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Commensurately modulated 1/4 and 1/5 phases of deuterated betaine calcium chloride dihydrate: a neutron structural study

OLIVIER HERNANDEZ,^{a,†} JEAN-MICHEL KIAT,^{a,b} ALAIN COUSSON,^a WERNER PAULUS,^{a,c} JOSE MARIA EZPELETA^d AND FRANCISCO JAVIER ZÚÑIGA^e

^aLaboratoire Léon Brillouin (CEA-CNRS), CEA/Saclay, 91191 Gif-sur-Yvette CEDEX, France, ^bLaboratoire de Structure, Propriétés et Modélisation des Solides (UMR du CNRS 8580), École Centrale, 92295 Châtenay-Malabry, France, ^cInstitut für Kristallographie, Jägerstraße 17–19, 52056 Aachen, Germany, ^dDepartamento de Física Aplicada II, Facultad de Farmacia, Universidad del País Vasco, Apartado 450, 01080 Vitoria-Gasteiz, Spain, and ^eDepartamento de Física de la Materia Condensada, Facultad de Ciencias, Universidad del País Vasco, Apartado 644, 48080 Bilbao, Spain. E-mail: hernand@bali.saclay.cea.fr

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Abstract

The structures of the commensurate 1/4 and 1/5 phases of the displacively modulated compound D-BCCD [deuterated betaine (trimethylammonioacetate) calcium chloride dihydrate, *i.e.* (CD₃)₃NCD₂COOCaCl₂(D₂O)₂ or CaCl₂·C₅D₁₁NO₂·2D₂O] have been determined by single-crystal neutron diffraction at 100 and 68 K, respectively. The structural model of the 1/4 phase is found to be quite different from that obtained previously from X-ray diffraction data of the hydrogenated compound. This discrepancy comes from the fact that X-ray irradiation induces in this compound an unusual time-dependent decrease of the intensity of high-order

satellite diffraction peaks. As a consequence and due to the commensurate nature of the phases investigated, X-ray diffraction failed to detect the large anharmonicity of the structural modulation which is clearly present in the two structures determined by neutron diffraction.

Comment

The structure determination of the low-temperature commensurately modulated 1/5 phase of the title compound [with a temperature range of stability of 53.3–75.2 K at atmospheric pressure (Unruh *et al.*, 1989)] was undertaken to check if, disregarding the change of the modulation periodicity, the modulated structure of BCCD remains at lower temperature globally close to those determined by X-ray diffraction at 90 (1/4 phase; Ezpeleta *et al.*, 1992) and 130 K (first incommensurate phase; Zúñiga *et al.*, 1991). Indeed, these two latter modulated structures were found to be very similar, being particularly well described by a single-harmonic modulation, whereas the qualitative conclusions of a recent neutron diffraction study (Hernandez *et al.*, 1996) indicate that the modulation on cooling becomes clearly anharmonic below 115 K. A second motivation for this work was to verify the group theory predictions of Pérez-Mato (1988), which give, assuming an unique order parameter of Λ_3 symmetry for the whole sequence of phase transitions, all the possible space groups of the different commensurate phases of the Devil's staircase-type phase diagram of BCCD. Finally, in order to obtain a complete set of data which can be compared to X-ray results, data collection by single-crystal neutron diffraction was undertaken not only in the 1/5 phase at 68 K, but also in the 1/4 phase at 100 K.

The structural model of the 1/4 phase obtained by means of neutron diffraction is different from that refined with the X-ray data (Ezpeleta *et al.*, 1992). A systematic comparison of equivalent interatomic distances and angles determined from these two models (see Table 1 for some typical examples) indicates that the organic betaine molecule appears more distorted along the *c* modulation axis in the 'neutron' model than in the 'X-ray' one, whereas for the distorted octahedron centred on the Ca atom, this effect is weaker. For instance, one observes that in these two models, the bond lengths N2—C32 and N4—C34 differ by 0.22 (2) and 0.16 (2) Å, respectively, while the angles O14—C44—C34 and C25—N3—C13 differ by 13 (2) and 13.5 (9)°, respectively. A similar comparison made for the atoms surrounding the Ca atoms, leads to differences of 0.11 (3) and 0.10 (3) Å for the bond lengths Ca1—O31 and Ca4—O12, respectively, and to a maximum angle difference of only 4.3 (6)° for the angle O23—Ca3—Cl8. The molecular diagram (Fig. 1) shows the formula unit of the 1/5 phase constituted by five inequivalent BCCD molecules. Two different geo-

† Present address: Laboratoire de Dynamique et Structure des Matériaux Moléculaires (UPRESA au CNRS 8024), UFR de Physique, Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq CEDEX, France.

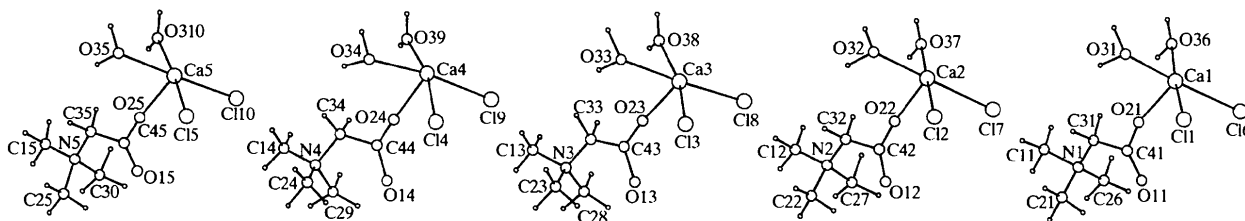


Fig. 1. Molecular diagram of the 1/5 phase of BCCD at 68 K, showing the formula unit, *i.e.* the five inequivalent BCCD molecules. All atoms are drawn as small circles of arbitrary radii.

metric configurations along the *c* modulation axis are clearly observed for the water molecules of the calcium octahedron and for the betaine molecules considered as rigid-body groups (Fig. 2). In a unit cell, two consecutive atom groups occupy one of the configurations and the following three groups occupy the second one, while the C3*i*—C4*i* bonds (*i* = 1–5) are almost superimposed along the *c* axis. Hence, the modulation describing the atomic displacements from the *Pnma* average structure in the 1/5 phase, but also in the 1/4 phase, is quite anharmonic, approaching a step-like form, in contrast to the results of the X-ray diffraction study of the 1/4 phase (Ezpeleta *et al.*, 1992).

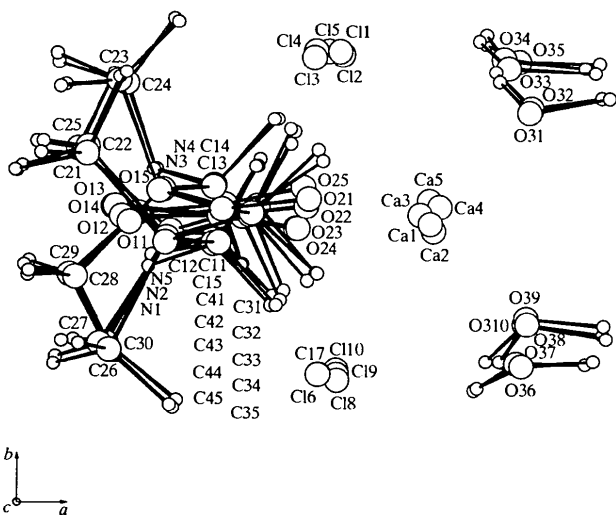


Fig. 2. View down the *c* modulation axis of part of the unit cell of the 1/5 phase of BCCD at 68 K, showing the effect of the anharmonic modulation. All atoms are drawn as small circles of arbitrary radii.

The X-ray model of the 1/4 phase published previously (Ezpeleta *et al.*, 1992) does not describe faithfully the real modulated structure of this phase. The explanation is intrinsic to the probe used and is given elsewhere (Hernandez *et al.*, 1999); X-rays induce in BCCD an unusually strong decrease of the intensity of diffraction satellite peaks with irradiation time. This effect is unusual insofar as its consequence depends mainly on the nature of these peaks (satellite reflections of different

order) being dramatic for third-order satellite peaks. Due to the superimposition of diffraction peaks specific to the commensurately modulated phases, this effect cannot be properly corrected, unlike the usual intensity decay during a diffraction experiment. As a consequence, any standard X-ray structural study of the modulated phases in BCCD, as is probably true for other incommensurate molecular crystals, will tend to underestimate the anharmonicity of the modulation, if present. Therefore, despite the higher reliability factors obtained, neutron diffraction appears more suited to the investigation of the modulated structure of such organic compounds, unless the acquisition time of the X-ray data is much lower than the irradiation time necessary to affect the measured intensities strongly (*e.g.* use of area-detector diffractometers). Finally, we confirm the *P*₂₁₂₁ space group predicted by Pérez-Mato (1988) for the 1/5 phase. The physical aspects and consequences of the present work, in particular the interpretation of the structural change which indeed occurs between the first incommensurate phase and the 1/4 phase, will be analysed elsewhere (Hernandez *et al.*, 1999).

Experimental

The title compound was prepared by slow evaporation from a saturated D₂O solution of fully deuterated pure chemicals.

D-BCCD 1/4 phase

Crystal data

CaCl₂·C₅D₁₁NO₂·2D₂O

M_r = 279.0

Orthorhombic

*P*₂₁*ca*

a = 10.82 (2) Å

b = 9.98 (2) Å

c = 43.13 (7) Å

V = 4657 (15) Å³

Z = 16

D_x = 1.592 Mg m⁻³

D_m not measured

Neutron radiation

λ = 1.528 Å

Cell parameters from 25

reflections

θ = 8.11–21.36°

μ = 0.0836 mm⁻¹

T = 100.0 K

Prism

7.5 × 4.5 × 3.5 mm

Colourless

Data collection

Orphée reactor (Saclay, France), 6T2 four-circle diffractometer

1639 reflections with

*F*² > 3σ(*F*²)

*R*_{int} = 0.037

ω scans between $2\theta = 0$ and 45° , ω - θ scans between $2\theta = 45$ and 80° , and ω - 2θ scans between $2\theta = 80$ and 120°
 Absorption correction: none
 3414 measured reflections
 1737 independent reflections

Refinement

Refinement on F
 $R = 0.084$
 $wR = 0.088$
 $S = 1.16$
 1639 reflections
 450 parameters
 Chebyshev weighting
 scheme: parameters
 1.08, 1.37 and 0.328

$\theta_{\max} = 49.96^\circ$
 $h = 0 \rightarrow 9$
 $k = 0 \rightarrow 10$
 $l = 0 \rightarrow 41$
 3 standard reflections
 every 200 reflections
 intensity decay: $<1.4\%$

$(\Delta/\sigma)_{\max} = 0.06$
 $\Delta\rho_{\max} = 1.51 \text{ Fm } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -1.10 \text{ Fm } \text{\AA}^{-3}$
 Extinction correction:
 Larson (1970)
 Extinction coefficient:
 139 (5)
 Scattering factors from
 Sears (1992)

Table 1. Selected geometrical parameters (\AA , $^\circ$) for the $1/4$ phase of D-BCCD

	Neutron	X-ray
Ca1—O31	2.28 (2)	2.389 (3)
Ca2—O22	2.21 (2)	2.231 (3)
Ca2—O33	2.31 (2)	2.355 (3)
Ca4—O24	2.14 (2)	2.225 (3)
Ca4—O12'	2.17 (2)	2.272 (3)
N1—C31	1.60 (1)	1.462 (4)
N2—C32	1.35 (1)	1.568 (5)
N2—C22	1.45 (1)	1.581 (5)
N3—C33	1.63 (1)	1.499 (4)
N4—C34	1.32 (1)	1.477 (4)
N4—C27	1.49 (1)	1.602 (6)
N4—C26	1.62 (1)	1.532 (5)
C31—C41	1.44 (1)	1.539 (5)
C33—C43	1.43 (1)	1.560 (6)
C34—C44	1.59 (1)	1.484 (6)
O11 ⁱⁱ —Ca1—Cl1	92.0 (4)	88.43 (7)
O23—Ca3—O13 ⁱⁱⁱ	171.4 (6)	174.4 (2)
O23—Ca3—Cl8	99.6 (5)	95.29 (8)
C32—N2—C22	112.8 (6)	103.71 (3)
C25—N3—C13	116.1 (6)	102.6 (3)
C28—N3—C33	109.2 (6)	121.0 (3)
C34—N4—C27	114.6 (6)	103.3 (3)
C27—N4—C26	104.9 (6)	117.3 (3)
O14—C44—C34	108.3 (8)	121.6 (4)

Symmetry codes: (i) $1+x, y, z$; (ii) $x - \frac{1}{2}, \frac{1}{2} - y, -z$; (iii) $x - \frac{1}{2}, y, \frac{1}{2} - z$.

D-BCCD 1/5 phase*Crystal data*

$\text{CaCl}_2 \cdot \text{C}_5\text{D}_{11}\text{NO}_2 \cdot 2\text{D}_2\text{O}$
 $M_r = 279.0$
 Orthorhombic
 $P2_12_12_1$
 $a = 10.82 (3) \text{ \AA}$
 $b = 9.98 (2) \text{ \AA}$
 $c = 53.93 (2) \text{ \AA}$
 $V = 5824 (21) \text{ \AA}^3$
 $Z = 20$
 $D_x = 1.591 \text{ Mg m}^{-3}$
 D_m not measured

Neutron radiation
 $\lambda = 1.528 \text{ \AA}$
 Cell parameters from 21 reflections
 $\theta = 14.77$ – 21.36°
 $\mu = 0.0915 \text{ mm}^{-1}$
 $T = 68.0 \text{ K}$
 Prism
 $7.5 \times 4.5 \times 3.5 \text{ mm}$
 Colourless

Data collection

Orphée reactor (Saclay, France), 6T2 four-circle diffractometer
 ω scans between $2\theta = 0$ and 45° , ω - θ scans between $2\theta = 45$ and 80° , and ω - 2θ scans between $2\theta = 80$ and 120°
 Absorption correction: none
 7098 measured reflections
 2456 independent reflections

2336 reflections with $F^2 > 3\sigma(F^2)$
 $R_{\text{int}} = 0.038$
 $\theta_{\max} = 52.17^\circ$
 $h = 0 \rightarrow 9$
 $k = 0 \rightarrow 10$
 $l = 0 \rightarrow 54$
 3 standard reflections
 every 150 reflections
 intensity decay: $<1.4\%$

Refinement

Refinement on F
 $R = 0.123$
 $wR = 0.154$
 $S = 1.03$
 2336 reflections
 562 parameters
 Chebyshev weighting
 scheme: parameters
 1.77, 1.38 and 0.331

$(\Delta/\sigma)_{\max} = 0.07$
 $\Delta\rho_{\max} = 1.89 \text{ Fm } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -2.00 \text{ Fm } \text{\AA}^{-3}$
 Extinction correction:
 Larson (1970)
 Extinction coefficient:
 134 (7)
 Scattering factors from
 Sears (1992)

The sample was initially characterized at room temperature. The structural model refined ($R = 0.0474$ and $S = 1.23$) confirms that previously published (Ezpeleta *et al.*, 1996). Refinement of the occupation parameters of the D-atom sites leads to a global rate of deuteration of 0.99. Next, the sample was mounted on the cold finger of a displax closed-cycle cryostat and cooled to 100.0 and 68.0 K for the data collections of the $1/4$ and $1/5$ phases, respectively. The high number of rejected measured reflections (rates of 0.257 and 0.269 for the $1/4$ and $1/5$ phases, respectively) is mainly explained by contamination of the profiles by aluminium powder reflections of the cryostat for ω - θ and ω - 2θ scans. For the $1/4$ phase, the starting parameters, excluding H atoms, were taken from the X-ray model published previously (Ezpeleta *et al.*, 1992); the D atoms which could not be generated geometrically (*i.e.* those of the water molecules) were located from difference Fourier synthesis. For the $1/5$ phase, the initial atomic positions in the fivefold commensurate supercell were generated from the aforementioned room-temperature asymmetrical unit. The space groups of both phases were chosen in such a way that they were compatible not only with the non-univocal systematic absences, but also with the group theory derivation of possible space groups (Pérez-Mato, 1988). The symmetry elements of the non-standard space groups $P2_1ca$ and $P2_12_12_1$ deduced for the $1/4$ and $1/5$ phases, respectively, were then determined so as to be compatible with the $P(Pnma):(1,s,-1)$ super space group (Pérez-Mato, 1991), with global phases of the modulation equal to $3\pi/8$ and to $3\pi/10$, respectively, or in other words, so as to maintain the standard origin of the $Pnma$ space group of the parent high-temperature phase. The non-standard symmetry cards used for the $P2_1ca$ and $P2_12_12_1$ space groups are thus: x, y, z ; $x + \frac{1}{2}, -y + \frac{1}{2}, -z$; $x, -y + \frac{1}{2}, z + \frac{1}{2}$; $x + \frac{1}{2}, y, -z + \frac{1}{2}$ and x, y, z ; $x + \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{7}{10}$; $-x, y + \frac{1}{2}, -z + \frac{1}{5}$; $-x + \frac{1}{2}, -y, z + \frac{1}{2}$, respectively. The refinement of both structures (by the full-matrix least-squares method) was achieved by applying soft restraints to interatomic distances. These restraints were progressively

relaxed until the final minimum was reached. No anisotropic displacement parameters can be applied and, due to systematic measurement errors, several isotropic displacement parameters remain physically non-reasonable, *i.e.* close to zero. Final difference Fourier maps display residual peaks. The label and distance of the closest atom sites are D260/0.71 Å and C33/0.98 Å for the 1/4 and 1/5 phases, respectively.

For both compounds, data reduction: *COLL5* (Lehmann & Larsen, 1974); program(s) used to refine structures: *CRYSTALS* (Watkin, Prout, Carruthers & Betteridge, 1996); molecular graphics: *CAMERON* (Watkin, Prout & Pearce, 1994); software used to prepare material for publication: *CRYSTALS*.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: FG1472). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Polymorphs of [(2*S*,3*S*)- α -Me-*N,N'*-bis-(salicylidene)butane-2,3-diaminato]bis-(pyridine)cobalt(III) tetrafluoroborate hydrate

SHOICHI SATO,^a TAKASHI FUKUDA,^b KAZUAKI ISHII,^b YOSHIHARU NAKANO^b AND YUKI FUJII^b

^a*X-ray Research Laboratory, Rigaku Corporation, Matsubara-cho 3-9-12, Akishima, Tokyo 196-8666, Japan.* and ^b*Department of Chemistry, Faculty Of Science, Ibaraki University, Bunkyo 2-1-1, Mito 310-8512, Japan. E-mail: sato@rigaku.co.jp*

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Abstract

The title compound, {2,2'-[butane-2,3-diylbis(nitrilo-1-ethylidene)diphenolato-*O,N,N',O'*]bis(pyridine-*N*)-cobalt(III) tetrafluoroborate hydrate, [Co(C₂₀H₂₂N₂O₂)(C₅H₅N)₂]BF₄·xH₂O or [Co{ α -Me-sal₂-(*S,S*)-bn}(py)₂]·BF₄·xH₂O (py is pyridine), showed polymorphs of crystals grown at the same time; one crystallized in the hexagonal system ($x = 1.5$) with a very long *c* axis and the other was in the monoclinic system ($x = 1.7$). The cell axes of the two structures were related simply to each other by $a_m \simeq a_h$, $b_m \simeq a_h + 2b_h$ and $c_m \simeq c_h/2$, where the axes of the hexagonal and monoclinic cells are identified by subscripts *h* and *m*, respectively. The complex cations, as well as the molecular arrangements in both structures, are quite similar to each other. The cation adopts octahedral coordination formed by the tetradentate salen-type Schiff base ligand in the basal plane and two *trans* pyridine ligands. The cation has an approximate twofold axis of rotation through the Co atom. The two methyl groups of the C—C bridge take an antiperiplanar conformation. The counter-ion is located nearly in the basal plane of the cation. The cations form dimers *via* π – π stacking between pyridine rings. Layers of cation dimers and anions stack alternately along *c*. The hexagonal structure includes 1.5 water molecules per Co atom and the monoclinic structure has 1.7 water molecules.

Comment

The molecular design of chiral tetradentate Schiff base complexes of manganese(III) and cobalt(III) is of great interest in the development of enantioselective oxygenation or hydrogenation catalysts for olefins or ketones (Jacobsen, 1993, and references therein; Katsuki, 1995; Nagata *et al.*, 1995; Bernardo *et al.*, 1996; Lam *et al.*, 1996). In the course of our investigation of Co^{III} complexes with chiral salen-type Schiff base ligands,