Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

A new crystal phase of barium nitroprusside trihydrate studied by neutron diffraction at 20 K

G. Chevrier,[a] J. M. Kiat,[a,b] J. A. Güida[c] and A. Navaza[d]*

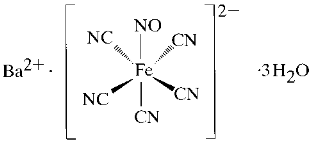
[a]Laboratoire Léon Brillouin, CEN Saclay, 91191 Gif-sur-Yvette, France, [b]Laboratoire des Structures, Propriétés et Modélisations des Solides, URA CNRS 8580, École Centrale de Paris, 92295 Châtenay-Malabry, France, [c]CEQUINOR (CONICET-UNLP), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 1900 La Plata, Argentina, and Universidad Nacional de Luján, 6700 Luján, Argentina, and [d]LPBC-CSSB, UMR CNRS 7033, Université Paris 13, 93017 Bobigny, France
Correspondence e-mail: anavaza@smbh.univ-paris13.fr

Received 11 December 2003
Accepted 8 January 2004
Online 10 February 2004

The crystal of barium pentacyanonitrosylferrate trihydrate {barium nitroprusside trihydrate, $Ba[Fe(CN)_5(NO)]\cdot 3H_2O$} has been studied by neutron diffraction at 20 K. The study was performed to characterize the structural phase generated by the phase transition undergone by the crystals at 80 K, at which temperature the unit-cell volume doubles. This crystal phase still exists at 20 K. The crystal structure, in space group *P*1, is completely ordered. The positional changes of the water molecules in the present structure with respect to those of the compound at 105 K are presented.

Comment

At room temperature, barium nitroprusside crystallizes as a trihydrate. The crystals of barium nitroprusside trihydrate, (I), undergo four phase transitions when the temperature decreases. The first neutron diffraction study of (I) detected two phase transitions occurring at 112 and 130 K (Navaza *et al.*, 1990). Comparison of the neutron structures at 140 and 295 K (Navaza *et al.*, 1992) confirmed the phase transition observed at 233 K by differential thermal analysis and ^{14}N NQR experiments (Güida, 1992; Murgich *et al.*, 1990). Recently, a new neutron diffraction study of (I) gave evidence of a fourth phase transition, at 80 K. At this temperature, commensurate superlattice reflections ($h\pm\frac{1}{2}\,k\,l$) appear, suggesting a doubling of the *a* cell parameter of the room-temperature crystal cell (Chevrier *et al.*, 2003). To determine the crystal phase below this transition temperature, a neutron diffraction data set, including superlattice reflections with a resolution of 1.2 Å, has been measured on a single crystal at 20 K. At this temperature, the three unit-cell angles are not 90° within standard uncertainty. The crystal cell volume is exactly double that at 105 K.



(I)

In this structure (space group *P*1), molecules of (I) occupy eight independent sites, labelled 1–8 in Fig. 1. The principal structural differences between the crystal models refined at 20 and 105 K are related to the positions of the water molecules. Table 1 presents distances and angles concerning these molecules.

In all the sites, water molecule *W*2, bonded to one Ba atom in a trigonal coordination, has atoms N3, N4, N5 and N6 as possible acceptors of weak hydrogen bonds. These contacts connect the nitroprusside anions along the [010] direction. The mean H21···N3, H21···N4, H22···N5 and H22···N6 distances [2.84 (13), 2.52 (15), 2.71 (15) and 2.63 (13) Å, respectively] are equivalent to those found at 105 K, but the shortening of H21···N4 in sites 1 and 3 [2.27 (3) and 2.34 (3) Å, respectively, at 20 K, and 2.63 and 2.45 Å, respectively, at 105 K] indicates that the contact forces between *W*2 and these N atoms are significantly strengthened, pointing to a hydrogen bond in these sites.

In sites 1, 2, 3 and 8, small positional variations are observed in water molecule *W*3. The molecular plane rotates by about 10° and the molecule is displaced by about 0.1 Å from its position at 105 K (Figs. 2*b* and 2*c*). By contrast, in sites 4, 5, 6 and 7, *W*3 rotates by about 80° around the O3—H32 direction and moves by about 0.6 Å, introducing significant changes in the hydrogen-bond system (Figs. 2*a* and 2*d*). As at 105 K, *W*3 forms hydrogen bonds with N atoms of the same nitroprusside anion. In all sites, *W*3 forms a hydrogen bond with atom N2 *via* atom H32. In sites 3, 5, 6 and 8, *W*3 acts as a donor to atom N3, and in the other sites as a donor to atom N6, *via* atom H31. *W*3 is also coordinated to one Ba atom. Its tetragonal coordination is completed by accepting from *W*4 the strongest hydrogen

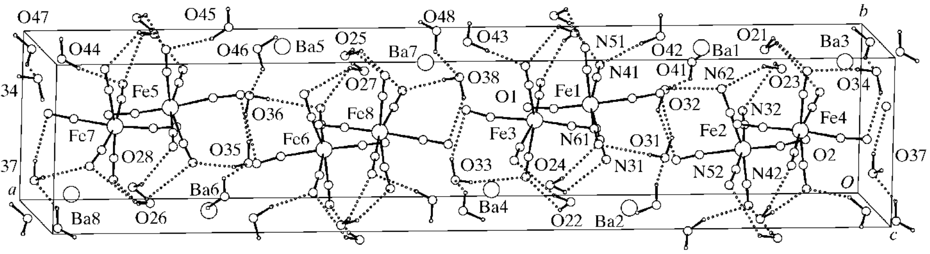


Figure 1
A perspective view of the unit-cell contents of (I) at 20 K. For the sake of clarity, only selected labels are included. The eight independent nitroprusside anions occupy sites differentiated by the last digit in the label. Dotted lines represent possible hydrogen bonds.

DOI: 10.1107/S0108270104000599

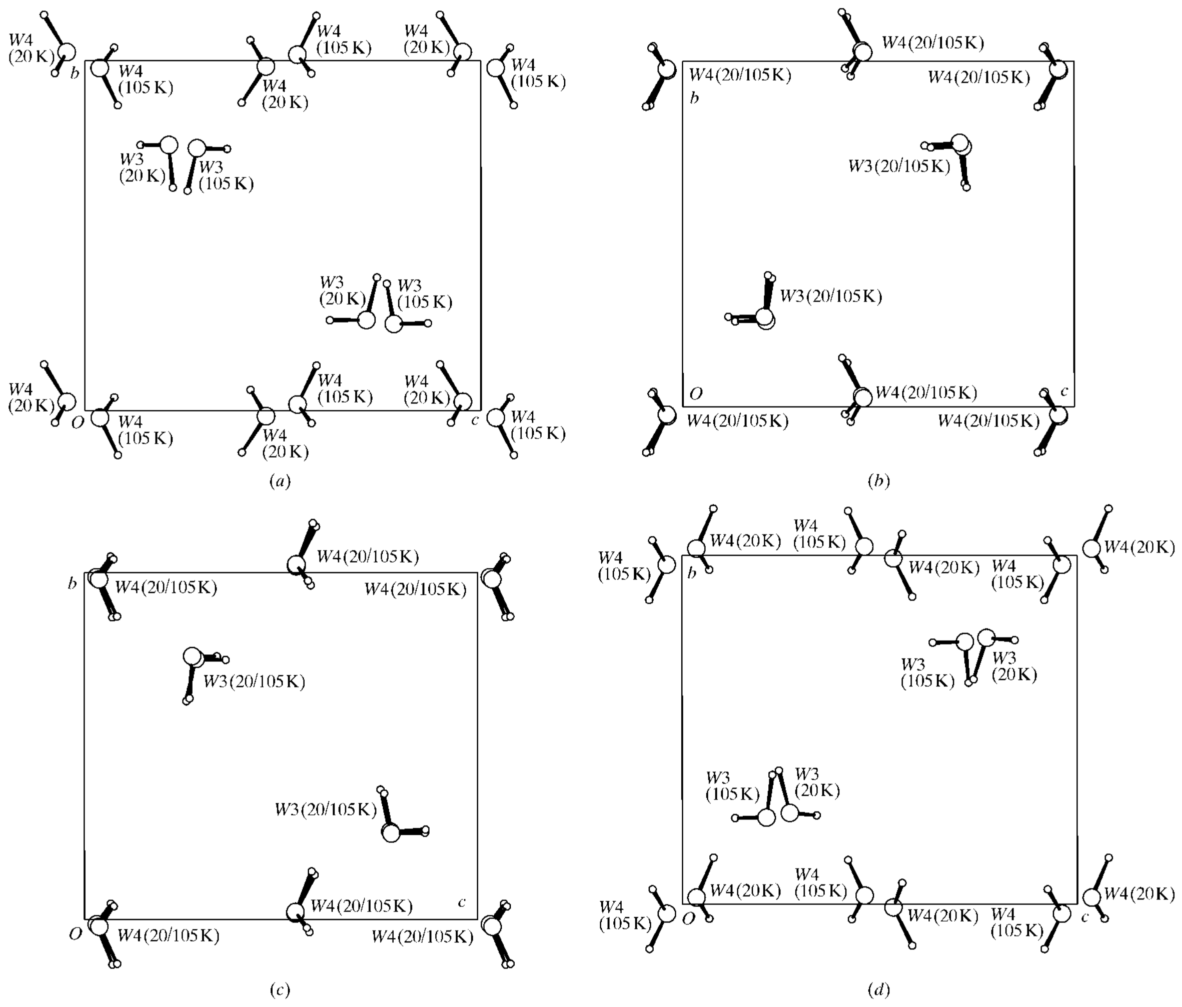


Figure 2
Unit-cell sections along the [100] direction, showing the differences between the *W*3 and *W*4 positions in the 20 and 105 K structures of (I). (*a*) $x = 0$, (*b*) $x = \frac{1}{4}$, (*c*) $x = \frac{1}{2}$, and (*d*) $x = \frac{3}{4}$.

bond of the structure [mean distances and angle: O4···O3 = 2.85 (3) Å, H42···O3 = 2.08 (4) Å and O4—H42···O3 = 137 (5)°].

In sites 1,2,3 and 8, *W*4 keeps the same orientation as in the structure at 105 K. The molecular plane rotates by less than 6° and the centre of gravity of the molecules is displaced by about 0.2 Å (Fig. 2*b* and 2*c*). However, in all other sites *W*4 moves to adopt a pseudocentrosymmetric position with respect to that occupied at 105 K, the molecular plane rotates by 170° around the *b* axis and the molecule is displaced by about 0.9 Å along the [010] direction (Figs. 2*a* and 2*d*). In all sites, *W*4 acts as a hydrogen-bond donor to *W*3 *via* atom H42. In sites 1, 2, 4 and 7, *W*4 is also a hydrogen-bond donor to atom N4 [mean distances and angle = 2.98 (4) Å, 2.18 (6) Å and 140 (4)°], and in all other sites to atom N5 [mean distances and angle = 2.98 (2) Å, 2.14 (3) Å and 145 (3)°], *via* atom H41. *W*4 is shared between two Ba atoms, giving a distorted tetrahedral coordination [mean Ba—O4—Ba angle = 160.3 (1)°].

In conclusion, this study unambiguously shows the positional redistribution of water molecules in (I) at 20 K which, breaking the translational symmetry satisfied at 105 K, induces the doubling of the *a* cell parameter.

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 by spontaneous concentration of saturated aqueous solutions kept in a thermostat slightly above room temperature, using the hanging-seed method.

Crystal data

$Ba[Fe(CN)_5(NO)]\cdot 3H_2O$
$M_r = 407.32$
Triclinic, $P1$
$a = 37.905$ (66) Å
$b = 7.694$ (7) Å
$c = 8.705$ (9) Å
$\alpha = 90.030$ (10)°
$\beta = 90.086$ (7)°
$\gamma = 90.146$ (2)°
$V = 2539$ (6) Å^3
$Z = 8$

$D_x = 2.131$ Mg m^{-3}
Neutron radiation
$\lambda = 1.548$ Å
Cell parameters from 32 reflections
$\theta = 15.6$–24.2°
$\mu = 0.16$ mm^{-1}
$T = 20$ (2) K
Parallepiped, brown–red
5.5 × 2.5 × 1.5 mm

i28 G. Chevrier *et al.* • Ba[Fe(CN)5(NO)]·3H2O *Acta Cryst.* (2004). C**60**, i27–i29

Data collection

Four-circle diffractometer, 6T2 beamline at Orphée reactor
ω 3 < 2θ < 50, ω–θ 50 < 2θ < 80, ω–2θ 80 < 2θ < 110
Absorption correction: numerical (*CRYSTAL SHAPE*; local program)
$T_{\min} = 0.498$, $T_{\max} = 0.794$
3218 measured reflections
3021 independent reflections
2676 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.012$
$\theta_{\max} = 55.0°$
$h = -36 \rightarrow 12$
$k = -8 \rightarrow 8$
$l = -9 \rightarrow 9$
2 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.068$
$wR(F^2) = 0.072$
$S = 3.44$
3021 reflections
565 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2)]$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.06$
$\Delta\rho_{\min} = -0.83$
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.00058 (2)

The crystal of (I), enclosed in a vanadium container under atmospheric conditions, was cooled directly to 20 K at a cooling rate of 3 K min^{-1}. The experimental conditions for cooling prevented the collection of a complete set of diffracted reflections. The structure of (I) at 20 K was solved in three steps. In the first step, the crystal structure of (I) at 140 K, placed in one half of the 20 K unit cell, was refined in space group *P*1 using the intensities of the data without the commensurate superlattice reflections. An average model was refined in this 'half cell'. High residual peaks were found on the difference Fourier maps around water positions *W*3 and *W*4. In the second step, the difference Fourier maps were also calculated in the same 'half cell' but without the contributions of *W*3 and *W*4. Eight possible positions for water molecules *W*3 and *W*4 were detected. In the last step, 85 acceptable models of (I) at 20 K were built into the 20 K unit cell, *via* combination of the possible positions of *W*3 and *W*4, and refined using all data. The criterion used to choose the final model was the best convergence of refinements in space group *P*1. High correlations and the low ratio of the refined parameters to the number of independent reflections obliged us to refine all atoms isotropically and to constrain the isotropic displacements of all atoms occupying pseudosymmetrical positions (Ba, Fe, C, nitrosyl N, nitrosyl O, cyanide N, water O2, water O3 and water O4) to be identical. The H—O and H$\cdots$H distances of the water molecules were restrained to 0.963 (5) and 1.511 (8) Å, respectively. The absolute value of the largest residual peak was less than 17% of the peak associated with a removed C atom.

Data collection: 4*c-edi* (Person *et al.*, 1995); cell refinement: 4*c-edi*; data reduction: *COLL*5 (Lehmann & Larsen, 1974); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993); 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: SQ1146). Services for accessing these data are described at the back of the journal.

References

Chevrier, G., Kiat, J. M., Güida, J. & Navaza, A. (2003). *Acta Cryst.* C**59**, i59–i62.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Güida, J. A. (1992). PhD thesis, University of La Plata, Argentina.

Lehmann, M. S. & Larsen, F. K. (1974). *Acta Cryst.* A**30**, 580–589.

Murgich, J., Bonalde, I. & Abanero, J. A. (1990). *Z. Naturforsch. Teil A*, **45**, 353–356.

Navaza, A., Chevrier, G., Schweiss, P. & Rigotti, G. (1992). *J. Solid State Chem.* **99**, 158–165.

Navaza, A., Schweiss, P., Alzari, P. M., Chevrier, G., Heger, G. & Güida, J. A. (1990). *J. Solid State Chem.* **89**, 23–30.

Pearce, L., Prout, C. K. & Watkin, D. J. (2000). *CAMERON*. Chemical Crystallography Laboratory, University of Oxford, England.

Person, C., Goukassov, A. & Kiat, J. M. (1995). 4*c-edi*. Laboratoire León Brillouin, France.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL*93. University of Göttingen, Germany.

Acta Cryst. (2004). C**60**, i27–i29 G. Chevrier *et al.* • $Ba[Fe(CN)_5(NO)]\cdot 3H_2O$ **i29**