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Neutron Diffraction Study on Single Crystals of Strontium Pentacyanonitrosyl Ferrate(II) Tetrahydrate (Strontium Nitroprusside Tetrahydrate)[1]

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The crystal structure of strontium nitroprusside tetrahydrate, $Sr[Fe(CN)_5NO] \cdot 4H_2O$, has been redetermined by neutron diffraction measurements on single crystals at room temperature (monoclinic, space group *C*2/*m*, (No. 12) $a = 20.07(2)$, $b = 7.591(8)$, $c = 8.397(9)$ Å, $\beta = 98.7(5)°$, $V = 1260(4)$ Å^3). Refinements of the structure using 867 observed structure factors converged to the final $R = 0.064$. Results confirm the oxygen–water disorder found by the X-ray diffraction study; i.e., the oxygen atom of one water molecule is located on two different sites, corresponding to general positions within the asymmetric unit, with occupation factors of 2/3 and 1/3. An infinie hydrogen bond network links the strontium coordination polyhedra along the [0 1 0] direction. All sites occupied by hydrogen atoms of the only water molecule not coordinated to a strontium ion, and acceptors of hydrogen bonds in this network, could not be determined. This fact suggests that this water molecule is affected by structural disorder and that it has free unabridged hydrogens. The water molecule, which does not belong to the hydrogen-bond network, is disordered on the symmetry plane *m*. Previous assignments of water IR absorption bands have been revised and improved on the basis of the new structural data. © 1996 Academic Press, Inc.

INTRODUCTION

One of the most interesting properties of the nitrosylpentacyanoferrate$^{(2-)}$ anion ($[Fe(CN)_5NO]^{2-}$) (1–4 and references therein) is, perhaps, the recently discovered possibility of exciting the anion to metastable electronic states. Also of interest is the bonding of water molecules, including hydrogen bonding, although weak, in the hydrated salts containing that anion. Crystallographic studies by neutron and X-ray diffraction are necessary to interpret the structural transformations suffered by crystals of these compounds after dehydration or phase transitions, all certainly related to the hydrogen-bonding system. The most studied of these are barium nitroprusside 3 and 6.5 hydrates. Crystallographic results about the water behavior show the structural importance of these molecules and their responsibility in the phase transitions observed (5, 6, and references therein).

Another system which is worth analyzing is strontium nitroprusside and its hydrates. For this salt three hydrates are known. Crystallization at room temperature leads to strontium nitroprusside tetrahydrate; lower hydrates are produced by controlled thermal (DTA; the dihydrate, at 72°C and the monohydrate, at 138°C) and P_4O_{10}-driven dehydration (see (7) and references therein to the obtainment of a mosaic of alligned microcrystals of the dihydrate which allowed a complete X-ray structure determination). X-ray crystallographic results show that the three hydrates have in common a water molecule coordinated to the strontium ion (7). As with barium nitroprusside 3 hydrate (8), strontium nitroprusside tetrahydrate ($Sr[Fe(CN)_5NO] \cdot 4H_2O$, SrNP) undergoes phase transitions when going from room temperature to 77° K (197, 192, 182, and 174° K) (9). The structure of this hydrate has been recently redetermined by X-ray diffraction (10). A positional disorder was observed for the oxygens of two water molecules and was solved on the basis of chemical

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criteria: two different sites in general positions, with occupation factors 2/3 and 1/3, are occupied by these molecules (W3, W4). Another water molecule, W1, with its environment involved in the disorder, has one hydrogen atom that appears to be free (11). It is to be noted that the motions of individual water molecules could not be discerned in the proton NMR relaxation measurements (11).

We have undertaken the neutron diffraction study of SrNP at room temperature in an attempt to confirm the disorder found by X-ray diffraction studies, to verify the existence of a hydrogen-bond network in SrNP (from the hydrogen positions) and also to provide a base for further studies about the phase transitions.

The packing of this structure and the two different strontium coordination polyhedra were amply described as a result of the X-ray diffraction studies (12, 7, 10).

EXPERIMENTAL AND STRUCTURE REFINEMENT

Large brown-red crystals were obtained by evaporation of an aqueous solution of SrNP at room temperature. A crystal of size $2.1 \times 3.5 \times 1.8$ mm^3 was sealed into an aluminum container. A complete neutron diffraction data set was obtained at constant temperature (298 K) employing the new four-circle diffractometer (6T2 channel, $\lambda = 1.611(5)$ 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 18 reflections. Space group $C2/m$ was verified from data collected within the $3° \leq 2\theta \leq 60°$ range. Reflection intensities were measured for $3° < 2\theta < 45°$ using the ω-step scan mode, $45° < 2\theta < 80°$ using the ω/θ-step scan mode, and $80° < 2\theta < 135°$ using the $\omega/2\theta$-step scan mode, in the Miller index ranges $-19 \leq h \leq 13$, $-8 \leq k \leq 8$, and $-7 \leq l \leq 9$ (2 to 5 sec/step, 35 steps, unique set). The ω-scan range was adjusted as a function of scattering angle to match the instrument resolution ($4 - 10\,\mathrm{tg}\theta + 16\,\mathrm{tg}^2\theta$). The intensities of two reference reflections (8 0 0) and (2 0 3), monitored every 100 measures, were essentially constant throughout the data collection period (5.3 days). Integrated reflection intensities were determined from scans by profile analysis. For the largest scattering angles no overlap of neighboring reflections was observed. Intensities were corrected for absorption using numerical methods, given the crystal faces $\langle 0\,0\,1\rangle$, $\langle 0\,0\,-1\rangle$, $\langle 2\,0\,0\rangle$, $\langle -2\,0\,0\rangle$, $\langle 0\,2\,0\rangle$, and $\langle 0\,-2\,0\rangle$ (measured absorption coefficient $\mu = 1.56$ cm^{-1}, minimum/maximum transmision factors (0.62/0.78). Of 2004 measured reflections, 1010 were independent ($R_{\mathrm{sym}} = \Sigma\| F_{\mathrm{O}}| - |F_{\mathrm{Oav}}\|/\Sigma|F_{\mathrm{O}}| = 0.017$) and 867 (having $|F|^2 > 3\,\sigma(|F|^2)$ were used in the refinements.

The water oxygen positions were determined from a difference Fourier map phased with the refined positions and isotropic thermal parameters of all atoms of the X-ray model, not belonging to water molecules. Subsequent difference maps gave positions of hydrogen atoms. As a consequence of disorder, O–H and H–H distances were restrained to 0.95 and 1.55 Å (e.s.d. 0.04 Å) during the refinements. The hydrogen occupation factors (o.f.) were estimated from the peak intensities on the difference Fourier maps, and later, adjusted to have homogeneous temperature factors. The full matrix least-squares refinement of 152 parameters based on $|F|$ values, with weights $\omega = 1/[\sigma^2(|F|) + 0.00023F^2]$, converged to the final $R = \Sigma\|F_{\mathrm{O}}| - |F_{\mathrm{C}}\|/\Sigma|F_{\mathrm{O}}| = 0.065$, and $R_\omega = [\Sigma\omega(|F_{\mathrm{O}}| - |F_{\mathrm{C}}|)^2/\Sigma\omega|F_{\mathrm{O}}|^2]^{0.5} = 0.073$ ($s = [(\Sigma\omega(|F_{\mathrm{O}}| - |F_{\mathrm{C}}|)^2/(N_{\mathrm{O}} - N_{\mathrm{V}})]^{0.5} = 3.1$ and $(\Delta/\sigma)_{\max} = 0.40$). H, Sr, and Fe atoms were refined isotropically. The relatively small $\|F_{\mathrm{O}}| - |F_{\mathrm{C}}\|$ differences for strong reflections obtained in the final cycles, including an empirical isotropic extinction parameter (max. correction: 3% on $|F|$ values), indicated that no correction for anisotropic extinction effects was required. Only 11 reflections remained with a $\|F_{\mathrm{O}}| - |F_{\mathrm{C}}\|/\sigma(F_{\mathrm{O}}) > 2.5$ There were no significant trends in the data analyzed as a function of $|F_{\mathrm{O}}|$ and sin θ. The absolute value of the largest residual peak in the last difference map was smaller than 0.08 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 (13).

Structure refinement was performed with SHELX76 program (14) on a VAX 3100 computer.

DISCUSSION

Final atomic parameters are shown in Table 1. In order to compare the structures of SrNP obtained by X-ray and neutron diffraction, Table 2 presents the cation environments in both structures; no significative differences are observed between positions of nonhydrogen atoms.

All water molecules present some positional disorder.

W1, the only molecule not coordinated to a Sr^{2+} cation, has two different environments in the crystal. In site 1, W1 is H-bond acceptor of W3 and W4; in site 2, it accepts hydrogen atoms from two W3 molecules as shown in Fig. 1 and Table 3. All parameters concerning these bonds are within the ranges for H bonds, but the angle H31–O1–H41 is 7° smaller than the lower limit for a water molecule that donates the two hydrogens and coordinates to two hydrogen atoms belonging to other water molecules (77°) (6). This diminution may be caused by the fact that W1 is relatively strongly H bonded as an acceptor and that it is only a H donor to N3. It was not possible to locate all sites of the W1 hydrogen atoms. In the X-ray model, H11 and O1 are on the symmetry plane m, but in this work H11, as well as H121, were refined in general positions with o.f. equal to 0.5 and 0.33, respectively. Probably, the X-ray assigned position to H11 is an average of several hydrogen sites. The indetermination of HW1 atoms renders impossi-

TABLE 1
Final Atomic Coordinates and Equivalent Isotropic Thermal Parameters with Their Estimated Standard Deviations

Atom	x	y	z	$B_{\mathrm{iso}}/B_{\mathrm{eq}}$
Sr*	0.1328(2)	0.0	0.2946(4)	1.70(6)
Fe*	0.4109(1)	0.0	0.2208(3)	1.61(5)
O	0.5504(3)	0.0	0.2601(6)	4.0(2)
N	0.4941(2)	0.0	0.2438(3)	2.2(1)
N(1)	0.3942(1)	0.2833(3)	−0.0437(3)	3.9(1)
N(2)	0.4039(1)	0.2863(3)	0.4769(3)	4.2(1)
N(3)	0.2557(2)	0.0	0.1847(5)	4.3(2)
C(1)	0.2999(2)	0.1782(4)	0.0553(3)	2.4(1)
C(2)	0.4060(2)	0.1792(4)	0.3811(3)	2.4(1)
C(3)	0.3139(3)	0.0	0.1969(5)	2.6(2)
O(1)	0.2860(4)	0.5	0.1739(8)	5.6(3)
H(11)*	0.2764(8)	0.472(2)	0.071(2)	7.5(3)
H(121)*	0.331(1)	0.551(3)	0.188(3)	8.6(3)
O(2)	0.5038(3)	0.5	0.2415(7)	3.5(2)
H(21)*	0.4759(7)	0.462(2)	0.151(1)	5.2(2)
H(22)*	0.4779(7)	0.538(2)	0.323(1)	5.4(2)
O(3)	0.7047(4)	0.2082(9)	0.3516(8)	4.9(2)
H(31)*	0.7325(7)	0.175(2)	0.279(1)	6.4(2)
H(321)*	0.689(1)	0.100(3)	0.387(3)	7.8(3)
H(322)*	0.733(2)	0.2177(3)	0.460(2)	6.8(3)
O(4)	0.2672(6)	0.425(2)	0.476(1)	5.1(3)
H(41)*	0.279(1)	0.435(3)	0.370(2)	6.9(3)
H(421)*	0.239(2)	0.530(3)	0.483(3)	5.7(3)
H(422)*	0.245(3)	0.320(3)	0.498(4)	7.7(3)

Note. $B_{\mathrm{eq}} = 4/3 \sum_i \sum_j \beta_{ij}\mathbf{a}_i\mathbf{a}_j$. Starred atoms were refined isotropically.

ble an accurate description the W1 environment in each crystal site.

W2, coordinated to a strontium ion, has its oxygen lying on the symmetry plane m and its two hydrogens in general position (o.f., 0.5), then it is disordered on the symmetry plane. When the hydrogen atoms are refined as lying on this plane, (as H21 in the X-ray model), large thermal parameters and abnormal values of H–O2 distance and of H21–O2–H22 angle are obtained. In each one of the two possible enanthiomeric positions of W2, only one of the hydrogen atoms has short contacts (2.52 Å) with one neighboring nitrogen atom, H21 $\cdots$ N1 or H22 $\cdots$ N1′ (N1′ is mirror related with N1).

The oxygen atoms of the other water molecules, W3 and W4, are in general positions. Their o.f. values were refined to 0.66 and 0.33, respectively. The same figures have been previously obtained in refinements with X-ray data. From the analysis of chemical contacts and using this result, the existence of an infinite network of hydrogen bonds of periodicity three times the cell parameter b, which connects two different strontium coordination polyhedra along the [0 1 0] direction, was proposed. One each of the hydrogen atoms of W3 and W4 was found with the same o.f. of its coordinating oxygen (H31, 0.66 and H41, 0.33). The other two hydrogen atoms are disordered on two positions (H321, H322, o.f., 0.33; H421, H422, o.f., 0.165). Figure 1 details the distribution of these hydrogen atoms along of the [0 1 0] direction showing the infinite hydrogen-bond network of periodicity 3b. In one period there are four sites crystallographically independent of the eight occupied by W3 molecules, and two of the four occupied by W4 molecules. In all positions, W3 and W4 are hydrogen bond donors to W1. They are acceptors of hydrogen bonds of other neighboring W3 or W4 molecules in sites 5, 6, and 8; in the other sites, C–O–C and the corresponding O–H–A angles are out of the hydrogen bond standard values. The different environments are completed by the strontium cation forming distorted tetrahedra as shown in Table 3.

The new structural information should help in improving

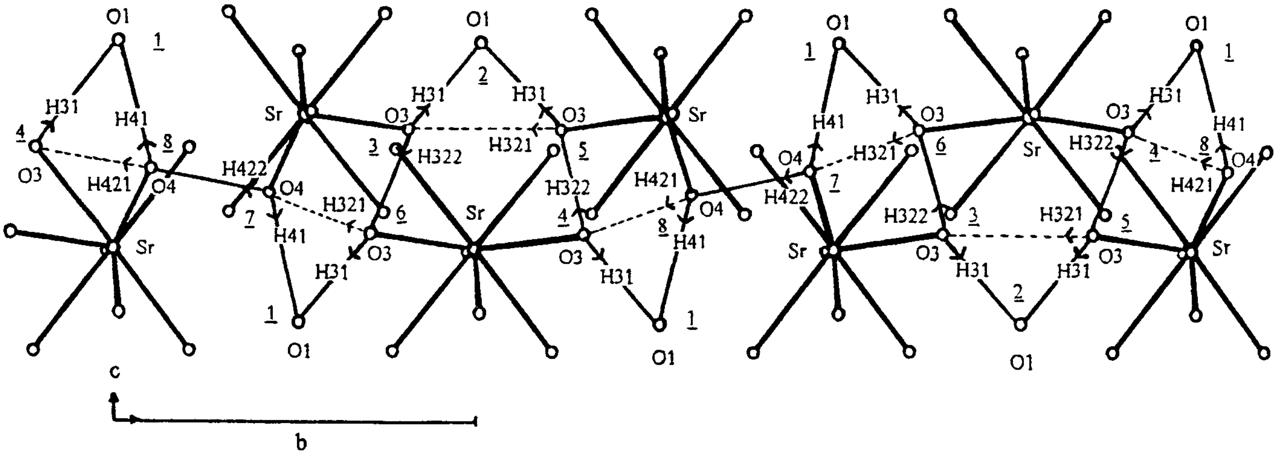

FIG. 1. Hydrogen bond network along the [0 1 0] direction. Hydrogen bonds are represented by weak lines; short contacts between water molecules with angles abnormal to allow hydrogen bonds, by dot-lines. (i) $x - 1/2, y + 1/2, z$; (ii) $-x + 1/2, -y + 1/2, -z$; (iii) $x - 1/2, -y + 1/2, z$; (iv) $x + 1/2, y + 1/2, z$; (v) $x, -y, z$; (vi) $x + 1/2, y - 1/2, z$; (vii) $-x + 3/2, -y + 1/2, -z + 1$; (viii) $-x + 1/2, -y + 1/2, -z + 1$.

TABLE 2
Cation Environments

Atom 1	Atom 2	d_{neut}	$d_{\text{X-ray}}$	Atom 1	Atom 2	d_{neut}	$d_{\text{X-ray}}$
Fe	N	1.65(1)	1.661(4)	N	O	1.12(2)	1.122(6)
Fe	**C(1)**	**1.928(9)**	**1.927(3)**	**C(1)**	**N(1)**	**1.148(9)**	**1.151(4)**
Fe	**C(2)**	**1.928(8)**	**1.928(3)**	**C(2)**	**N(2)**	**1.151(9)**	**1.143(4)**
Fe	C(3)	1.93(1)	1.933(4)	C(3)	N(3)	1.16(1)	1.150(6)
Sr	N(3)	2.77(2)	2.753(4)	Sr	O(2)	2.56(1)	2.575(4)
Sr	**N(2)$^{\text{ii}}$**	**2.70(1)**	**2.707(3)**	**Sr**	**N(1)$^{\text{i}}$**	**2.66(1)**	**2.753(4)**
Sr	**O(3)$^{\text{iii}}$**	**2.65(1)**	**2.656(4)**	**Sr**	**O(4)$^{\text{ii}}$**	**2.63(1)**	**2.646(6)**

A1	A2	A3	A1–A2–A3		A1	A2	A3	A1–A2–A3	
N	Fe	C(3)	179.2(6)	179.5(2)	**N**	**Fe**	**C(1)**	**95.0(4)**	**94.6(1)**
C(1)	Fe	C(1)$^{\text{iv}}$	89.2(1)	89.2(1)	**N**	**Fe**	**C(2)**	**94.3(4)**	**94.4(1)**
C(2)	Fe	C(2)$^{\text{iv}}$	89.9(1)	90.1(1)	**C(1)**	**Fe**	**C(2)**	**89.7(3)**	**89.6(1)**
C(1)	**Fe**	**C(3)**	**85.6(4)**	**85.8(1)**	**C(2)**	**Fe**	**C(3)**	**85.1(4)**	**85.3(1)**
C(1)	**Fe**	**C(2)$^{\text{iv}}$**	**170.8(2)**	**171.0(1)**	**N(1)**	**C(1)**	**Fe**	**179.2(7)**	**179.3(2)**
O	N	Fe	179.7(5)	179.5(4)	**N(2)**	**C(2)**	**Fe**	**179.7(4)**	**180.0(4)**
N(3)	C(3)	Fe	179.1(1)	179.4(4)					

Note. Distances (Å) and angles (°) occurring twice due to the crystallographic plane are printed in bold type (i) $x - 1/2, y - 1/2, z$; (ii) $x, -y, z$; (iii) $-x + 1/2, -y + 1/2, -z$; (iv) $-x + 1/2, -y + 1/2, -z + 1$.

the interpretation of the vibrational behavior of the water molecules in SrNP, already considered by Della Védova *et al.* (7) on the basis of the previous crystallographic information (12) (see also (15)).

Present results show that there are, strictly, at least 9 structurally different types of water molecules and 12 different OH bonds, a variety that, in principle, implies an unsourmountable challenge for the interpretation of crystallization water vibrational spectra. Anyway, the assignments could be improved but taking into account that the results of the present work correspond to room temperature and the reported detailed IR spectra of deuterium substituted SrNP, containing isolated H_2O, DHO, and D_2O molecules (obtained at adequate isotropic dilutions), were run at low temperature to improve definition and resolution of the bands (7). Now we know that when lowering the temperature, SrNP experiences phase changes, as mentioned above, that can bring about concomitant spectral modifications.

It is to be noted that multiplicity of stretching bands is higher in the spectra region corresponding to deuterated water molecules than in the region of nondeuterated species (8 and 5, respectively).

In fact, the spectra are not so complicated as they should be ideally because not all structural differences among water molecules are big enough to originate separated bands under the resolution reached in the low temperature spectra. This puts a limit, therefore, to the possibility of improving previous assignments (7).

The spectroscopically best defined water molecule seems to be W2 (previous W3) (7, 15), coordinated to strontium ion and with its two hydrogen atoms very weakly, if bonded at all, to a nitrogen atom each. It fulfils structural-spectroscopic correlations of Berglund *et al.* (16), Mikenda (17), and Amalvy and Aymonino (18) to a very few if any cm^{-1}. An exception is made of the O2–H22 stretching wavenumber when calculated from the H22 ⋯ N2 distance (17) (2.87 Å), because the difference between the calculated (2687 cm^{-1}) and the experimental (2650 cm^{-1}) values amounts to 37 cm^{-1} but it must be taken into account that the H22 ⋯ N2 distance is much larger due to the low O2–H22 ⋯ N2 angle (120°).

Mean $\tilde{\nu}_{\text{as}}$ and $\tilde{\nu}_{\text{s}}$ values, both for W2 (H_2O) and W2 (D_2O), agree quite well (to 1 cm^{-1}) with $\tilde{\nu}$(OH) and $\tilde{\nu}$(OD) of isolated W2 (HOD) molecules, pointing to a highly symmetric HOH structure. In spite of being practically nonhydrogen bonded, ν_{as}, $\tilde{\nu}_{\text{s}}$, and $\tilde{\delta}$ wavenumbers are distinctly lower than corresponding values for gaseous water due to the influence of the strongly polarizing Sr^{2+} cation (16).

Coordination to two hydrogen atoms (H31, H41) and a hydrogen bond to N3, although weak, should also lower wavenumbers of W1 but to slightly below those of W2, as predicted by Amalvy and Aymonino (18). $\tilde{\nu}$(O1–H121) should be therefore very similar to $\tilde{\nu}$(O2–H21) and $\tilde{\nu}$(O2–H22), all three hydrogens acting as non(hydrogen) bonded. $\tilde{\nu}$(O1–H11 ⋯ N3) should be distinctly lower. This difference does not manifest itself in the OH stretching region but apparently it occurs in the OD region.

W3 and W4 molecules are the tightest hydrogen bonded, the O47–H41 ⋯ O1 hydrogen bond being the strongest of all. O3–H321 groups seem to be free of hydrogen bond-

TABLE 3
Water Molecule Structures and H Bonds

Molecule		Site	A	C	O–H	H–A	O–A	O–C	H–H	H–O–H	H–O–C	C–O–C	O–H–A
W1	O1	1		H31^{i}				2.00(1)	1.49(6)	103(2)	123(1)	70(1)	
				H41				1.75(2)			145(1)		
	H11		N3^{ii}		0.89(2)	2.16(1)	3.00(1)				139(2)		160(1)
	H121				0.97(2)						102(2)		
	O1	2		H31^{i}				2.00(1)	1.49(6)	103(2)	123(1)	84(1)	
				H31^{iii}				2.00(1)			103(1)		
	H11		N3^{ii}		0.89(2)	2.16(1)	3.00(1)				104(1)		160(1)
	H121				0.97(2)						140(1)		
W2	O2			Sr^{iv}				2.56(1)	1.56(2)	111(1)	128(1)		
	H21		N1		0.93(1)	2.52(1)	3.42(1)				121(0		163(3)
	H22		N2		0.97(1)	2.87(1)	3.44(1)						120(3)
W3	O3	3		Sr^{iv}				2.65(1)	1.55(2)	109(1)	119(1)	140(1)	
				H321^{v}				2.38(1)			101(1)		
	H31		O1^{vi}		0.92(2)	2.00(1)	2.86(1)				109(1)		154(1)
	H322		O3^{i}		1.00(2)	1.95(2)	2.93(1)				109(1)		166(1)
	O3	4		Sr^{iv}				2.65(1)	1.55(2)	109(1)	119(1)	151(1)	
				H421^{v}				1.82(2)			90(1)		
	H31		O1^{vi}		0.92(2)	2.00(1)	2.86(1)				109(1)		154(1)
	H322		O3^{vii}		0.94(1)	1.95(2)	2.93(1)				62(5)		166(1)
	O3	5		Sr^{iv}				2.65(1)	1.45(3)	108(2)	119(1)	100(1)	
				H322^{vii}				1.95(2)			109(1)		
	H31		O1^{vi}		0.92(2)	2.00(1)	2.86(1)				127(2)		154(1)
	H321		O3^{vii}		0.94(1)	2.38(5)	3.16(0)				101(2)		141(2)
	O3	6		Sr^{iv}				2.65(1)	1.45(3)	108(2)	119(1)	100(1)	
				H322^{vii}				1.95(2)			90(1)		
	H31		O1^{vi}		0.92(2)	2.00(1)	2.86(1)				127(2)		154(1)
	H321		O4^{v}		0.94(1)	2.09(2)	2.63(1)				101(2)		115(2)
W4	O4	7		Sr^{viii}				2.63(1)	1.62(9)	116(7)	113(2)	125(1)	
				H321^{i}				2.09(2)			84(2)		
	H41		O1		0.96(2)	1.75(2)	2.68(1)				112(2)		165(2)
	H422		O4^{vii}		0.95(3)	1.89(1)	2.79(1)				105(3)		158(4)
	O4	8		Sr^{viii}				2.63(1)	1.52(7)	103(5)	113(2)	103(1)	
				H422				1.89(1)			104(1)		
	H41		O1		0.96(2)	1.75(2)	2.68(1)				99(2)		165(2)
	H421		O3^{i}		0.98(2)	1.82(2)	2.63(1)				135(3)		137(3)

Note. Distances in (Å) and angles in (°). H–O–C angles are presented in the following order: H1–O–C1, H1–O–C2, H2–O–C1, and H2–O–C2. H–H distances are included for the sake of comparison with theoretical 1.55 Å. (i) $x - 1/2, y + 1/2, z$; (ii) $-x + 1/2, -y + 1/2, -z$; (iii) $x - 1/2, -y + 1/2, z$; (iv) $x + 1/2, y + 1/2, z$; (v) $x, -y, z$; (vi) $x + 1/2, y - 1/2, z$; (vii) $-x + 3/2, -y + 1/2, -z + 1$; (viii) $-x + 1/2, -y + 1/2, -z + 1$.

ing due to the unfavorable geometrical relations with potential hydrogen acceptors (O3 and O4).

Table 4 presents the proposed assignments according to the present nomenclature and the more detailed structural data now available. The new proposal introduces some modifications to the previously reported assignments (7). The modifications are indicated with italics. The assignments try to fulfil Berlung *et al.* (16) and Mikenda (17) relations, including $\tilde{\nu}$(OH)/$\tilde{\nu}$(OD) ratios which should be about 1.35 (17). Doubtful assignment for W4(HOD ··· O4) implies a distinct $\tilde{\nu}$(OH)/$\tilde{\nu}$(OD) ratio (1.33).

It is to be noted that assignments of bands at 2682, 2625, and 2527 cm^{-1} are still doubtful because structural-spectroscopic correlations do not help much in these cases to cope with ambiguities. These bands, due to deuterated species, seem to have no visible counterparts in the spectral

TABLE 4
Revised Assignments of Water (Normal and Deuterated) IR Absorption Bands (cf. 7, 15)

Wavenumber	Assignment
3629	W1, W2 (H_2O, ν_{as})
3594	W1, W2 (HDO)
3557	W1, W2 (H_2O, ν_s)
3504	*W*3, W4 (DOH ··· O)
3355	*W*4 (DOH ··· *O*1)
2700	W1, W2 (D_2O), ν_{as})
2682	*W*1 (D_2O, ν_{as})? (see text)
2650	W1, W2 (HOD)
2625	*W*1 (HOD ··· N3)? (see text)
2597	*W*1, W2 (D_2O, ν_s)
2586	*W*3, W3 (HOD ··· O)
2527	*W*4 (*HOD* ··· *O*4)? (see text)
2480	*W*4 (HOD ··· *O*1)
1664 br	*W*3, *W*4 (H_2O, δ)
1610	W2 (H_2O, δ)
1597	*W*1 (H_2O, δ)
1450 br	*W*3, *W*4 (HOD, δ)
1424	W2 (HOD, δ)
1411	*W*1 (HOD, δ)
1213 br	*W*3, *W*4 (D_2O, δ)
1190	W2 (D_2O, δ)
1176	*W*1 (D_2O, δ)

Note. Wavenumbers in cm^{-1}. New assignments in italics.

region of nondeuterated water molecules. Anyway, assignments are suggested according to reasons given above.

CONCLUSIONS

SrNP is the first structure refined with data collected on the new four-circle diffractometer built on the channel 6T2 at the Orphée reactor. This neutron diffraction study confirms, without ambiguities, the water disorder in solid of SrNP, and also the infinite hydrogen bond network, of periodicity three times the cell parameter *b*, which was only suggested by previous X-ray study.

Furthermore, these new structural results allow the improvement of previous assignments of hydration water IR absorption bands.

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