s'écarteraient de positions centrosymétriques, joue de manière négligeable (f'' vaut respectivement: 0,36; 0,19; 0,009); les mesures des réflexions ne seraient donc pas altérées par la présence d'une macle par hémiédrie dans l'échantillon utilisé. Nous notons en outre que si la symétrie cristalline est $P1$ les diverses réflexions ont un module différent de ce qu'il est si la symétrie est $P\bar{1}$. Il faut encore noter que l'existence systématique d'une macle polysynthétique par hémiédrie amoindrirait le signal de second harmonique.

Compte tenu de ces considérations, nous avons essayé de reconstituer un modèle de structure de symétrie $P1$ à partir des résultats de l'affinement dans $P\bar{1}$ avec atomes dédoublés, en nous basant sur trois hypothèses: (i) dans les chaînes d'octaèdres $CdCl_6$ les arêtes non communes correspondent aux plus grandes distances $Cl–Cl$; (ii) la pseudo-symétrie par un pseudo axe binaire de direction $[1\bar{1}0]$ observée dans le modèle $P\bar{1}$ se retrouve dans le modèle $P1$; (iii) les forces de liaison de valence électrostatique doivent se situer pour Cd et Ca entre 2,06 et 1,94 unités de valence. Ceci nous a conduit à envisager plusieurs modèles également vraisemblables qui malheureusement ne peuvent pas être testés à l'aide des programmes classiques d'affinement par moindres carrés puisque la fonction minimisée, $\sum_i w_i(|F_o|-|F_c|)_i^2$ n'est pas adaptée pour ce cas de structure pseudo-symétrique (Rae, 1974). Nous comptons reprendre ce problème après avoir adapté un programme qui minimise $\sum_i w_i|F_o-F_c|_i^2$ comme Rae (1974) le propose.

Les tests de génération de second harmonique ont été effectués au CNET (Bagneux) par M Le Person que nous remercions très vivement.

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Structure Refinement of Strontium Nitrate, Sr(NO₃)₂, and Barium Nitrate, Ba(NO₃)₂

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Abstract. Sr(NO₃)₂: $M_r = 211.63$, cubic, $Pa3$, $a = 7.7813$ (2) Å [McMurdie *et al.* (1975).*Natl Bur. Stand. (US) Monogr.* **12**, 31], $U = 471.15$ Å³, $Z = 4$, $D_x = 2.98$ Mg m⁻³, μ[neutrons $\lambda = 0.8972$ (2) Å] = 0.002 mm⁻¹, room temperature. Ba(NO₃)₂: $M_r = 261.35$, $Pa3$, $a = 8.1184$ (2) Å [Swanson *et al.* (1974). *Natl Bur. Stand. (US) Monogr.* **11**, 14], $U = 535.07$ Å³, $Z = 4$, $D_x = 3.24$ Mg m⁻³, $\mu = 0.002$ mm⁻¹, room temperature. The atomic arrangements were refined at room temperature with single-crystal neutron diffraction data: Sr(NO₃)₂ to $R = 0.020$ ($R_w = 0.019$) for 330 reflections and Ba(NO₃)₂ to $R = 0.024$ ($R_w = 0.022$) for 351 reflections. The N–O bond lengths (uncorrected for thermal vibration) are 1.2467 (5) and 1.2465 (6) Å, the deviations of the N atoms from the planes defined by the O atoms of the nitrate groups are 0.005 (1) and 0.006 (1) Å, respectively. The amplitudes of the thermal vibrations have normal values.

Introduction. The isotypic cubic nitrates of lead, barium, strontium, and calcium are reported in the

literature to belong to the crystal class 23 or $2/m\bar{3}$. Morphological studies (Wulff, 1880) indicated tetartoedric symmetry. X-ray investigations by Vegard (1922), Jäger & Van Melle (1928) and Vegard & Bilberg (1931) led, however, to the conclusion that they crystallize in space group $Pa3$. The centrosymmetric symmetry was confirmed by Kleber (1955, 1957) on the basis of new morphological studies. In powder neutron diffraction studies of $Pb(NO_3)_2$ and $Ba(NO_3)_2$, Hamilton (1957) and Lutz (1960) assumed space group $Pa3$ and reported for the nitrate groups remarkably strong oscillations (librations) around the N atoms, and N—O bond lengths of 1·27 and 1·23 Å, respectively. Lutz (1960) stated that any deviation of the nitrate groups from planarity had to be very small. He suggested an anisotropic temperature factor for the O atom with the longest axis of the ellipsoid of vibration perpendicular to the N—O bond within the plane of the nitrate group. In a single-crystal neutron diffraction study of $Ba(NO_3)_2$, Birnstock (1967) reported the observation of (very weak) $hk0$ reflections violating space group $Pa3$ and refined its crystal structure in space group $P2_13$ with approximately 90 observed reflections to $R = 0·07$. From a crystal-chemical point of view his results are remarkable in three respects: (1) the two crystallographically independent nitrate groups have different bond lengths, N—O = 1·275 (8) and 1·225 (10) Å; (2) both nitrate groups have the shape of a rather flat trigonal pyramid with heights of 0·10 (1) and 0·12 (1) Å, respectively; (3) the environments of these groups differ considerably [the three Ba atoms closest to the nitrate groups deviate from the planes defined by the three O atoms of the NO_3 groups by −0·10 (1) and +0·40 (1) Å, respectively; the positive and negative signs designate the location on the same or on the opposite side as compared with the N atom of the nitrate group]. In contrast to Birnstock's (1967) results, physical properties such as piezoelectric, linear electrooptic and nonlinear optic effects or optical activity which should be present in space group $P2_13$ could not be detected by very sensitive measurements (Haussühl, 1977), and Raman spectroscopic data were also found to be in agreement with space group $Pa3$ (Brooker, 1979).

In order to contribute to the solution of the problem of the symmetry of the compounds under discussion, as well as to confirm or disprove the features of the atomic arrangement in barium nitrate reported by Birnstock (1967), it seemed worthwhile to refine again the crystal structures of $Sr(NO_3)_2$ and $Ba(NO_3)_2$.

Experimental. The crystals used for the measurements were grown from aqueous nitric acid solutions at about 323 K. Three-dimensional X-ray data for $Sr(NO_3)_2$ were collected at room temperature with Mo $K\alpha$ radiation on an automatic four-circle diffractometer and showed no violation of space group $Pa3$. Structure refinements using $SHELX76$ (Sheldrick, 1976) and $RFINE4$ (Finger & Prince, 1975) in space groups $P2_13$

and $Pa3$ both led to $R \sim 0·03$; the resultant atomic coordinates, however, differ considerably. As a consequence of the X-ray radiation used, the quality of the large class of reflection intensities to which the Sr atoms do not contribute was considerably affected by fluorescence radiation. As these reflections are very important for the accurate location of the light atoms, a neutron diffraction study was carried out.

Single crystals of $Sr(NO_3)_2$ and $Ba(NO_3)_2$ (ca 50 mm^3) {90 mm^3}* were mounted on the automatic four-circle $P3$ neutron diffractometer at the FR2 reactor, Kernforschungszentrum Karlsruhe [wavelength 0·8972 (2) Å]. Before the measurements were performed both crystals were quenched several times in liquid nitrogen in order to increase their mosaic structure (Heger & Kuhs, 1979). The remaining extinction effects had to be corrected in the structure refinements.

The decision on the correct space group was taken with reference to the following arguments. In space group $P2_13$ two crystallographically different nitrate groups would occur and by that increase the number of free parameters in the structure refinement from 16 ($Pa3$) to 28. E statistics to test for a centre of symmetry could not show acentric symmetry because of the atomic positions in the unit cell. However, as no reflections violating space group $Pa3$ were observed the refinements were performed initially in $Pa3$, and as it was possible to refine the structures to satisfactorily low reliability indices, the space group in which the title compounds crystallize is established to be $Pa3$ with one type of nitrate group only.

Absorption corrections were not considered necessary (see *Abstract*); the 1322 {2502} measured reflections with $\sin\theta/\lambda \leq 0·85$ Å^{-1} (automatically adjusted $\omega/2\theta$ scan) were averaged to give 485 {543} unique reflections of which 335 {357} had $I \geq 2\sigma(I)$. Refinements using isotropic extinction correction, anisotropic thermal parameters for all atoms and unit weights were carried out in Karlsruhe with XRAY76 (Stewart, 1976) and in Vienna with the 1980 update of XRAY72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972), $SHELX76$ (Sheldrick, 1976), $RFINE4$ (Finger & Prince, 1975) and $SFLS-5$ (Prewitt, 1966); these led to almost identical results† with R values of about 0·021 {0·026} (Nowotny & Heger, 1982). The neutron scattering lengths were taken from Koester (1977). Final refinements were carried out using $RFINE4$ (Finger & Prince, 1975) with the weighting scheme $w = \{[\sigma_F^2 + (pF^2)]^{1/2} \times (1 - 3x^4 + 2x^6)\}^{-1}$, where $x = |F_o - F_c|/[\sigma(F)\Delta F_{max}]$. The most balanced error distribution was found for $p = 0·02$ and $\Delta F_{max} = 2·0$ (which caused 5 {6} reflections with $|F_o - F_c| > \Delta F_{max}$ to be rejected). Final R values are: $Sr(NO_3)_2$: $R = 0·021$, $R_w = 0·023$ for 335 reflections and 0·020, 0·019 for

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* Where appropriate, data in curly brackets refer to $Ba(NO_3)_2$.

† Except $SHELX76$, probably because of its 'empirical (and physically dubious) isotropic extinction correction parameter' [program description (Sheldrick, 1976)].

330 reflections; $Ba(NO_3)_2$: $R = 0.025$, $R_w = 0.027$ for 357 reflections and 0.024, 0.022 for 351 reflections.* Geometrical calculations were carried out with *KRISTALLCHEMIE* (Nowotny & Zobetz, 1982).

Discussion. Final refined parameters are given in Table 1, interatomic distances and angles in Table 2.

The arrangement of metal (M^{2+}) ions in the crystal structures of $Sr(NO_3)_2$ and $Ba(NO_3)_2$ corresponds to a cubic face-centred Bravais lattice. They are connected by nitrate groups with the N atoms on the threefold axes and are twelve-coordinated by O atoms.

The coordination polyhedron around M^{2+} can be visualized as a considerably distorted cuboctahedron with broken square faces.† The square faces of the cuboctahedron are divided into two triangles by the longest edges of the convex polyhedron $[O-O = 3.947$ $\{4.132\}$ Å]. The angle between these two faces is very flat (about 1.4°). The mean length of the 24 edges of the cuboctahedron (neglecting the 'diagonal' of the 'square face') is 2.79 $\{2.93\}$ Å, which is very close to the mean $M-O$ distance of 2.78 $\{2.91\}$ Å. These mean $M-O$ distances are in good agreement with those

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* Lists of structure factors and an analysis of the anisotropic temperature factors for both compounds, and a table giving examples of mean $M-O$ distances within MO_n coordination polyhedra have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38495 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† The space-filling polyhedron in an arrangement with ideal cuboctahedral coordination is a dodecahedron. The space-filling polyhedron around M^{2+} (calculated assuming equal partition between all atoms) is a distorted dodecahedron which is a combination of two different rhombohedra. The superficial areas of their faces differ by less than 20%. Some data about space-filling polyhedra and coordination are summarized in Table 3.

Table 1. *Atomic parameters*

Occupied positions [after *International Tables for X-ray Crystallography* (1952)]: M: 4(a), N: 8(c), O: 24(d).

	$Sr(NO_3)_2$	$Ba(NO_3)_2$
$M: x = y = z$	0	0
β_{ii}	0.00412 (6)	0.00444 (6)
β_{ij}	0.00006 (5)	0.00010 (6)
N: $x = y = z$	0.34510 (4)	0.35139 (4)
β_{ii}	0.00467 (5)	0.00596 (5)
β_{ij}	0.00019 (3)	0.00102 (4)
O: x	0.27376 (7)	0.28553 (8)
y	0.28503 (7)	0.29105 (8)
z	0.47538 (6)	0.47627 (7)
β_{11}	0.00824 (8)	0.01020 (9)
β_{22}	0.00804 (8)	0.00914 (9)
β_{33}	0.00514 (7)	0.00762 (8)
β_{12}	0.00164 (5)	0.00350 (7)
β_{13}	0.00185 (5)	0.00370 (7)
β_{23}	0.00152 (5)	0.00310 (6)

The temperature factor is of the form
$$T = \exp\left[-(h^2\beta_{11} + \cdots + 2hk\beta_{12} + \cdots)\right].$$

Table 2. *Selected interatomic distances* (Å) *and angles* (°)

t: type of $M-O$ distance(s), defined by first occurrence in table. The point symmetry of the M^{2+} position is 3. Therefore, the 12 surrounding O atoms build up a 6 + 6 coordination with two different types (a, b) of $M-O$ distances within each distorted cuboctahedron.
r: remark.
n: number of equivalent values.

t	r*	n	$Sr(NO_3)_2$	$Ba(NO_3)_2$
MO_{12} polyhedron				
$M-O$	a	6	2.7153 (5)	2.8789 (6)
$M-O$	b	6	2.8381 (5)	2.9414 (6)
$O-O$	a, b	1	6	2.1594 (10)	2.1589 (12)
$O-O$	b, b	2	6	2.9114 (10)	3.0521 (12)
$O-O$	a, a	2	6	3.0126 (10)	3.2029 (12)
$O-O$	a, b	2	6	3.0829 (10)	3.3190 (12)
$O-O$	a, b	3	6	3.9082 (10)	4.1000 (12)
$O-O$	a, b	4	6	3.9473 (10)	4.1316 (12)
Nitrate group				
$N-O$		3	1.2467 (5)	1.2465 (6)
$O-O$		3	2.1594 (10)	2.1589 (12)
$O-N-O$		3	120.00 (06)	120.00 (07)
$M-O-N$	b	3	94.11 (03)	96.61 (03)
$M-O-N$	a	3	100.12 (03)	99.69 (03)
$M-O-M$	a, b	3	164.43 (02)	161.01 (02)
Short N–N distances				
N–N		5	1	4.1754 (6)	4.1794 (6)
N–N		6	6	4.1626 (6)	4.3803 (6)

* (1) Joined edge between cuboctahedron and nitrate group. (2) Edge of cuboctahedron. (3) Diagonal of the 'square face' of the cuboctahedron that is not an edge of the convex MO_{12} polyhedron. (4) Diagonal of the 'square face' of the cuboctahedron that is an edge of the convex MO_{12} polyhedron. (5) *Via* $\bar{1}$ (middle of the octahedral hole). (6) Nearest N neighbours not on the threefold axis.

Table 3. *Data for space-filling polyhedra* (*based on* r_M : $r_N : r_O = 1 : 1 : 1$) *and coordination*

	Sr	N	O	Ba	N	O
Coordination numbers						
Referred to greatest gap ($\Delta d/d$)	18	3	1	18	3	1
Referred to Hoppe (1970)	10.9	3.6	4.8	11.2	3.6	4.9
Referred to O'Keeffe (1979)	10.8	3.3	3.3	11.2	3.3	3.3
Space-filling polyhedra						
Total number of faces (n.o.f.)	12	16	21	12	10	17
n.o.f. > 1% of greatest face	12	10	13	12	10	15
n.o.f. > 10% of greatest face	12	7	12	12	7	12
Volume (Å³)	15.35	7.27	14.65	17.82	7.35	16.81

Faces of space-filling polyhedron around M^{2+}

M	n.o.f.	Superficial area (Å²)	Normalized superficial area (%)
Sr	6	3.047	100.0
	6	2.490	81.7
Ba	6	3.275	100.0
	6	2.854	87.2

occurring in comparable structures [some examples (De Villiers, 1971; Köhl, 1973; Drofenik & Golič, 1979; Effenberger, 1980; Miyake, Minato, Morikawa & Iwai, 1978) have been deposited]. The six shortest edges of the cuboctahedron ($O-O = 2.159$ Å) are edges of six (different) nitrate groups.
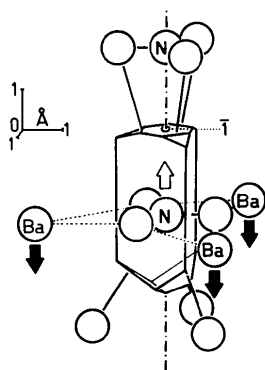
Fig. 1. Environment of the nitrate groups in $Ba(NO_3)_2$ with space-filling polyhedron around the N atom (calculated assuming equal partition between all atoms). Unmarked circles denote O atoms; arrows indicate deviations mentioned in the text.

The nitrate groups are extremely flat trigonal pyramids. The N—O bond length of 1·247 Å is in very good agreement with general experience (cf., for example, Leclaire, 1979). In both compounds the N atom of the nitrate group is shifted slightly from the centre of gravity of the three O atoms towards the nearest centre of symmetry (Fig. 1) giving a pyramidal height of 0·005 (1) {0·006 (1)} Å. Although these deviations are very small, their e.s.d.'s indicate that they are significant.

The MO_{12} polyhedra are connected by bridging nitrate groups (Wells, 1975). Each nitrate group links together three different MO_{12} polyhedra so that the nitrate groups belong to class III_6 within the classification of Leclaire (1979) and the cuboctahedra are connected via corners.

As mentioned above, the M^{2+} ions are arranged in the form of a cubic face-centred Bravais lattice. Two nitrate groups related by a centre of symmetry are located in each octahedral hole of this M^{2+} arrangement. Each nitrate group has three M^{2+} ions as neighbours. In relation to the oxygen plane of the nitrate group, these neighbouring cations are in both compounds on the opposite side of the 'vertex' of the (extremely flat) NO_3 pyramid. (The environment of the nitrate group is shown in Fig. 1.)

Each O atom is surrounded by one N atom (N—O = 1·247 Å) and two M atoms (M—O = 2·715 and 2·838 {2·879 and 2·941} Å) in the form of a flat pyramid. The elevation of the O atom from the N—M—M plane is 0·119 (1) {0·183 (1)} Å. The vertex of this flat pyramid points in the same direction as the vertex of the NO_3 pyramid. This corresponds to observations of similar deviations in carbonates (cf. Zemann, 1981). A further polarity in the environment of the nitrate group comes from the neighbouring O atoms with more distant neighbours at the side of the N apex [N—O ≥ 3·6880 (6) {3·8735 (7)} Å; the three nearer O atoms on the opposite side have N—O distances of 3·1000 (5) {3·3011 (6)} Å].

The thermal vibration of M^{2+} is nearly isotropic in both compounds. The anisotropic temperature factors of N show an almost spherical shape in $Sr(NO_3)_2$ and a somewhat more elliptical shape in $Ba(NO_3)_2$ (the r.m.s. amplitude parallel to the threefold axis is 27% greater than in the perpendicular directions). The longest axis (1) of the clearly anisotropic thermal vibration ellipsoid of O is approximately perpendicular to the plane defined by the nitrate group,* the medium-length axis points approximately perpendicular to the N—O bond within the plane of the nitrate group and the shortest in the direction of the N—O bond. These results are not in agreement with the suggestion of a remarkably large oscillation (libration) of the O atoms around the N atom in the nitrate group (Hamilton, 1957; Lutz, 1960).

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* The threefold axis is positioned between (1) and the normal (n) to the N—M—M plane. The angle between (1) and the threefold axis is 12·6 {6·5}°, the angle between (n) and the threefold axis is 5·7 {8·7}°, and the angle between (1) and (n) is 18·2 {14·5}°.

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Calcium Sulfat Subhydrat, CaSO₄.0,8H₂O

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Abstract. $M_r = 150 \cdot 6$, trigonal, $P3_1 21$, $a = 6 \cdot 968$ (8), $c = 6 \cdot 410$ (4) Å, $V = 269 \cdot 5$ Å^3, $Z = 3$, $D_x = 2 \cdot 63$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0 \cdot 7107$ Å, $\mu = 20 \cdot 24$ cm^{-1}, room temperature, $F(000) = 228$. Using 286 reflexions with $I > 3\sigma(I)$, including Friedel pairs, one of the two possible enantiomorphous space groups could be rejected by statistical methods (final $R = 0 \cdot 05$). Chains of alternating Ca^{2+} and SO_4^{2-} ions parallel to the c axis form the framework of a tunnel structure in which four water molecules are randomly distributed over five tunnel positions. The Ca^{2+} ion is surrounded by six SO_4^{2-} groups (similar to the arrangement in anhydrite) and one water molecule, counting the nine nearest O atoms (distances 2·45–2·66 Å).

Einleitung. Im System CaSO₄–H₂O sind die auch als Mineralien bekannten Phasen CaSO₄ (Anhydrit) und CaSO₄.2H₂O (Gips) strukturell hinreichend charakterisiert (Atoji & Rundle, 1958; Cheng & Zussman, 1963; Cole & Lancucki, 1974; Kirfel & Will, 1980). Demgegenüber liegen über Phasen der Zusammensetzung CaSO₄.xH₂O $(0 < x < 2)$ nur unzureichende oder widersprüchliche Berichte vor. Der als Halbhydrat (Hemihydrat) bezeichneten Phase CaSO₄.½H₂O wird einmal monokline (Gallitelli, 1933), dann wieder trigonale Symmetrie (Gaubert, 1934; Caspari, 1934) zugeordnet. Eine einheitliche Auffassung über den zeolithischen Charakter des Wassers

besteht unter diesen Autoren nicht. Eine erhebliche stöchiometrische Breite bezüglich des Wassergehalts $(0 < x < \frac{2}{3})$ für pseudohexagonale Phasen wird bei Bunn (1941) erörtert. In der jüngeren Literatur berichten Bushuev & Borisov (1982) über die Phasen CaSO₄.½H₂O (trigonal, $P3_1 21$) und CaSO₄.0,67H₂O (monoklin, $I2$); an Einkristallen mit 0,67H₂O wurde eine Röntgenstrukturanalyse durchgeführt (Bushuev, 1982).

Eine genaue Charakterisierung der bei der Dehydratation von Gips entstehenden Phasen ist wünschenswert. Diese Produkte rücken wegen der Verfahren zur Entschwefelung der Rauchgase mit CaCO₃ bei der Verbrennung von Kohle in der Wirbelschicht zunehmend in das Blickfeld des Interesses. Erste Ergebnisse der in diesem Zusammenhang unternommenen röntgenographischen und thermoanalytischen Untersuchungen an CaSO₄.½H₂O sind kürzlich vorgestellt worden (Frik & Kuzel, 1982). Diese Arbeiten werden durch die im folgenden beschriebene Einkristall-Rötgenstrukturanalyse von der trigonalen Phase CaSO₄.0,81H₂O ergänzt.

Experimentelles. In einen Exsiccator wird eine Kristallisierschale mit einer nur knapp den Boden bedeckenden, 0,01 molaren Lösung von CaCl₂ in H₂O gegeben. Nach einmalig angelegtem (Wasserstrahl-)Vakuum sorgt eine Schale mit konz. H₂SO₄ einerseits für den Wasserentzug, andererseits für eine ausreichende