water lost.

Experimental

Aqueous solutions of barium nitrate and potassium cyanate were mixed and allowed to evaporate at room temperature. Well-formed, highly transparent, cubes were obtained in high yield. These showed no anomalies under a polarising microscope. The crystals are stable in a closed vial but lose water slowly when exposed in the laboratory for several weeks. Differential scanning calorimetry was carried out with a Perkin-Elmer DSC-1B instrument as described previously [3].

Structure Determination

A crystal 0.3 mm on edge was mounted in a Lindemann glass capillary. Data were collected on a Stoe Stadi II diffractometer for one quadrant of reciprocal space to a θ limit of 25°. No loss of intensity of standard reflections was detected during the data collection.

All calculations were performed on the Dundee University Prime 6350 computer using the SHELXS [4], SHELX76 [5], XANADU [6] and PLUTO [7] program packages. Atomic scattering parameters were from the International Tables for X-ray Crystallography [8].

Lorentz, polarisation and absorption corrections were applied to the data. From the 17463 measured reflections 899 unique data for which $F > 3\sigma F$ were used in the final refinement. The two unique Ba atoms were identified from a Patterson map. The structure developed normally with conventional least-squares refinement and difference syntheses. At R 0.080 features close to the cell origin were interpreted as six-fold disordered partially occupied NCO^- ions. Refinement continued to R 0.039 with anisotropic temperature parameters for the Ba atoms and all other atoms isotropic. Hydrogen atoms were not included. At this stage several light atom parameters were oscillating and further refinement was deemed to be unjustified.

Crystallographic Data

Cubic, $F43c$ (219), $a = 26.52(1)$ Å, $V = 18652$ Å^3, $D_x = 2.82$, $D_m = 2.48$, $F(000) = 14144$, Mo Kα radiation, $\lambda = 0.71069$ Å, $\mu = 52.07$ cm^{-1}, $T = 293$ K.

Final Refinement

Minimising $\Sigma w(|F_o| - |F_c|)^2$, 55 refined parameters, $R = 0.039$, $R_w = 0.081$, $w = 1.0000/((\sigma_F)^2 + 0.0024922F^2)$, max. $\Delta/\sigma = 1.5$, max. features on difference map 1.17, −1.11 e/Å^{-3}.

Results and Discussion

Atomic coordinates and isotropic temperature parameters are given in Table 1. Figure 1 shows the structure. The unit-cell contents are given in Table 2.

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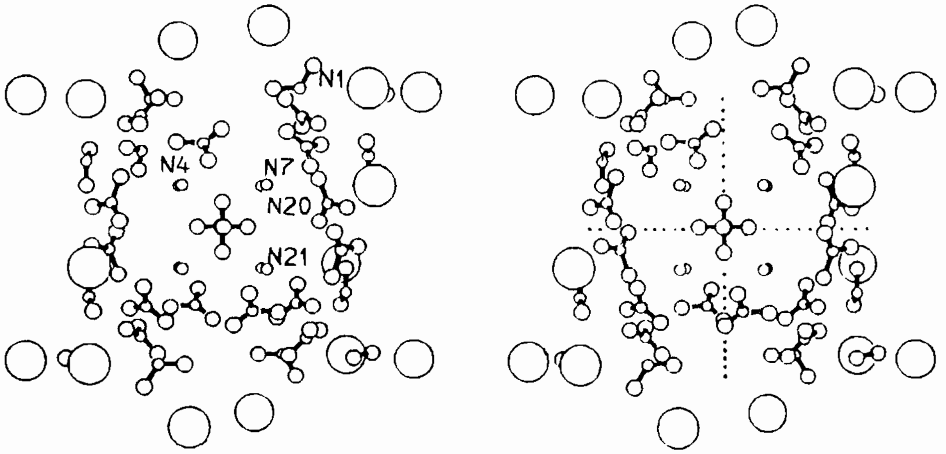

Fig. 1. $Ba(NO_3)_2{\cdot}2H_2O$: stereo-pair showing contents of part of the cubic unit-cell viewed down an axis. The cyanate ion is at the cell origin in the centre of the figure.

TABLE 1. $Ba(NO_3)_2{\cdot}2H_2O$: coordinates ($\times 10^4$) and isotropic temperature parameters ($\times 10^3$) for the non-hydrogen atoms with e.s.d.s in parentheses

	x/a	y/b	z/c	U_{eq} [a]
Ba1	2500	2500	2500	15(1)
Ba2	3641(1)	2503(1)	726(1)	19(1)
N1	1276(4)	2500	2500	20(2)
O2	2500	2500	802(4)	32(2)
O3	2907(3)	2468(6)	1511(3)	27(2)
N4	2102(5)	−433(5)	1504(5)	35(3)
O5	2436(4)	9637(4)	1199(3)	32(2)
O6	1942(4)	−104(4)	1788(3)	33(2)
O7	1915(4)	−894(4)	1556(4)	30(2)
N8	1462(4)	1462(4)	1462(4)	26(4)
O9	1529(4)	1100(4)	1759(4)	31(2)
N10	766(3)	766(3)	766(3)	40
N11	766(3)	766(3)	−766(3)	40
ON10	766(3)	766(3)	766(3)	60
ON11	766(3)	766(3)	−766(3)	60
O21	378(4)	3270(4)	9325(4)	25(2)
O22	345(6)	1757(7)	9356(7)	67(5)
C23	0	0	5000	156(45)
O24	0	0	555(16)	57(10)

[a] $U_{eq} = (1/3)\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i{\cdot}\mathbf{a}_j$.

The nitrate ion sites at N10 and N11 and the cyanate ion site C23 are partially occupied, containing 32 anions between them out of a possible 72. An accurate division of the occupancies was not possible but acceptable temperature parameters were obtained for the following model. The cyanate site is close to fully occupied. The N10 and N11 sites are 50% occupied by nitrate and up to 50% occupied by water molecules. Nitrate ions at N10 and N11 are disordered by rotation about the three-fold axis, the cell body diagonal. The oxygen atoms were not located and are assumed to be smeared over annuli about this axis.

TABLE 2. Unit-cell contents

Atom	Position	Site symmetry
Ba1	8b	23
Ba2	96h	general position
		nitrate ions fully occupied
N1	48g	2
N4	96h	general position
N8	32e	3
		nitrate ions partially occupied and disordered
N10	32e	3
N11	32e	3
		cyanate ions partially occupied and disordered
C23	8a	23
		water molecules
O21	96h	general position
O22	96h	general position

The nitrate ions have an average N–O distance of 1.25(2) Å. The distance 1.47(2) Å for C(23)–O(24) is an average C–O and C–N distance in OCN^-. Attempts to interpret this distance in detail are inappropriate.

Both Ba atoms are twelve-coordinate. Ba(1) has six symmetry positions of the nitrate ion at N(1), each bidentate through the two O(3) atoms related by the two-fold axis through N(1). Thus all the Ba(1)–O(3) distances are identical, 2.837(7) Å. The crystallographic symmetry of the $[Ba(NO_3)_6^{4-}]$ fragment is T (23) (Fig. 2(a)) showing much larger deviations from T_h than in the ammonium [9] and pyridinium [10] salts of the very similar $Ce(NO_3)_6^{2-}$ ion. The angle between the normals to the opposed pairs of mean planes Ba(1), O(3), O(3)′, N(1) is 19.2(2)°. In $Cs_2NaLa(NO_3)_6$ the O-coordinated $La(NO_2)_6^{3-}$ anion has crystallographic T_h symmetry [11]. Ba(2) has

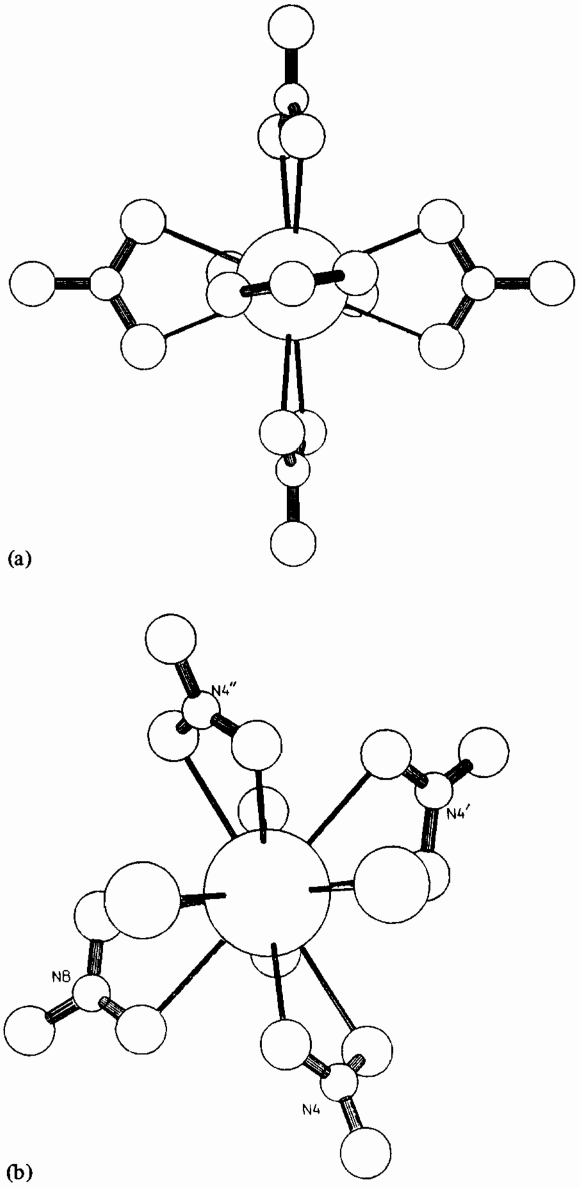

Fig. 2. (a) Coordination environment of Ba(1), symmetry *T*. (b) Coordination environment of Ba(2), viewed along the bisector of the angle O(21)–Ba(2)–O(22), which is the direction of the pseudo two-fold rotation axis. The nitrate group at N(1) is hidden by Ba(2).

two water molecules and five bidentate nitrate ions, with an average Ba–O distance 2.933(30) Å. Table 3 contains the individual distances to Ba(2). Figure 2(b) shows that there is an approximate two-fold rotation axis along Ba(2)–N(1). The coordination polyhedron is close to a tetra-capped cube [4 + 4 + 4] arrangement, reminiscent of the [3 + 3 + 3] tricapped trigonal prism coordination of $La(H_2O)_9^{3+}$ [12]. O(3) bridges Ba(1) and Ba(2), with an angle of 159.0(3)° at O(3). O(2) bridges Ba(2) and Ba(2)′. The environment of Ba(2) atom is shown in Fig. 2(b).

TABLE 3. Ba(2)–O distances (Å)[a]

O(2)	3.032(1)
O(3)	2.850(7)
O(5)	2.929(3)
O(7)	2.966(4)
O(5)′	2.925(3)
O(6)′	2.883(4)
O(6)″	2.950(3)
O(7)″	2.948(4)
O(9)	2.949(4)
O(9)′	2.970(3)
O(21)	2.878(5)
O(22)	2.922(5)

[a] Listed in bidentate pairs.

The unit-cell contents are approximately $96[Ba(NO_3)_2 \cdot 2H_2O] \cdot 8[Ba(NO_3)(NCO)] \cdot yH_2O$. The close agreement of the unit-cell dimensions of the present compound (26.52(1) Å) and the ClO_2-containing sample reported by Garrini and Riganti (26.46 Å) suggests that the latter must have a very similar structure. Presumably the bent ClO_2^- can fit into the large site at the origin as easily as linear NCO^-, with appropriate disorder, although the published analysis requires more ClO_2 than can be accommodated in this way. It seems likely that the crystals described in 1854 were also of this class, with an unknown impurity anion. If no impurity anion is present to occupy the site at the origin the structure becomes unstable. Nitrate ion is too large for this site and a stoichiometric but disordered $Ba(NO_3)_2 \cdot 2H_2O$ is not formed at room temperature.

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