

to the 2.69 Å distance, which represents the closest approach allowed by rotation about the bonds.

This behavior contrasts with that of the phenethylamines and the phenylisopropylamines previously studied, in which the amine side chain tends to be maximally extended (Bergin, 1971, and references cited therein). Some evidence is thus provided for an attraction (possibly electrostatic) between the NH_3^+ group and the aromatic ring. The three methoxy groups adopt a configuration similar to that observed in reserpine (Karle & Karle, 1968); *i.e.*, the two outer methoxy groups are approximately coplanar with the benzene ring and the center group is nearly perpendicular to the plane of the ring (Table 3). The N-Br distances of 3.311 and 3.314 Å are normal for amine hydrobromides (Wunderlich, 1969).

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References

- BERGIN, R. (1971). *Acta Cryst.* **B27**, 2139-2146.
 ERNST, S. R. (1973). Ph. D. Dissertation, University of Utah, Salt Lake City, Utah.
 HEFFTER, A. (1898). *Ber. dtsh. chem. Ges.* **31**, 1193-1199.
 JOHNSON, C. K. (1970). *ORTEP*. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
 KARLE, J. & KARLE, I. (1968). *Acta Cryst.* **B24**, 81-91.
 STEWART, J. A., KUNDELL, F. A. & BALDWIN, J. C. (1970). The X-RAY System of Crystallographic Programs, Computer Science Center, Univ. of Maryland, College Park, Maryland.
 WUNDERLICH, J. A. (1969). *Acta Cryst.* **B25**, 1436-1443.

SHORT COMMUNICATIONS

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Acta Cryst. (1973). **B29**, 1546

A new crystal structure study of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. By B. RIBAR and V. DIVJAKOVIĆ, *Faculty of Science, Physics Department, Novi Sad, Yugoslavia*, and R. HERAK and B. PRELESNIK, *Boris Kidrič Institute, Belgrade, Yugoslavia*

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The unit cell has $a=6.277(7)$, $b=9.157(9)$, $c=14.484(10)$ Å, $\beta=98.6(2)^\circ$. The structure contains $\text{Ca}_2(\text{H}_2\text{O})_8(\text{NO}_3)_4$ dimers, joined by hydrogen bonds.

Introduction

The X-ray structure analysis of calcium nitrate tetrahydrate was recently carried out by Leclaire & Monier (1970). The structure was solved in the space group $P2_1/c$ on the basis of photographic data for 680 reflexions, giving a final R value of 0.051. As part of a series of studies of the crystal structures of hydrated nitrates of bivalent metals, we have undertaken an independent X-ray crystal structure analysis of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. From the data for 1194 independent non-zero reflexions in the space group $P2_1/n$, the atomic parameters were derived and a final R index of 0.088 was achieved. Abrahams & Keve (1971) consider that duplicate measurements of the material being studied considerably increase the chances that the crystallographic results reported are indeed typical of that material. Hence, it may be useful to present our results as well, although the data from both determinations are in good agreement.

The colourless, transparent and hygroscopic crystals of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were prepared by the slow evaporation of the CaO solution in HNO_3 in the presence of P_2O_5 . The lattice parameters were determined from Weissenberg $h0l$ and $hk0$ photographs, calibrated with a Debyeogram of

germanium. The standard deviations were estimated from several film measurements. The crystal data obtained are presented in Table 1.

Table 1. *Crystal data for $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$*

Crystal system:	Monoclinic	
a	6.277 (7) Å	6.268 (6) Å*
b	9.157 (9)	9.116 (9)
c	14.484 (10)	14.830 (10)
β	98.6 (2)°	106.5 (3)°
Z	4	4
D_{meas}	1.88 g cm ⁻³	1.88 g cm ⁻³
D_{calc}	1.90	1.90
Space group	$P2_1/n$	$P2_1/c$

* The data of Leclaire & Monier (1970).

Three-dimensional intensity data ($0kl \rightarrow 3kl$ and $h0l \rightarrow h5l$) were collected from two spherical crystals sealed in Lindemann capillaries; integrated multiple films and the equi-inclination Weissenberg technique were used. The

intensities were measured photometrically and corrected for Lorentz, polarization and absorption effects. A total of 1194 independent reflexions was collected.

The position of the calcium atom was found from a three-dimensional Patterson function, and the positions of the oxygen and nitrogen atoms from the two successive Fourier syntheses. The structure was refined by full-matrix least-squares calculations, firstly with isotropic and later with anisotropic thermal parameters for all atoms. Unit weights were assumed for all the reflexions. The refinement converged at $R=0.088$. The atomic scattering factors were taken from *International Tables for X-ray Crystallography*. In the analysis the programs *VINCA 1* (local data reduction program), *FORDAP*, *NUCLS*, *SADIANA* and *ORFFE*

(from Ibers's system of crystallographic programs) were used with the CDC 3600 computer.

The crystal structure of the compound, the environment of the calcium ion and the geometry of the nitrate groups revealed by Leclaire & Monier are confirmed. The crystal structure is built of $\text{Ca}_2(\text{H}_2\text{O})_8(\text{NO}_3)_4$ dimers, joined by hydrogen bonds. Two crystallographically non-equivalent nitrate groups are slightly distorted.

The final atomic position and thermal parameters are shown in Table 2. Below the values determined in this study are the corresponding values found by Leclaire & Monier, transformed to the present cell. The bond distances and angles referring to the coordination of the calcium atom, the geometry of nitrate groups and possible hydrogen

Table 2. *Final atomic parameters* ($\times 10^4$) *with estimated standard deviations*

The temperature factors are of the form: $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2lh\beta_{31} + 2kl\beta_{23})]$.

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ca	395 (3)	897 (2)	3669 (1)	69 (4)	32 (2)	14 (1)	2 (4)	6 (1)	2 (1)
	393 (4)	898 (2)	3670 (1)	123 (7)	56 (2)	24 (1)	-3 (4)	38 (2)	2 (1)
O(1)	219 (13)	2134 (10)	6739 (5)	153 (24)	70 (12)	19 (3)	2 (15)	15 (7)	-2 (6)
	240 (13)	2117 (7)	6731 (5)	115 (30)	90 (9)	19 (4)	-2 (13)	17 (10)	5 (5)
O(2)	817 (14)	1213 (8)	5415 (5)	248 (28)	23 (10)	22 (4)	-20 (13)	19 (8)	-11 (5)
	833 (12)	1210 (6)	5415 (5)	192 (30)	50 (9)	21 (4)	13 (12)	14 (9)	5 (4)
O(3)	1124 (16)	3556 (9)	5654 (6)	277 (32)	28 (9)	38 (5)	-24 (15)	23 (10)	-4 (6)
	1165 (14)	3544 (7)	5658 (5)	254 (33)	55 (9)	38 (5)	41 (13)	18 (10)	0 (5)
O(4)	239 (15)	2309 (9)	2133 (6)	187 (27)	39 (10)	39 (5)	19 (14)	22 (11)	1 (6)
	224 (14)	2314 (7)	2121 (5)	169 (30)	63 (10)	35 (4)	24 (13)	23 (10)	7 (5)
O(5)	1137 (16)	1343 (12)	865 (5)	258 (30)	119 (15)	15 (4)	20 (18)	18 (8)	16 (6)
	1083 (14)	1345 (8)	846 (5)	266 (35)	139 (13)	15 (4)	7 (15)	27 (10)	12 (5)
O(6)	1580 (15)	153 (9)	2181 (5)	247 (29)	48 (11)	24 (4)	-54 (15)	18 (8)	-7 (5)
	1570 (14)	156 (7)	2171 (5)	267 (32)	61 (9)	26 (4)	41 (13)	25 (11)	9 (5)
O(7)	1813 (13)	4635 (10)	7814 (6)	130 (23)	55 (11)	34 (4)	6 (14)	-14 (8)	-16 (6)
	1808 (12)	4634 (7)	7813 (5)	45 (29)	90 (10)	37 (4)	-12 (12)	-1 (9)	15 (5)
O(8)	1243 (14)	4639 (10)	853 (6)	144 (24)	58 (11)	30 (4)	-7 (14)	-16 (8)	11 (6)
	1204 (13)	4632 (7)	839 (5)	112 (29)	70 (4)	36 (4)	-22 (12)	-11 (10)	13 (5)
O(9)	3150 (16)	2791 (10)	3965 (6)	241 (31)	61 (12)	31 (4)	-36 (16)	11 (9)	4 (6)
	3176 (13)	2795 (7)	3984 (5)	229 (33)	71 (9)	33 (4)	-54 (13)	21 (10)	1 (5)
O(10)	3090 (16)	1961 (12)	8849 (7)	238 (32)	93 (14)	50 (5)	-84 (18)	-27 (11)	24 (8)
	3071 (15)	1966 (8)	8859 (6)	222 (40)	109 (11)	54 (5)	78 (16)	-22 (12)	-26 (6)
N(1)	720 (15)	2330 (10)	5936 (6)	119 (25)	26 (10)	18 (4)	-19 (15)	5 (8)	-3 (5)
	747 (15)	2334 (8)	5947 (6)	53 (37)	52 (11)	30 (5)	4 (14)	-8 (12)	4 (6)
N(2)	987 (16)	1292 (11)	1702 (6)	129 (26)	49 (13)	22 (4)	3 (16)	4 (9)	2 (6)
	958 (16)	1284 (9)	1684 (7)	69 (34)	74 (13)	34 (6)	-26 (15)	11 (12)	-1 (6)

Table 3. *Interatomic distances and angles*

(a) involving oxygen atoms about calcium

Ca-O(8 ^l)	2.414 (9)	2.438*	Ca-O(2)	2.525 (8)	2.510
Ca-O(9)	2.442 (9)	2.451	Ca-O(2 ^{ll})	2.519 (9)	2.499
Ca-O(7 ^{lll})	2.449 (8)	2.451	Ca-O(4)	2.562 (9)	2.563
Ca-O(10 ^{lll})	2.475 (10)	2.469	Ca-O(1 ^{ll})	2.853 (9)	2.824
Ca-O(6)	2.477 (9)	2.468			

(b) involving nitrate groups

N(1)-O(1)	1.262 (12)	1.230*	N(2)-O(4)	1.251 (13)	1.253
N(1)-O(2)	1.278 (12)	1.284	N(2)-O(5)	1.230 (12)	1.218
N(1)-O(3)	1.233 (12)	1.219	N(2)-O(6)	1.278 (12)	1.272
	O(1)-N(1)-O(2)	118.0 (9)°		117.1*	
	O(1)-N(1)-O(3)	121.7 (10)		123.6	
	O(2)-N(1)-O(3)	120.2 (9)		119.4	
	O(4)-N(2)-O(5)	123.5 (10)		122.7	
	O(4)-N(2)-O(6)	115.9 (9)		115.6	
	O(5)-N(2)-O(6)	120.5 (10)		121.6	

Table 3 (cont.)

(c) involving the possible hydrogen bonds

O(7)–O(1)	2.865 (12)	2.865*
O(7)–O(8 ^{iv})	2.993 (13)	2.968
O(8)–O(8 ⁱⁱⁱ)	2.797 (16)	2.739
O(4)–O(8)	2.956 (12)	2.924
O(6)–O(9)	2.748 (13)	2.737
O(5)–O(8)	3.019 (14)	2.998

The superscripts refer to the following transformations of the atomic coordinates.

No symbol	x	y	z
i	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
ii	$-x$	$-y$	$1-z$
iii	$x-\frac{1}{2}$	$\frac{1}{2}-y$	$\frac{1}{2}+z$
iv	$-x$	$1-y$	$1-z$

* The data of Leclaire & Monier.

bonds joining the $\text{Ca}_2(\text{H}_2\text{O})_8(\text{NO}_3)_4$ dimers are given in Table 3.

We have used the two sets of data to calculate a half normal probability analysis (Abrahams & Keve, 1971). The experimental values of Δ_j/σ_j (where Δ_j is the difference between the corresponding j th coordinate and σ_j is the pooled standard deviation) plotted against the expected values of Δ_j/σ_j (Hamilton & Abrahams, 1972) are given in Fig. 1. The plot is linear indicating that there are no systematic errors in either measurement. The slope of about 1.1 for all the points shows that the standard deviations are underestimated by about 10%. The average of the two sets of results should give a better estimate of the true data for $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$.

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A new polytype of silicon carbide, 189R. Its structure and growth. By M. DUBEY, U. S. RAM and G. SINGH, *Department of Physics, Banaras Hindu University, Varanasi 221005, India*

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A new 189-layered rhombohedral modification of silicon carbide has been discovered. Its structure is based on the 21R phase instead of one of the usual basic structures 6H, 15R and 4H, and has been found to be $[(34)_843]_3$ in Zhdanov notation. The studies on this polytype provide new information regarding the growth of polytypic crystals.

Introduction

Usually silicon carbide structures are found to be based on one of the basic structures 6H, 15R and 4H. Recently we have found a number of structures which are based on other structures like 21R (33R, 147R, Ram, Dubey & Singh, 1973a, b) etc. instead of one of the basic phases. Although a large number of polytypes of SiC are known by now, 189R was found to be of special interest because it is one of the few newly found structures which are based on a structure (21R) other than the usual phases. The structure and growth mechanism of this polytype is reported in the present paper.

Experimental details

The crystal containing 189R was a bluish-black piece of silicon carbide of size $3.0 \times 2.0 \times 1.5$ mm with a well devel-

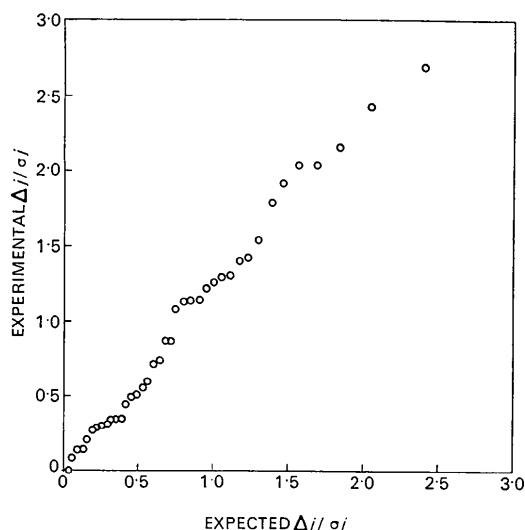


Fig. 1. The half-normal probability plot of Δ_j/σ_j for the two sets of 39 positional coordinates.

References

- ABRAHAMS, S. C. & KEVE, E. T. (1971). *Acta Cryst.* **A27**, 157–165.
International Tables for X-ray Crystallography (1962). Vol. III, pp. 202–207. Birmingham: Kynoch Press.
 LECLAIRE & MONIER, I. C. (1970). *C.R. Acad. Sci. Paris*, **271**, 1555–1557.
 HAMILTON, W. C. & ABRAHAMS, S. C. (1972). *Acta Cryst.* **A28**, 215–218.

oped (0001) face. The crystal surface was examined under the optical microscope and spiral features were observed over a wide area of the surface.

Single-crystal X-ray diffraction patterns show that almost all the crystal is a well ordered 21R structure and only a small region parallel to (0001) near the top gives reflexions due to other polytypic structures. Two polytypes 189R and 259H or 777R were found in a small region of the specimen near two different corners, intergrown in parallel orientation with the 21R structure. Fig. 1(a) is a c -axis oscillation photograph of 189R and Fig. 1(b) shows the reflexions of 259H or 777R. Fig. 1(c) is another c -axis oscillation photograph in a different range which shows 189R spots, but a careful observation of these reflexions shows that each of these spots are split up into 3 or 4 finer spots. These fine spots correspond to an undefined high-period polytype whose structure is strongly based on the 189R phase.