Structure of Barium Nitroprusside Trihydrate below the 233-K Phase Transition, Using Neutron Diffraction Data

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The crystal structure of barium nitroprusside trihydrate, $Ba[Fe(CN)_5NO] \cdot 3H_2O$, at 140 K temperature and its differences with the room-temperature structure are reported. It has been determined using neutron diffraction data [$F(000) = 418$ fm, $D_x = 2.13$ g cm^{-3}, $\mu = 0.6$ cm^{-1} (evaluated), space group $Pca2_1$ (29), orthorhombic, $Z = 4$, $a = 18.933(16)$, $b = 7.646(8)$, $c = 8.640(7)$ Å, $V = 1250(4)$ Å^3]. A final R-factor of 0.049 was obtained using 1094 observed structure factors. A rearrangement of water molecules occurs at the 233-K phase transition involving the loss of the symmetry m of the space group $Pcam$ of the high-temperature structure with a rotation of 6.5° of the nitroprusside ion around the [1 0 0] direction. A positional disorder is found for only one water molecule. Possible hydrogen bonds are analyzed.   © 1992 Academic Press, Inc.

Introduction

The importance of barium nitroprusside (BaNP) derives from several physical properties:

—BaNP belongs to a nitroprusside family for which long-living electronic metastable states of the anion are produced by laser irradiation at low temperatures (*1*).

—Its crystal packing is an excellent system to study correlation effects (Davydov splitting) due to strongly polar optic modes (*2, 3*) and also the coupling of IR radiation

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to longitudinal optic (LO) vibrations associated with these modes (4).

—BaNP crystals undergo three phase transitions when going from room temperature to 77 K (5–8).

Several cristallographic and spectroscopic studies on (BaNP) have been performed using X-ray (9–12) and neutron diffraction (5), as well as IR (6, 13), P-NMR (14), DSC (15), DTA (6), and ^{14}N-NQR (7, 8) spectroscopy.

DTA (6) and ^{14}N-NQR (7) experiments detected three phase transitions (DTA, 233.4, 130.2, and 118.0 K; ^{14}N-NQR, 233, 131, and 118 K) but none were observed in the DSC (15) study. Whilst DTA (6) results suggested three second-order transitions, ^{14}N-NQR (7) spectroscopy has been interpreted in terms of a weak first-order transition at 131 K and a pseudo-second-order, or very weak first-order transition, at 118 K.

Previous neutron diffraction studies (5) put into evidence the two structural phase transitions at 130(3) and 112(4) K. The behavior of selected reflections as a function of temperature was analyzed in the range between 295 and 77 K, however, for the high-temperature transition (233 K) no indication of anomalies in reciprocal space could be observed. At intermediate temperatures between the two transitions detected, the appearance of commensurate superlattice reflections suggested a duplication of the crystal parameter $a = 18.933$ Å. Below 112 K, additional reflections, forbidden in the room-temperature space group, were observed, and the superlattice reflections disappeared. The unsatisfactory results concerning the positioning of water molecules in the room-temperature structure suggested that phase transitions might be associated to displacements of these molecules.

We have undertaken the neutron diffraction study of BaNP at 140 K in an attempt to determine the structural changes produced by the first phase transition and to

provide a basis to study the other ones. We report here the crystal structure at 140 K and its differences with the room-temperature structure.

Experimental

A complete neutron diffraction data set was obtained at 140(3) K from a fragment (approximate dimensions 1.8 × 4.3 × 4.4 mm) of the same crystal studied at 295 K (5), employing the four-circle diffractometer 5C2 (P110, $\lambda = 0.831$ Å) at the Orphée reactor (CEN Saclay). The low temperature was attained cooling the specimen within a closed-cycle refrigerator. Unit-cell parameters and orientation matrix for data collection were determined from the refinement of 18 centered reflections in the range $25° < 2\theta < 52°$. A contraction of the a cell parameter was observed with a ratio of 0.976, while b and c remained constant within experimental errors. Reflection intensities were measured using the ω-scan mode (1.5 to 2 sec/step, 35 steps) for $3° < 2\theta < 75°$ and the $\omega/2\theta$-scan (1.5 sec/step, 35 steps) for $75° < 2\theta < 85°$, covering the Miller index ranges $0 \leq h \leq 27$, $0 \leq k \leq 11$, and $-12 \leq l \leq 14$. Both scan modes were adjusted as a function of the scattering angle to match the instrument resolution ($10 - 27\text{tg}\theta + 50\text{tg}^2\theta$). As in the room-temperature measurements, an overlap of neighboring reflections h, k, l and $h + 1, k, l$ was observed. The systematic extinctions corresponding to the space group $Pca2_1$ (which are the same as those of its supergroup $Pbcm$) were strictly respected.

The intensities of two reference reflections (0 6 6 and 12 0 0), monitored every 100 measured reflections, were essentially constant throughout the data collection period (12 days). Integrated reflection intensities were determined from the scans by profile analysis. Of 4856 measured reflections 2202 were independent ($R_{sym} = \Sigma$

$\||F_O| - F_{Oav}\|/\Sigma|F_O| = 0.007)$ and 1094, (having $|F|^2 > 5 \sigma(|F|^2)$, were used in the calculations. Despite the small absorption effects (evaluated coefficient $\mu = 0.6$ cm^{-1}), absorption corrections were applied by numerical methods given the zone faces $\langle 1\ 0\ 0 \rangle$, $\langle 0\ 1\ 0 \rangle$, $\langle 0\ 0\ 1 \rangle$ (minimum/maximum transmission factors of 0.87/0.76).

Structure Solution and Refinements

The first attempts to determine the BaNP structure at 140 K were performed in the space group *Pbcm* of BaNP at 295 K. Water molecules were placed from a difference Fourier map phased with the refined positions and isotropic thermal parameters of all the atoms, not belonging to water molecules. Contrary to the situation at room temperature, no splitting of OW3 was observed at 140 K. Full-matrix least-squares refinement of 121 parameters (anisotropic thermal parameters for all atoms) based on $|F|$ values converged to unsatisfactory agreement factors, $R = \Sigma\||F_O| - |F_C|\|/\Sigma|F_O| = 0.10$ and $R_w = [\Sigma\omega(|F_O| - |F_C|)^2/\Sigma\omega|F_O|^2]^{0.5} = 0.15$, with high thermal parameters for the hydrogen atoms. Consequently, the structural study was restarted in the subgroup *Pca2*$_1$.

Atomic positions of BaNP at 295 K, extended to the noncentric group *Pca2*$_1$, were used as starting parameters for the refinements. The model consisted of one nitroprusside ion, one Ba atom, and three water molecules, of which two were disordered over two sites (W3 and W4). High correlations obliged us to begin refinements with O–H and H–H distances restrained to 0.95 and 1.55 Å, respectively (estimated e.s.d 0.02 Å); these restrictions were gradually relaxed as refinement progressed. A small dumping factor was applied for the same reason. During the first cycles, occupation factors of the splitted W3 and W4 water molecules were refined. Only anisotropic temperature factors for the nitrogen atom of

the cyanides, the oxygen of the nitrosyl, and the water molecule W2 atoms were included. The relatively small $\||F_O| - |F_C|\|$ differences for strong reflections in the final cycles of structure refinement, including an empirical isotropic extinction parameter (max. correction: 5% on $|F|$ values), indicated that no correction for anisotropic extinction effects were required. The final full-matrix least-squares refinement of 147 parameters, based on $|F|$ values, and with weights $\omega = 1/(\sigma^2(|F_O|) + 0.0054 |F_O|^2)$, converged to $R = 0.049$, and $R_w = 0.066$ ($s = [(\Sigma\omega(|F_O| - |F_C|)^2/(N_O - N_V)]^{0.5} = 0.84$). From a total of 1094 reflections used in the refinement, 35 reflections remained in the last cycle with $\||F_O| - |F_C|\|/\sigma(F_O) > 2$. The absolute value of the largest residual peak was smaller than 0.07 of a removed N peak, used as a reference. The neutron scattering lengths were taken from the "International Tables for X-ray Crystallography" (1974) (*16*).

The results unambiguously show, in comparison with previous results (*5*):

—only one position for the W3 molecule,

—a shortening of the distance between nonequally occupied positions of the two oxygen atoms (O4 and O5) of the divided W4 molecule,

—one position (occupation factor 1) for one of the hydrogen (H41) bonded to O4/O5 (the thermal factor *U* does not suggest splitting)

—different occupation factors of the other hydrogen atoms bonded to O4/O5 (H42 and H51).

Final atomic parameters are presented in Table I. To compare the positional parameters with those of the room temperature structure (*5*), (x, y, z) should be read as ($-y + 1$, x, z).

Computer used: MICROVAX II. Programs: SHELX76 (*17*), SYBYL(*18*), ORTEP II (*19*)

Discussion

In order to compare the differences between the structures of BaNP at 295 and 140 K, we show in Table II selected bond distances and angles at both temperatures.

The W3 and W4 sites in the high-temperature form are statistically disordered about a plane and a symmetry center, respectively, suggesting the presence of two enantiomorphous structures in the crystal, distinct only for W3 and W4 positions. In the 140-K form, the significant changes in water molecules occupancy, together with the shift of their positional parameters, clearly show that the crystal undergoes a structural modification. A rearrangement of water molecules is produced at the 233-K transition that involves the loss of the symmetry plane m of the space group $Pcam$ of the high-temperature structure. A small rotation of the W2 molecule is observed, the W3 molecule occupies only one site with H31 located on the pseudo-special position m and the oxygen atom of W4 molecule is split (O4 and O5), although H41 occupies only one position.

The most outstanding consequence of the phase transition is a rotation of 6.5° of the nitroprusside anions around an axis passing through the Fe atom and parallel to the [1 0 0] direction (Fig. 1). This rotation implies also the breaking of the cristallographic

TABLE I

FINAL ATOMIC COORDINATES, OCCUPATION FACTORS, AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS FOR $Ba_2[Fe(CN)_5NO] \cdot 3H_2O$

	x	y	z	U_{eq}/U_{Iso}	s.o.f
BA	0.3972(2)	0.9281(4)	0.25	0.008(0)*	1.0
FE	0.6621(1)	0.5814(2)	0.2495(4)	0.007(0)*	1.0
O1	0.8090(2)	0.5453(4)	0.2497(5)	0.026(2)	1.0
N1	0.7499(1)	0.5571(3)	0.2509(4)	0.012(0)*	1.0
N2	0.5010(1)	0.6515(3)	0.2412(4)	0.024(2)	1.0
N3	0.6291(2)	0.2888(4)	0.4876(4)	0.029(2)	1.0
N4	0.6555(2)	0.8514(4)	0.5155(4)	0.018(2)	1.0
N5	0.6609(2)	0.8745(3)	0.0045(3)	0.025(2)	1.0
N6	0.6354(2)	0.3066(3)	−0.0049(4)	0.008(2)	1.0
C2	0.5611(2)	0.6217(3)	0.2431(5)	0.011(0)*	1.0
C3	0.6409(2)	0.4000(4)	0.4004(4)	0.011(1)*	1.0
C4	0.6585(2)	0.7502(4)	0.4147(4)	0.010(0)*	1.0
C5	0.6644(2)	0.7674(4)	0.0969(4)	0.012(1)*	1.0
C6	0.6464(2)	0.4099(4)	0.0901(4)	0.012(1)*	1.0
O2	0.2530(2)	0.8867(4)	0.2477(5)	0.021(2)	1.0
H1	0.2229(4)	0.8788(5)	0.3336(5)	0.043(2)	1.0
H2	0.2267(4)	0.9316(5)	0.1624(5)	0.034(2)	1.0
O3	0.4763(3)	0.2489(5)	0.2883(5)	0.033(1)*	1.0
H31	0.5073(5)	0.2550(5)	0.3703(5)	0.064(1)*	1.0
H32	0.4687(4)	0.3674(5)	0.2677(5)	0.048(1)*	1.0
O4	0.5167(3)	0.0234(5)	0.0398(5)	0.016(1)*	0.7
H41	0.5204(5)	0.1338(5)	0.0877(5)	0.053(1)*	1.0
H42	0.5558(5)	−0.0410(5)	0.0774(5)	0.043(1)*	0.7
O5	0.4982(5)	0.0448(5)	0.0019(5)	0.021(1)*	0.3
H51	0.4641(5)	0.1176(6)	−0.0313(6)	0.047(1)*	0.3

Note. Starred atoms were refined isotropically.

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33}).$$

symmetry m which was respected by the nitroprusside ion in the 295-K phase. This loss of symmetry was also detected by ^{14}N-NQR (*8*) spectroscopy: at 233 K the number
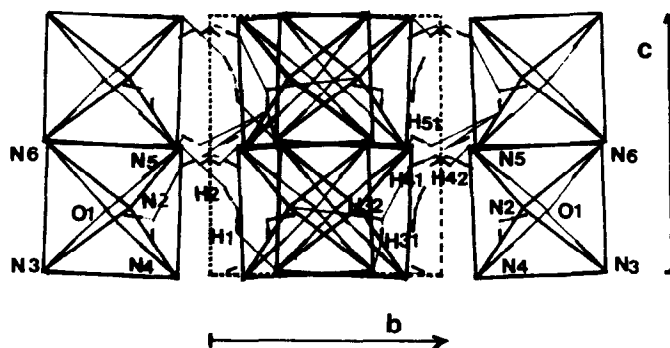

FIG. 1. SYBYL (*18*) view of the nitroprusside anion packing along the *a* axis with the water molecules contacts. It can be seen the ±6.5° rotation of the anions around the [1 0 0] direction. The unit cell is represented by dots–lines and the water contacts and O bonds with the weakest lines.

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TABLE II

Selected Bond Distances (Å) and Angles (°) in BaNP at 140 K (First Column), and in BaNP at Room Temperature (Second Column) (5), without Correction for Thermal Motion According to the Riding Model

		Water molecules			
O(2)–H(1)	0.937(7)	0.906(6)	O(2)–H(2)	0.953(6)	0.906(6)
H(1)–H(2)	1.535(6)	1.416(9)	O(2)–N(3)^i	3.406(5)	3.443(4)
H(1)–N(3)^i	2.562(7)	2.610(9)	O(2)–N(4)^{ii}	3.574(5)	3.548(4)
H(1)–N(4)^{ii}	2.890(6)	2.903(9)	O(2)–N(5)^{ii}	3.285(5)	3.443(4)
H(2)–N(5)^{ii}	2.369(6)	2.610(9)	O(2)–N(6)^i	3.450(5)	3.548(4)
H(2)–N(6)^i	2.897(6)	2.903(9)	O(2)–Ba	2.748(5)	2.771(5)
H(1)–O(2)–H(2)	108.5(6)	102.4(7)	O(2)–H(1)–N(4)^{ii}	130.8(4)	129(1)
O(2)–H(2)–N(5)^{ii}	161.0(4)	153(1)	O(2)–H(1)–N(3)^i	149.8(4)	153(1)
O(2)–H(2)–N(6)^i	118.1(4)	129(1)	N(3)^i–O(2)–N(5)^{ii}	104.1(2)	103.7(1)
N(3)^i–O(2)–N(6)^i	76.8(1)	74.5(1)	N(4)^{ii}–O(2)–N(5)^{ii}	80.1(1)	79.2(1)
Ba –O(2)–H(1)	127.3(5)	123.4(5)	Ba –O(2)–H(2)	118.9(5)	123.4(5)
Ba –O(2)–N(3)^i	136.5(2)	136.7(1)	Ba –O(2)–N(5)^{ii}	117.9(1)	118.3(1)
O(3) –H(31)	0.921(9)	0.96(2)	O(3) –H(32)	0.935(6)	0.96(2)
O(3) –H(41)	2.116(7)	2.31(1)	O(3) –Ba^{iii}	2.893(6)	2.91(1)
H(31)–H(32)	1.435(8)	1.466(f)	O(3) –O(4)	2.858(6)	2.97(1)
O(3) –O(5)	2.955(6)	2.97(1)	O(3) –N(2)	3.140(5)	3.13(1)
H(32)–N(2)	2.268(5)	2.36(1)	O(3) –N(3)	3.380(7)	3.66(1)
H(31)–N(3)	2.532(9)	2.72(2)	H(31)–O(4)^{iv}	2.623(6)	2.78(2)
H(31)–O(5)^{iv}	2.561(6)	2.78(2)	O(3) –O(4)^{iv}	3.012(6)	3.103(9)
O(3) –O(5)^{iv}	2.946(6)	3.103(9)			
H(31)–O(3)–H(32)	101.3(6)	106.3(f)	O(3)–H(31)–O(4)^{iv}	106.1(5)	101(1)
O(3) –H(31)–O(5)^{iv}	105.7(5)	104(1)	O(3)–H(31)–N(3)	153.3(7)	168(1)
O(3) –H(32)–N(2)	155.0(7)	136.4(8)			
O(4) –H(41)	0.943(6)	0.96(1)	O(5) –H(41)	1.091(7)	1.52(2)
O(4) –H(42)	0.947(9)	0.96(2)	O(5) –H(51)	0.90(1)	0.96(2)
O(4) –Ba^{iii}	2.991(6)	2.98(1)	O(5) –Ba^{iii}	3.008(7)	3.058(9)
O(4) –Ba^i	3.011(5)	3.058(9)	O(5) –Ba^i	2.950(8)	2.98(1)
O(4) –N(2)^{iii}	3.347(5)	3.32(1)	O(5) –N(2)^i	3.235(5)	3.32(1)
O(4) –N(4)^i	3.404(7)	3.44(1)	O(5) –N(4)^i	3.02(1)	3.10(1)
O(4) –N(5)^{iii}	2.974(7)	3.10(1)	O(5) –N(5)^{iii}	3.344(9)	3.44(1)
O(4) –N(6)	3.145(6)	3.13(1)	O(5) –N(6)	3.280(9)	3.74(1)
O(4) –O(3)	2.858(6)	2.97(1)	O(5) –O(3)	2.955(6)	3.10(1)
O(4) –O(3)^v	3.012(6)	3.10(1)	O(5) –O(3)^v	2.946(6)	2.97(1)
H(41)–O(3)	2.116(7)	2.31(1)	H(51)–N(4)^i	2.31(1)	2.31(1)
H(41)–N(6)	2.669(9)	2.53(1)	H(51)–N(2)^i	2.723(6)	2.79(2)
H(42)–N(5)^{iii}	2.18(1)	2.31(1)	O(4) –O(5)	0.507(9)	0.9(2)
H(42)–N(2)^{iii}	2.934(6)	2.79(2)			
H(41)–O(4) –H(42)	104.9(8)	107(2)	H(41)–O(5) –H(51)	96.2(6)	106(1)
O(4) –H(41)–O(3)	134.7(6)	125(1)	O(5) –H(41)–O(3)	131.6(8)	125(1)
O(4) –H(41)–N(6)	111.9(7)	121(1)	O(5) –H(41)–N(6)	114.8(6)	97.8(6)
O(4) –H(42)–N(5)^{iii}	140.1(5)	138.7(8)	O(5) –H(51)–N(2)^i	117.2(8)	115(1)
O(4) –H(42)–N(2)^{iii}	107.8(6)	103(1)	O(4) –H(51)–N(4)^i	135.3(7)	138.7(8)

TABLE II—*Continued*

Fe Coordination					
Fe–N(1)	1.673(3)	1.665(3)	N(1)–O(1)	1.122(4)	1.116(5)
Fe–C(2)	1.938(4)	1.931(4)	C(2)–N(2)	1.159(4)	1.156(4)
Fe–C(3)	1.945(4)	1.932(2)	C(3)–N(3)	1.158(4)	1.148(2)
Fe–C(4)	1.926(4)	1.929(2)	C(4)–N(4)	1.166(4)	1.150(2)
Fe–C(5)	1.940(4)	1.929(2)	C(5)–N(5)	1.146(4)	1.150(2)
Fe–C(6)	1.925(4)	1.932(2)	C(6)–N(6)	1.158(4)	1.148(2)
N(1)–Fe–C(2)	177.0(2)	177.2(1)	N(1)–Fe–C(3)	97.0(2)	95.8(1)
N(1)–Fe–C(4)	96.0(2)	94.5(1)	N(1)–Fe–C(5)	93.7(2)	94.5(1)
N(1)–Fe–C(6)	94.8(2)	95.8(1)	C(2)–Fe–C(3)	85.9(2)	86.2(1)
C(2)–Fe–C(4)	83.1(2)	83.5(1)	C(2)–Fe–C(5)	83.5(2)	83.5(1)
C(3)–Fe–C(4)	88.5(2)	89.7(5)	C(3)–Fe–C(5)	169.4(2)	169.6(1)
C(3)–Fe–C(6)	87.8(1)	88.3(1)	C(4)–Fe–C(5)	90.8(2)	90.4(8)
C(4)–Fe–C(6)	169.0(2)	169.6(1)	C(5)–Fe–C(6)	91.0(2)	89.7(1)
O(1)–N(1)–Fe	178.0(3)	177.7(3)	N(2)–C(2)–Fe	177.7(2)	177.3(3)
N(3)–C(3)–Fe	178.2(3)	179.5(2)	N(4)–C(4)–Fe	179.1(3)	177.8(2)
N(5)–C(5)–Fe	175.2(3)	177.8(2)	N(6)–C(6)–Fe	178.5(4)	179.5(2)
Ba Coordination					
Ba–O(2)	2.749(5)	2.771(5)	Ba–N(2)	2.888(4)	2.889(4)
Ba–N(3)[i]	2.853(4)	2.846(2)	Ba–N(4)[vi]	2.818(4)	2.852(3)
Ba–N(5)[vii]	2.885(4)	2.852(3)	Ba–N(6)[viii]	2.844(4)	2.846(2)
Ba–O(3)[ix]	2.893(6)	2.910(1)	Ba–O(4)[ix]	2.991(6)	2.985(8)
Ba–O(5)[ix]	3.008(7)	3.056(6)	Ba–O(4)[viii]	3.008(8)	3.056(6)
Ba–O(5)[viii]	2.950(8)	2.985(8)			

Note. Symmetry codes: (i) $x - 0.5, -y + 1, z$; (ii) $x - 0.5, -y + 2, z$; (iii) $x, y - 1, z$; (iv) $-x + 1, -y, z + 0.5$; (v) $-x + 1, -y, z - 0.5$; (vi) $-x + 1, -y + 2, z - 0.5$; (vii) $-x + 1, -y + 2, z + 0.5$; (viii) $-x + 1, -y + 1, z + 0.5$; (ix) $x, y + 1, z$.

of CN sites changes from three to five. Conversely, no appreciable changes in the $[Fe(CN)_5NO]^{2-}$ octahedron are observed between both crystal structures at 140 and 295 K: superposing the Fe coordination polyhedra via a least-squares process and fixing the Fe atoms at the same position, the structures fit one another very well (root mean square distance: 0.037 Å; the largest difference is found between the oxygen atoms of nitrosyl 0.06 Å).

No significant variations in H1 · · · N4 and H2 · · · N6 distances and O2–H1 · · · N4/O2–H2 · · · N6 angles are observed. The shortening of H1 · · · N3 and H2 · · · N5 distances indicates that the contact forces between the W2 water molecule and these nitrogen atoms are strengthened. Thus W2 should be a hydrogen-bond donor having as acceptors N3 and N5 nitrogen atoms. These water molecules interconnect therefore the $[Fe(CN)_5NO]^{2-}$ octahedra along the [0 1 0] direction. W2 is not a hydrogen-bond acceptor, and its trigonal coordination is completed by the Ba cation.

The W3 water molecule is an acceptor for only one hydrogen bond, O4/O5–H41 · · · O3, which is the strongest hydrogen bond in the structure. W3 is also coordinated to the Ba cation forming a distorted tetrahedron with a mean angle of 109° and a dispersion of 20°. This molecule involves two-center hydrogen bonds with N2 (through H32) and N3 (through H31) as acceptors, but in the
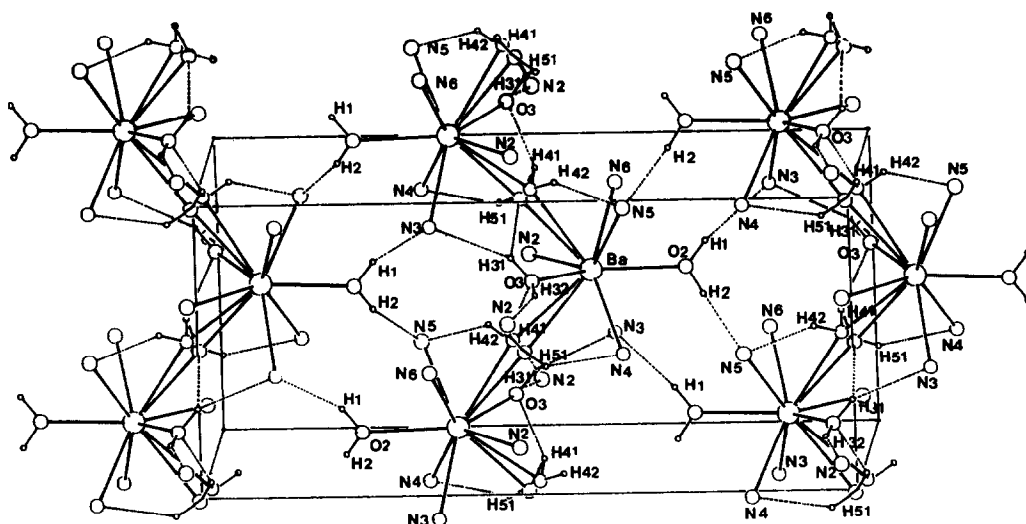
FIG. 2. ORTEP (*19*) drawing showing chains of the Ba polyhedra with the possible hydrogen bonds..

neighborhood of H31 are also located the O4/O5 atoms suggesting a bifurcated three-center hydrogen bond (sum of O3–H31 · · · N3, O3–H31 · · · O4/O5 and O4/O5–H31 · · · N3 angles of 350.4°/346.1°).

Assuming the existence of O3–H31 · · · O4/O5 bonds, the water molecule W4/W5 would have an unusual penta-coordination with three electron-acceptor neighbors. However, considering the two-coordination for the lone-pairs of W4/W5 (only with the two Ba cations), this water molecule can be reclassified under a very distorted tetrahedral coordination [mean angle 108(27)°/104(32)°]. The increase of H41 · · · N6 and H42 · · · N2 distances and the decreasing of O4–H41 · · · N4 and O4–H42 · · · N2 angles suggest that W4/W5 forms 2 two-center hydrogen bonds: O4–H41 · · · O3 and O4–H42 · · · N5/O5–H51 · · · N4.

By means of the O3–H31 · · · O4/O5 hydrogen bonds, W3 and W4/W5 water molecules form an helix of dimers along the [0 0 1] direction. Moreover, if O3–H31 · · · O4/O5 bonds are taken as granted, an infi-

nite network of water molecules results along the same direction.

The very slight changes suffered by the coordination polyhedron around Ba (triply capped trigonal prism with OW2, OW3, and N2 atoms capping the polyhedron faces), may be explained in terms of the modifications previously described. Due to the simultaneous coordination of W4/W5 to two Ba cations, infinite chains of coordination polyhedra parallel to the [0 0 1] direction are formed, which are bonded by W2 · · · N and O3–H32 · · · N2 hydrogen bonds along the [1 0 0] and [0 1 0] direction, respectively. The other water contacts are produced within the polyhedra chains. (Fig. 2)

The phase transition at 233 K is thus characterized by positional changes of water molecules and the nitroprusside anions, with concomitant enhancement of the hydrogen-bond forces. More extensive structural studies of the other transitions are in progress at 121 and 81 K to elucidate more details of the water behavior in this peculiar system of weak hydrogen bonds.

Acknowledgments

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