

An ordered low-temperature phase of barium nitroprusside trihydrate studied by neutron diffraction

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Received 17 March 2003

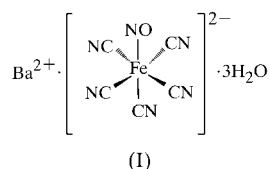
Accepted 9 May 2003

Online 11 June 2003

Crystals of barium pentacyanonitrosylferrate trihydrate (barium nitroprusside trihydrate), $\text{Ba}[\text{Fe}(\text{CN})_5(\text{NO})]\cdot 3\text{H}_2\text{O}$, have been studied by neutron diffraction in order to examine the structural behaviour of the compound in the 20–120 K temperature range and to determine the structure at 105 K. The results show the existence of a new crystal phase of the compound at 80 K (with a duplicated a parameter), which still exists at 20 K. The crystal structure at 105 K shows a rearrangement of the water molecules, which results in an ordered structure with $P1$ symmetry. Two of the four independent nitroprusside cations are rotated by 4.5° around the $[100]$ direction.

Comment

Barium nitroprusside trihydrate, (I), belongs to the nitroprusside family, in which the nitroprusside anion can be photoexcited reversibly to two long-living metastable states at low temperature (Zöllner *et al.*, 1989; Guida *et al.*, 1993; Soria *et al.*, 2002; Woike *et al.*, 2002, and references therein). The nitroprusside anion is currently being used in the search for new materials that combine photochromic and magnetic or electroconducting properties in the same crystal (Bellouard *et al.*, 2001, and references therein; Zorina *et al.*, 2002).



X-ray diffraction studies of (I) at room temperature (Lanfranconi *et al.*, 1973; Retzlaff *et al.*, 1989) indicate the presence of weakly bonded water molecules and the existence

of strong dipolar interactions between the nitrosyl ligands. The peculiar system of weak hydrogen bonds induces phase transitions in the crystals of (I); three of these hydrogen bonds have been detected by DTA (at 233.4, 130.2 and 118.0 K) and ^{14}N NQR (at 233, 131 and 118 K) experiments (Murgich *et al.*, 1990; Guida, 1992). As a consequence of its characteristic crystal packing, (I) has been used to study the origin and magnitude of correlation (Davidov) splitting effects due to the coupling between strongly polar vibrations of neighbouring anions in the crystal lattice (Piro *et al.*, 1987; Guida *et al.*, 1992).

From an analysis of the behaviour of selected reflections as a function of temperature, decreasing from 295 to 77 K, the first neutron diffraction study of (I) detected phase transitions at 130 and 112 K (Navaza *et al.*, 1990). Between these two temperatures, commensurate superlattice reflections appear, suggesting a duplication of the crystal a parameter. Below 112 K, additional reflections, which are forbidden at room temperature for space group $Pbcm$, are observed and the superlattice reflections disappear. However, near 233 K, no anomaly in reciprocal space could be detected; a comparison of the neutron structures at 140 and 295 K confirmed this phase transition (Navaza *et al.*, 1990, 1992).

The neutron crystal structure at 295 K was refined in space group $Pbcm$. At this temperature, positional disorder affects two water molecules, *viz.* $W3$ and $W4$. The neutron structure at 140 K shows positional disorder of molecule $W4$ only, and this structure was refined in space group $Pca2_1$. NMR studies have further shown that the positional disorder of the water molecules is dynamic (Tritt-Goc & Pislewski, 1994; Tritt-Goc, 1995).

We have undertaken a new neutron diffraction study of (I) in an attempt to confirm the existence of a fourth phase transition at 80 K, which was suggested by anomalies observed in Raman and IR spectra (Guida, 1992), and to determine the structure below 112 K.

The intensity evolution of selected reflections was analyzed as a function of temperature in the 20–140 K range. As an example, Fig. 1 shows the behaviour of the 071 reflection, which is forbidden in space groups $Pbcm$ and $Pca2_1$. Similar behaviour was observed at the time of the first neutron diffraction study of (I). At 20 K, the 071 reflection and two commensurate superlattice reflections, *viz.* $+\frac{1}{2}71$ and $-\frac{1}{2}71$, are visible. The latter begin to vanish at 80 K and disappear completely at 95 K, whereas the 071 reflection increases in intensity, reaching its maximum at 105 K and disappearing at 130 K. Between 110 and 130 K, the commensurate reflections are present. These results confirm the existence of another crystal phase of (I) at 80 K, which still exists at 20 K.

To determine the crystal phase of (I) between 80 and 110 K, a complete neutron diffraction data set has been collected at 105 K. These measurements show the significant intensity of some reflections forbidden by the $Pca2_1$ space group and its subgroups $P2_1$ and Pc . Thus, the space group of (I) at 105 K is $P1$. The cell volume is slightly greater (2%) than that at 140 K but is equivalent to that at room temperature. The angle α is not 90° within standard uncertainty.

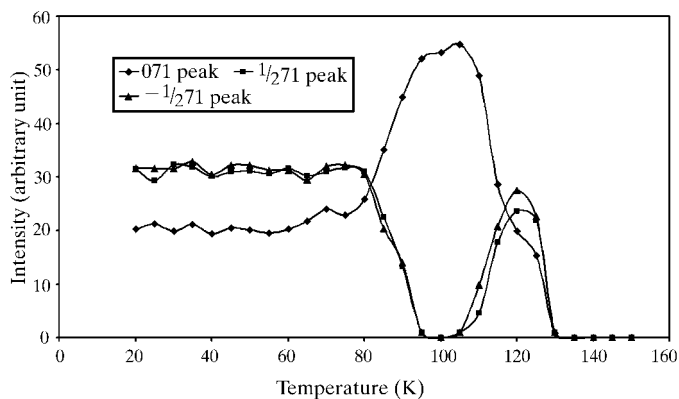


Figure 1
The variation of the 071 reflection and of the $\frac{1}{2}71$ and $-\frac{1}{2}71$ superlattice reflection intensities with increasing temperature (20–140 K).

In this structure, molecules of (I) occupy four independent sites, labelled 1, 2, 3 and 4 in Fig. 2 and Table 1. The increasing number of anions in the asymmetric unit was foreseen by Murgich *et al.* (1990) using ^{14}N NQR spectroscopy. Large positional variations of the W2, W3 and W4 water molecules are observed, which break the $Pca2_1$ symmetry of the 140 K crystal phase.

Molecule W2, coordinated to the Ba^{2+} anion, connects the nitroprusside anions along the [010] direction. In the structure at 105 K, we observed a significant increase of the average $\text{H1}\cdots\text{N3}$ (2.85 Å) and $\text{H2}\cdots\text{N5}$ (2.71 Å) distances (–2.56 and 2.37 Å, respectively, at 140 K), and a decrease of the $\text{H1}\cdots\text{N4}$ (2.50 Å) and $\text{H2}\cdots\text{N6}$ (2.62 Å) distances (2.89 and 2.90 Å, respectively, at 140 K). This distance variation indicates that the interactions between molecule W2 and atoms N4 and N6 are particularly strengthened in sites 3 and 4 (Table 2).

At 295 K, molecule W3 is crystallographically disordered over two positions, as shown in Fig. 3. At 140 K, molecule W3 occupies a single position and is involved in a two-centre hydrogen bond with atoms N2 (*via* atom H32) and N3 (*via* atom H31) of the same nitroprusside anion. At 105 K, in sites 1 and 2, molecule W3 rotates 80° around the $\text{O3}–\text{H32}_{140}$ axis and moves by 0.6 Å. In sites 3 and 4, the changes are not

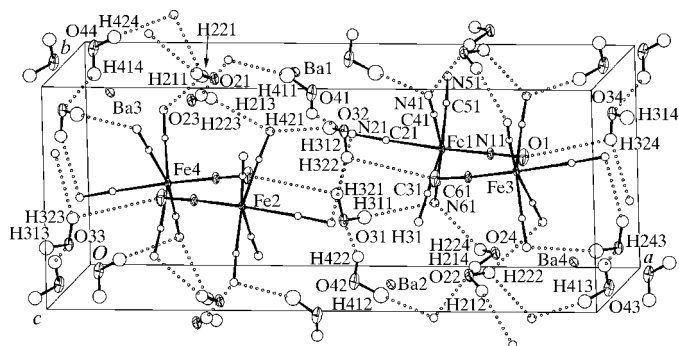


Figure 2
A perspective view of the unit cell of (I). For the sake of clarity, only a few labels are included. The four independent pseudosymmetric nitroprusside anions occupy sites differentiated by the last number in the name. Dotted lines represent possible hydrogen bonds.

significant. The $\text{O3}–\text{H32}\cdots\text{N2}$ hydrogen bond exists for all four sites, but the $\text{O3}–\text{H31}\cdots\text{N3}_{140}$ interaction is replaced by an $\text{O3}–\text{H31}\cdots\text{N6}$ interaction in sites 1 and 2 (Table 2).

Molecule W4 is disordered over two positions, with an occupancy of 0.5 at 295 K, and of 0.7 and 0.3 at 140 K (labelled W4 and W5, respectively, in Fig. 3); one of the W4 H atoms is in the same position as one of the W5 H atoms. At 105 K, W4 has an occupancy of 1 in the four non-equivalent sites. In sites 3 and 4, molecule W4 keeps the same orientation as $W4_{140}$ and forms similar hydrogen bonds. In sites 1 and 2, molecule W4 rotates 170° around the $\text{O5}–\text{H51}_{140}$ axis and moves more than 0.7 Å, such that the $\text{O4}–\text{H41}\cdots\text{N4}$ hydrogen bonds are significantly reinforced. The rotation of molecule W3 (sites 1 and 2) permits this molecule to accept a hydrogen bond from the new position of molecule W4, *via* atom H42 (Table 2).

The principal structural differences between the four independent nitroprusside anions refined at 105 K and the nitroprusside anion refined at 140 K are related to the acceptor atoms of the hydrogen bonds. The C–N bond distances are a little longer at 105 K [$\langle\text{C}–\text{N}\rangle_{105} = 1.178$ (8) Å *versus* $\langle\text{C}–\text{N}\rangle_{140} = 1.157$ (8) Å], particularly for the C4–N4 bond corresponding to sites 3 and 4 [1.20 (1)–1.21 (1) *versus* 1.166 (4) Å]. Furthermore, in sites 3 and 4, the C3–Fe–C4 angles are larger [90.8 (6)–90.2 (6) *versus* 88.5 (2) $^\circ$], the C5–Fe–C6 angles are smaller [88.8 (6)–88.3 (6) *versus* 91.0 (2) $^\circ$], the Fe–C4–N4 angles are smaller [174 (1)–176 (1) *versus* 179.1 (3) $^\circ$] and the Fe–C5–N5 angles are larger [178 (1)–178 (1) *versus* 175.2 (3) $^\circ$] at 105 K. The nitroprusside anions occupying sites 3 and 4 retain the same orientation as those of the structure at 140 K, while the nitroprusside anions occupying sites 1 and 2 rotate $\sim 4.5^\circ$ around the [100] axis.

The coordination polyhedron around the Ba^{2+} cation is a triply capped trigonal prism, with atoms OW2, N2 and OW3 capping the polyhedron faces. Molecules W2 and W3 are coordinated to one Ba^{2+} atom and molecule W4 is shared between two consecutive cations, thus forming infinite chains of coordination polyhedra parallel to the [001] direction. The chains located in the (0yz) and ($\frac{1}{2}yz$) unit-cell planes are not structurally equivalent, and the differences may be explained

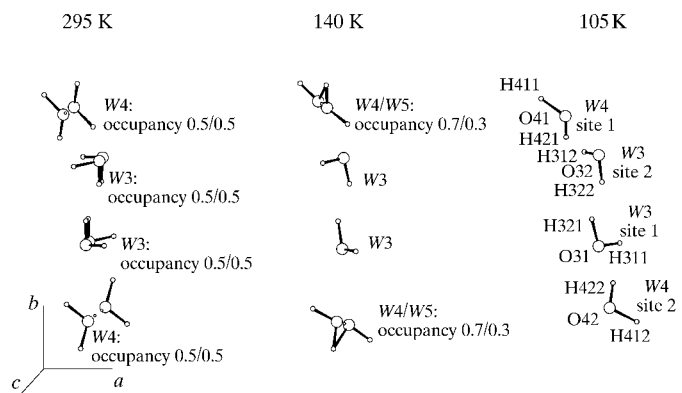


Figure 3
The positions of the disordered W3 and W4/W5 water molecules lying close to the $a/2$ plane at 295, 140 and 105 K (sites 1 and 2). The perspective view is the same as in Fig. 2.

in terms of positional variations of molecules *W3* and *W4*. The rotation and the high displacement of molecule *W4* in sites 1 and 2 induce some geometric differences. As observed in the structure at 140 K, the O3—H31···N3 hydrogen bonds corresponding to sites 3 and 4 reinforce the intrachain cohesion, while the O3—H31···N6 hydrogen bonds observed in sites 1 and 2 connect consecutive chains in the [010] direction.

In conclusion, positional changes of the water molecules induce an ordered structure in space group *P1*, with concomitant changes to the hydrogen bonding and a rotation of 4.5° of the nitroprusside cations lying in sites 1 and 2. The present study confirms the existence of a fourth phase transition, at 80 K, in crystals of (I).

These results show the important role played by weakly bonded water molecules in these low-temperature phase transitions.

Experimental

Compound (I) was obtained by stirring together stoichiometric quantities of silver nitroprusside (prepared by precipitation from stoichiometric amounts of sodium nitroprusside and silver nitrate solutions) and barium chloride solution. Silver chloride was separated from the solution by filtration and the liquid was concentrated in a vacuum rotary evaporator at room temperature, producing crystals of (I). Large single crystals were grown from small crystals, using the hanging-seed method, by spontaneous concentration of saturated aqueous solutions kept in a thermostat slightly above room temperature.

Crystal data

Ba[Fe(CN) ₅ (NO)]·3H ₂ O	$D_x = 2.120 \text{ Mg m}^{-3}$
$M_r = 407.31$	Neutron radiation
Triclinic, <i>P1</i>	$\lambda = 1.548 (5) \text{ \AA}$
$a = 19.01 (9) \text{ \AA}$	Cell parameters from 33 reflections
$b = 7.694 (16) \text{ \AA}$	$\theta = 15.5\text{--}24.2^\circ$
$c = 8.72 (2) \text{ \AA}$	$\mu = 0.16 \text{ mm}^{-1}$
$\alpha = 90.040 (3)^\circ$	$T = 105 (2) \text{ K}$
$\beta = 90.003 (5)^\circ$	Parallelepiped, brown-red
$\gamma = 89.994 (5)^\circ$	$5.5 \times 2.5 \times 1.5 \text{ mm}$
$V = 1276 (7) \text{ \AA}^3$	
$Z = 4$	

Data collection

Orphee four-circle 6T2 reactor diffractometer	$R_{\text{int}} = 0.007$
ω -2 θ scans	$\theta_{\text{max}} = 55.0^\circ$
Absorption correction: numerical (laboratory program)	$h = -18 \rightarrow 6$
$T_{\text{min}} = 0.498$, $T_{\text{max}} = 0.793$	$k = -8 \rightarrow 8$
2453 measured reflections	$l = -9 \rightarrow 9$
2415 independent reflections	2 standard reflections
2260 reflections with $I > 2\sigma(I)$	every 100 reflections
	intensity decay: none

Refinement

Refinement on F^2	$w = 1/(\sigma^2 F_o^2)$
$R[F^2 > 2\sigma(F^2)] = 0.078$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$wR(F^2) = 0.087$	$\Delta\rho_{\text{max}} = 0.98 \text{ fm \AA}^{-3}$
$S = 3.75$	$\Delta\rho_{\text{min}} = -1.09 \text{ fm \AA}^{-3}$
2415 reflections	Extinction correction: <i>SHELXL97</i>
340 parameters	Extinction coefficient: 0.00229 (10)
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected bond lengths (Å).

Fe1—N11	1.683 (17)	O3—N13	1.149 (19)
Fe1—C21	1.933 (19)	O4—N14	1.113 (18)
Fe1—C61	1.937 (15)	N21—C21	1.185 (15)
Fe1—C31	1.943 (15)	N22—C22	1.172 (15)
Fe1—C51	1.944 (16)	N23—C23	1.168 (16)
Fe1—C41	1.965 (15)	N24—C24	1.170 (16)
Fe2—N12	1.673 (17)	N31—C31	1.179 (13)
Fe2—C52	1.926 (15)	N32—C32	1.178 (14)
Fe2—C42	1.937 (16)	N33—C33	1.190 (14)
Fe2—C32	1.941 (16)	N34—C34	1.185 (14)
Fe2—C62	1.944 (15)	N41—C41	1.163 (14)
Fe2—C22	1.963 (19)	N42—C42	1.194 (14)
Fe3—N13	1.675 (16)	N43—C43	1.200 (14)
Fe3—C43	1.913 (16)	N44—C44	1.206 (14)
Fe3—C33	1.946 (16)	N51—C51	1.152 (14)
Fe3—C23	1.95 (2)	N52—C52	1.182 (14)
Fe3—C53	1.949 (16)	N53—C53	1.168 (15)
Fe3—C63	1.953 (15)	N54—C54	1.166 (15)
Fe4—N14	1.676 (16)	N61—C61	1.175 (13)
Fe4—C44	1.910 (16)	N62—C62	1.171 (13)
Fe4—C34	1.931 (15)	N63—C63	1.169 (13)
Fe4—C64	1.937 (16)	N64—C64	1.171 (14)
Fe4—C24	1.95 (2)	C32—N32	1.178 (14)
Fe4—C54	1.963 (16)	C42—N42	1.194 (14)
O1—N11	1.136 (18)	C43—N43	1.200 (14)
O2—N12	1.120 (18)	C64—N64	1.171 (14)

Table 2
Hydrogen-bonding geometry (Å, °).

<i>D</i> — <i>H</i> ··· <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> — <i>H</i> ··· <i>A</i>
O21—H211···N44 ⁱ	0.87 (3)	2.63 (3)	3.46 (2)	160 (3)
O21—H221···N54 ⁱ	0.98 (3)	2.65 (3)	3.37 (2)	130 (2)
O21—H221···N64	0.98 (3)	2.62 (3)	3.49 (2)	148 (2)
O22—H212···N43 ⁱⁱ	1.03 (4)	2.53 (3)	3.52 (2)	163 (3)
O22—H222···N53 ⁱⁱ	0.92 (4)	2.66 (3)	3.39 (2)	137 (3)
O22—H222···N63	0.92 (4)	2.69 (3)	3.48 (2)	144 (3)
O23—H213···N42 ⁱ	0.92 (4)	2.45 (3)	3.33 (2)	161 (3)
O23—H223···N62	0.90 (4)	2.62 (3)	3.42 (2)	148 (3)
O24—H214···N41 ⁱⁱ	1.03 (4)	2.41 (3)	3.41 (2)	161 (3)
O24—H224···N61	1.03 (4)	2.57 (3)	3.45 (2)	143 (3)
O31—H311···N61	0.91 (4)	2.52 (3)	3.37 (2)	155 (3)
O31—H321···N21	0.97 (4)	2.23 (3)	3.12 (2)	153 (3)
O31—H321···O4	0.97 (4)	3.12 (3)	3.61 (2)	113 (3)
O32—H312···N62	0.94 (4)	2.52 (3)	3.40 (2)	155 (3)
O32—H322···N22	0.91 (4)	2.31 (3)	3.17 (2)	160 (3)
O32—H322···O3	0.91 (4)	3.14 (4)	3.54 (3)	110 (3)
O33—H313···N33 ⁱⁱⁱ	0.98 (4)	2.48 (3)	3.40 (2)	156 (3)
O33—H323···N23 ⁱⁱⁱ	0.91 (4)	2.28 (3)	3.14 (2)	156 (3)
O33—H323···O2	0.91 (4)	3.14 (3)	3.58 (2)	112 (3)
O34—H314···N34 ^{iv}	0.91 (3)	2.53 (3)	3.39 (2)	159 (3)
O34—H324···N24 ^{iv}	0.96 (4)	2.23 (3)	3.14 (2)	157 (3)
O34—H324···O1	0.96 (4)	3.14 (4)	3.57 (3)	109 (2)
O41—H411···N42 ⁱ	1.07 (4)	2.12 (3)	3.05 (2)	142 (3)
O41—H421···O32	0.87 (3)	2.14 (3)	2.83 (2)	136 (3)
O42—H412···N41 ⁱⁱ	1.05 (3)	2.12 (3)	3.03 (2)	145 (3)
O42—H422···O31	0.87 (3)	2.17 (3)	2.85 (2)	135 (3)
O43—H413···N53 ^v	0.94 (3)	2.18 (3)	2.97 (2)	143 (3)
O43—H423···O33	0.96 (3)	2.09 (3)	2.86 (2)	137 (3)
O44—H414···O34 ⁱⁱⁱ	0.92 (3)	2.14 (3)	2.87 (2)	136 (3)
O44—H424···N54 ⁱ	0.96 (3)	2.18 (3)	3.00 (2)	142 (3)

Symmetry codes: (i) $x, 1 + y, z$; (ii) $x, y - 1, z$; (iii) $x - 1, y, z$; (iv) $1 + x, y, z$; (v) $x - 1, y - 1, z$.

The crystal, enclosed in an aluminium container under atmospheric conditions, was cooled to 20 K at a rate of 3 K min⁻¹. The cooling experimental conditions prevented the collection of a complete set of diffracted reflections. The structure of (I) at 105 K was determined in space group *P1*. Water molecules were located in

difference Fourier maps, and were phased with refined positions and isotropic displacement parameters for all nitroprusside atoms. High correlations and the low ratio of the number of refined parameters to the number of independent reflections obliged us to refine the H and cyanide atoms isotropically, and to constrain the isotropic or anisotropic displacement parameters of all atoms occupying pseudo-symmetric positions to be identical. The absolute value of the largest residual peak was smaller than 20% of the peak associated with a removed C atom.

Data collection and cell refinement: *4c_edi* (Person *et al.*, 1995); data reduction: *COLL5* (Lehmann & Larsen, 1974); program(s) used to solve structure: *SHELXL93* (Sheldrick, 1993); program(s) used to refine structure: *SHELXL93*; molecular graphics: *CAMERON* (Pearce *et al.*, 2000); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1015). Services for accessing these data are described at the back of the journal.

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