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S. C. Abrahams, J. L. Bernstein, and R. Liminga

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Pyroelectric $Ba(NO_2)_2 \cdot H_2O$: Room temperature crystal structure

S. C. Abrahams and J. L. Bernstein

Bell Laboratories, Murray Hill, New Jersey 07974

R. Liminga

Institute of Chemistry, University of Uppsala, Box 531, S-75121 Uppsala, Sweden
and Bell Laboratories, Murray Hill, New Jersey 07974
(Received 18 January 1980; accepted 14 February 1980)

Barium nitrite monohydrate, $Ba(NO_2)_2 \cdot H_2O$, is strongly pyroelectric at room temperature and crystallizes in the hexagonal system with space group $P6_5$, or the enantiomorphous $P6_1$, and with six formulas in the unit cell. The lattice constants at 298 K are $a = 7.07490 \pm 0.00003$ and $c = 17.89087 \pm 0.00012$ Å ($\lambda CuK\alpha_1 = 1.540598$ Å). The integrated intensities of most reflections within a quadrant of reciprocal space having radius $(\sin\theta)/\lambda \leq 1.15$ or 1.08 Å^{-1} were measured on two different crystals, each with different diffractometer, resulting in 3218 $Fmeas$ for one set and 3671 $Fmeas$ for the second set of independent structure factors. The crystal structure was solved from Patterson and Fourier series, and refined by the method of least squares. The final agreement factor $R = 0.026$ for the first set, 0.018 for the second set of $Fmeas$. The two sets of $Fmeas$ and the derived structural parameters are compared using normal probability plot analysis. The two NO_2^- ions have a mean N–O distance of 1.246 ± 0.002 Å and O–N–O angle of $114.2 \pm 0.2°$. The Ba^{2+} ion is coordinated by nine oxygen and one nitrogen atoms at an average distance of 2.899 Å. The water molecule has a weighted mean O–H distance of 1.04 ± 0.03 Å and H–O–H angle of $102.7° \pm 4.3°$: it is hydrogen bonded to two independent NO_2^- ions by an O–H⋯O bond of 2.878 Å and an O–H⋯N bond of 2.951 Å.

INTRODUCTION

A strong pyroelectric effect in $Ba(NO_2)_2 \cdot H_2O$ was first reported by Gladkii and Zheludev,[1] who also measured the temperature dependence of the piezoelectric, elastic, and thermal expansion coefficients.[2] No evidence for a phase transition was found between 80 and 330 K: the crystal loses water of hydration above 335 K. A fuller set of tensor properties was measured by Haussühl at room temperature.[3] The linear and non-linear optical properties together with the phase-matching conditions have been independently reported.[4,5] Elucidation of the origin of the strong pyroelectric and, by contrast, small piezoelectric coefficients, the considerable birefringence in $Ba(NO_2)_2 \cdot H_2O$ crystals, and also the relative roles filled by the nitrite ion in this material and in ferroelectric[6] $NaNO_2$, KNO_2, and $AgNa(NO_2)_2$, requires the detailed atomic arrangement to be known. Accordingly, the crystal structure of $Ba(NO_2)_2 \cdot H_2O$ has been determined and is reported herein.

EXPERIMENTAL

Murray Hill. A sphere of radius[7] 0.1235(5)mm was ground from a crystal grown in Uppsala (see below) and mounted on a Pyrex capillary with random orientation. All reflections with $0 \leq h \leq 10$, $0 \leq k \leq 10$, $-20 \leq l \leq 20$ and $(\sin\theta)/\lambda \leq 1.15$ Å^{-1} were measured, by use of an Enraf–Nonius CAD-4 diffractometer controlled by a PDP 11/40-8e computer under Enraf–Nonius software,[8] with graphite monochromatized MoKα radiation. An $\omega-2\theta$ scan was used over an angular scan range of $0.60° + 0.347° \tan\theta$. In measuring the integrated intensities, backgrounds were taken by extending the scan 25% on each side, with maximum time per reflection of 120 s. Three standard reflections, checked every hour, varied less than 1.0%.

The integrated intensities of 4539 reflections were corrected for Lorentz, polarization, and absorption[9] effects. Equivalent reflections were averaged and resulted in 4119 independent $Fmeas$ of the form $F(hk \cdot l)$ and $F(hk \cdot \bar{l})$. Standard deviations were derived from the expression $\sigma^2 F^2 meas = V_1 + V_2$,[10] where the variance V_1 is the sum of the variance attributable to counting statistics plus 38×10^{-4} $(Fmeas)^4$, the estimate of all factors varying monotonically with scattering angle. The variance V_2 is the larger of that given by the deviation among equivalent members of a form or 157×10^{-4} $(Fmeas)^4$, the estimate of error associated with determination of the crystal radius and with long-term variations in the measurements. A total of 3218 of the 4119 independent $Fmeas$ had $F^2 meas > 3\sigma F^2 meas$. The remainder were omitted from the subsequent analysis. A correction for isotropic extinction was made[11] in course of the refinement: the coefficient value was $4.72(16) \times 10^3$ and the maximum correction was 35.7%, in $F(00\bar{6})$. The magnitudes of the 3218 $Fmeas$ and $\sigma Fmeas$ used in the least-squares analysis, on the final absolute scale, are given in Ref. 12.

Uppsala. Transparent colorless hexagonal prisms of $Ba(NO_2)_2 \cdot H_2O$ were grown from aqueous solution at room temperature by slow evaporation. Several weeks' growth gave crystals with maximum dimensions of 20 mm. A sphere of diameter 0.240(5) mm was ground and etched in ethanol–water to remove surface damage. Intensities were measured with this sphere at room temperature using a PDP-8a computer controlled Enraf–Nonius CAD-4 diffractometer. Graphite-monochromatized MoKα radiation was used with an $\omega-2\theta$ step-scan over a range $0.80° + 0.35° \tan\theta$. Background corrections were made by a profile-analysis method.[13] The maximum time spent on a reflection was 240 s. Eight of the nine standard reflections having integrated
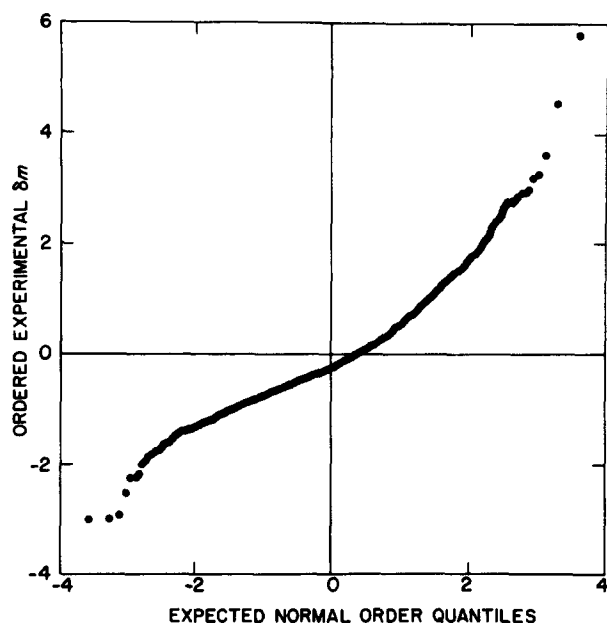
FIG. 1. Normal probability δm_i plot (see text) of the 2569 measured structure factors common to the Murray Hill and Uppsala sets.[12]

intensities less than 2×10^5 counts decreased by about 3% on average in course of measurement. The ninth standard [$I(1\bar{1} \cdot 1) \simeq 3 \times 10^5$ counts] increased by about 25%, indicative of a change in crystal perfection. About midway through data collection there was a sudden discontinuous decrease in all standards by about 6%, probably due to a change within the x-ray tube. A scaling function, derived from the average individual scaling functions for the eight consistent standards, was used for correcting the measured intensities. All $hk \cdot \bar{l}$ reflections with $(\sin\theta)/\lambda \leq 0.89$ $Å^{-1}$ and all $hk \cdot l$ reflections with $(\sin\theta)/\lambda \leq 1.08$ Å were measured, resulting in a total of 4803 integrated intensities.

The variances in $I(hk \cdot l)$ were estimated from the Poisson counting statistics, the scatter observed in the standard reflections, and the uncertainty in the scaling function.[14] The intensities of equivalent reflections within the $\{hk \cdot l\}$ and $\{hk \cdot \bar{l}\}$ subsets were averaged and the standards excluded, giving 4181 independent values of $F(hk \cdot l)$. The integrated intensities were corrected for Lorentz, polarization, and absorption effects. The minimum and maximum transmission factors were 0.27 and 0.32. The internal agreement indicator R_{int} $= \sum ||Fmeas| - |\overline{Fmeas}|| \div \sum |Fmeas| = 0.018$. The final isotropic extinction coefficient[11] was $9.02(23) \times 10^3$ and the maximum correction was 60%, in $F(00\bar{6})$. The 21 strongest reflections were omitted from the final refinement: the largest extinction correction in the reflections included was 18% for $F(21\bar{2})$. The magnitudes of the 3671 $Fmeas$ and $\sigma Fmeas$, with $Fmeas > 3\sigma Fmeas$, are given in Ref. 12.

COMPARISON OF MURRAY HILL AND UPPSALA Fmeas

The use of different crystal spheres in the two experiments resulted in two sets of $Fmeas$ that initially ap-

peared to differ significantly. Examination showed that one set was of the form $F(hk \cdot l)$, the other $F(kh \cdot \bar{l})$. Both were right-handed. Transformation of one set to the form of the other eliminated the apparent systematic differences and led, for the 2559 common reflections, to the δm plot[15] shown in Fig. 1, ($\delta m = [m_i(1) - k\, m_i(2)]$ $\div [\sigma^2\, m_i(1) + k^2\, \sigma^2\, m_i(2)]^{1/2}$, where $m_i(1)$ is ith $Fmeas$ of the Murray Hill set, $m_i(2)$ is the corresponding ith $Fmeas$ of the Uppsala set, $\sigma^2\, m_i$ is the variance of the ith $Fmeas$, and k is the scale factor between the two sets of $Fmeas$). In the absence of systematic error in the $Fmeas$, and with individual values of $\sigma Fmeas$ well determined, the δm plot should be linear with unit slope and zero intercept. The characteristic S shape of the plot in Fig. 1 indicates some systematic error is present. The similarity in the two sets of experimental procedures suggests that the principal source of error lies in one or both methods used for assigning $\sigma Fmeas$. The need to double the Uppsala values of $\sigma Fmeas$, noted in subsequent refinement, may be significant. The slope of the plot in Fig. 1, $S = 0.78$, shows that the pooled standard deviation is overestimated by about 28%.

CRYSTAL DATA

$Ba(NO_2)_2 \cdot H_2O$ has formula weight (fw) $= 247.37$. The hexagonal unit cell has lattice constants $a = 7.07490(3)$, $c = 17.89087(12)$ Å at 298 K, as measured with $CuK\alpha_1$ $= 1.540598$ Å on a modified version[16] of Bond's precision lattice constant diffractometer.[17] Lattice constants obtained by least-squares refinement based on 30 values of $\theta(10° < \theta < 45°)$, measured from a powder photograph recorded by using a Guinier–Hägg XDC-700 focussing camera with $CrK\alpha_1$ radiation ($\lambda = 2.289753$ Å) and with Si ($a = 5.431065$ Å) as an internal standard, are $a = 7.0747(3)$, $c = 17.8935(12)$ Å. Haussühl found $a = 7.076(7)$, $c = 17.898(18)$ Å. The two latter sets of values do not differ significantly from the more accurate lattice constants used in this paper. The unit cell volume is 775.52 $Å^3$. $Dm = 3.179(3)$ gcm^{-3},[3] $Dx = 3.178$ g cm^{-3} for 6 fw per unit cell.

The absorption coefficient[18] for $MoK\alpha$ radiation is 7.65 mm^{-1} and, for the spheres measured, μR (Murray Hill) $= 0.983$, μR (Uppsala) $= 0.914$. $F(000) = 672e$. The wavelength dispersion of the refractive indices has been measured independently[4,5]: at 1.064×10^{-6} m, $n_0 = 1.59651$ and $n_e = 1.50743$. Crystals of $Ba(NO_2)_2 \cdot H_2O$ are optically active, with rotation at 300 K ranging from 6 deg mm^{-1} at 0.75×10^{-6} m to about 100 deg mm^{-1} at 0.4×10^{-6} m.[19] Both laevo- and dextrorotatory crystals are expected to grow from aqueous solution, with one chirality forming in space group $P6_1$, the other in $P6_5$. The diffraction symmetry is $6/m$, the only systematic absenses are $00 \cdot l$ for $l \neq 6n$. The pyroelectric properties confirm[3] the space group to be $P6_1$ or $P6_5$, not $P6_122$ or $P6_522$ as previously proposed.[20]

SOLUTION AND REFINEMENT OF THE STRUCTURE

The barium atom position was readily located from the three-dimensional Patterson function. Following coordinate refinement by the method of least squares, the barium atom was used to determine the phase angles

TABLE I. Atomic position coordinates of
Ba(NO₂)₂·H₂O at 298 and 296 K.[a]

Atom	x	y	z
Ba	0.426 76(3)	0.849 80(2)	0
	0.426 76(2)	0.849 79(2)	0
N(1)	0.246 2(5)	0.028 4(6)	0.145 8(2)
	0.245 5(3)	0.027 4(3)	0.145 6(1)
N(2)	0.564 2(6)	0.117 5(7)	0.325 5(3)
	0.563 8(4)	0.118 3(5)	0.325 6(2)
O(1)	0.437 3(4)	0.101 0(5)	0.122 9(2)
	0.436 5(3)	0.100 2(3)	0.123 2(1)
O(2)	0.107 9(4)	0.862 8(5)	0.111 6(2)
	0.107 6(3)	0.862 6(3)	0.111 6(1)
O(3)	0.582 5(5)	0.288 6(5)	0.298 0(2)
	0.584 9(4)	0.289 5(3)	0.298 0(1)
O(4)	0.615 5(6)	0.012 9(6)	0.283 2(3)
	0.616 1(4)	0.013 5(4)	0.283 0(2)
O(W)	0.231 1(4)	0.156 0(5)	0.416 4(2)
	0.231 6(3)	0.156 5(3)	0.416 2(1)
H(1)	0.171(15)	0.027(14)	0.384(5)
	0.175(9)	0.050(9)	0.379(3)
H(2)	0.091(7)	0.165(8)	0.441(3)
	0.102(8)	0.181(8)	0.422(3)

[a]Upper lines refer to Murray Hill results (298 K),
lower lines to Uppsala results (see text).

for evaluation of the three-dimensional Fourier series.
Atomic scattering factors for the neutral (Murray Hill)
or ionized (Uppsala) atoms were taken from the *International Tables for X-Ray Crystallography*,[18] as were
the corrections for anomalous dispersion. No parameter was found to change as much as one estimated
standard deviation on exchanging form factors for
ionized atoms with those for neutral atoms. Calculations in Murray Hill were made on the Honeywell 6080
computer using the ORFLS-3 program,[21] and in Uppsala
on the IBM 1800, NORD 10, and IBM 370/155 computers.[22] The two independent nitrogen and five oxygen
atom positions were found by an examination of the resulting electron density function. Further least-squares
refinement, using anisotropic temperature coefficients
followed by three-dimensional difference Fourier series,
led to the location of the two independent hydrogen atoms

Final refinement with the Murray Hill *Fmeas*[12] included the position coordinates of all atoms but with
anisotropic temperature coefficients only for Ba, N,
and O and isotropic coefficients for H. Iterations were
continued until all non-H atom parameter shifts became
less than 0.02 and those of the H atoms less than 0.1 of
the corresponding standard deviation. The residual
electron density in a difference Fourier series was
evaluated at close intervals. The resulting distribution
contained no maxima or minima exceeding ±1.4 $e\,Å^{-3}$
and is regarded as featureless. The final position
parameters are given in Table I, the anisotropic temperature coefficients in Table II.

Refinement with the Uppsala *Fmeas*[12] gave thermal

parameters for H that were consistently negative. These
parameters were hence held constant at the equivalent
B value for O(W), resulting in an oscillation of the H
atom position coordinates by about 1–3 standard deviations. The mean of the oscillating *xyz* values for H
were used, without variation, in the final cycles of
least-squares refinement to avoid a resulting slight
instability in the coordinates of the heavier atoms. It
was noted from the value of S (cf. Table III) that the
variances in the observed structure factors were underestimated by about a factor of two, hence these were
all multiplied by two before the final refinements to
bring them closer to their absolute values. The final
magnitudes of the atomic coordinates are given in Table
I, with the temperature coefficients in Table II. The
agreement indicators for both sets of data are in
Table III.

COMPARISON OF THE TWO SETS OF ATOMIC, POSITION, AND TEMPERATURE PARAMETERS

The Murray Hill and Uppsala sets of atomic position
coordinates and anisotropic temperature coefficients
listed in Tables I and II may readily be compared in a
δp normal probability plot.[15] The comparison is made
by plotting the ordered values of δp_i $(=[p_i(1)-p_i(2)]/$
$[\sigma^2 p_i(1)+\sigma^2 p_i(2)]^{1/2}$, where $p_i(1)$ is the ith parameter
of the Murray Hill set, $p_i(2)$ the corresponding parameter of the Uppsala set, and $\sigma^2 p_i$ is the variance of the
ith parameter) against the expected half-normal order
quantiles,[18] as shown in Fig. 2. The three largest δp_i

TABLE II. Anisotropic temperature coefficients for
Ba(NO₂)₂·H₂O at 298 and 296 K.[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ba	814(3)	688(3)	113(1)	652(4)	58(2)	−25(2)
	856(3)	724(2)	112(1)	691(4)	58(1)	−26(1)
N(1)	105(5)	125(6)	18(1)	116(9)	9(3)	−8(3)
	106(4)	114(4)	17(1)	93(3)	4(1)	−11(1)
N(2)	144(7)	158(7)	21(2)	155(11)	28(5)	38(5)
	140(5)	163(5)	20(1)	151(8)	28(3)	39(3)
O(1)	80(4)	163(7)	20(1)	46(8)	6(3)	−38(4)
	84(3)	175(5)	20(1)	63(7)	2(2)	−37(3)
O(2)	89(5)	110(5)	24(1)	54(8)	−5(3)	4(4)
	98(4)	120(4)	23(1)	60(6)	2(2)	−5(3)
O(3)	234(10)	129(6)	24(1)	229(13)	66(5)	25(4)
	242(7)	135(4)	26(1)	232(9)	74(3)	20(3)
O(4)	169(8)	129(7)	41(2)	184(12)	36(6)	21(5)
	181(5)	143(5)	38(1)	216(9)	32(4)	29(4)
O(W)	94(4)	120(5)	18(1)	97(8)	2(3)	−11(3)
	102(3)	117(4)	16(1)	90(6)	−4(2)	−8(2)
H(1)	3.3(1.6)					
	1.8					
H(2)	0.4(8)					
	1.8					

[a]Based on the exponential expression $-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2$
$+\beta_{12}hk+\beta_{23}kl+\beta_{13}hl)$. Values of β_{ij} are $\times 10^5$ for Ba, $\times 10^4$
for N and O. Isotropic values in $Å^2$ are given for H. See
footnote to Table I.

TABLE III. Structural refinement indicators for $Ba(NO_2)_2 \cdot H_2O$. [a]

Parameters varied[b]	Number of variables[c]	R	wR	S
xyz, B	41	0.0453	0.0619	1.349
	41	0.0442	0.0644	2.556
$xy\bar{z}$, B	41	0.0478	0.0649	1.412
	41	0.0468	0.0685	2.719
xyz, β_{ij}	81	0.0256	0.0354	0.777
	73	0.0175	0.0276	1.100
$xy\bar{z}$, β_{ij}	81	0.0295	0.0404	0.885
	73	0.0228	0.0364	1.454

[a]See Ref. 10 for definitions of R, wR, and S. Upper lines give Murray Hill, lower lines Uppsala, results.
[b]All models are corrected for extinction, each has a single variable scale factor. Models with xyz coordinates are in space group $P6_5$, those with $xy\bar{z}$ coordinates are in space group $P6_1$.
[c]For 3218 independent Murray Hill $Fmeas$, 3671 independent Uppsala $Fmeas$. The model with 41 variables corresponds to isotropic temperature factors for all atoms: that with 81 variables to anisotropic temperature coefficients for all atoms except hydrogen which are treated isotropically: that with 73 variables has no hydrogen atom parameters varied.

correspond to β_{11}, β_{22}, and β_{12} for Ba, the fourth to H(2)z, and the fifth to O(3)x. The remaining 72 ranked deviates, derived from Tables II and III, form an acceptably near-linear array with slope of 1.20 and zero intercept. The two sets of results are hence drawn from the same normal distribution, despite the small systematic error in $Fmeas$ or $\sigma Fmeas$ detected in Fig.

TABLE IV. Root-mean-square amplitudes of thermal vibration along the principal ellipsoid axes in $Ba(NO_2)_2 \cdot H_2O$ at 298 and 296 K. [a]

Atom	1	2	3
Ba	0.114 Å	0.123 Å	0.142 Å
	0.117	0.125	0.142
N(1)	0.135	0.152	0.176
	0.140	0.146	0.175
N(2)	0.144	0.166	0.207
	0.140	0.167	0.207
O(1)	0.121	0.152	0.226
	0.125	0.155	0.224
O(2)	0.125	0.166	0.198
	0.131	0.173	0.195
O(3)	0.134	0.154	0.246
	0.133	0.159	0.255
O(4)	0.140	0.172	0.263
	0.139	0.180	0.255
O(W)	0.133	0.149	0.177
	0.137	0.155	0.165

[a]Excluding the hydrogen atoms. The estimated standard deviations are about 0.001 Å for Ba and 0.003 Å for N and O.
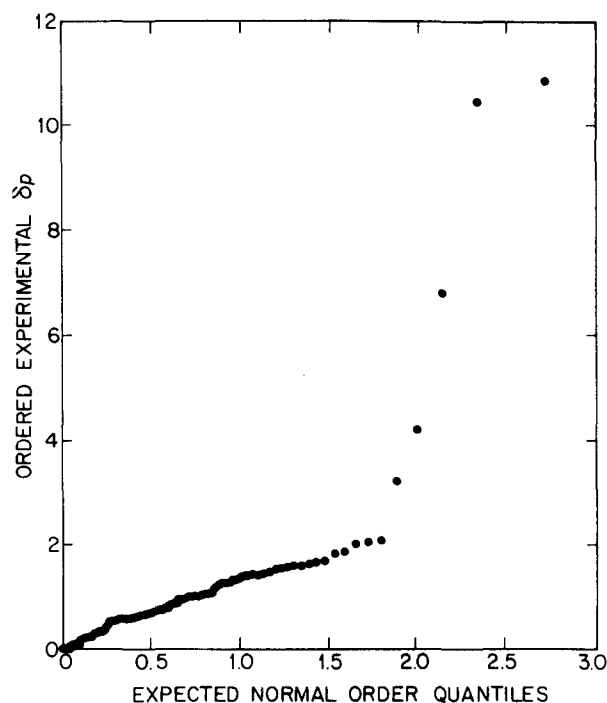
FIG. 2. Half-normal probability δp_i plot (see text) of 77 atomic parameters common to the two sets given in Tables I and II.

1, except for the five outliers. The largest deviate, Ba (β_{11}), with value 10.82 corresponds to a difference of only 5.1% in the coefficient. This difference may be associated with inadequate discrimination in both experiments against thermal diffuse scattering, leading to small but different apparent decreases in the temperature factors. The deviate of 4.20 for H(2)z is probably related to the oscillation in coordinate values found for this atom in one of the structural refinements. The deviate of 3.21 for O(3)x is possibly due to an underestimation of its pooled standard deviation that is larger than average.

AMPLITUDES OF VIBRATION

The agreement indicators of Table III may be used to test the hypothesis that the atomic vibrations in $Ba(NO_2)_2 \cdot H_2O$ are isotropic rather than anisotropic. The experimental ratio wR (isotropic)/wR (anisotropic) = 1.749 for the Murray Hill results, 2.333 for the Uppsala results, based on the model with xyz coordinates (see next section for the absolute atomic configuration). The Hamilton ratio[23] $\mathfrak{R}_{40,3137,0.005} = 1.001$, hence the hypothesis is confidently rejected at the half-percent significance level. The anisotropy present is evident on examination of the root-mean-square amplitudes of thermal vibration along the principal ellipsoid axes, given in Table IV. The ratio of maximum to minimum amplitude varies from 1.25 for Ba to over 1.8 for O(3). The magnitudes of the RMS amplitudes in $Ba(NO_2)_2 \cdot H_2O$ are comparable with those reported in similar hydrates, such as $Ni(IO_3)_2 \cdot 2H_2O$. [24]

ABSOLUTE CONFIGURATION

The atomic arrangement of $Ba(NO_2)_2 \cdot H_2O$ in Table I is given for space group $P6_5$ in a right-handed coordinate

TABLE V. Interatomic distances and angles in Ba(NO₂)₂·H₂O at 297 K.[a]

N(1)–O(1)	1.249(3) Å	N(2)–O(3)	1.249(4) Å
N(1)–O(2)	1.244(3)	N(2)–O(4)	1.240(4)
O(W)–H(1)	0.96(6)	O(W)···O(4)	2.878(3)
O(W)–H(2)	1.08(4)	O(W)···N(1)	2.951(5)
Ba–O(1)	2.772(2)	Ba–O(W)	2.863(2)
–O(1)	2.807(2)	–O(2)	2.881(2)
–O(3)	2.834(2)	–O(W)	2.956(2)
–O(4)	2.849(2)	–O(2)	3.049(2)
–O(3)	2.857(2)	–N(2)	3.127(3)
O(1)–N(1)–O(2) 114.1(2)°		O(3)–N(2)–O(4) 114.2(3)°	
H(1)–O(W)–H(2) 102.7(4.3)		O(W)–H(2)···O(4) 140.2(4.3)	
		O(W)–H(1)···N(1) 163.8(4.2)	

[a]Distances, angles and standard deviations given are weighted means derived from the individual Murray Hill and Uppsala results. The standard deviations have been corrected by the factor 1.2, see text.

system. An arrangement of opposite chirality exists in the enantiomorphous space group $P6_1$. The absolute configuration, or choice of space group in this case, can be related to the measured structure factors[12] by making use of Friedel's law violations caused by the anomalous scattering of $MoK\alpha$ radiation by barium and, to a lesser extent, by nitrogen and oxygen. The structure factors in Ref. 12 include terms of the form $F(hk \cdot l)$ and $F(hk \cdot \bar{l})$, allowing the hypothesis to be tested that the model corresponding to the atomic arrangement in $P6_1$ fits the experimental data better than that in $P6_5$. The theoretical value of $wR(P6_1)/wR(P6_5)$, for 3218 independent F_{meas} and 81 variables, at the half-percent confidence level, is $\Re_{1,3137,0.005} = 1.0012$;[23] the experimental values from Table III are 1.141 and 1.319 for the two independent sets of measurements. The hypothesis may thus be rejected with safety. The coordinates of Table I hence represent the absolute configuration for optically active Ba(NO₂)₂·H₂O in space group $P6_5$ in terms of the Miller indices and structure factors of Ref. 12.

Examination of the same group of nine pairs of Friedel related reflections, see Table I of Ref. 25, used to determine the absolute sense of the pyroelectric coefficient p_3 and piezoelectric coefficient d_{33} showed excellent agreement between the signs of $(|F(hk \cdot l)| - |F(hk \cdot \bar{l})|)$ for both measured and calculated structure factors.[12] It may be noted that the chances of the Murray Hill and Uppsala crystals having the same chirality, as found experimentally, are 50% since the spheres studied were ground from unrelated crystals.

INTERATOMIC DISTANCES AND ANGLES

The interatomic distances and angles in Ba(NO₂)₂·H₂O were calculated from the two independent sets of position coordinates in Table I and the lattice constants given in the "Crystal Data" section. The two sets of coordinates and standard errors have previously been shown to belong to the same normal distribution hence the best values, as given in Table V, are weighted means. The given errors are the standard deviations

in these weighted means multiplied by the factor 1.20 taken from Fig. 2.

The geometry of the nitrite ion, with mean N–O distance of 1.246(2) Å and O–N–O angle of 114.2(2)°, is in close accord with previously published results. The N–O bond length in NaNO₂ at room temperature is found[26] to be 1.244(4) Å with, apparently, slightly smaller values at higher temperatures. The O–N–O angle is given as 115.6(3)° at room temperature and as slightly smaller above. An N–O bond length of 1.22(2) Å is reported in trigonal KNO₂,[27] with O–N–O = 115.3(3.4)°: in K₃Cu(NO₂)₃, the N–O distance appears to be distributed over the range 1.13(3) Å to 1.26(2) Å.[28] The average N–O distance in the four independent NO₂⁻ ions in K₃[Hg(NO₂)₄]NO₃, found by neutron diffraction,[29] is 1.239(4) Å.

The coordination number (C.N.) of the barium atom depends on the distance that is considered to be reasonable as the limiting interatomic contact. Table V lists eight Ba–O contacts less than 3 Å, with two others of 3.049 and 3.127 Å. The average Ba–O/N distance from Table V for C.N. = 8 is 2.852 Å, for C.N. = 10 it is 2.899 Å. The effective Ba²⁺ radius for C.N. = 8 is 1.56 Å, for C.N. = 10 is 1.66 Å.[30] The coordination of oxygen in Ba(NO₂)₂·H₂O is between three and four, with radius between 1.22 and 1.24 Å. The predicted Ba–O distance is hence about 2.79 Å for C.N. = 8 and 2.89 Å for C.N. = 10: the match for C.N. = 10 suggests the limiting contact distance be taken at about 3.13 Å. The Ba²⁺ ion environment is shown in Fig. 3. One NO₂⁻ ion forms a bidentate and five other NO₂⁻ ions monodentate O–Ba contacts. Similar arrangements of NO₂⁻ ions about a metal ion are reported,[28] for example in K₃Cu(NO₂)₃. Two water molecules make additional O–Ba contacts: one NO₂⁻ ion forms an N–Ba contact approximately along the nitrite two-fold axis.

The water molecule dimensions as measured in this study by x-ray diffraction are in good agreement with
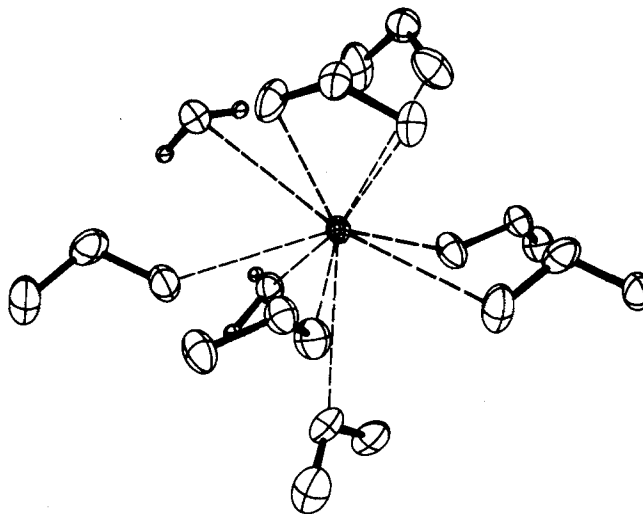

FIG. 3. Environment of Ba²⁺ ion in Ba(NO₂)₂·H₂O. The Ba²⁺ ion is depicted crosshatched, the H atoms by small circles, and the Ba–O and Ba–N contacts by dashed lines. Two water molecules and seven nitrite ions surround the Ba²⁺, see text.
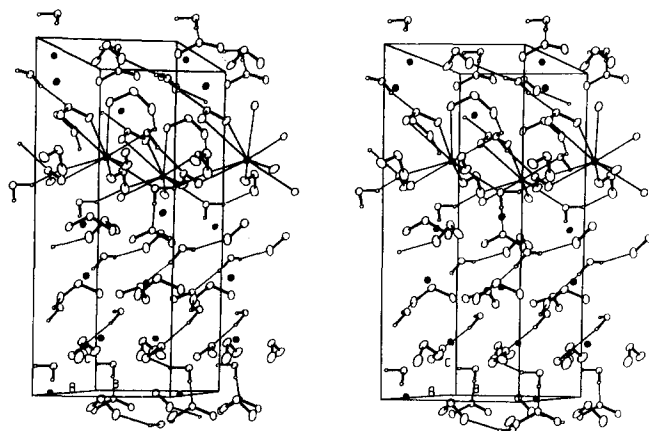
FIG. 4. Stereoview of the Ba(NO$_2$)$_2$·H$_2$O structure. The ellipsoids are shown at the 30% probability level.

the accepted O–H distance of about 0.96 Å and H–O–H angle of 108°.[31] The water molecule forms hydrogen bonds to both independent nitrite ions, with an O(W)···O(4) distance of 2.878(3) Å and an O(W)···N(1) distance of 2.951(5) Å. The importance of the contribution of these hydrogen bonds and of the ionic contacts about the Ba^{2+} ion to the stability of crystalline Ba(NO$_2$)$_2$·H$_2$O is evident from the stereoview of the atomic arrangement presented in Fig. 4. The measured O···O distance is near the average value[31] of 2.81 Å, that of O···N is within the reported range[32] 2.76–3.13 Å.

PYROELECTRIC AND PIEZOELECTRIC COEFFICIENTS

The pyroelectric p_3 and piezoelectric d_{33} coefficients have been remeasured as $14(1) \times 10^{-5}$ C m^{-2} K^{-1} and $3.1(2) \times 10^{-12}$ C N^{-1} respectively. The absolute sign of these coefficients, and their relation to the atomic arrangement, will be discussed elsewhere.[25]

ACKNOWLEDGMENT

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