

## Neutron Diffraction Analysis of Barium Nitroprusside Trihydrate at Room Temperature

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Received February 9, 1990

The crystal structure of barium nitroprusside trihydrate,  $\text{Ba}[\text{Fe}(\text{CN})_5\text{NO}]\cdot 3\text{H}_2\text{O}$ , at room temperature has been refined using neutron diffraction measurements ( $F(000) = 41.8$ ,  $D_x = 2.13 \text{ g cm}^{-3}$ ,  $\mu = 0.6 \text{ cm}^{-1}$  (evaluated), space group *Pbcm* (57), orthorhombic,  $Z = 4$ ,  $a = 7.620(7)$ ,  $b = 19.394(17)$ , and  $c = 8.631(8) \text{ \AA}$ ,  $V = 1276(4) \text{ \AA}^3$ ). A final  $R$  factor of 0.060 was obtained using 1349 observed structure factors. The nitroprusside ion in  $\text{Ba}[\text{Fe}(\text{CN})_5\text{NO}]\cdot 3\text{H}_2\text{O}$  presents a distorted octahedral configuration similar to that found in other nitroprusside salts determined by X-ray and neutron diffraction methods. Its polar axis lies in a symmetry plane, which also includes the  $\text{Ba}^{2+}$  and the oxygen of one of the water molecules. A positional disorder of the other two water molecules is observed. Two structural phase transitions were found at 130(3) and 112(4) K; they were analyzed from the evolution of selected reflections as a function of temperature in the range between 295 and 77 K. © 1990 Academic Press, Inc.

### Introduction

Barium nitroprusside (BaNP) was studied several years ago by X-ray diffraction (1), as well as by IR (2) and P-NMR (3) spectroscopy. The first crystal structure determination, based on visually estimated photographic data, showed the presence of two molecules of water of hydration, and the subsequent spectroscopic results were interpreted on this basis.

Recently, interest in BaNP has been renewed, in particular because it is the second of the nitroprusside salts where a long-living electronic metastable state of the anion was produced by laser irradiation at low temperature (4). This state was first detected for  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$  (5) and it is known to occur in other nitroprussides as well (6). In addition, and as a consequence of its characteristic crystal packing, BaNP constitutes an excellent system to study correlation (Davydov) splitting effects due to strongly polar optic modes (7) and also the coupling to IR radiation of longitudinal

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optic (LO) vibration associated with these modes (8).

Two independent redeterminations of the crystal structure have been performed by X-ray diffraction, one in the previously reported (1) noncentrosymmetric space group  $Pca2_1$  (9) (noncentrosymmetric X-ray model, NC-XRM) and the other in the centrosymmetric space group  $Pbcm$  (10) (C-XRM) which contains  $Pbc2_1$  as a subgroup. Despite the different space group assignments, both studies revealed that the compound is in fact a trihydrate and provided essentially the same atomic positions for all atoms with the exception of a single water molecule (a relative displacement of about 0.4 Å). On this basis all spectroscopic measurements were reinterpreted (11) and references therein). Electrostatic energy calculations were performed in space group  $Pca2_1$  to place the missing H atoms in theoretical positions. Based on this complete model, a hydrogen bonding scheme was proposed (9) but it could not be satisfactorily used for the reinterpretation of the P-NMR spectra (12).

We have undertaken a neutron diffraction study of this compound in an attempt to determine precisely the positions of the water molecules and to examine the structural behavior at low temperature. We report here the crystal structure at room temperature.

Certain reflections monitored as a function of temperature between 295 and 77 K revealed two structural phase transitions at about 112 and 130 K. These were confirmed by subsequent DSC (13) and  $^{14}\text{N}$ -NQR (14) studies which also showed the existence of a third phase transition at about 232 K.

## Experimental

Single crystals were obtained by slow evaporation of a Ba nitroprusside solution at 30°C. Large crystals were grown from small ones suspended in saturated solution.

A complete data set was obtained at 295 K from an orange-red crystal of dimensions  $3.0 \times 4.4 \times 4.3 \text{ mm}^3$  employing the four-circle diffractometer 5C2 (P110) at the Orphée reactor (CEN Saclay), using neutrons with 0.831 Å wavelength. Unit cell parameters and the orientation matrix for data collection were determined from the refinement of 18 centered reflections in the range  $29^\circ < 2\theta < 52^\circ$ . Reflection intensities were measured for  $4^\circ < 2\theta < 75^\circ$ , using the  $\omega$ -step scan mode, in the Miller index ranges  $0 \leq h \leq 11$ ;  $-28 \leq k \leq 0$ ;  $0 \leq l \leq 12$  and  $-11 \leq h \leq 0$ ;  $0 \leq k \leq 17$ ;  $-12 \leq l \leq 0$ . The  $\omega$ -scan range was adjusted as a function of scattering angle to match the instrument resolution.

The intensity of two reference reflections (060 and 008) monitored every 100 measured reflections was essentially constant throughout the data collection period (15 days). The method of intensity integration is described elsewhere (15). The large lattice parameter  $b = 19.394 \text{ Å}$  induced some overlap of neighboring reflections  $hkl$  and  $h, k \pm 1, l$  as shown by a precise examination of profiles at large scattering angles. From 3772 reflections measured, 2213 were independent and only 1349 having  $|F|^2 > 5 \sigma(|F|^2)$  were used in the calculations. Due to the small absorption effects ( $\mu = 0.6 \text{ cm}^{-1}$ ) no correction was applied to the diffraction data. The very good agreement between symmetry-related reflection intensities,  $R_{\text{sym}} = \sum ||F_0| - |F_{0\text{av}}|| / \sum |F_0| = 0.005$ , and the relative small  $||F_0| - |F_c||$  differences for strong reflections observed during the final cycles of structure refinement pointed to almost negligible extinction effects. The full matrix least-squares refinement of 109 parameters based on  $|F|$ 's, with weights  $w = 1/\sigma^2(|F|)$ , converged to final  $R = \sum ||F_0| - |F_c|| / \sum |F_0| = 0.060$  and  $R_w = [\sum w(|F_0| - |F_c|)^2 / \sum w |F_0|^2]^{0.5} = 0.078$  ( $s = [(\sum w(|F_0| - |F_c|)^2 / (N_0 - N_v))]^{0.5} = 3.69$  and  $(\Delta/\sigma)_{\text{max}} = 0.013$ ). Two water molecules (W3 and W4) were restrained to the ideal

geometry (Distance O–H = 0.963 (5) Å, angle H–O–H = 107 (.1)°) and were refined with an overall isotropic temperature factor; 48 reflections remained in the last refinement with a  $| |F_0| - |F_c| | / \sigma(F_0) > 2$ . The neutron scattering lengths were taken from the international Tables for X-Ray Crystallography (16). Structure refinement was performed with the SHELX76 (17) program on a MicroVAX II computer and with XFLS (18) on a CONVEX C1-XP computer.

A series of selected reflections was recorded as a function of temperature between 170 and 77 K in steps of 2 K. The results point out two phase transitions. The most significant change in intensity was observed for the (701) reflection.

## Results and Discussion

### (I) Room Temperature Structure

Both structural models derived from X-ray data, NC-XRM and C-XRM, show water molecules with unusually large thermal parameters (OW3 in NC-XRM (9), OW3 and OW4 in C-XRM (10)). These water molecules lie on "pseudo-special" or special positions, respectively. First attempts to refine these two models using the neutron data with hydrogen atoms located from difference Fourier maps were not satisfactory since thermal parameters were too high and O–H distances not correct. A maximum entropy approach using X-ray data (19) showed the possibility of occupational disorder for OW3 and OW4. Consequently, a structural model incorporating this disorder was refined in both space groups; lack of significant improvement in the noncentrosymmetric group according to the Hamilton test (20) led us to keep the *Pbcm* group for subsequent analysis. This centric space group is also supported by recent NQR measurements which show only six <sup>14</sup>N lines, as expected from the three inequivalent CN ligands of [Fe(CN)<sub>5</sub>NO]<sup>2-</sup>

ion at the *Pbcm* site symmetry *m* (21). Work in this space group implies that the two enantiomorphous structures, distinct only for W3 and W4 positions, are present in the crystal.

Reduced thermal parameters for OW3 and OW4, which are no longer constrained by symmetry, are obtained by taking into account such a positional disorder. However, the final *R* factor remains rather high, and most of the residual peaks on a final differences Fourier map are located in the region of W3 and W4, so the present model at room temperatures does not provide a satisfactory description of the geometrical arrangement of hydration water molecules W3 and W4. Structural analysis at low temperature, above and below the transition temperatures, would eventually help to clarify this point, considering that water rearrangement is probably responsible for the observed structural transitions.

Final atomic positions and equivalent isotropic thermal parameters are shown in Table I. Relevant bond distances and angles, except for the centrosymmetric positions of W3 and W4 (corresponding to one of the enantiomorphous structures), are presented in Table II.

The nitroprusside ion presents the usual distorted octahedral configuration (Tables IIa and III). Its NCFeNO polar axis lies on a mirror plane (*m*) coincident with one of the bisectors of adjacent CN ligands. The distance from the iron atom to the least-squares mean plane of the *cis*-carbon atoms is 0.173(2) Å. As expected, distances and angles between nitroprusside atoms are not significantly different from those determined by X-ray diffraction, both in the C-XRM (10) as well as in an equivalent disordered model (DC-XRM) (22). However, there are some small differences with the neutron crystallographic data of sodium nitroprusside (15) which show an Fe–N–O angle slightly smaller and distances Fe–C more dispersed. The equivalent isotropic

TABLE I  
POSITIONAL AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS AND  
THEIR E.S.D.'S FOR Ba[Fe(CN)<sub>5</sub>NO].3H<sub>2</sub>O

Atom	x	y	z	$U_{iso}^a$
Ba	0.0722(4)	0.3973(2)	0.250	0.0165(13)
Fe	0.4163(2)	0.6596(1)	0.250	0.0133(6)
O(1)	0.4563(7)	0.8022(2)	0.250	0.0442(23)
N(1)	0.4438(2)	0.7448(1)	0.250	0.0203(8)
N(2)	0.3384(4)	0.5034(1)	0.250	0.0423(14)
N(3)	0.6961(2)	0.6300(1)	0.4987(2)	0.0447(10)
N(4)	0.1328(2)	0.6590(1)	0.5042(2)	0.0438(9)
C(2)	0.3720(4)	0.5615(2)	0.250	0.0243(13)
C(3)	0.5918(2)	0.6407(1)	0.4059(2)	0.0240(8)
C(4)	0.2380(2)	0.6606(1)	0.4086(2)	0.0242(8)
O(2)	0.1146(6)	0.2553(2)	0.250	0.0427(23)
H(2)	0.087(2)	0.2281(4)	0.168(1)	0.0959(62)
O(3)	-0.264(1)	0.4667(6)	0.212(1)	0.0970(24)
H(31)	-0.275(3)	0.5051(8)	0.142(2)	0.0970(24)
H(32)	-0.368(2)	0.4671(9)	0.276(2)	0.0970(24)
O(4)	-0.024(1)	0.5128(5)	0.462(1)	0.0791(19)
H(41)	-0.136(1)	0.5238(8)	0.417(2)	0.0791(19)
H(42)	0.057(2)	0.5484(7)	0.431(2)	0.0791(19)

<sup>a</sup>  $U_{iso}$  defined as  $(1/3)(U_{11} + U_{22} + U_{33})$ .

Note. Symmetry codes. (i)  $X, Y, 1/2 - Z$ . (ii)  $-X, 1 - Y, Z - 1/2$ . (iii)  $1 - X, 1 - Y, 1 - Z$ . (iv)  $1 - X, 1 - Y, Z - 1/2$ . (v)  $-X, 1 - Y, 1 - Z$ . (vi)  $1 - X, Y - 1/2, 1/2 - Z$ . (vii)  $1 - X, Y - 1/2, Z$ . (viii)  $-X, Y - 1/2, 1/2 - Z$ . (ix)  $-X, Y - 1/2, Z$ . (x)  $X - 1, Y, Z$ . (xi)  $X - 1, Y, 1/2 - Z$ . (xii)  $-X, 1 - Y, 1/2 + Z$ .

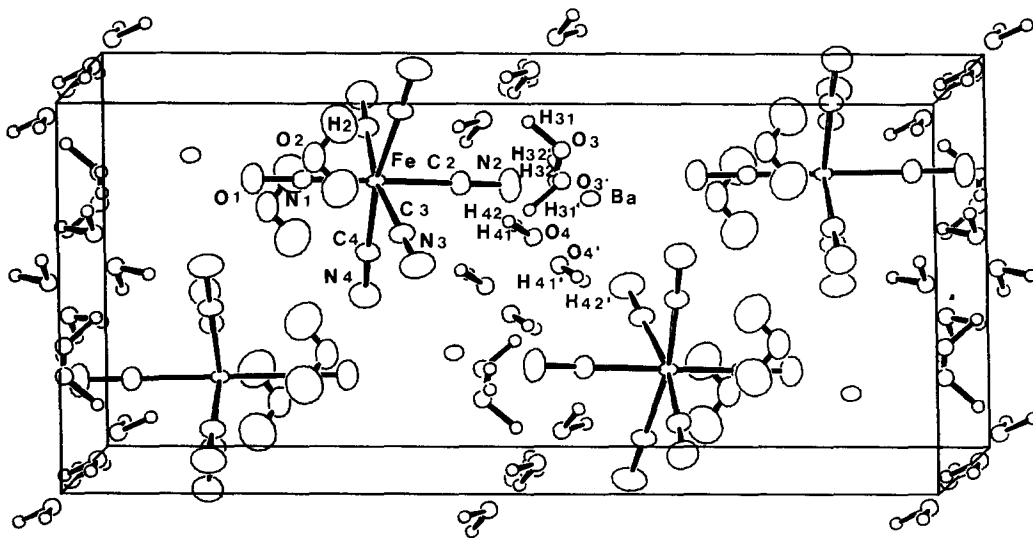


FIG. 1. ORTEP drawing (20) of the unit cell content of Ba<sub>2</sub>[Fe(CN)<sub>5</sub>NO].3H<sub>2</sub>O.

TABLE II  
SELECTED BOND DISTANCES (Å) AND ANGLES (°) CONCERNING Fe, Ba, AND WATER OXYGEN ATOMS

(a)									
Fe	N(1)	1.665(3)	Fe	C(2)	1.931(4)	Fe	C(3)	1.932(2)	
Fe	C(4)	1.929(2)	N(1)	O(1)	1.116(5)	C(2)	N(2)	1.156(4)	
C(3)	N(3)	1.148(2)	C(4)	N(4)	1.150(2)				
N(1)	Fe	177.2(1)	C(2)	Fe	86.2(1)	C(3)	Fe	C(4)	89.72(5)
N(1)	Fe	95.8(1)	C(3)	Fe	169.6(1)	C(2)	Fe	C(4)	83.5 (1)
N(1)	Fe	94.5(1)	C(3)	Fe	88.28(8)	C(4) <sup>i</sup>	Fe	C(4)	90.42(8)
O(1)	N(1)	177.7(3)	N(2)	C(2)	177.3(3)	N(3)	C(3)	Fe	179.5(2)
N(4)	C(4)	177.8(2)							
(b)									
Ba	O(2)	2.771(5)	Ba	O(4)	2.985(8)	Ba	O(4) <sup>ii</sup>	3.056(6)	
Ba	O(3)	2.91(1)	Ba	N(2)	2.889(4)	Ba	N(3) <sup>iii</sup>	2.846(2)	
Ba	N(3) <sup>iv</sup>	2.846(2)	Ba	N(4) <sup>v</sup>	2.852(2)	Ba	N(4) <sup>vi</sup>	2.852(3)	
O(2)	H(2)	0.906(6)	O(2)	Ba	2.771(5)	O(2)	N(3) <sup>iii</sup>	3.425(3)	
O(2)	N(3) <sup>iv</sup>	3.425(3)	O(2)	N(4) <sup>v</sup>	3.289(4)	O(2)	N(4) <sup>vi</sup>	3.289(4)	
O(2)	N(3) <sup>vi</sup>	3.548(4)	H(2)	N(3) <sup>vi</sup>	2.903(9)	O(2)	N(3) <sup>vii</sup>	3.548(4)	
O(2)	N(4) <sup>viii</sup>	3.443(4)	H(2)	N(4) <sup>viii</sup>	2.610(9)	O(2)	N(4) <sup>ix</sup>	3.443(4)	
Ba	O(2)	N(3) <sup>vii</sup> 136.7(1)	O(2)	O(2)	N(3) <sup>vii</sup> 74.5(1)	O(2)	H(2)	N(3) <sup>vii</sup> 129(1)	
Ba	O(2)	N(4) <sup>vi</sup> 118.3(1)	O(2)	O(2)	N(4) <sup>ix</sup> 79.2(1)	O(2)	H(2)	N(4) <sup>viii</sup> 153(1)	
H(2)	O(2)	H(2) <sup>i</sup> 102.4(7)	O(2)	O(2)	N(4) <sup>ix</sup> 103.7(1)				
O(3)	O(3) <sup>j</sup>	0.66(2)	O(3)	O(4)	2.97(1)	O(3)	O(4) <sup>ii</sup>	3.103(9)	
O(3)	N(2) <sup>x</sup>	3.13(1)	O(3)	N(4) <sup>ii</sup>	3.19(1)	O(3)	Ba	2.91(1)	
O(3)	N(3) <sup>xi</sup>	3.66(1)	O(3)	N(4) <sup>v</sup>	3.599(9)				
O(3)	H(41)	2.31(1)	O(3)	H(31)	0.96(2)	O(3)	H(32)	0.96(2)	
H(31)	N(3) <sup>xi</sup>	2.72(2)	H(31)	O(4) <sup>ii</sup>	2.78(2)	H(32)	N(2) <sup>x</sup>	2.36(1)	
O(3)	H(31)	O(4) <sup>ii</sup> 101(1)	O(3)	H(31)	N(3) <sup>xi</sup> 168(1)	O(3)	H(32)	N(2) <sup>x</sup> 136.4(8)	
O(4)	O(4) <sup>j</sup>	0.9(2)	O(4)	O(3)	2.97(1)	O(4)	O(3) <sup>vii</sup>	3.10(1)	
O(4)	Ba	3.056(6)	O(4)	Ba <sup>xii</sup>	3.056(6)	O(4)	N(3) <sup>x</sup>	3.131(9)	
O(4)	N(4)	3.10(1)	O(4)	N(2)	3.32(1)	O(4)	N(2) <sup>vii</sup>	3.46(1)	
O(4)	H(41)	0.96(2)	O(4)	H(42)	0.96(2)	H(41)	N(3) <sup>x</sup>	2.53(1)	
H(41)	O(3)	2.31(1)	H(42)	N(4)	2.31(1)				
O(4)	H(41)	O(3)	O(4)	H(41)	N(3) <sup>x</sup> 126(1)	O(4)	H(42)	N(4)	138.7(8)

Note. Numbers in parentheses are estimated standard deviations in the least significant digits. Symmetry codes are given in the footnote to Table I.

TABLE III  
 ANGLES BETWEEN LEAST SQUARES PLANES THROUGH THE ATOMS OF THE  
 NITROPRUSSIDE ION

1	$d(\text{\AA})$	2	$d(\text{\AA})$	3	$d(\text{\AA})$
Fe	0.001(1)	Fe	-0.001 (1)	C(3)	0.000(2)
O(1)	0.095(4)	O(1)	0.095(4)	C(4)	0.000(2)
N(1)	0.037(1)	N(1)	0.037(1)	C(3) <sup>i</sup>	0.000(2)
N(2)	0.075(2)	N(2)	0.075(2)	C(4) <sup>i</sup>	0.000(2)
C(2)	0.022(2)	C(2)	0.022(2)		
N(3) <sup>i</sup>	-0.037(2)	N(4) <sup>i</sup>	-0.044(2)		
N(4)	-0.044(2)	N(3)	-0.037(2)		
C(3) <sup>i</sup>	-0.025(2)	C(4) <sup>i</sup>	-0.018(2)		
C(4)	-0.018(2)	C(3)	-0.025(2)		
4	$d(\text{\AA})$	5	$d(\text{\AA})$	Planes	Angle (°)
C(3)	0.048(2)	N(3)	0.000(2)	1-2	90.0
C(4)	0.071(2)	N(4)	0.000(2)	1-3	90.5
C(3) <sup>i</sup>	0.048(2)	N(3) <sup>i</sup>	0.000(2)	1-4	89.3
C(4) <sup>i</sup>	0.071(2)	N(4) <sup>i</sup>	0.000(2)	1-5	90.9
N(3) <sup>i</sup>	-0.052(2)			2-3	90.5
N(4) <sup>i</sup>	-0.067(2)			2-4	89.3
N(3)	-0.052(2)			2-5	90.9
N(4)	-0.067(2)			3-4	179.7
				3-5	0.5
				4-5	179.8

Note. Symmetry codes are given in the footnote to Table I.

thermal parameters are about 10% lower than those found in the DC-XRM for all nitroprusside atoms except Fe (25% lower).

An ORTEP drawing (20) of the content of the unit cell is shown in Fig. 1. The nitroprusside anions are piled up along the *c* axis, with the NO groups disposed in a nearly antiparallel fashion (4).

The coordination polyhedron around Ba<sup>2+</sup> can be described as a triply capped trigonal prism (tctp, c.n. 9) (23) with the OW2, N2, and OW3 atoms capping the polyhedron faces (Table IIb). Two of the water molecules (W2 and W3) are coordinated to a single cation, while the third one (W4) is shared between such cations.

The occupational disorder found for W3 and W4 water molecules at room temperature renders difficult an unambiguous description of the hydrogen bonding network.

Nevertheless, selected distances and angles concerning water molecules are present in Table IIc.

### (II) Phase Transitions

When decreasing from room temperature to 77 K, additional reflections forbidden in space group *Pbcm* [ $h0l$  ( $h = 2n + 1$ );  $0kl$  ( $k = 2n + 1$ ): 701, 709, 307, 507, 038, 058, 071, 075, 095, 0 11 3, 0 11 7 . . .] appeared. This observation prompted a study on the intensities of these reflections as a function of temperature. Figure 2 shows the results corresponding to the (701) reflection. Lowering temperature from 295 K, two superlattice reflections ( $7 \pm 0.5$  1) appear at about 126 K. They disappear below 108 K and simultaneously the (701) reflection, forbidden in the space group *Pbcm*, is observed. The intensity of these reflections is

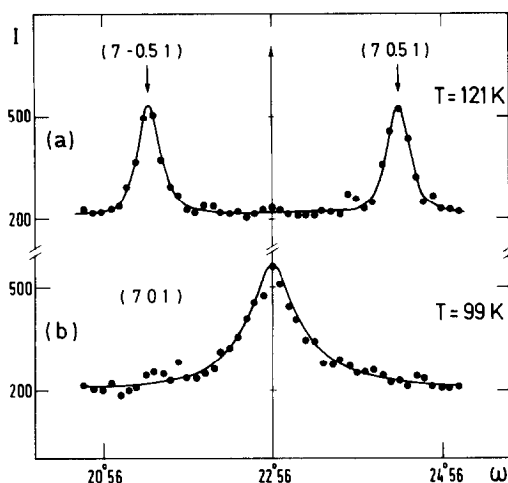


FIG. 2.  $\omega$  scans of the (7 0 1) reflection. (a) Example of the observation between 112 and 130 K. (b) Example of the observation below 112 K.

about 0.5% of the largest intensity in the unreduced data set (004). This behavior is reversible: increasing temperature from 77 K, the (701) reflection disappears above 115 K and the two superlattice reflections are only observed between 115 and 133 K. These results evidence two structural transitions for the barium nitroprusside at 112(4) and 130(3) K.

Recent DSC and  $^{14}\text{N}$ -NQR experiments on powder or single crystal samples of  $\text{BaNp}$  show three phase transitions which confirm our results (DSC: 115, 128 and 231 K (13),  $^{14}\text{N}$ -NQR: 118, 131, and 233 K (14)). To characterize the third anomaly at about 231 K another study by neutron diffraction was performed, however, no indication of the anomaly in reciprocal space were observed. It is likely that the background increase due to the diffuse scattering of disordered H atoms may have prevented the detection of eventual superlattice peaks.

### Acknowledgments

We thank Dr. Rigotti for suggesting this work and Dr. Aymonino and Dr. Piro for critical reading of the manuscript.

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