

et al., 1983b) indicate that only a small error, a shortening of around 0.01 Å, can be expected from the ECP treatment on tellurium. We have not considered or included relativistic effects in these calculations but they could be of importance for such a heavy element as tellurium. There are, however, no references in the literature concerning these effects on bond lengths in tellurium compounds.

If the difference between the calculated and experimental Te—O bond distances in K_2TeO_3 , is used to extrapolate the geometry of a hypothetical (experimental) free tellurite ion, we obtain a Te—O distance of 1.83 Å. The value, extrapolated from experimental results, employed for example by Brown (1974) in the valence-bond theory, is slightly shorter, 1.813 Å.

These quantum-chemical calculations and comparison with experiments give us a good starting point for our further studies of the stereochemistry of tellurium(IV)—oxygen compounds.

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Absolute Chirality and Crystal Structure of Barium Nitrite Monohydrate, $Ba(NO_2)_2 \cdot H_2O$

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Abstract

The absolute chirality of barium nitrite monohydrate, $Ba(NO_2)_2 \cdot H_2O$ [$M_r = 247.4$, hexagonal, space group $P6_1$, $a = 7.070$ (1), $c = 17.886$ (2) Å, $V = 774.3$ Å³, $R = 0.017$ for 1792 observed reflections] has been determined at room temperature through a combination of X-ray diffraction and optical study. For a

crystal that is optically dextrorotatory in the visible region of the spectrum, the space group is found to be $P6_1$. Classical polarizability theory is successfully used to calculate the optical rotation and refractive indices in this crystal and results in good agreement with experiment are obtained. Using the results of these calculations and the principles of anisotropic polarizability theory, a correlation between the sign of the observed optical rotation and the arrangement of the atoms in the crystal structure is established. The

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interactions of most importance to the optical rotation are shown to be those between the highly polarizable Ba ions (Ba^{2+}) and the O atoms of the water molecules $[\text{O}(W)]$. The interdependence of the Ba^{2+} and $\text{O}(W)$ species in their response to the propagating electromagnetic field results in the consideration of polarizable Ba— $\text{O}(W)$ 'units' giving a quasimolecular contribution to the optical rotation. A structural helix of these Ba— $\text{O}(W)$ units is identified as the principal structural origin of the optical rotation.

Introduction

Barium nitrite monohydrate, $\text{Ba}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$, is well known as a strong pyroelectric material (Gladkii & Zheludev, 1965; Liminga, Abrahams & Bernstein, 1980). Other properties of the material have been extensively investigated, including its piezoelectric, electrooptic, dielectric, elastic and thermoelastic behaviour (Haussühl, 1978). However, it remains potentially technically useful because of its pyroelectric response which is comparable with that of LiTaO_3 . Reasonably large (several mm) crystals of optical quality may be obtained from aqueous solution by slow evaporation.

The crystal structure of $\text{Ba}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$ has been well determined by Abrahams, Bernstein & Liminga (1980), who established that the material crystallizes in one of the polar enantiomorphic space groups $P6_1$ or $P6_5$. The crystallographic point symmetry thus allows the material to display optical activity. The observation of optical activity in $\text{Ba}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$ has been reported by several authors, but principally by Burkov, Kizel, Perekalina, Kozlova & Semin (1973), who measured and fitted the dispersion curve over the visible region of the spectrum. The material shows a substantial optical rotation of 17°mm^{-1} at a wavelength of 4800 \AA for light propagating along the unique axis. $\text{Ba}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$ is optically uniaxial negative and quite highly birefringent ($\Delta n = -0.1050$ at 4765 \AA ; Abdullaev, Vasil'eva, Dobrzhanskiĭ & Polivanov, 1977).

Our interest in this material was to establish the correlation between the optical rotation and its crystal structure. The relationship between its pyroelectric and piezoelectric behaviour and its crystal structure has already been established (Liminga *et al.*, 1980) but, although the structural chirality of their crystal was determined at this time, no association with the optical hand was made. The study of the relationship between crystal structure and optical rotation in a polar crystal requires careful thought, as pointed out by Stadnicka, Glazer & Moxon (1985) in their analogous work on $\alpha\text{-LiIO}_3$.

Experimental

Crystals of $\text{Ba}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$ were grown by slow evaporation from aqueous solution at room tempera-

ture. After several weeks, transparent colourless hexagonal prisms of several mm in length but of rather small cross section were obtained. The crystals appeared to be generally of good optical quality. One was cut and polished on (001) to a thickness of $\sim 1 \text{ mm}$. This hexagonal cross section, when viewed in conoscopic illumination between crossed polars, gave a good uniaxial figure (Fig. 1a) which showed no variation with position in the slice. There was no evidence of twin boundaries of the type described by both Liminga *et al.* (1980) and Gallagher, Abrahams, Wood, Schrey & Liminga (1981). On insertion of a quarter-wave plate above the crystal, Airy's spiral for the crystal was obtained (Fig. 1b) which demonstrated that the crystal was optically dextrorotatory.

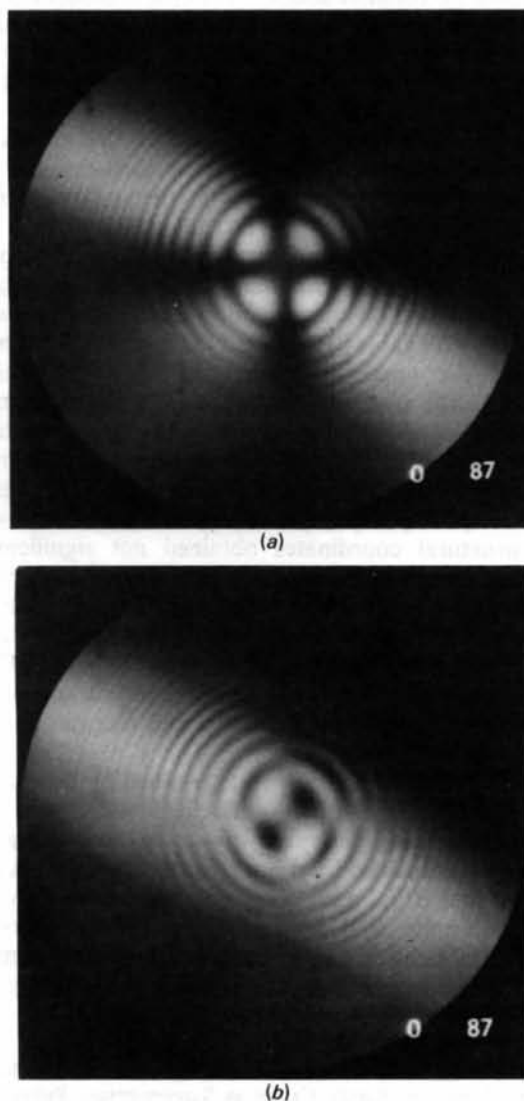


Fig. 1. (a) Uniaxial conoscopic figure for a (001) section of $\text{Ba}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$. (b) Airy's spiral for dextrorotatory $\text{Ba}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$.

A sphere of diameter < 0.25 mm ($\mu R > 0.983$) was ground from the dextrorotatory section and was examined using X-ray techniques. Laue photographs showed that the sphere was a good single crystal suitable for structure determination.

Data collection

A data set sufficient for the independent determination of both structural polarity and chirality was necessary. The $+z$ direction may be fixed relative to the known crystal structure (Abrahams *et al.*, 1980) by comparing the observed and calculated intensity differences between pairs of symmetry-inequivalent reflections hkl and $kh\bar{l}$. These reflections, chosen because the descriptions of the structure using opposite choices of $+z$ are related by a twofold rotation about $[110]$ (see Stadnicka *et al.*, 1985), have large differences in intensity and allow us to fix the $+z$ direction unambiguously *independently of chirality*. Once the direction of the $+z$ axis is fixed relative to the known structure, Bijvoet pairs of reflections, hkl and $kh\bar{l}$, sensitive to the effects of anomalous scattering, can be used to determine the structural chirality. The details of the data collection and refinement are presented in Tables 1 and 2.*

Comparison of the corrected intensities of pairs of observed reflections hkl and $kh\bar{l}$ with calculated intensities based on the structural model of Abrahams *et al.* (1980) (Table 3) indicated that our choice of axes showed the opposite polarity to their convention. Therefore the structural model adopted for refinement was that of Abrahams *et al.* with their structural coordinates (X_A, Y_A, Z_A) for all atoms transformed according to $X = Y_A, Y = X_A, Z = 1 - Z_A$. The refinement in space group $P6_5$ was very straightforward with the structural coordinates obtained not significantly different from those previously published. An identical refinement in space group $P6_1$ was performed simply by reversing the signs of the f'' terms. The latter refinement gave the lower R factors (Table 1). Final refinements in $P6_1$ using appropriately transformed coordinates gave the coordinates and thermal parameters listed in Table 2.

The absolute chirality was determined by comparing the observed Bijvoet-pair differences with those calculated assuming the space group $P6_1$ and using the parameters obtained from our refinement (Table 4). It is evident that ΔF_{calc}^2 and ΔF_{obs}^2 always agree in sign and compare quite well in magnitude for all pairs of reflections considered. Therefore the results demonstrate conclusively that the correct space group for optically dextrorotatory $\text{Ba}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$ is $P6_1$.

* Lists of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51764 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Summary of the experimental conditions and refinement details

Crystal colour, shape and size	Colourless sphere, diameter < 0.25 mm
Linear absorption coefficient (cm^{-1})	78.64
Diffractometer	Enraf-Nonius CAD-4
Radiation	Graphite-monochromated Mo K α
Scan mode	$\omega-2\theta$
No. of reflections and angular range for lattice parameters	25, $6 < \theta < 21^\circ$
Lattice parameters (\AA)	7.070 (1), 17.886 (2)
Maximum $(\sin \theta)/\lambda$ (\AA^{-1})	0.59
Ranges of h, k and l	-1 to 10, -1 to 10, -26 to 26
Intensity control	Monitored hourly, variation $< 1.2\%$
Number of reflections measured	3158
Number of unique observed reflections	1792 [$F_o^2 > 2.5\sigma(F_o^2)$]
R_{int}^* on F	0.022 [all reflections having $F_o > 5\sigma(F_o)$]
Absorption correction	Sphere < 0.25 mm ($0 \leq \theta \leq 25^\circ$)
Max. and min. absorption corrections	3.598, 3.342
Model structure	From Abrahams <i>et al.</i> (1980)
Atomic scattering factors, f' and f''	<i>International Tables for X-ray Crystallography</i> (1974), neutral atoms
Refinement method	Full-matrix least squares (XTAL2.4)
No. of parameters	82
R, wR ($P6_5$)	0.017, 0.015
R, wR ($P6_1$)	0.023, 0.022
χ^2 (goodness of fit, $P6_1$)	2.4
Weighting scheme	$1/\sigma^2(F_o)$
Maximum (average) Δ/σ	0.05 (0.019)
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e \AA^{-3})	1.02, 1.07
Isotropic extinction parameter †	0.103 (3)
Max. and min. extinction factors	1.0, 0.83

$$* R_{\text{int}} = (\sum \{N \sum [w(F - F)^2]\} / \sum [(N - 1) \sum (wF^2)])^{1/2}$$

$$† \chi^2 = [\sum (w |F_{\text{obs}} - F_{\text{calc}}|^2) / (N_{\text{ref}} - N_{\text{var}})]^{1/2}$$

‡ Extinction calculated after Zachariasen (1967).

Stadnicka *et al.* (1985) have pointed out that there are four possible descriptions of a polar, chiral crystal described by point group 6. Relative to Abrahams *et al.* (1980) we have found both the opposite polarity and chirality. The structure of Abrahams *et al.* and our structure [both illustrated in Figs. 2(a) and 2(b)] may be transformed into each other by the operation $m(001)$ which reverses both chirality and polarity.

Optical rotation

A correlation was now sought between the sign of the observed optical rotation and the structural arrangement of the atoms on helices using the guidelines put forward by Glazer & Stadnicka (1986) (hereafter GS). In summary, these guidelines state:

(i) The highly polarizable atoms are the major contributors to the optical rotation.

(ii) The directions of the shortest distances between polarizable atoms tend to correspond to the directions of highest polarizability.

(iii) The contribution to the optical rotation is largest for helices with short interatomic distances and low pitches.

(iv) The sign of the optical rotation is determined by the orientation of the anisotropic polarizabilities of the polarizable atoms in the plane perpendicular to the helix axis. When the component tangential to the helix is larger, plane polarized light rotates in the same sense as that in which the helix is described. When the radial

Table 2. Fractional coordinates and thermal parameters (\AA^2) for space group $P6_1$, with *e.s.d.*'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba	0.84994 (3)	0.42685 (3)	-0.0012 (5)	0.01213 (9)	0.01474 (9)	0.01724 (8)	0.00574 (8)	-0.00070 (8)	0.00152 (8)
N1	0.0293 (5)	0.2463 (5)	0.1443 (5)	0.022 (1)	0.021 (1)	0.026 (2)	0.012 (1)	-0.001 (1)	0.004 (12)
N2	0.1164 (6)	0.5649 (5)	0.3243 (5)	0.034 (2)	0.023 (2)	0.038 (2)	0.013 (1)	0.006 (2)	0.006 (2)
O(N)1	0.1030 (5)	0.4378 (4)	0.1214 (5)	0.032 (2)	0.015 (1)	0.033 (1)	0.006 (1)	-0.011 (1)	0.002 (1)
O(N)2	0.8628 (4)	0.1078 (4)	0.1108 (5)	0.020 (1)	0.016 (1)	0.035 (2)	0.004 (1)	-0.001 (1)	0.001 (1)
O(N)3	0.2902 (5)	0.5860 (5)	0.2972 (5)	0.023 (1)	0.040 (2)	0.044 (2)	0.018 (1)	0.009 (1)	0.019 (1)
O(N)4	0.0127 (5)	0.6155 (5)	0.2814 (5)	0.029 (2)	0.035 (2)	0.060 (2)	0.019 (1)	0.004 (2)	0.006 (2)
O(W)	0.1556 (5)	0.2312 (4)	0.4152 (5)	0.019 (1)	0.019 (1)	0.025 (1)	0.008 (1)	-0.002 (1)	0.00 (1)
H1	0.044 (9)	0.190 (9)	0.385 (3)	$U_{\text{non}} = 0.039$					
H2	0.167 (7)	0.118 (8)	0.432 (3)	$U_{\text{non}} = 0.027$					

Table 3. Observed and calculated differences (ΔF^2) for pairs of (inequivalent) reflections hkl and $h\bar{k}l$

The ΔF^2_{calc} values are computed using the structural coordinates of Abrahams *et al.* (1980) and the ΔF^2_{obs} values are obtained from our observed data. The results allow us to assign the direction of $+z$ opposite to that of Abrahams *et al.* The differences are calculated by:

$$\Delta F^2 = \frac{F^2(hkl) - F^2(h\bar{k}l)}{\frac{1}{2}[F^2(hkl) + F^2(h\bar{k}l)]} \times 100\%.$$

<i>hkl</i>	ΔF^2_{obs}	ΔF^2_{calc}
2 1 3	+28.75	-28.33
3 1 1	-18.56	+25.02
2 1 0	+92.08	-91.26
2 1 8	+22.61	-34.49
1 3 5	+30.22	-30.69
1 2 9	+100.34	-109.93
2 1 9	-109.84	+102.65
1 2 10	-56.13	+64.86
2 1 10	+63.27	-59.13
2 3 2	+31.75	-32.08
1 4 2	-56.49	+52.26
4 1 2	+51.44	-58.56

Table 4. Observed and calculated Bijvoet differences (ΔF^2) for pairs of reflections hkl and $h\bar{k}l$ sensitive to anomalous scattering

The ΔF^2_{calc} values are computed assuming the space group $P6_1$, and the structural coordinates from our refinement. The $\times F^2_{\text{obs}}$ are the intensity differences from our observed data. The differences are calculated by:

$$\Delta F^2 = \frac{F^2(hkl) - F^2(h\bar{k}l)}{\frac{1}{2}[F^2(hkl) + F^2(h\bar{k}l)]} \times 100\%.$$

<i>hkl</i>	ΔF^2_{obs}	ΔF^2_{calc}
0 1 4	7.94	6.40
1 1 2	11.56	10.03
0 2 1	7.43	6.33
0 0 6	9.0	6.25
0 2 2	13.48	15.06
2 1 4	7.32	7.99
0 3 4	9.07	7.2
4 2 5	3.66	3.59
1 5 1	3.60	3.86
2 1 8	7.43	5.50
3 2 6	9.90	6.06
2 1 10	9.47	6.66

component is larger, the plane of polarization rotates in the opposite sense to that of the helix.

The presence of the screw axis in space group $P6_1$ ensures that there are many 'symmetric-structural' (after GS) helical arrangements of atoms described by the space-group symmetry. We are particularly interested in helices consisting of highly polarizable atoms. If Pauling's (1927) atomic polarizability volumes are taken as a reasonable starting point, the O

atoms involved in the polar $(\text{NO}_2)^-$ and H_2O groups must be considered the most polarizable species. There are five distinct types of O atom in the $\text{Ba}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$ unit cell. Four of these [O(N)1–O(N)4, Fig. 2b] belong to the $(\text{NO}_2)^-$ groups and the remaining oxygen type [O(W)] belongs to the H_2O group. In considering the relative sizes of the polarizability volumes assigned to O(N) and O(W), two factors are taken into account *i.e.* (a) the bond lengths between a given O atom and the surrounding atoms, and (b) the nature of the H_2O and $(\text{NO}_2)^-$ groups. In general, the Ba–O(W) distances are longer than the Ba–O(N) distances suggesting that the O(W) electrons, being less rigidly bound, should be more able to respond to the electromagnetic field. In the H_2O groups, there is ionic charge separation in the H–O bonds. However, in the $(\text{NO}_2)^-$ groups, there is a degree of covalency in the N–O interactions which reduces the polarizability volume which may be assigned to an individual O(N). Therefore, on average, the O(W) are considered to occupy a larger polarizability volume than the O(N). Because of the complexity of the structure, attempts to predict the orientation

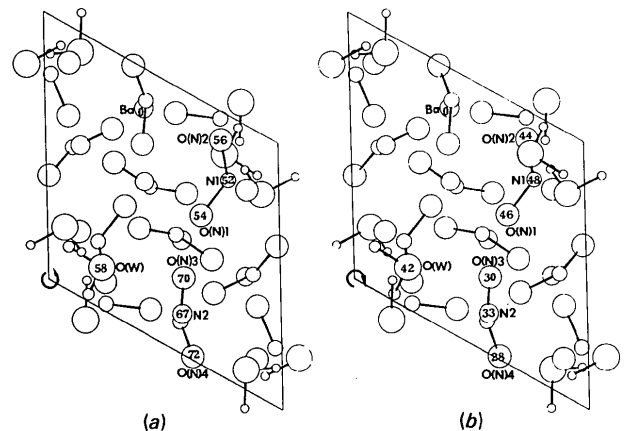


Fig. 2. The $\text{Ba}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$ structure viewed along $[001]$. (a) Our form of the structure (space group $P6_1$). (b) The structure of Abrahams *et al.* (1980) (space group $P6_3$). The arrows at the origin indicate the opposite chiralities of the structures (a) and (b) and follow senses of the helices of O atoms formed about this point (not joined in the figures). The opposite structural polarities are revealed by consideration of the NO_2 groups which show dipole moments respectively pointing into (a) and out of (b) the page.

of the anisotropic polarizability ellipsoids for the O atoms were not made. Instead, the orientations were computed using the program of Devarajan & Glazer (1986) (hereafter DG) which calculates optical rotation and birefringence for crystals when supplied with structural data and input polarizability volumes for the important atoms. The results of the calculations are compared with experimental values in deciding the optimum values for the input polarizability volumes. The experimental value for the optical rotation, $17.327^\circ \text{ mm}^{-1}$ at the chosen wavelength (4800 Å) was calculated from the expression for the best fit to the observed dispersion curve of Burkov *et al.* (1973). The values for the refractive indices ($n_o = 1.6303$, $n_e = 1.5259$) were taken from Abdullaev *et al.* (1977).

Input polarizability volumes were supplied for the two types of O atom O(N) and O(W) [no distinction was made between the theoretically distinguishable O(N)1–O(N)4 in order to limit the number of parameters]. The best fit to the experimental data obtained was $\rho_{\text{calc}} = 8.76^\circ \text{ mm}^{-1}$, $n_{o \text{ calc}} = 1.6303$, $n_{e \text{ calc}} = 1.5259$ for input polarizability volumes $\alpha^{O(W)} = 3.35 \text{ \AA}^3$ and $\alpha_{O(N)} = 1.68 \text{ \AA}^3$. This result was quantitatively disappointing ($\rho_{\text{calc}} \approx \frac{2}{3}\rho_{\text{obs}}$) although it did demonstrate independently that the arrangement of atoms in space group $P6_1$ corresponded to an optically dextrorotatory result. The small dextrorotation calculated can be explained using a structural helix theory of optical rotation with reference to the calculated polarizability ellipsoids (Fig. 3*a*). Centred on the origin are two RS1/6 (in the terminology of GS) helices, *i.e.*, helix (1) (*ABCDEF*) consisting of O(W) atoms with polarizability ellipsoids radial to the helix and helix (2) (*GHIJKL*) consisting of O(N)2 atoms with polarizability ellipsoids tangential. Anisotropic polarizability theory [Ramachandran (1951) and GS] predicts that helix *ABCDEF* gives a dextrorotatory contribution to the optical rotation (*i.e.* against the sense of the helix) and that *GHIJKL* gives a laevorotatory contribution (*i.e.* with the sense of the helix). In assessing which of these two opposite contributions has the greater magnitude, we must consider several factors, *e.g.*, the interatomic bond length in each helix, the degree of anisotropy of the polarizability ellipsoids and the size of the polarizability volumes for the atoms involved. The O(N)2–O(N)2 distance in helix (2) (3.340 Å) slightly exceeds the O(W)–O(W) distance in helix (1) (3.313 Å) and the input polarizability for the O(N) is much smaller than that for the O(W). The degree of anisotropy in both the O(N)2 and O(W) polarizability ellipsoids is approximately the same. Hence, we expect helix (1) consisting of O(W) atoms having a much higher overall polarizability volume and a shorter interatomic distance to predominate, resulting in a net dextrorotation.

The importance of the other atomic species, *i.e.*, the Ba and the N atoms, to the optical rotation was then

Table 5. *Final calculated values (using program of DG) for the refractive indices and optical rotation in dextrorotatory barium nitrite*

Isotropic input polarizabilities (Å ³)			$n_{o \text{ calc}}$	$n_{e \text{ calc}}$	ρ_{calc} (° mm ⁻¹)
$\alpha_{O(N)}$	$\alpha_{O(W)}$	α_{Ba}	($n_{o \text{ obs}} = 1.6303$)	($n_{e \text{ obs}} = 1.5259$)	($\rho_{\text{obs}} = 17.327$)
1.22	2.21	2.90	1.6191	1.5343	+17.327

considered. In $\text{Ba}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$ the N atom is effectively a high-valency cation and therefore has a negligible polarizability. However, barium (Ba^{2+}) may be highly polarizable as found by Tessman, Katta & Shockley (1953) and Pohl (1978) in fitting refractive index data for barium compounds. The Ba^{2+} were introduced into the calculation and the three polarizability volumes α_{Ba} , $\alpha_{O(W)}$ and $\alpha_{O(N)}$ were adjusted to obtain the excellent fit to the experimental data listed in Table 5. The polarizability volume ($\alpha_{Ba} = 2.90 \text{ \AA}^3$) for Ba^{2+} is comparable with the values used by the authors above and exceeds the polarizability volumes for both O(W) and O(N). Clearly the inclusion of the Ba atoms is very important to the calculation of the optical rotation in this material. However, optical rotation, refractive indices and birefringence cannot be simultaneously fitted considering the Ba and O(W) alone, as the O(N) must be included. The calculated birefringence is very sensitive to the value assumed for the polarizability of the O(N), demonstrating the importance of the polarizability anisotropy of the $(\text{NO}_2)^-$ group to the optical anisotropy of the material. This effect was also observed by Hirotsu, Yanagi & Sawada (1968) in NaN_2 .

The effect of the inclusion of the Ba^{2+} can be seen with reference to Fig. 3(*b*). Relative to Fig. 3(*a*), the O(N)2 (which now take a smaller overall polarizability volume) are less anisotropic so that the laevorotation produced by helix (2) (*GHIJKL*) is reduced. However, the O(W) in helix (1) (*ABCDEF*) have polarizability ellipsoids oriented neither significantly radial nor tangential to the helix. Hence, helix (1) does not now contribute directly to the optical rotation whereas previously it produced a dextrorotation. The most obvious difference between Figs. 3(*a*) and 3(*b*) is the presence of the Ba atoms (*MNOPQR*) in the latter represented by large, slightly anisotropic polarizability ellipsoids. These are linked into a star-like helix (*ANBOCPDQERFM*, Fig. 3*b*) by the O(W) through Ba–O(W) bonding distances of 2.863 and 2.956 Å. The Ba–Ba bond length in the RS1/6 helix (3) (*MNOPQR*), which is formed by the Ba atoms alone, is 4.707 Å, a very long interatomic bond length for a helix to be effective in influencing the optical rotation. Careful examination of the structure did not reveal any new structural helices involving the O(N), O(W) and Ba so that attention was focussed on the helices at the origin. Even though the Ba–Ba bonding distance is as large as 4.707 Å, their slightly radially oriented

polarizability ellipsoids would be expected to produce a small dextrorotatory contribution to the optical rotation on their own. A stronger link between a pair of neighbouring Ba atoms is made through a bridging O(W). Indeed, it is the presence of the two O(W)

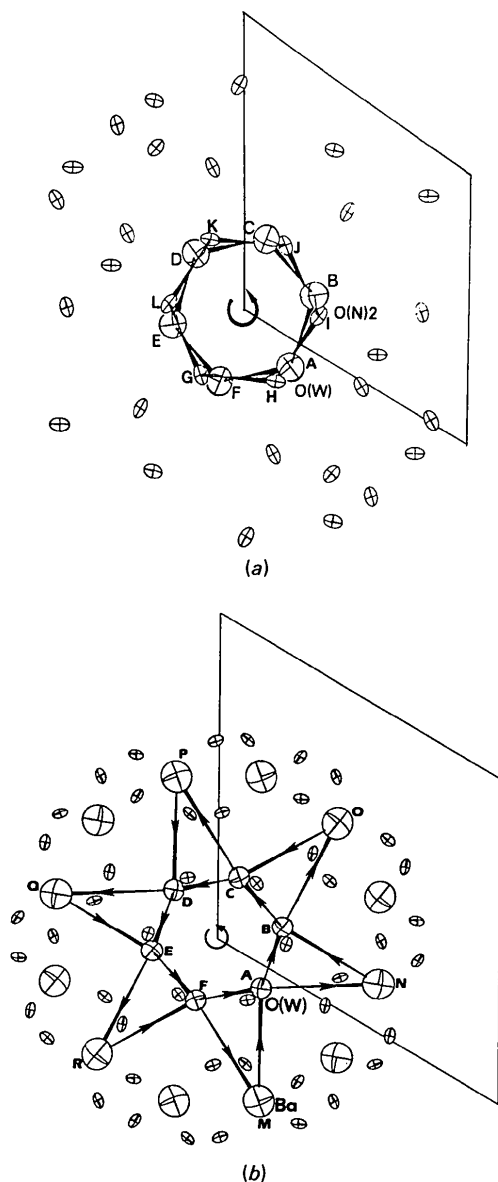


Fig. 3. (a) View of dextrorotatory Ba(NO₂)₂·H₂O along [001] showing the polarizability ellipsoids for the O atoms only. The polarizability ellipsoids shown correspond to a calculated optical rotation of +8.36° mm⁻¹ arising from the larger dextrorotatory contribution of the O(W) atoms on helix ABCDEF which supercedes the laevorotatory contribution of the O(N)2 atoms on the helix GHIJKL. (b) View of dextrorotatory Ba(NO₂)₂·H₂O along [001] including Ba atoms and O atoms. The polarizability ellipsoids shown correspond to the final calculated optical rotation of 17.33° mm⁻¹. The figure ANBOCPDQERFM is identified as the principal structural origin of the optical rotation in Ba(NO₂)₂·H₂O.

atoms bonded to each Ba that forces its polarizability ellipsoid around into the radial orientation [as can readily be confirmed by omitting the O(W) from the calculation]. Therefore, through a cooperative interaction between the Ba and the O(W) atoms, an arrangement of anisotropically polarizable units resulting in an optical dextrorotation is produced. We can consider that the optical rotation arises physically from the helical arrangement of polarizable Ba(O(W))₂ 'groups' (i.e., the complete figure ANBOCPDQERFM) expressing the importance of the Ba–O(W) interaction, rather than simply through a helix of Ba atoms alone. This cooperative physical interpretation is consistent with the point-dipole approach, which attaches an individual independent oscillator to each atomic site, since it simply expresses the importance of interatomic 'dipole–dipole' interactions in determining the optical rotation. The Ba–O(W) interactions here are particularly marked because both atoms are assigned high polarizability volumes (implying that the induced polarizability of each is enhanced by the presence of the other) and because these atoms are relatively closely bound in the crystal structure.

The importance of the whole entity ANBOCPDQERFM is demonstrated by calculating its individual effect by including only Ba and O(W) atoms in the calculation. This gives an increase in the calculated optical rotation to 25.5° mm⁻¹ [for the same α_{Ba} and $\alpha_{\text{O(W)}}$ as before]. Considering the polarizability ellipsoids (Fig. 4), it is clear that the increased calculated optical rotation can be explained both by the increased anisotropy of the Ba ellipsoids in their radial configuration [resulting from the absence of the influence of the O(N) atoms at bonding distances 2.881 and 3.049 Å] and by the absence of the helix (2) of O(N)2 atoms (which previously gave a laevorotation). Meanwhile, the O(W) atoms forming helix (1) now show polarizability ellipsoids oriented tangentially to the helix. Therefore,

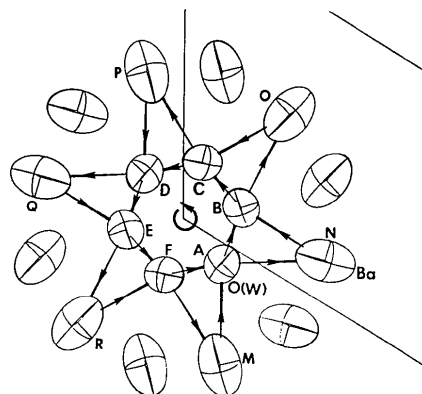


Fig. 4. Polarizability ellipsoids for Ba and O(W) atoms only showing the effect of considering the entity ANBOCPDQERFM in isolation. The polarizability ellipsoids shown correspond to a calculated optical rotation of ~25° mm⁻¹.

the O(*W*) atoms, if considered in isolation, would provide a laevorotatory contribution to the optical rotation. However, when the interactions between the O(*W*) and the Ba atoms are considered, *i.e.*, the figure *ANBOCPDQERFM*, a considerable dextrorotation results which more than outweighs any laevorotation produced by the O(*W*)'s alone. These observations clearly demonstrate that these rather unusual structural helices can indeed independently account for the observed optical rotation in Ba(NO₂)₂·H₂O.

The independence of helices of type *ANBOCPDQERFM* in their interactions with the propagating electromagnetic field is demonstrated by computing the effect of artificial expansion of the unit cell in the (001) plane [in a similar way to Thomas (1988)]. The calculated optical rotation is observed to undergo a steady decrease because the number of effective helices per unit volume is decreased as the cell volume is increased, *i.e.*, it is a dilution effect. However, the orientations of the polarizability ellipsoids of the Ba and O(*W*) atoms forming an individual *ANBOCPDQERFM* helix remains virtually unchanged throughout the expansion process showing that the important Ba—O(*W*) interactions already identified *within* the helix predominate over any interhelix interactions.

The Ba—O(*W*) helix *ANBOCPDQERFM* has a star-like shape in projection, with the re-entrant angles O(*W*)—Ba—O(*W*) appearing very acute. This type of structural feature was previously commented upon by Stadnicka, Glazer & Koralewski (1987) in their study of α-NiSO₄·6H₂O. In the latter, the re-entrant angles in the oxygen helix associated with the optical rotation (Fig. 5) are caused by strong hydrogen bonding between the O1 and O3 atoms which lie on the helix and atoms O4 and O5 which do not. In the case of Ba(NO₂)₂·H₂O, the more exaggerated re-entrant angles occur because the O(*W*) atoms in the helix *ANBOCPDQERFM* are hydrogen bonded to both the independent (NO₂)⁻ groups [bond lengths O(*W*)—O(N)4 = 2.878, O(*W*)—N1 = 2.957 Å] tending to

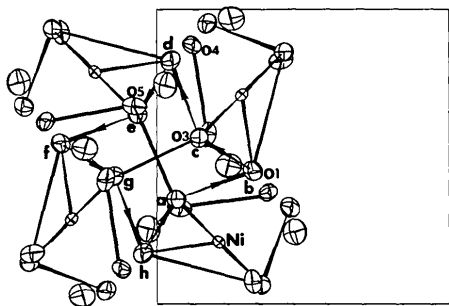


Fig. 5. View of α-NiSO₄·6H₂O along [001] including polarizability ellipsoids for the O and Ni atoms only [after Stadnicka *et al.* (1987)]. The sharp re-entrant angles in the helix *abcdefgh* are analogous to (although less exaggerated than) those shown by the helix *ANBOCPDQERFM* (Figs. 3b and 4).

force an O(*W*) away from its associated Ba atoms. Other weaker O—O bonding interactions also contribute to this effect.

In Ba(NO₂)₂·H₂O, the predominating interactions important to the optical rotation are those between the Ba and O(*W*) atoms. The effect of large dipole—dipole interactions tends to force the polarizability ellipsoid of the Ba atom to lie along the Ba—O(*W*) bonding directions. In combination with the exaggerated re-entrant angle in the helix, this results in the Ba atom's polarizability ellipsoid being forced into a radial orientation. The large value of the input polarizability volume for the Ba atom certainly assists this effect. The re-entrant angles are less marked in the helix of O atoms in NiSO₄·6H₂O and the polarizability ellipsoids of the O1 atoms at the external vertices do not have a radial orientation. This difference results not only because of the different geometrical characteristics of the helix but also because of the dissimilar bonding environments for the atoms concerned. The O1—O3 interactions in α-NiSO₄·6H₂O do not dominate the optical rotatory behaviour to the same extent as the Ba—O(*W*) interactions in Ba(NO₂)₂·H₂O.

Concluding remarks

Optically dextrorotatory Ba(NO₂)₂·H₂O has been shown to crystallize in space group *P6₁*. The structural origin of the optical rotation has been interpreted using anisotropic polarizability theory and the interatomic interactions of primary importance have been identified as those between the Ba²⁺ ions and the O atoms from the water molecules. The arrangement of the anisotropically polarizable Ba²⁺ and O(*W*) on an unusual structural helix showing exaggerated re-entrant angles has led to a quasimolecular interpretation of the optical rotation in this structure in terms of polarizable Ba—O(*W*) units. Calculations have also shown that, as expected, consideration of the (NO₂)⁻ groups [through the polarizability of the O(N) atoms] is essential for the correct modelling of the optical anisotropy of the material. Results in very good agreement with experiment have been obtained from calculations in the classical point-dipole approximation for a material in which there is some deviation from its basic assumptions. In particular, despite the fact that the (NO₂)⁻ group is a polarizable entity having an extended charge distribution that cannot be simply modelled in this approximation, the results of the calculations are very encouraging.

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Single-Crystal X-ray Study of the Decagonal Phase of the System Al–Mn

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Abstract

A single crystal of the metastable decagonal phase of the system Al–Mn with the composition $\text{Al}_{0.78(2)}\text{Mn}_{0.22(2)}$ and approximate dimensions $0.25 \times 0.13 \times 0.08 \text{ mm}^3$ has been investigated by various X-ray film methods and on a four-circle diffractometer. The diffraction pattern can be indexed using four reciprocal lattice vectors pointing to the vertices of a pentagon $a_1^* = a_2^* = a_3^* = a_4^* = 0.2556 (1) \text{ \AA}^{-1}$ and one normal to them parallel to the tenfold axis $a_5^* = 0.08065 (5) \text{ \AA}^{-1}$ [$a_5 = 12.400 (7) \text{ \AA}$]. The X-ray photographs indicate that this two-dimensionally quasicrystalline phase is highly ordered. Nevertheless, a considerable amount of diffuse scattering is observed in the reciprocal lattice layers perpendicular to the tenfold axis.

Introduction

Since the discovery of the first quasicrystalline phase, which was icosahedral (Shechtman, Blech, Gratias &

Cahn, 1984), numerous new quasicrystals have been detected, some of which have one-dimensional lattice periodicity. In a few cases the point symmetry of these two-dimensional quasicrystals has been found to be octagonal or dodecagonal (Kuo, 1987a). Mostly, however, they show decagonal symmetry. Such phases have been prepared in the systems Al–Mn, Al–Fe, Al–Ru, Al–Pt, Al–Pd, Al–Cr(Si), Al–Co, Al–Ni(Si), Al–Rh and Al–Os (Kuo, 1987b). With the exception of the icosahedral phase of the system Al–Li–Cu (Mai, Zhang, Hui, Huang & Chen, 1987; van Smaalen, Bronsveld & de Boer, 1987) all single-crystal diffraction studies of quasicrystals have been performed by electron scattering because of the lack of large single crystals. Since the electrons have a very short wavelength, leading to a large radius of the Ewald sphere and also a stronger interaction with matter than X-rays, an interpretation of the diffraction patterns in terms of a simple kinematical approach and thus a quantitative structure determination is in most of the cases not possible. Furthermore, surface effects and structural changes during specimen preparation might obscure the bulk information.

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