

Hydrogen-Bonding System in Barium Nitroprusside 6.5-Hydrate

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The hydrogen-bond system in barium nitroprusside 6.5-hydrate, $[\text{Ba}_2(\text{H}_2\text{O})_{10}][\text{Fe}(\text{CN})_5\text{NO}]_2 \cdot 3\text{H}_2\text{O}$, has been determined by neutron diffraction on monocrystals. Results show the compound to be orthorhombic, space group $Cmc2_1$ (36), $a = 16.008(43)$, $b = 11.550(3)$, $c = 16.648(5)$ Å, $V = 3078(3)$ Å³, $Z = 4$. Refinement of the structure, using 973 observed structure factors, converged to the final R_w factor of 0.058. The 2 independent barium atoms, separated 4.60 Å, share a plane of three water molecules forming dimeric tetravalent units. The nitroprusside anions deviate from the C_4 ideal symmetry, but this deviation is less than that observed in other nitroprussides. The 10 crystallographically independent water molecules have been classified according to their coordination. Analysis of the H-bond strength, together with a comparison of the packing of the two known barium nitroprusside hydrates (3-hydrate and 6.5-hydrate), suggests that the water molecules labeled as W(1), W(7), W(8), and W(9) could be lost during the partial dehydration of 6.5-hydrate into 3-hydrate. © 1995 Academic Press, Inc.

INTRODUCTION

Various hydrates exist for many nitroprusside salts. For barium nitroprusside (BaNP: $\text{Ba}[\text{Fe}(\text{CN})_5\text{NO}]$), two hydrates are known. Crystallization from an aqueous solution of BaNP at temperatures above 290 K produces to the trihydrate (BaNP-3), whereas the 6.5-hydrate (BaNP-6.5) is obtained at lower temperatures.

Recently, DTA experiments on BaNP-6.5 in the range 320–600 K have shown that water molecules are lost at 337 and 418 K. Diminution of the sample mass after partial dehydration (8 hr at 345 K), suggested that the compound evolves to BaNP-3. IR spectra and powder X-ray diffractograms confirm that most of the product in these dehydrated samples is BaNP-3 (1).

The BaNP-3 has been extensively investigated as a consequence of interest in the long-lived electronic metastable

state of the anion produced by laser irradiation at low temperature, its characteristic crystal packing, its phase transitions, and its peculiar system of weak hydrogen bonds (2–17). The BaNP-6.5 was studied by X-ray diffraction on monocrystals by P. Klüfers and S. Haussühl (18): though no hydrogen atom position was determined, the water molecules were ordered in a system of H-bonds applying rules given by Falk and Knap (19). This hydrate is of particular interest because

—it has 10 crystallographically independent water molecules,

—the instability of the crystals in a water-unsaturated atmosphere could be related to the H-bond system,

—crystals evolve to BaNP-3,

—BaNP-6.5 also presents the long-lived electronic metastable state (9).

We have undertaken a neutron diffraction study to complete the structural knowledge of BaNP-6.5 by determining the configuration of the water molecules and the precise H-bond system.

EXPERIMENTAL AND STRUCTURE REFINEMENT

Large orange-red single crystals were obtained by evaporation of an aqueous solution of BaNP at 280 K. A crystal of size $6.6 \times 5.4 \times 4$ mm was coated with an oil film and sealed into an aluminum container. A complete neutron diffraction data set was obtained at constant temperature (280 K) employing the four-circle diffractometer 5C2 (P110, $\lambda = 0.831$ Å) at the Orphée reactor of CEN Saclay. Unit cell parameters and orientation matrix for data collection were determined from the refinement of setting angles of 23 reflections. Space group $Cmc2_1$ was verified from data collected within the range $3^\circ \leq 2\theta \leq 30^\circ$. Reflection intensities were measured for $3^\circ < 2\theta < 70^\circ$, using the ω -step scan mode, in the Miller index ranges $-22 \leq h \leq 0$; $-16 \leq k \leq 0$; $0 \leq l \leq 25$ (1.5 to 4 sec/step, 35 steps). The ω -scan range was adjusted as a function of scattering angle to match the instrument resolution ($8.5 - 28.7 \tan \theta + 46.7 \tan^2 \theta$). Two reference reflections ($0 \bar{4} 8$) and ($5 \bar{1} \bar{7}$) were monitored every 3 hr throughout

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the data collection period (4 days). Despite the precautions taken to prevent crystal decomposition, a severe linear decay of intensities of 0.38% per hour was observed. Integrated reflection intensities were determined from scans by profile analysis. For the largest scattering angles no overlap of neighbouring reflections was observed. Intensities were corrected for linear decay and for absorption using numerical methods given the crystal faces $\langle 2\ 1\ 0 \rangle$, $\langle 1\ 3\ 3 \rangle$, $\langle 3\ \bar{1}\ \bar{3} \rangle$, $\langle 2\ 1\ 0 \rangle$, $\langle 0\ 0\ 2 \rangle$, $\langle 3\ 1\ 3 \rangle$, $\langle \bar{1}\ \bar{3}\ \bar{3} \rangle$, and $\langle 0\ 0\ \bar{2} \rangle$ (evaluated coefficient $\mu = 1.04\ \text{cm}^{-1}$, minimum/maximum transmission factors 0.68/0.78). From 2553 independent reflections measured, only 973 having $|F|^2 > 3\sigma(|F|^2)$ were used in the calculations.

All hydrogen atoms were located from difference Fourier maps calculated with the X-ray structure model. There is no occupational or orientational disorder in the structure. Thermal parameters of only six atoms (N(1), N(3), N(4), N(5), O(5) and O(9)) were refined anisotropically as a consequence of the small number of observed reflections. The full matrix least-squares refinement of 179 parameters based on $|F|$ values, with weights $\omega = 1/\sigma^2(|F|)$, converged to the final $R = \sum ||F_O| - |F_C|| / \sum |F_O| = 0.062$, and $R_w = [\sum \omega(|F_O| - |F_C|)^2 / \sum \omega |F_O|^2]^{0.5} = 0.058$ ($s = [(\sum \omega(|F_O| - |F_C|)^2 / (N_O - N_V))]^{0.5} = 2.6$ and $(\Delta/\sigma)_{\text{max}} = 1.04$). The relatively small $||F_O| - |F_C||$ differences for strong reflections obtained in the final cycles, including an empirical isotropic extinction parameter (maximum correction 4% on $|F|$ values), indicated that no correction for anisotropic extinction effects was required. Only 14 reflections remained with $||F_O| - |F_C||/\sigma(F_O) > 2$. The absolute value of the largest residual peak in the last difference map was smaller than 0.09 at the peak of a removed C used as a reference. The neutron scattering lengths were taken from the *International Tables for X-Ray Crystallography* (20).

Structure refinement was performed with the SHELX76 program (21) on a VAX 4200 computer. All pictures were drawn using the ORTEP program (22).

DISCUSSION

Final atomic parameters are shown in Table 1. Positional parameters of nonhydrogen atoms compare well with those of the X-ray structure (18). The equivalent isotropic thermal parameters are about 9% lower than those found in the X-ray structure. Diminution of thermal parameters determined from neutron diffraction was also observed for the BaNP-3 (6). Bond lengths were not corrected for thermal motion; thus they may suffer from a slight artificial shortening.

1. Anions and Cations

Relevant bond distances and angles relative to nitroprusside anion (NP: $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$) and barium cations are presented in Table 2.

TABLE 1
Positional and Thermal Parameters and Occupation Factor in BaNP6.5 Hydrate

Atom	x	y	z	$U_{\text{iso}}/U_{\text{eq}}$	s.o.f
Ba(1)	0.000	0.7071(8)	0.4986(7)	0.016(1)	0.5
Ba(2)	0.000	0.3246(8)	0.4212(8)	0.022(1)	0.5
Fe	0.2584(2)	0.2546(3)	0.2429(4)	0.015(1)	1.0
N(1)	0.1496(3)	0.2475(5)	0.0900(4)	0.035(2)	1.0
N(2)	0.3536(3)	0.4478(4)	0.1540(5)	0.037(1)*	1.0
N(3)	0.3824(4)	0.0917(5)	0.1585(5)	0.044(1)*	1.0
N(4)	0.1435(4)	0.4358(5)	0.3223(5)	0.040(1)*	1.0
N(5)	0.3794(3)	0.2991(5)	0.3851(4)	0.036(1)	1.0
O	0.1738(5)	0.0756(7)	0.3203(6)	0.038(1)	1.0
N	0.2078(3)	0.1471(4)	0.2886(4)	0.021(1)	1.0
C(1)	0.1898(4)	0.2510(5)	0.1478(5)	0.021(1)	1.0
C(2)	0.3167(3)	0.3766(5)	0.1875(5)	0.018(1)	1.0
C(3)	0.3368(4)	0.1525(5)	0.1912(5)	0.025(1)	1.0
C(4)	0.1865(4)	0.3715(5)	0.2902(5)	0.024(1)	1.0
C(5)	0.3351(4)	0.2817(5)	0.3316(5)	0.022(1)	1.0
O(1)	0.1001(4)	0.4998(7)	0.5008(6)	0.028(1)	1.0
H(11)	0.154(1)	0.501(1)	0.478(1)	0.053(2)	1.0
H(12)	0.110(1)	0.476(1)	0.555(1)	0.047(2)	1.0
O(2)	0.000	0.6023(8)	0.6541(8)	0.026(1)	0.5
H(21)	0.048(1)	0.552(1)	0.663(1)	0.057(2)	1.0
O(3)	0.000	0.9349(9)	0.5686(8)	0.030(1)	0.5
H(31)	0.047(1)	0.967(1)	0.598(1)	0.052(2)	1.0
O(4)	0.000	0.5775(9)	0.3538(8)	0.033(1)	0.5
H(41)	0.047(1)	0.564(1)	0.323(1)	0.051(2)	1.0
O(5)	0.000	0.2262(9)	0.2732(7)	0.039(2)*	0.5
H(51)	0.000	0.143(1)	0.257(1)	0.058(2)	0.5
H(52)	0.000	0.272(1)	0.224(1)	0.051(2)	0.5
O(6)	0.000	0.2355(9)	0.5765(8)	0.037(2)	0.5
H(61)	0.043(1)	0.248(1)	0.606(1)	0.108(2)	1.0
O(7)	0.1616(6)	0.2361(8)	0.4700(6)	0.045(1)	1.0
H(71)	0.171(1)	0.158(1)	0.483(1)	0.074(2)	1.0
H(72)	0.205(1)	0.271(1)	0.485(1)	0.091(2)	1.0
O(8)	0.000	0.9773(9)	0.2682(8)	0.042(2)	0.5
H(81)	0.046(1)	0.944(1)	0.250(1)	0.089(2)	1.0
O(9)	0.2176(6)	0.9853(9)	0.4900(7)	0.055(2)*	1.0
H(91)	0.185(1)	0.930(1)	0.459(1)	0.068(2)	1.0
H(92)	0.202(1)	0.975(1)	0.544(1)	0.076(2)	1.0
O(10)	0.000	0.0817(10)	0.4261(9)	0.046(2)	0.5
H(101)	0.000	0.040(1)	0.473(1)	0.044(2)	0.5
H(102)	0.000	0.032(1)	0.381(1)	0.066(2)	0.5

Note. Starred atoms were refined anisotropically. $U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

All atoms of NP are in general positions. The angles O–N–Fe ($179.1(7)^\circ$) and C(2)–Fe–N ($178.5(4)^\circ$) characterize the deviation from the C_{4v} ideal symmetry of the anion. The NP is less distorted in this structure than in the sodium nitroprusside (23) and BaNP-3 (3, 6) neutron structures. The distance from the iron atom to the least-squares mean plane of the *cis* carbon atoms is $0.131(4)\ \text{\AA}$.

The two independent barium atoms lie on the crystallographic mirror plane *m*. Ba(1) coordinates four CN groups of different NP and five water molecules, Ba(2) two CN groups and seven water molecules. Distances around

TABLE 2
Environments of Cations

Fe Coordination			
Fe-N	1.677(6)	N-O	1.120(9)
Fe-C(1)	1.926(8)	C(1)-N(1)	1.160(8)
Fe-C(2)	1.927(7)	C(2)-N(2)	1.155(7)
Fe-C(3)	1.926(7)	C(3)-N(3)	1.150(8)
Fe-C(4)	1.940(7)	C(4)-N(4)	1.146(8)
Fe-C(5)	1.945(8)	C(5)-N(5)	1.156(8)
N-Fe-C(1)	94.7(3)	N-Fe-C(2)	178.5(4)
N-Fe-C(3)	93.7(3)	N-Fe-C(4)	92.6(3)
N-Fe-C(5)	94.6(3)	C(1)-Fe-C(2)	84.2(3)
C(1)-Fe-C(3)	89.4(3)	C(1)-Fe-C(4)	90.6(3)
C(1)-Fe-C(5)	170.6(3)	C(2)-Fe-C(3)	85.3(3)
C(2)-Fe-C(4)	88.4(3)	C(2)-Fe-C(5)	86.5(3)
C(3)-Fe-C(4)	173.7(3)	C(3)-Fe-C(5)	91.5(3)
C(4)-Fe-C(5)	87.4(3)		
O-N-Fe	179.1(7)	N(1)-C(1)-Fe	178.7(6)
N(2)-C(2)-Fe	178.1(5)	N(3)-C(3)-Fe	178.3(6)
N(4)-C(4)-Fe	175.6(7)	N(5)-C(5)-Fe	178.5(6)

Ba(1) Coordination			
Ba(1)-O(1)	2.88(1)	Ba(1)-O(4)	2.84(2)
Ba(1)-O(2)	2.86(2)	Ba(1)-N(1) ⁱ	2.89(1)
Ba(1)-O(3)	2.88(1)	Ba(1)-N(5) ⁱⁱ	2.90(1)

Ba(2) Coordination			
Ba(2)-O(1)	2.90(1)	Ba(2)-O(4)	3.13(2)
Ba(2)-O(5)	2.71(2)	Ba(2)-O(6)	2.78(2)
Ba(2)-O(7)	2.90(1)	Ba(2)-O(10)	2.81(2)
Ba(2)-N(4)	3.11(1)		

Note. Distances in Å occurring twice by *m* crystallographic plane are printed in bold type. Superscripts should be interpreted as follows:

ⁱ $x, \bar{y}, z + \frac{1}{2}$;

ⁱⁱ $\bar{x} + \frac{1}{2}, y + \frac{1}{2}, z$.

Ba(2) are more dispersed. W4, W1, and its mirror related W1' are shared by the two cations; dimeric tetravalent units, with Ba(1)-Ba(2) distance 4.60 Å, are so formed (Fig. 1).

II. Water Structure and Hydrogen Bonds

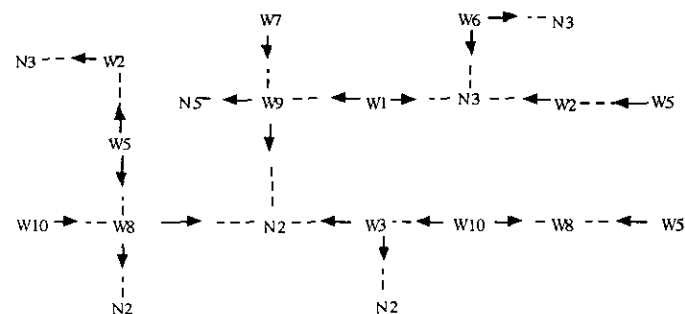
Ten water molecules are crystallographically inequivalent. Seven of these occupy sites of C_s symmetry (mirror planes), and the remaining three sites C_1 (no symmetry). In two of the seven cases C_s , the mirror plane contains the water molecule (m_{\parallel}); in the other five, it is perpendicular to the water plane (m_{\perp}). Five water molecules are coordinated to a single cation, three are shared between Ba(1) and Ba(2), and the final two are not coordinated to barium atoms. Table 3 presents the 10 molecules classified according to the types defined by Ferraris and Franchini-Angela (24). W7 was included in class 1 despite being a donor of only one hydrogen (in all classes of FF classification (24) expanded by Chiari and Ferraris (25), each of the two hydrogens forms H-bonds).

Almost all the values in Table 3 are within the range of those that characterize the H-bonds as a function of type of acceptor as presented by Chiari and Ferraris (25, 26). The large thermal parameters observed for some hydrogen atoms may be associated to a weakness or absence of hydrogen bonds (long distances $H \cdots A$ and $O \cdots A$). The shortening of O-H and H \cdots H distances (W8 and W7 molecules) is related to this effect. In W6 the distance $H \cdots H$ is abnormally short, and the long distance $H \cdots A$ (2.38 Å) is accompanied by a limit angle A-O-W-A (76°) and by a severely bent angle OW-H \cdots A (138°). This may be a consequence of a disorder, but attempts to find a split position for this molecule were not concluding.

New values can be joined to the CF (25, 26) table of bond lengths and angles arranged according to the subdivision in classes: angle A \cdots OW \cdots A for classes 1D (W10, W5), 1'J (W6), 2B (W1, W4), 2E (W8, W9), and 2H (W2, W3). The C \cdots OW \cdots C angle in W8 is 6° smaller than the limit of the class 2E).

The minimum value of repulsive contact is found between W1 and W2 (distance $H(12) \cdots H(21)$: 2.24 Å).

Fig. 2a shows the infinite network of H-bonds, schematized below (W4 is not involved):



III. Packing Description

The structure can be described as formed by planes normal to the [100] direction, containing alternately nitroprusside anions and W9 molecules (NP-planes), then dimeric units and W8 molecules (D-planes) (Fig. 2b).

In the D-planes, the dimeric entities are stacked along the [0 1 0] direction; the distance between nearest cations of different dimers is 7.25 Å. These dimers are hydrogen bonded along [0 1 0] by W10, and along [0 0 1] by W5; these two water molecules also bond the same W8. The oxygens of W2, W3, W4, W6, and W8 (the five molecules m_{\perp}) lie on the D-planes, and, via the H-bonds, are connected to the contiguous NP-planes.

In the NP-planes the NP anions form columns parallel to the a and b axes with the NO dipoles oriented at 62° of the polar axis 2₁. The [0 1 0] NP columns are joined along [0 0 1] via the H-bonds donated by W9. This water,

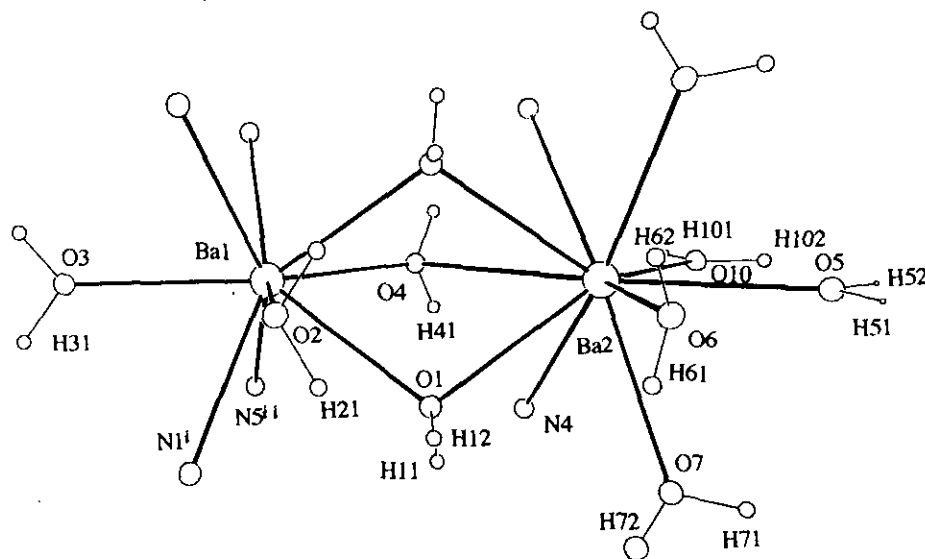


FIG. 1. Dimeric unit in BaNP6.5 hydrate. (i) $\bar{x}, \bar{y} + 1, z + \frac{1}{2}$; (ii) $\bar{x} + \frac{1}{2}, \bar{y} + \frac{1}{2}, z$.

TABLE 3
Water Molecule Structure and H-Bonds

Class	Molecule	Site symmetry	Acceptor atoms (A)	Coordinated atoms (C)	O-H	H...A	O...A	O...C	H...H	H-O-H	H-O-C	A-O-C	C-O-C A-O-A	O-H-A
1D	W5	O(5)		Ba(2)				2.71(2)	1.57(3)	108.(2)			133.(1)	
		H(51)	m_1	O(8) ⁱⁱ	0.99(2)	1.92(2)	2.88(2)				130.(1)	116.(1)	160.(2)	
	W10	O(10)		Ba(2)	0.97(2)	1.87(2)	2.8(2)	2.81(2)	1.54(3)	111.(2)	122.(1)	110.(1)	—	163.(2)
		H(101)	m_1	O(3) ⁱⁱ	0.92(2)	2.00(2)	2.92(2)				124.(1)	127.(1)	120.(1)	171.(2)
	W7	H(102)		Ba(2)	0.95(3)	1.97(3)	2.90(2)	2.90(1)	1.41(2)	105.(2)	125.(2)	113.(1)	—	162.(2)
		O(7)	1	O(9) ⁱⁱ	0.94(2)	2.14(2)	3.05(2)				123.(1)	129.(1)	—	165.(2)
1'J	W6	H(71)		Ba(2)	0.84(2)			2.78(2)	1.37(4)	106.(3)	—	—	—	—
		H(72)	m_1	N(3) ⁱⁱⁱ	0.85(2)	2.37(2)	3.07(2)				118.(1)	100.(1)	76.(1)	138.(2)
2B	W1	O(1)	1	Ba(1) Ba(2)				2.88(1) 2.90(1)	1.48(2)	106.(1)	120.(1) 109.(1)	127.(1) 119.(1)	86.(1)	
		H(11)		O(9) ^{iv}	0.94(2)	2.08(2)	2.93(2)				110.(1)	112.(1)	106.(1)	150.(2)
	W4	H(12)	m_1	Ba(1) Ba(2)	0.95(2)	1.90(2)	2.84(1)	2.84(2) 3.12(2)	1.50(3)	108.(2)	108.(1) 92.(1)	103.(1) 62.(1)	101.(1)	171.(1)
		O(4)		N(4) ^v	0.92(2)	2.14(2)	2.87(1)				125.(1)	117.(1)	106.(1)	135.(1)
2H	W2	O(2)	m_1	Ba(1) H(52) ^{viii}				2.86(2) 1.87(2)	1.53(3)	104.(2)	113.(1) 111.(1)	110.(1) 125.(1)	104.(1)	
		H(21)		N(3) ⁱⁱⁱ	0.97(2)	2.01(2)	2.93(1)						80.(1)	156.(1)
	W3	O(3)	m_1	Ba(1), H(101) ^{ix}				2.88(1) 2.00(2)	1.49(3)	101.(2)	124.(1) 100.(1)	126.(1) 96.(1)	103.(1)	
		H(31)		N(2) ^{vi}	0.97(2)	2.10(2)	3.06(1)				100.(1)	93.(1)	100.(1)	174.(1)
2E	W8	O(8)	m_1	H(102) ^{ix} H(51) ^{ix}				1.97(3) 1.92(2)	1.47(3)	113.(2)	117.(1) 114.(1)	129.(1) 93.(1)	77.(1)	
		H(81)		N(2) ^{vii}	0.89(2)	2.27(2)	3.04(1)				111.(1)	116.(1)	101.(1)	146.(1)
	W9	O(9)	1	H(11) ^{vii} H(71) ^{ix}				2.08(2) 2.14(2)	1.54(2)	107.(2)	122.(1) 111.(1)	119.(1) 116.(1)	105.(1)	
		H(91)		N(5) ^{vii}	0.97(2)	2.21(2)	3.17(1)				113.(1)	116.(1)	119.(1)	175.(1)
		H(92)		N(2) ^{vi}	0.95(2)	2.22(2)	3.06(1)				94.(1)	72.(1)	148.(1)	

Note. Bold type character indicate that atoms, angles or distances are repeated by symmetry. Class 1: one bond to the bisector of the lone pairs. Class 1': one bond to one of the lone pairs. Class 2: two bonds to the lone pairs (tetrahedral arrangement). m_1 : the crystallographic mirror plane contains the water molecules. m_1 : the mirror plane is perpendicular to the water plane. Superscripts should be interpreted as follows: (i) $\bar{x}, \bar{y} + 1, z - \frac{1}{2}$; (ii) $\bar{x}, \bar{y} - 1, z$; (iii) $\bar{x} + \frac{1}{2}, \bar{y} + \frac{1}{2}, z + \frac{1}{2}$; (iv) $\bar{x} + \frac{1}{2}, \bar{y} + \frac{1}{2}, z$; (v) \bar{x}, \bar{y}, z ; (vi) $\bar{x} + \frac{1}{2}, \bar{y} - \frac{1}{2}, z + \frac{1}{2}$; (vii) $\bar{x} + \frac{1}{2}, \bar{y} + \frac{1}{2}, z$; (viii) $\bar{x}, \bar{y} + 1, z + \frac{1}{2}$; (ix) $\bar{x}, \bar{y} + 1, z$.

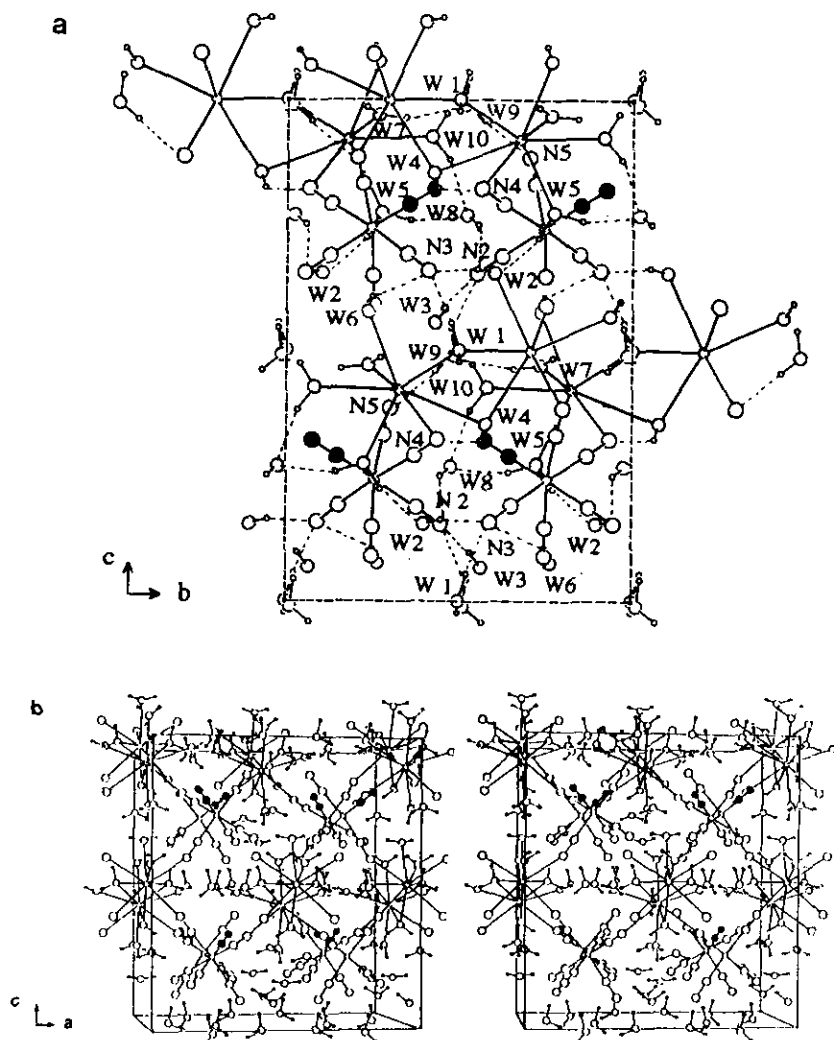


FIG. 2. (a) Packing projection of the BaNP6.5 hydrate along $[1\ 0\ 0]$. The dotted lines represent hydrogen bonds. (b) ORTEP stereoscopic view of the structure along $[0\ 1\ 0]$. Atoms of the NO groups are represented in black.

being acceptor for W1 and W7, participates also to link the NP and D-planes. The three water molecules, W1, W7, and W9, are placed into channel cavities parallel to $[0\ 1\ 0]$ bounded by columns of NP and of barium atoms.

CONCLUDING REMARK

In the BaNP-3,³ the barium atoms coordinate five nitrogen atoms of different NP and four water molecules, with one water shared by two cations (2, 3, 6, 10, 14, 16). So the coordination polyhedra are connected in infinite chains parallel to the c' axis of the crystal, intercepting

the (a', b') plane in $(0, 0)$ and $(0, 0.5)$. The NP anions are arranged, also along the c' direction, in double intercalated chains with the NO dipoles oriented in an antiparallel fashion. These double chains pass, in the (a', b') plane, through $(0.45, 0.25)$ and $(0.55, 0.75)$ points.

In crystals of BaNP-6.5, the elimination of W9, W7, and W1, together with W8 (water molecule weakly bonded and not coordinated to cations), would lead to a compound of the same chemical composition and packing as BaNP-3. A rotation of NP anions, such that the NO dipoles orient parallel to c the axis and antiparallel to the b direction, and a small translation in the c direction would give the double intercalated chains observed in BaNP-3 (the NP displacement being possible in the empty $[0\ 1\ 0]$ channels). Furthermore, after the loss of the two W1 only one water molecule (W4) would remain between Ba(1) and

³ Crystallographic data at room temperature: space group $Pbcm$, crystal parameters $a' = 7.620(7)$, $b' = 19.394(17)$, $c' = 8.631(8)$ Å.

Ba(2). If W10 were also coordinated to the neighboring Ba(1) in the [0 1 0] direction, infinite chains of cation coordination polyhedra could be so formed with four coordinated water molecules around each cation. This analysis leads to an equivalence of the crystal axes of both hydrates: a , b , c of BaNP-6.5 as compared to $2a'$, c' and b' of BaNP-3.

Lists of observed and calculated structure factors and anisotropic thermal parameters have been deposited as supplementary material.

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