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Neutron Structure Refinement of Barium Oxalate–Oxalic Acid Dihydrate, $BaC_2O_4.H_2C_2O_4.2H_2O$ and of Related Nonstoichiometric Hydrates

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Abstract. $BaC_2O_4.H_2C_2O_4.2H_2O$, $M_r = 351{\cdot}38$, monoclinic, $C2/c$, $a = 14{\cdot}446\ (2)$, $b = 5{\cdot}4175\ (6)$, $c = 12{\cdot}450\ (1)$ Å, $\beta = 116{\cdot}17\ (1)^\circ$, $V = 874\ (4)$ Å^3, $Z = 4$, $D_x = 2{\cdot}669$ Mg m^{-3}, $\lambda = 1{\cdot}2651$ Å, $\mu(n) = 0{\cdot}137$ mm^{-1}, $F(000) = 269{\cdot}94$, room temperature, final $R = 0{\cdot}021$ for 768 independent reflections. The neutron refinement of the crystal structure of the dihydrate compound confirms the structure previously reported from X-ray measurements. The positions of the two kinds of H atoms are determined and the environment and geometry of the water molecules analysed. The crystal structures of mosaic crystals with various water contents ε, from dehydration of single crystals followed by rehydration with H_2O or D_2O, were also refined. Only limited changes of the structural parameters of the dihydrate mosaic crystals with respect to the single-crystal ones are observed ($R = 0{\cdot}022$ and $0{\cdot}045$ for the hydrogenated and deuterated crystals, respectively). In mosaic crystals with $\varepsilon \neq 2$, the initial crystallographic sites of water are preserved whatever the water content ($\varepsilon = 0{\cdot}7$, $R = 0{\cdot}072$; $\varepsilon = 0{\cdot}3$, $R = 0{\cdot}058$). However, the oxalate ions in such crystals present abnormally large displacement parameters along the y direction; this is tentatively explained by the random removal of water molecules which leads to the formation of two intermolecular distances along this direction.

Introduction. Previous thermogravimetry and X-ray diffraction studies of the thermal dehydration of barium oxalate–oxalic acid dihydrate BaC_2O_4.-

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Table 1. *Experimental data and structure refinement parameters for barium oxalate* $1/1/\varepsilon$ $(0 < \varepsilon \leq 2)$

	(I)	(II)	(III)	(IV)	(V)
Crystal size (mm)	2 × 1 × 0·85	1·8 × 1·5 × 0·95	1·35 × 1 × 0·75	1·35 × 1·15 × 0·6	1·2 × 1·1 × 0·5
No. and θ (°) range of reflections used for refinement of lattice parameters	15 16–38	16 6·5–38	16 16–34·5	16 11–39	10 6·5–40·5
Scan range θ (°)	5–50	5–40	5–50	5–50	5–50
Scan type	$\omega:2\theta$	$\omega:\theta$	$\omega:2\theta$	$\omega:2\theta$	$\omega:2\theta$
Range of h	$0\rightarrow15$	$0\rightarrow14$	$0\rightarrow16$	$0\rightarrow16$	$0\rightarrow18$
k	$0\rightarrow6$	$0\rightarrow5$	$0\rightarrow6$	$0\rightarrow6$	$0\rightarrow5$
l	$-14\rightarrow12$	$-12\rightarrow10$	$-14\rightarrow12$	$-14\rightarrow12$	$-14\rightarrow12$
Standard reflections and averaged intensity variation (%)	040, $22\bar{3}$, 600 4·7	400, 040, 002 5·1	040, $22\bar{3}$, 600 7·8	$\bar{4}00$ 4·2	400, 020, $00\bar{2}$ 8·7
No. of reflections measured	877	527	871	715	1029
No. of unique reflections	768	487	812	678	756
Program system	*PROMETHEUS*	*SHELX76*	*SHELX76*	*SHELX76*	*SHELX76*
No. of reflections used in refinement	661	403	593	420	504
Rejection criterion	$F^2 < 3\sigma(F^2)$	$F < 4\sigma(F)$	$F < 4\sigma(F)$	$F < 4\sigma(F)$	$F < 4\sigma(F)$
Transmission factors for absorption correction	0·868–0·898	0·911–0·949	—	0·957–0·975	0·955–0·976
Extinction parameters	$Z_{11} = 0{\cdot}2460 \times 10^8$ $Z_{22} = 0{\cdot}1288 \times 10^8$ $Z_{33} = 0{\cdot}8508 \times 10^8$ $Z_{13} = -0{\cdot}8696 \times 10^8$	—	—	—	—
No. of refined parameters	96	96	98	79	82
R (wR)	0·021 (0·021)	0·022 (0·017)	0·045 (0·049)	0·072 (0·082)	0·058 (0·049)
Weighting scheme	$w = [\sigma^2(F^2)]^{-1}$	$w = k[\sigma^2(F) + \lvert g\rvert.F^2]^{-1}$ $k = 1{\cdot}5070$ $g = 9 \times 10^{-6}$	$w = k[\sigma^2(F) + \lvert g\rvert.F^2]^{-1}$ $k = 1{\cdot}4053$ $g = 3{\cdot}9 \times 10^{-4}$	$w = k[\sigma^2(F) + \lvert g\rvert.F^2]^{-1}$ $k = 1{\cdot}2570$ $g = 1{\cdot}9 \times 10^{-3}$	$w = k[\sigma^2(F) + \lvert g\rvert.F^2]^{-1}$ $k = 1{\cdot}3574$ $g = 1{\cdot}7 \times 10^{-4}$

$H_2C_2O_4.2H_2O$ showed that this compound can gradually lose its water and give rise to a series of nonstoichiometric hydrates designated as $BaC_2O_4.H_2C_2O_4.\varepsilon H_2O$ with $0 \leq \varepsilon \leq 2$ (Mutin, Watelle & Dusausoy, 1979; Mutin & Watelle, 1979; Mutin, Watelle-Marion, Dusausoy & Protas, 1972). The main framework of the crystalline structure of the dihydrate is preserved during the loss of water. Depending on the P, T conditions imposed on the sample, the anhydrous β-salt structure can arise after complete dehydration and transient formation of the intermediate defect anhydrous α salt, or for non-zero ε values.

During the dehydration, several anomalies related to structural and thermodynamical parameters were found at a chemical composition close to $\varepsilon = 1$ (Mutin *et al.*, 1979). Compared with prereactional changes observed in $Ca(OH)_2$ (Chaix-Pluchery, Bouillot, Ciosmak, Niepce & Freund, 1983; Chaix-Pluchery, Pannetier, Bouillot & Niepce, 1987; Chaix-Pluchery & Niepce, 1988), the structural features of the dehydration and those of the involved atom motions are reminiscent of pretransitional changes since they occur before the structure change. However, a fundamental difference with $Ca(OH)_2$ is that these changes are associated with a modification of the chemical composition of the initial material.

The crystal structures of the dihydrate compound as well as of the anhydrous α salt have been investigated by X-ray diffraction (Mutin *et al.*, 1979; Mutin *et al.*, 1972; Dusausoy, Protas, Mutin & Watelle, 1970). A further investigation using neutron diffraction is reported in this paper. A series of crystals with different water contents has been used in order to localize the H atoms in the unit cell of the dihydrate compound and also to specify the structural modifications taking place in the oxalate at compositions close to $\varepsilon = 1$.

In the following, the dihydrate, the nonstoichiometric hydrates and the α and β anhydrous salts will be designated as 1/1/2, $1/1/\varepsilon$, α 1/1/0 and β 1/1/0, respectively, for convenience.

Experimental. The kinetics of dehydration of the oxalate dihydrate are very slow; therefore, the crystals with given compositions were prepared before the diffraction experiments and then sealed off in Lindemann tubes: single crystal [$2H_2O$ denoted by (I)] or mosaic crystals obtained by dehydration of 1/1/2 followed by rehydration with H_2O [$2H_2O$ and εH_2O denoted by (II) and (V) respectively] or with D_2O [$2D_2O$ and εD_2O denoted by (III) and (IV) respectively]. They are prismatic crystals grown from a mixture of an oxalic acid solution and an acidified barium chloride solution. Well shaped crystals were selected for the neutron experiments.

Neutron diffraction measurements were performed on the four-circle diffractometer D8 installed on a thermal-neutron beam tube in the reactor hall of the Institut Laue–Langevin (Grenoble). The wavelength of neutrons was 1·2651 Å. The Lindemann tubes containing the crystals were fixed on a goniometer head. The measurements were made at room temperature. Experimental details on data acquisition and analysis are given in Table 1 for each crystal. Lattice parameters calculated from the first collection of data for each crystal are reported in Table 2.

Table 2. *Lattice parameters* (Å *and* °) *for barium oxalate* $1/1/\varepsilon$ $(0 < \varepsilon \leq 2)$

E.s.d.'s are given in parentheses and refer to the last digit.

	(I)	(II)	(III)	(IV)	(V)
a	14·446 (2)	14·445 (4)	14·446 (3)	15·083 (15)	15·264 (10)
b	5·4175 (6)	5·414 (2)	5·414 (1)	5·024 (8)	4·929 (4)
c	12·450 (1)	12·458 (4)	12·447 (2)	12·371 (8)	12·351 (8)
β	116·17 (1)	116·18 (2)	116·25 (2)	117·93 (5)	118·34 (4)

Data reduction was carried out using the program *COLL5N* (Lehmann & Wilson, 1975). Integrated intensities were evaluated by the $\sigma(I)/I$ criteria (Lehmann & Larsen, 1974) and corrected for Lorentz and absorption effects (program *DATAP*; Coppens, Leiserowitz & Rabinowitch, 1965). The structure refinement was carried out with the least-squares method. All atoms were allowed to vibrate anisotropically except those of water molecules in compounds with $\varepsilon \neq 2$. The neutron scattering lengths were taken equal to 5·28, 6·65, 5·805, −3·7409 and 6·67 fm for Ba, C, O, H and D atoms, respectively (Koester & Rauch, 1981).

The structure refinement of the 1/1/2 single crystal was performed after extinction correction of the data using the crystallographic program system *PROMETHEUS* (Zucker, Perenthaler, Kuhs, Bachmann & Schulz, 1983). The extinction correction was calculated in the formalism of Becker & Coppens (1974, 1975). The best results were obtained by assuming a Lorentzian anisotropic mosaic distribution (type I extinction). The structure of the other crystals was refined using the crystallographic program *SHELX* (Sheldrick, 1976) without any extinction correction because of their mosaic structure. The refinement parameters and final R factors are reported in Table 1. $\Delta/\sigma_{\max} < 0{\cdot}01$ in the last cycle of refinement.

Discussion.

Crystal structure of 1/1/2.

(1) *Comparison between the X-ray and neutron diffraction results.* The crystal structure of 1/1/2 single crystal (I) is essentially that reported from X-ray data (Mutin *et al.*, 1979; Dusausoy *et al.*, 1970). The final positional parameters and equivalent isotropic B are listed in Table 3. Fig. 1(*a*) shows the projection of the 1/1/2 structure on the (010) plane. The nomenclature used for crystallographically equivalent atoms is given at the bottom of Table 3. For the sake of clarity, the O atoms of the water molecules are denoted by W instead of O.

The additional information given by the neutron refinement concerns the positions of the H atoms in the directions expected from the X-ray study (Dusausoy *et al.*, 1970) (Fig. 1 and Table 3).

Table 3. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic B* (Å^2) *for barium oxalate* $1/1/\varepsilon$ $(0 < \varepsilon \leq 2)$

The five lines relative to each atom refer to crystals (I) to (V) respectively.

$$B_{eq} = (8\pi^2/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}*
Ba	½	6655 (3)	¼	1·39 (5)
		6661 (5)		2·1 (1)
		6651 (8)		1·7 (1)
		6684 (16)		2·4 (2)
		6700 (10)		1·8 (1)
C(1)	2349 (1)	8402 (1)	380 (1)	1·14 (2)
	2348 (1)	8404 (3)	380 (1)	1·85 (6)
	2349 (2)	8408 (4)	382 (2)	1·51 (7)
	2374 (3)	8348 (16)	428 (4)	5·9 (3)
	2379 (2)	8311 (8)	446 (2)	3·0 (1)
O(1)	3025 (1)	9163 (2)	1337 (1)	1·88 (3)
	3025 (1)	9163 (4)	1338 (1)	2·56 (7)
	3028 (2)	9150 (6)	1345 (2)	2·26 (9)
	3025 (4)	9178 (25)	1396 (5)	8·6 (4)
	3038 (3)	8911 (12)	1454 (3)	5·3 (2)
O(2)	1397 (1)	8931 (2)	−65 (1)	1·69 (3)
	1400 (1)	8937 (4)	−61 (1)	2·38 (6)
	1399 (2)	8935 (5)	−64 (2)	2·08 (9)
	1425 (3)	8776 (15)	−19 (4)	4·1 (2)
	1449 (2)	8852 (9)	−2 (3)	3·0 (1)
C(2)	4758 (1)	1098 (1)	181 (1)	1·17 (2)
	4760 (1)	1100 (3)	183 (1)	1·82 (6)
	4757 (2)	1101 (4)	181 (2)	1·60 (7)
	4761 (3)	1218 (9)	157 (3)	2·5 (1)
	4761 (2)	1234 (5)	142 (2)	1·62 (8)
O(3)	4870 (1)	1319 (2)	1203 (1)	1·87 (4)
	4869 (1)	1321 (3)	1200 (1)	2·54 (7)
	4865 (2)	1308 (5)	1201 (2)	2·2 (1)
	4895 (5)	1515 (11)	1195 (4)	4·1 (2)
	4881 (3)	1560 (7)	1194 (3)	2·6 (1)
O(4)	4252 (1)	2585 (2)	−699 (1)	1·53 (3)
	4249 (1)	2587 (4)	−697 (1)	2·22 (6)
	4256 (2)	2563 (6)	−705 (2)	1·90 (9)
	4274 (3)	2723 (11)	−760 (4)	2·7 (2)
	4263 (2)	2760 (7)	−777 (3)	1·9 (1)
H(1)	3911 (1)	4149 (3)	−402 (1)	2·66 (6)
	3912 (2)	4158 (7)	−401 (3)	3·6 (1)
	3964 (13)	3977 (42)	−442 (15)	5·8 (9)
	3834 (17)	4399 (50)	−529 (20)	4·4 (8)
	3817 (4)	4531 (13)	−489 (5)	3·2 (3)
W	3183 (1)	4016 (3)	2150 (1)	2·66 (5)
	3181 (2)	4025 (6)	2156 (2)	3·3 (1)
	3182 (3)	4011 (7)	2149 (3)	3·2 (1)
	3096 (10)	4126 (34)	1953 (11)	2·2 (6)
	3087 (15)	4172 (48)	1954 (18)	2·6 (7)
H(3)	2724 (2)	4125 (4)	2492 (2)	4·5 (1)
	2733 (3)	4140 (9)	2479 (4)	5·5 (2)
	2711 (8)	4142 (20)	2495 (10)	5·0 (4)
	2756 (28)	4298 (79)	2370 (35)	8·5 (9)
	2680 (36)	4248 (110)	2357 (45)	5·4 (9)
H(2)	3156 (2)	2358 (4)	1893 (2)	3·69 (9)
	3158 (3)	2339 (10)	1890 (4)	5·1 (2)
	3159 (7)	2320 (18)	1903 (8)	3·9 (4)
	3137 (20)	2450 (75)	1933 (23)	5·8 (7)
	3057 (25)	2140 (76)	1798 (31)	3·1 (8)

With regard to the main features of the stacking, the X-ray results are also confirmed. Two distinct C_2O_4 groups are evidenced. The bond lengths and angles determined in both groups (Fig. 2) agree with the identification proposed from the X-ray refinement, *i.e.* a $C_2O_4^{2-}$ ion and an oxalic acid molecule. Both groups are connected by a strong hydrogen bond O(4)—H(1)···O(2). This gives rise to chains inside the structure (Fig. 1*b*) which are linked to the water molecules by a weak hydrogen bond W—H(2)···O(1). A second bond between H(3) and O(1^{vi})* could also be considered (Fig. 1*a*); it would allow the chains to be weakly linked together. Due to the weakness of the hydrogen bonds from the water

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* Symmetry code: (i) $\bar{x}, \bar{y}, \bar{z}$; (ii) $x+\frac{1}{2}, y+\frac{1}{2}, z$; (iii) $\bar{x}+\frac{1}{2}, \bar{y}+\frac{1}{2}, \bar{z}$; (iv) $\bar{x}, y, \bar{z}+\frac{1}{2}$; (v) $x, \bar{y}, z+\frac{1}{2}$; (vi) $\bar{x}+\frac{1}{2}, y+\frac{1}{2}, \bar{z}+\frac{1}{2}$; (vii) $x+\frac{1}{2}, \bar{y}+\frac{1}{2}, z+\frac{1}{2}$; (viii) $x, y+1, z$.

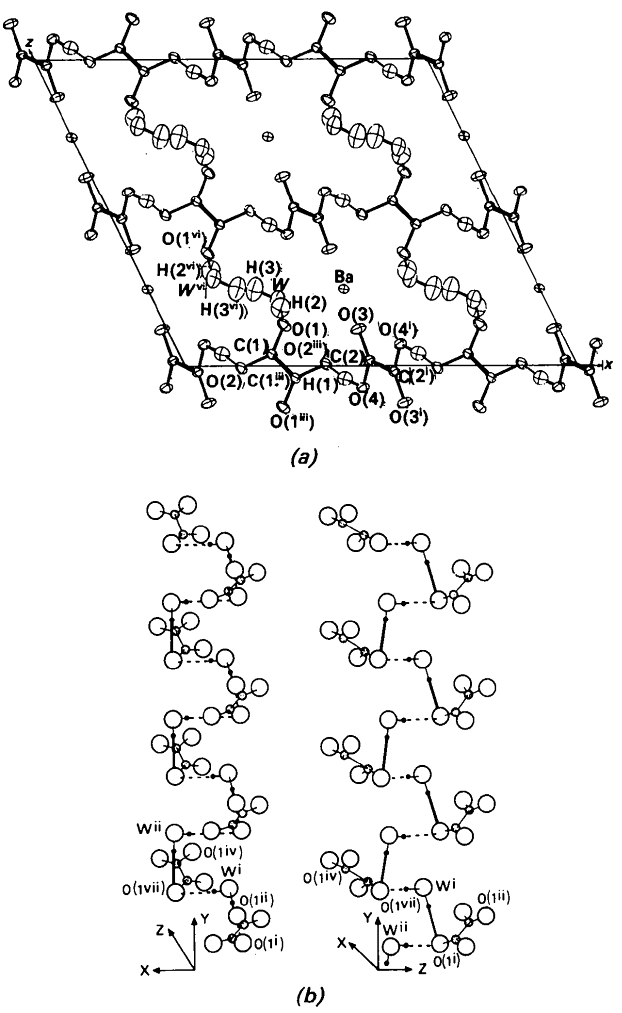

Fig. 1. (*a*) Projection of the 1/1/2 structure on the (010) plane. (*b*) Schematic drawing of the hydrogen-bond network.

molecules, the latter are only loosely bound to the other atoms and the cohesion is completely ensured by the barium ions which are surrounded by twelve O atoms forming an almost regular icosahedron. The bond lengths in the barium coordination polyhedron are reported in Fig. 3. However, the water molecules link the oxalate ions along the **b** direction (Fig. 1*b*); this hydrogen-bond network controls the length of the *b* axis as evidenced by the change in this cell parameter upon dehydration: $b = 5{\cdot}4175$ Å, $\varepsilon = 2$; $b = 4{\cdot}88$ Å, $\varepsilon = 0$ (Mutin *et al.*, 1979). The main effect of dehydration is a large contraction (by about 10%) of the *b* axis and a smaller lengthening of *a* (by 6·5%). The *c* axis is only weakly affected by the dehydration.

With regard to the anisotropic displacement parameters of the different atoms,* it is worth noting that they are always slightly higher along the *y* direction than along the other directions, except for the water molecules for which it is the opposite.

(2) *Bonding of the water molecules.* A single kind of water molecule is evidenced in the oxalate structure. The related bond lengths and angles are given in Fig. 4.

In order to specify the environment and the geometry of the water molecule in this crystalline structure, we have referred to the classification of hydrate water molecules proposed by Ferraris & Franchini-Angela (1972) and Chiari & Ferraris (1982). From the distances *W*···O shown in Fig. 5 and due to the orientation of the *W*—H bonds, only two hydrogen

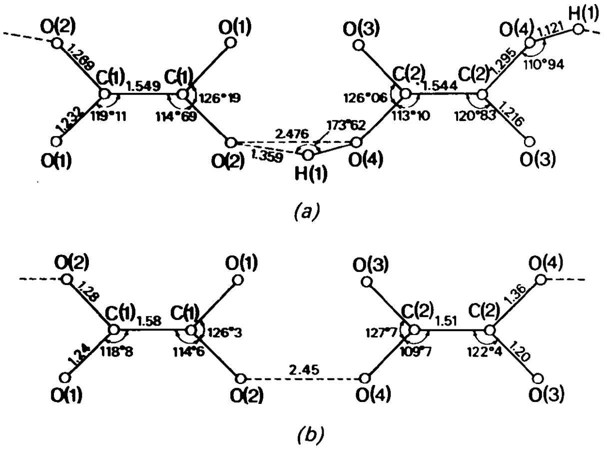

Fig. 2. Bond lengths (Å) and angles (°) of the C_2O_4 groups in the 1/1/2 structure, calculated (*a*) from neutron data (this work) and (*b*) from X-ray data (Dusausoy, Protas, Mutin & Watelle, 1970).

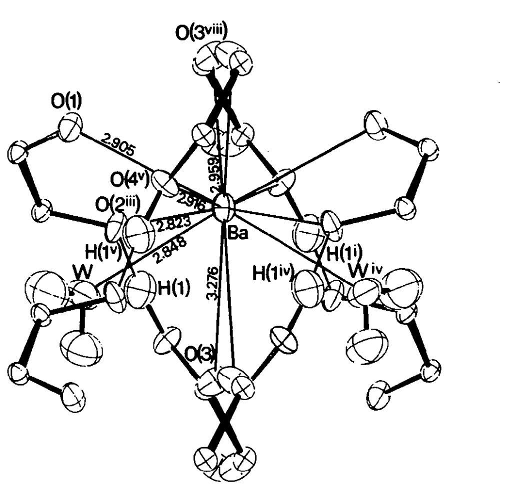

Fig. 3. Bond lengths (Å) in the barium coordination polyhedron, calculated from neutron data (1/1/2 structure).

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* Lists of anisotropic displacement parameters [for crystals (I), (II), (III), (IV) and (V)] and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51998 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

bonds can be considered, W—H(2)—O(1) and W—H(3)—O(1^{vi}). The distances and angles of these hydrogen bonds are given in Fig. 4. The second is a limiting case of a hydrogen bond but can still be considered as such because two hydrogen bonds are usually donated by the water molecule in most hydrates.

W coordinates only a single Ba^{2+} cation. Therefore, the water molecule belongs to class 1 (type *D*) or to class 1′ (type *J*) in the Ferraris classification. Comparison of the values of bond lengths and angles reported in Fig. 4 of this paper and the averaged values in Table 3 of Chiari & Ferraris (1982) indicates better correspondence with class 1. The value of the angle between $W\cdots$Ba and the plane of the water molecule (ε_1 in Fig. 4), about 19°, is also in favour of class 1 and shows that the cation tends to lie along the bissector of the lone-pair orbitals (Ferraris & Franchini-Angela, 1972).

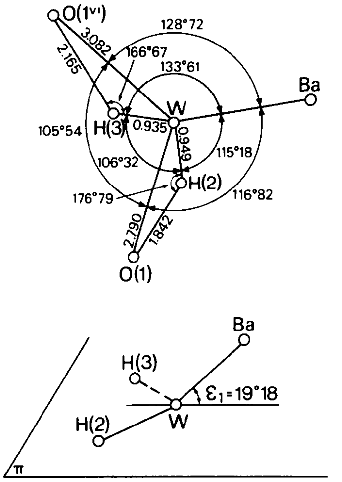

Fig. 4. Bond lengths (Å) and angles (°) characteristic of the water molecule (1/1/2 structure).

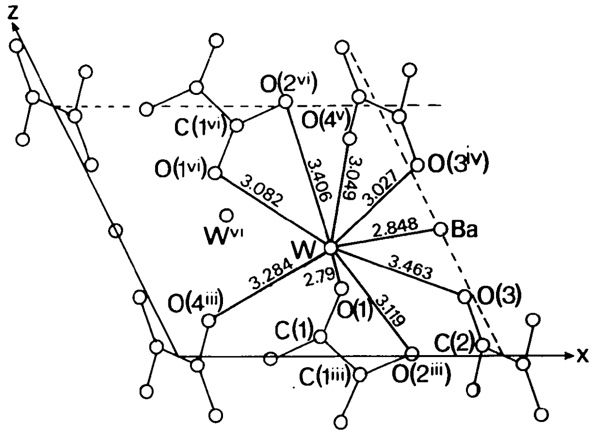

Fig. 5. Environment of the water molecules in the 1/1/2 structure (distances in Å).

(3) *Structure of the rehydrated mosaic crystal* 1/1/2 (II). Owing to the strong mosaic structure of the rehydrated crystal, the structure refinement could be carried out without any extinction correction. The positional parameters are very close to those of the original single crystal (Table 3) but the displacement parameters are slightly larger for the rehydrated compound. This difference probably originates from a disorder created in the structure by the mosaic nature of the crystal.

(4) *Influence of deuteration.* After dehydration of 1/1/2 followed by rehydration with D_2O [crystal (III)], only the hydrogen sites belonging to the water molecule were assumed to be deuterated. However, the initial refinement showed this not to be true because an isotopic H↔D exchange between the water and oxalic acid molecules is taking place, even at room temperature. Therefore, the rate of isotopic substitution of every hydrogen (deuterium) site had to be refined. Owing to large correlations, the occupancy and displacement parameters of these sites were first refined alternatively. In the final stages of the refinement, all parameters were allowed to vary. Thus, the deuteration rate was estimated to be about 51% for the oxalic acid molecule and about 59% for water. Such an isotopic exchange indicates that a chemical reaction takes place between the two kinds of hydrogen sites and that a selective deuteration of the water molecules is not feasible.

The structural parameters are close to those obtained for the crystal rehydrated with H_2O (Table 3). Only small differences are observed in the hydrogen/deuterium atomic positions.

Nonstoichiometric hydrates

The P–T phase diagram of the system 1/1/2, 1/1/0, H_2O is given in Fig. 6. In the hatched zone of Fig. 6, the dihydrate compound gradually loses water without any structure change, which gives rise to a series of nonstoichiometric hydrates designated as $1/1/\varepsilon$ with $0 \leq \varepsilon \leq 2$. In the particular case of a chemical composition close to $\varepsilon = 1$, several anomalies were observed in the isothermal $\varepsilon(P)_T$ and isobaric $\varepsilon(T)_P$ curves and in the temperature evolution of the lattice parameters, although this composition does not correspond to a separate phase from either a structural or a thermodynamical point of view (Mutin *et al.*, 1979).

The water molecules are located on well defined lattice sites in the dihydrate structure. The comparison between the 1/1/2 and the α 1/1/0 crystal structures investigated by X-ray diffraction showed that the loss of water does not result in any considerable change in the framework arrangement. The water vacancy is thus defined as the site previously occupied by the H_2O dipole in the 1/1/2 structure. One may wonder how the ε molecules are distributed in the framework of the nonstoichiometric phase and in particular when half of the molecules have left the structure. The study of intermediate $1/1/\varepsilon$ structures was undertaken to elucidate this point. Two phases with different water compositions were investigated: ε close to 1 [crystal (IV) rehydrated with D_2O vapour] and ε close to 0 [crystal (V) rehydrated with H_2O vapour].

(1) *Refinement conditions and determination of* ε. In order to determine the precise composition ε of these two crystals, the site occupancy of the water atoms was included as an additional parameter in the refinement. In the case of the crystal prepared to be close to 1/1/1, the refinement turned out to be more complicated due to partial rehydration of the crystal with heavy water. As for 1/1/2 rehydrated with D_2O, all hydrogen sites were assumed to be partially deuterated. Three hydrogen site occupation factors were refined in this compound to take into account both the stoichiometry ε and the isotopic exchange between H and D on the two hydrogen sites. Due to the large number of parameters to refine in the two nonstoichiometric crystals, the water atoms [crystals (IV) and (V)] as well as H(1) [crystal (IV)] were restricted to vibrate isotropically. The refinement of the water site occupation factor led to $\varepsilon = 0{\cdot}7$ for crystal (IV) (calculated from the *W* site occupation factor) and to $\varepsilon = 0{\cdot}3$ for crystal (V). In 1/1/0·7, the deuteration rate was about 51% for the oxalic acid molecule and about 82% for the water molecule.

(2) *Structural parameters and disorder*. The positional parameters of 1/1/0·3 (Table 3) as well as the corresponding lattice parameters (Table 2) are very close to those of α 1/1/0 as determined by X-ray diffraction (Mutin *et al.*, 1979). The parameters of 1/1/0·7 (Tables 3 and 2) are neither those of the 1/1/2 nor those of the 1/1/0 but appear to be intermediate between both structures.

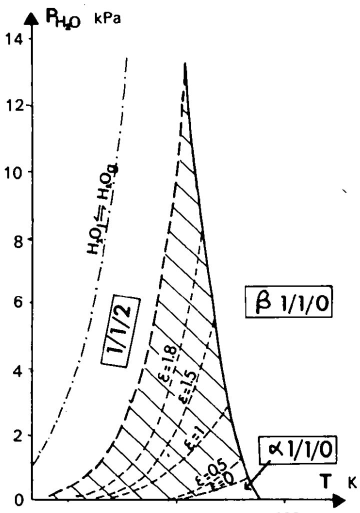

Fig. 6. *P–T* phase diagram of the system 1/1/2, 1/1/0, H_2O.

In both compounds, the three non-equivalent atoms of the $C_2O_4^{2-}$ ion exhibit abnormally large (and physically unrealistic for thermal vibrations) displacement parameters along the *y* direction [$0{\cdot}1013 \le U_{22} \le 0{\cdot}2514$ and $0{\cdot}0606 \le U_{22} \le 0{\cdot}1278$ for C(1), O(1), O(2) in 1/1/0·7 and 1/1/0·3, respectively]. This suggests an alternative structural model in which every atom of the oxalate ion is split between two different positions. A refinement of this model leads to two extreme positions for the oxalate ion, separated by about 0·45 Å in 1/1/0·3 and 0·65 Å in 1/1/0·7 ($R = 0{\cdot}074$, $wR = 0{\cdot}089$ for 1/1/0·7 and $R = 0{\cdot}061$, $wR = 0{\cdot}049$ for 1/1/0·3). This most likely results from the random elimination of water molecules from the structure and can be explained from the hydrogen-bonding network of the crystal. Indeed, the distance between two (C_2O_4) molecules (Fig. 1*b*) along the *y* direction is essentially controlled by the presence of the water molecules through the formation of O(1)—H(2)—*W*—H(3)···O(1) bonds. The removal of part of the water will therefore yield to the formation of two kinds of (C_2O_4)—(C_2O_4) distances along the *y* axis and the length of the *b* axis will be determined by the weighted sum of these elementary (C_2O_4)—(C_2O_4) distances which can be estimated from the structure of the limiting compositions $\varepsilon = 2$ and $\varepsilon = 0$: $d = 2{\cdot}71$ Å if a water molecule is present and $d = 2{\cdot}44$ Å if one is not (Mutin *et al.*, 1979). As the removal of the water molecules takes place randomly, this disorder shows up in a diffraction experiment as a splitting of the oxalate ions in two 'ghost' molecules. This does not occur for the oxalic acid molecules where intermolecular distance is determined by the Ba—O distances which are not affected by dehydration.

The diffraction experiment does not enable differentiation between a statistical model in which all Ba atoms are bonded to a single water molecule and an alternative model in which half the Ba are bonded to two water molecules while the others are not bonded to any, and thus does not provide clues to explain the different anomalies previously observed (Mutin *et al.*, 1979) in the system $1/1/\varepsilon$ at the composition $\varepsilon = 1$.

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Structure of Bis(benzaldehyde azine)dichloropalladium(II)

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Abstract. $[Pd(C_{14}H_{12}N_2)_2]Cl_2$, $M_r = 593·86$, monoclinic, $P2_1/n$, $a = 11·922$ (3), $b = 7·908$ (2), $c = 13·982$ (3) Å, $\beta = 103·89$ (2)°, $V = 1279·6$ (6) Å^3, $Z = 2$, $D_x = 1·54$, $D_m = 1·564$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 9·08$ cm^{-1}, $F(000) = 600$, $T = 298$ K, $R = 0·0319$ for 1170 significant reflections. The Pd^{II} ion is in a *trans* square-planar arrangement surrounded by two Cl and two N atoms. This planar geometry is rigorously imposed by the presence of a crystallographic inversion center at the Pd^{II} ion. Only one of the two N atoms in each benzalazine ligand is bonded to the Pd ion. The long chains in these ligands are in a zigzag shape approximately perpendicular to the $PdCl_2N_2$ plane.

Introduction. The coordination chemistry of benzalazine and its derivatives is rarely explored, although there are several interesting possible bonding modes for the coordination of this ligand to metal ions. To date, no example of a metal complex containing a coordinated azine is known. The reaction of benzalazine with $Fe_3(CO)_{12}$ led to the formation of $(\mu\text{-}C_6H_5CHN)_2Fe_2(CO)_6$ and an *ortho*-metallated complex $(o\text{-}C_6H_4CH_2N{-}N{=}CHC_6H_5)\text{-}Fe_2(CO)_6$ (Nametkin, Tyurin, Trusov, Batsanov & Struchkov, 1981, and references cited therein). The reaction of ketone azines with Cp_2Zr resulted in the formation of $Cp_2Zr(N{=}CR_2)_2$ (Erker, Frömberg, Krüger & Raabe, 1988). In an attempt to synthesize Pd–benzalazine complexes from the reactions of $PdCl_2$ and $PdCl_2(CH_3CN)_2$ with the ligand in chloroform solutions, we obtained white and pale-yellow precipitates, respectively. Both precipitates have the same empircial formula, $(PhCHNNCHPh)_2Cl_2Pd$. In order to distinguish between the structures of these two isomers, an X-ray structural determination of the pale-yellow crystal was undertaken. In this paper, we report the results of the investigation.

Experimental. The palladium complex was prepared by the addition of 2 equivalents of benzalazine to $PdCl_2(CH_3CN)_2$ in chloroform. The undissolved material was filtered. A crystalline product was obtained by evaporation of the filtrate. The product was redissolved in chloroform and pale-yellow crystals were grown by slow evaporation of the solvent in a refrigerator. A crystal of size 0·16 × 0·15 × 0·08 mm was selected for X-ray intensity measurement. D_m was determined by flotation in a mixture of carbon tetrachloride and *n*-hexane. A MicroVAX II computer-controlled Nicolet *R*3*m*/*V* diffractometer equipped with a graphite monochromator (Mo $K\alpha$ radiation, $\lambda = 0·71073$ Å) was used for intensity-data collection. The unit-cell parameters were determined by a least-squares fit of 22 reflection peaks with $6·0 \leq 2\theta \leq 24·0°$. $\theta/2\theta$ scan data were collected at room temperature (298 K) out to a 2θ limit of 50·0° (h $-13\rightarrow 13$, k $0\rightarrow 9$, l $0\rightarrow 15$) with a variable scan speed of 2·93–14·65° min^{-1}. Three standard reflections were monitored every 50 reflections and showed no signs of crystal deteriora-

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