Low temperature phases of strontium nitroprusside tetrahydrate (Sr[Fe(CN)$_5$NO]·4H$_2$O). Refinement of the neutron structure at 60 K

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The behavior of Sr[Fe(CN)$_5$NO]·4H$_2$O between room temperature and 77 K has been investigated by X-ray powder diffraction (XRD), differential thermal analysis (DTA), and infrared spectroscopy (IRS). DTA puts into evidence five phase transitions—at 152.7, 174.3, 183.0, 193.0, and 199.5 K—when temperature is increased very slowly. When decreasing the temperature, XRD detects a change of space group below 153 K—from $C2/m$ to $P2/m$— already reported as a result of a neutron diffraction study performed at 130 K. The $P2/m$ space group remains at least down to 60 K. The structure at this temperature (monoclinic, space group $P2/m$, $Z = 4$, $a = 19.765(21)$ Å, $b = 7.540(5)$ Å, $c = 8.384(1)$ Å, $\beta = 98.87(1)°$, $V = 1236(16)$ Å^3) has been refined to a final R factor 0.077 using 687 observed structure factors. Of the two series of IR spectra obtained when cooling the sample (first series) and when heating the previously cooled sample (second series), only a feature of the first series of spectra seems to be related with the transition observed at 153 K.

KEY WORDS: Strontium nitroprusside; neutron diffraction; DTA; IR; X-ray powder diffraction.

Introduction

This work is part of a series of structural studies of solid nitroprusside hydrates directed towards establishing the relation between the

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structural behavior of these compounds and the presence of weakly bonded water of crystalliza-tion molecules.[1,2]

The crystal structure of Sr[Fe(CN)$_5$NO]·4H$_2$O (SrNP4W) has been determined previously by X-ray diffraction at room temperature and by neutron diffraction (ND) at 300 (ND300) and 130 K (ND130) on single crystals.[2–4] At room temperature, the space group is $C2/m$ and at 130 K the space group is $P2/m$.[2–4] Water disorder has been observed and, when going from room tem-perature to 130 K, the hydrogen atoms positions change as a consequence of rotation of the planes of the four independent water molecules.[4] In the meantime, X-ray powder diffraction (XRD), dif-ferential thermal analysis (DTA), and infrared

spectroscopy (IRS) studies were begun in an attempt to improve the structural study of SrNP4W below room temperature, up to 77 K. Five transitions were detected by DTA at 152.7, 174.3, 183.0, 193.0, and 199.5 K when heating slowly the pre-cooled samples (results previously advanced).[3,5] PMR reports confirmed such results.[6,7] We have also performed a neutron diffraction study of SrNP4W at 60 K (ND60) to verify if new structural modifications are produced when going from 130 K to that temperature. As samples submitted to XRD suffered unavoidable dehydration, the presence of the di- and the monohydrate was detected allowing the determination of the respective space groups.

Experimental

Preparation of samples

SrNP·4H$_2$O (C$_5$H$_8$FeN$_6$O$_5$Sr) was obtained in the usual way through silver nitroprusside (prepared by precipitation from stoichiometric amounts of sodium nitroprusside and silver nitrate solutions) by stirring the solid with a solution of strontium chloride in stoichiometric quantity. Silver chloride was separated from the solution by filtration and the liquid was concentrated in a rotator vacuum evaporator at room temperature to obtain red crystals of SrNP4W. Big single crystals were grown for DTA and ND measurements by the hanging seed method with spontaneous concentration of a saturated aqueous solutions kept in a thermostat slightly above room temperature.

Differential thermal analysis

DTA measurements were performed with a homemade apparatus able to detect up to 0.1% C$_p$ anomalies at heating rates between 1 and 5 K/h, which ensure quasi-static thermodynamic conditions.[8] The core of the instrument is a thick-walled (1 cm thickness) aluminium cylindrical vessel, 10.5 × 17.5 cm filled with high-density polystyrene, which contains the sample and the reference. As samples, big single crystals (about 2 × 1 × 1 cm^3) of SrNP4W were used. The reference was a 4.51 g aluminium cylinder. Runs were performed with temperature increasing spontaneously very slowly (about 3 K/h) from about 90 K up to room temperature.

Neutron diffraction

Two different single crystals, closed into an aluminium container at atmospheric conditions, were cooled with the same cooling rate (ca. 3 K/min) from room temperature to 130 and 60 K, respectively; the first one in two steps, to 205 and to 130 K and the second directly to 60 K. The neutron structure of ND130 has been previously described;[4] the crystal data, data collection, and refinement conditions concerning the neutron structure ND60 are given in Table 1 and the refined parameters in Table 2.

Structure refinement was performed with the SHELXL93 program,[10] on a Hewlett Packard Vectra VA PC.

X-ray powder diffraction

Data were collected in the $\omega/2\theta$ step mode (step size: 0.016°, scan time by step: 10 s) with the prototype spectrometer of the C.P.S. Laboratory (École Centrale de Paris),[11] using radiation of 1.39223 Å (Cu Kβ, graphite monochromator) and scintillation detector. The powdered sample, prepared by grinding SrNP·4H$_2$O single crystals in a humid atmosphere and spreaded on a plane holder, was covered with a plastic film with the idea of avoiding its dehydration. The temperature was controlled to ±0.1 K with a Meric cryostat. Cooling between measuring steps was produced with cold (dry) nitrogen flowing under partial vacuum. Samples suffered partial dehydration produced by the dry nitrogen despite the protection.

Table 3 includes the temperature and the 2θ range corresponding to the different runs. The diffractograms were fitted with the *Fullprof* program (Profile matching)[12] to obtain cell parameters.

Table 1. Crystal Data, Data Collection and Refinements Conditions

Crystal data

Chemical formula	$C_5H_8FeN_6O_5Sr$
CCDC No.	CCDC-1003/6082
$F(000)$	448
D_c (g cm^{-3})	2.005
Crystal system	Monoclinic
Space group	$P2/m$, refinements with $C2/m$
a (Å)	19.765(21)
b (Å)	7.540(5)
c (Å)	8.384(1)
β (°)	98.87(1)
V (Å^3)	1234(16)
No. of reflections for lattice parameters	31 (32 < 2θ < 46°)
Radiation	Orphée reactor, CEN Saclay
Wavelength (λ Å)	1.526(5), λ/2 contamination < 1.9 × 10^{-4}
Absorption coefficient (μ cm^{-1})	1.56 (measured)
Temperature (K)	60
Crystal color	Red-brown
Crystal faces (Miller indices)	(100), (010), and (001)
Crystal size (mm)	5.0 × 3.4 × 1.75

Data collection

Diffractometer	Four-circle diffractometer (6T2 channel)
Data collection range and scan mode	ω-scan for 2 < 2θ < 50°, ω/θ-scan for 50 < 2θ < 80°, ω/2θ-scan for 80 < 2θ < 120°, (41 steps, 2–4 s/step for 2 < 2θ < 50°, 3–5 s/step for 80 < 2θ < 120°) adjusted as a function of the scattering angle to match the instrument resolution 6–8tgθ + 18tg^{2}θ
Index range (omitting $h + k = 2n + 1$)	−13 < h < 18 −8 < k < 8 −8 < l < 9
No. of reflections measured	1244
R_{int}	0.015
No. of independent reflections	722
No. of reflections with $F_o > 2\sigma$ (F_o)	687
Standard reflections, variation	($\overline{420}$) and (022), all the 100 measures, constant during data collection period: 6 days
Absorption correction type	Numerical methods using crystal shape
Transmission factors (T_{min}, T_{max})	0.4928, 0.7316

Refinement

Refinement method	Full matrix least squares on F^2
No. of parameters refined	136
Weighting scheme	$\omega = 1/\sigma^2(F^2)$
R for all and observed reflections, $R\omega$	0.077, 0.080, 0.012
Goodness of fit, all and observed reflections	3.67, 3.67
Extinction correction method	SHELXL
Extinction coefficient	0.00138(1)
Sources of atomic scattering factors	International tables of crystallography (1974)[9]

Table 2. Final Fractional Atomic Coordinates, Occupation Factors, and Thermal Parameters

Atom	x	y	z	sof	$U_{iso}/U_{eq}{}^a$
Sr	0.1327(3)	0.0000	0.2945(6)	0.50	0.012(1)
Fe	0.4134(3)	0.0000	0.2205(5)	0.50	0.011(1)
O	0.5556(6)	0.0000	0.2640(8)	0.50	0.019(2)
N	0.4979(3)	0.0000	0.2465(5)	0.50	0.011(1)
N1	0.3964(2)	0.2852(5)	−0.0441(4)	1.00	0.023(1)
N2	0.4034(2)	0.2887(5)	0.4746(4)	1.00	0.031(1)
N3	0.2562(4)	0.0000	0.1792(6)	0.50	0.029(2)
C1	0.4027(2)	0.1802(6)	0.0556(5)	1.00	0.015(1)
C2	0.4074(2)	0.1800(6)	0.3791(5)	1.00	0.019(1)
C3	0.3162(5)	0.0000	0.1953(7)	0.50	0.017(2)
O1	0.2887(5)	0.5000	0.1729(12)	0.50	0.030(2)
H11*	0.2773(9)	0.5000	0.0684(28)	0.50	0.054(5)
H12*	0.3336(17)	0.5577(36)	0.1936(32)	0.50	0.070(9)
O2	0.5018(5)	0.5000	0.2437(10)	0.50	0.019(2)
H21*	0.4717(8)	0.4611(21)	0.1499(20)	0.50	0.023(4)
H22*	0.4749(10)	0.5000	0.3214(24)	0.50	0.049(4)
O3	0.2060(5)	0.2938(15)	0.3548(9)	0.75	0.035(2)
H31*	0.2346(8)	0.3273(21)	0.2797(19)	0.75	0.048(4)
H321*	0.1891(17)	0.4001(57)	0.3700(43)	0.375	0.054(9)
H322*	0.2381(14)	0.2616(46)	0.4583(32)	0.375	0.035(7)
O4	0.2656(15)	0.4250(33)	0.4709(27)	0.25	0.025(5)
H41*	0.2785(17)	0.4247(47)	0.3738(45)	0.25	0.026(8)
H421*	0.2303(37)	0.5000	0.4860(75)	0.16	0.013(14)
H422*	0.2323(33)	0.3641(99)	0.4665(68)	0.17	0.028(13)

Note. Estimated standard deviations are in parantheses.
$^a U_{eq} = (1/3)\Sigma\Sigma\ U_{ij}\ a_i^* a_j^*\ \boldsymbol{a}_i \boldsymbol{a}_j$. Starred atoms were refined isotropically.

Infrared spectra

A Bruker 113v FTIR instrument was used between 4000 and 250 cm^{-1}, with a CsI beam splitter and a DTGS detector. One hundred scans were accumulated for each spectrum. Resolution was 2.0 cm^{-1}. The spectrophotometer was provided with an Oxford OX8ITL variable temperature optical cell and attached temperature control setup. Nujol mulls of powdered samples were spread between CsI disks, and positioned at the tip of the cryostat. Two series of measurements were made stepwise, keeping the temperature constant for 0.5 h in each stage, in the range 77–290 K. The first series implied cooling the sample in the stepwise manner from room temperature down to 77 K and the second series implied heating it after a quick cooling to 77 K. No dehydration of the samples was observed.[5]

Table 3. Experimental Conditions and Refined Parameters of the Three Hydrates as a Function of Temperature

Spectrum reference	Temperature (K), 2θ range	Hydrate, space group	Refined parameters: a (Å), b (Å), c (Å), β (°)	Volume (Å^3)	Number of refined parameters	R_{bragg} (%)	χ^2
NP300	300, 7–38	SrNP·4H$_2$O, $C2/m$	20.090(8), 7.609(4), 8.406(4), 98.78(3)	1270(2)	16	2.19	1.83
		SrNP·2H$_2$O, $Pcmm$	19.40(4), 7.51(1), 8.323(7)	1213(6)		1.40	
NP266	266, 7–36	SrNP·4H$_2$O, $C2/m$	20.031(7), 7.610(3), 8.391(4), 98.74(3)	1264(2)	22	2.35	1.48
		SrNP·2H$_2$O, $Pcmm$	18.91(1), 7.504(6), 8.343(7)	1184(3)		2.25	
		SrNP·H$_2$O, $Pmmm$	20.99(2), 7.486(5), 7.291(7)	1146(3)		2.98	
NP231	231, 7–38	SrNP·4H$_2$O, $C2/m$	20.012(8), 7.588(4), 8.416(4), 98.85(3)	1263(2)	23	2.29	1.46
		SrNP·2H$_2$O, $Pcmm$	18.83(2), 7.48(2), 8.39(2)	1181(6)		3.53	
		SrNP·H$_2$O, $Pmmm$	20.91(2), 7.47(1), 7.28(1)	1137(5)		2.17	
NP205	205, 7–41	SrNP·4H$_2$O, $C2/m$	19.978(7), 7.577(3), 8.422(3), 98.89(2)	1260(2)	23	1.91	0.95
		SrNP·2H$_2$O, $Pcmm$	18.75(2), 7.48(1), 8.398(5)	1177(4)		2.98	
		SrNP·H$_2$O, $Pmmm$	20.78(2), 7.483(9), 7.265(7)	1130(4)		2.39	
NP196	195.5, 7–38	SrNP·4H$_2$O, $C2/m$	19.97(1), 7.577(4), 8.421(4), 98.89(3)	1259(2)	22	1.78	1.47
		SrNP·2H$_2$O, $Pcmm$	18.75(2), 7.48(2), 8.40(1)	1178(6)		2.22	
		SrNP·H$_2$O, $Pmmm$	20.77(6), 7.50(2), 7.26(1)	1130(9)		1.39	
NP189	189, 7–41	SrNP·4H$_2$O, $C2/m$	19.956(7), 7.576(4), 8.421(4), 98.95(2)	1258(2)	23	1.91	1.10
		SrNP·2H$_2$O, $Pcmm$	18.72(1), 7.515(8), 8.400(5)	1181(3)		1.04	
		SrNP·H$_2$O, $Pmmm$	20.68(2), 7.50(1), 7.248(7)	1123(4)		1.41	
NP178	178, 7–38	SrNP·4H$_2$O, $C2/m$	19.957(9), 7.579(5), 8.420(6), 98.89(3)	1258(3)	23	2.04	1.36
		SrNP·2H$_2$O, $Pcmm$	18.71(2), 7.49(1), 8.41(2)	1180(6)		1.44	
		SrNP·H$_2$O, $Pmmm$	20.62(3), 7.519(8), 7.24(1)	1123(5)		2.85	
NP165	165, 7–41	SrNP·4H$_2$O, $C2/m$	19.926(8), 7.574(4), 8.413(5), 98.85(3)	1255(2)	23	1.53	1.06
		SrNP·2H$_2$O, $Pcmm$	18.68(2), 7.487(8), 8.43(1)	1178(4)		1.41	
		SrNP·H$_2$O, $Pmmm$	20.63(3), 7.50(1), 7.22(1)	1117(6)		1.77	
NP146	146.4, 7–38	SrNP·4H$_2$O, $P2/m$	19.94(1), 7.576(5), 8.420(5), 98.89(3)	1257(2)	20	1.67	1.22
		SrNP·2H$_2$O, $Pcmm$	18.68(5), 7.44(3), 8.45(2)	1175(11)		1.81	
		SrNP·H$_2$O, $Pmmm$	20.56(6), 7.47(2), 7.22(2)	1109(9)		0.74	

Results and discussion

Differential thermal analysis

SrNP4W shows a rich DTA behavior. When the cooled sample is heated very slowly, five distinct peaks are produced, as shown in Fig. 1. Mean results from several runs were the following: $T_1 = 152.7 \pm 3.3$ K, $T_2 = 174.3 \pm 0.4$ K, $T_3 = 183.0 \pm 0.5$ K, $T_4 = 193.0 \pm 1.0$ K, and $T_5 = 199.5 \pm 0.6$ K.[3] PMR results are in very good accordance with these results (transitions reported at 174, 182, 192, and 197 K).[6,7] The first transition (at 152.7 K) is exothermic and the other four endothermic. Heat amounts involved in the transitions, referred to the last (199.5 K), are $Q_1/Q_5 = -0.82 \pm 0.04$, $Q_2/Q_5 = 1.57 \pm 0.08$, $Q_3/Q_5 = 1.98 \pm 0.10$, $Q_4/Q_5 = 1.10 \pm 0.05$, $Q_5 = 1$ (taken as reference).

Neutron diffraction

The neutron structure at 130 K put into evidence a modification of the crystal symmetry:[4] the room temperature space group $C2/m$ changes to $P2/m$ as a consequence of rotation of the planes of the four independent water molecules. At 60 K the space group is also $P2/m$: the intensities of reflections with $h + k = 2n + 1$ are observed. Figure 2 reproduces the profiles of selected reflections. No appreciable changes between the refined structures ND130 and ND60 are detected. Fe and Sr coordination polyhedra resulting from two structures superpose strictly within standard deviations. Selected bond distances and bond angles concerning the water molecules are presented in Table 4.

X-ray powder diffraction

Despite the precautions taken, samples of SrNP4W suffered partial dehydration. The presence of the di- and the monohydrate was detected in all diffractograms through the respective most conspicuous diffraction lines.[5] Table 3 summarizes the results obtained. As an example, the observed and calculated powder diffractograms at 146.4 K (NP146) are presented in Fig. 3. It is to be noted that to fit correctly these diffractograms (see Fig. 4 for the NP300 case), the *Pcmm*
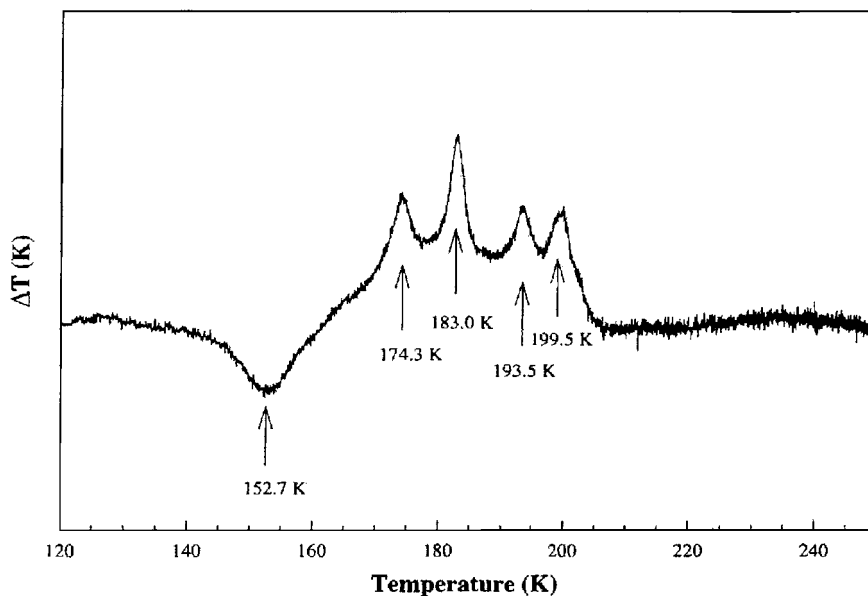

Fig. 1. ΔT vs. T_s curve from the DTA experiment. ΔT: difference between sample (T_s) and reference temperatures.
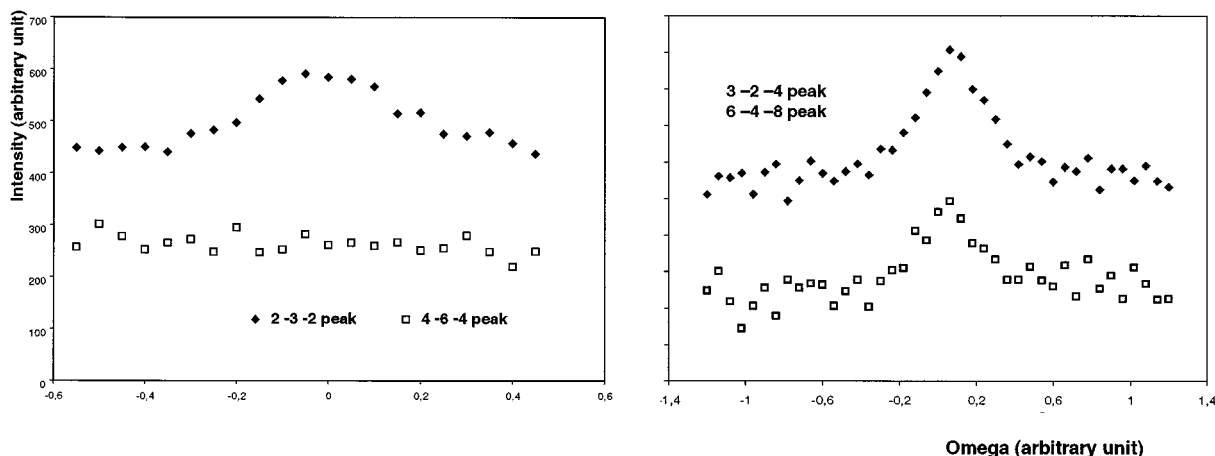
Fig. 2. Selected reflections [$(2\bar{3}2)$, $T = 130$ K and $(3\bar{2}4)$, $T = 60$ K] normally unobserved in the space group $C2/m$, indicate the change to space group $P2/m$. They are not a $\lambda/2$ effect (rate of contamination: 2.5×10^{-4}).

space group for SrNP2W had to be used instead of the *Ccmm* group reported in a previous X-ray study performed with the mosaic of nearly parallel crystals that kept the external shape of the original SrNP·4H$_2$O single crystal after partial dehydration.[13] Figure 5 shows the variation of the cells volumes as a function of temperature, which seems to be linear in general but below 266 K for the dihydrate and above ca. 153 K for the tetrahydrate.

Infrared spectra

Two series of spectra were obtained at selected temperatures: when gradually cooling the sample (first series) and when heating it, previously cooled directly to 77 K (second series).

Bands due to water appear, at room temperature, in the following spectral ranges.[3,5,14]

- HO stretchings (νHO): 3800–3400 cm^{-1}. The two well defined sharp bands at 3635 and 3562 cm^{-1} (3629 and 3557 cm^{-1} in.[3]) were assigned to the antisymmetric and the symmetric H$_2$O stretchings of the W1 and W2 water molecules (which are very weak hydrogen donors) with the contribution, perhaps, of the stretching band of the

free HO group of W3.[3] The broad band that follows them, centred at about 3450 cm^{-1}, should be due to the hydrogen bonded HO groups of W3 and W4.
- H$_2$O deformations (δH$_2$O): 1750–1550 cm^{-1}. The broad band at 1649 cm^{-1} (1664 cm^{-1} in.[3]) is assigned to W3 and W4, the peak of 1613 (1610) cm^{-1} to W2 and the shoulder in 1604 (1597) cm^{-1} to W1.
- H$_2$O librations (LH$_2$O), characterized by a strong increase in intensity with cooling: 900–350 cm^{-1}. Features are the weak broad band at ca. 557 cm^{-1} and the very badly defined shoulders at ca. 465 and ca. 385 cm^{-1}. It is to be noted that LW3 and LW4 are expected to lie at higher wavenumbers than LW1 and LW2.

Spectral ranges for anion bands are as follows.

- NO stretching first overtone (2νNO): 3950–3850 cm^{-1}.
- CN stretchings (νCN): 2175–2100 cm^{-1}.
- NO stretching (νNO): 2050–1850 cm^{-1}.
- FeNO deformation (δFeNO) and FeN stretching (νFeN) (in decreasing order of wavenumbers): 700–600 cm^{-1}.
- FeC stretchings (νFeC) and FeCN deformations (δFeCN) (mixed): 550–250 cm^{-1}.

Table 4. Selected Bond Distances (Å) and Bond Angles (°) Concerning W1, W2, W3, and W4 Water Molecules at 60 K (First Column) and at 130 K (Second Column), Without Correction for Thermal Motion According to the Riding Model

Molecule		A[a]	C[b]	O—H	H—A	O—A	O—C	H—O—H	O—H—A
W1	1 O1		H31[c]				1.98(2), 1.96(1)	105(2), 103(2)	
			H41				1.82(4), 1.96(1)		
		H11	N3[d]	0.87(3), 0.88(2)	2.07(3), 2.10(2)	2.95(1), 2.99(1)			176(2), 175(1)
		H12		0.98(4), 0.91(2)					
	2 O1		H31[c]				1.98(2), 1.96(1)	105(2), 103(2)	
			H31[e]				1.98(2), 1.96(1)		
		H11	N3[d]	0.87(3), 0.88(2)	2.07(3), 2.10(2)	2.95(1), 2.99(1)			176(2), 175(1)
		H12		0.98(4), 0.91(2)					
W2	3 O2		Sr[f]				2.56(1), 2.54(1)	103(2), 106(1)	
		H21	N1	0.96(2), 0.95(1)	2.42(2), 2.46(1)	3.35(2), 3.38(1)			164(2), 162(1)
		H22	N2	0.90(3), 0.90(2)	2.60(2), 2.61(1)	3.31(2), 3.36(1)			142(2), 141(1)
		H22	N2[g]		2.60(2), 2.61(1)	3.32(2), 3.36(1)			142(2), 141(1)
W3	4 O3		Sr[f]				2.65(1), 2.64(1)	107(2), 106(2)	
			H321[h]				2.34(1), 2.35(1)		
		H31	O1[i]	0.94(2), 0.97(1)	1.98(4), 1.96(1)	2.86(1), 2.86(1)			154(1), 153(1)
		H322	O3[j]	1.02(3), 1.05(3)	1.82(3), 1.80(3)	2.84(2), 2.85(1)			179(1), 178(2)
	5 O3		Sr[f]				2.65(1), 2.64(1)	107(2), 106(2)	
			H421[i]				1.92(2), 1.96(1)		
		H31	O1[i]	0.94(2), 0.97(1)	1.98(4), 1.96(1)	2.86(1), 2.86(1)			154(1), 153(1)
		H322	O3[j]	1.02(3), 1.05(3)	1.82(3), 1.80(3)	2.84(2), 2.85(1)			179(2), 178(2)
	6 O3		Sr[f]				2.65(1), 2.64(1)	98(2), 100(2)	
			H322[j]				1.82(2), 1.80(1)		
		H31	O1[i]	0.94(2), 0.97(1)	1.98(2), 1.96(1)	2.86(1), 2.86(1)			154(1), 153(1)
		H321	O3[h]	0.88(5), 0.95(1)	2.36(5), 2.35(1)	3.11(2), 3.16(0)			146(3), 143(2)
	7 O3		Sr[f]				2.65(1), 2.64(1)	98(2), 100(2)	
			H322[j]				1.82(2), 1.80(1)		
		H31	O1[i]	0.94(2), 0.97(1)	1.97(2), 1.96(1)	2.86(1), 2.86(1)			154(1), 153(1)
		H321	O4[i]	0.88(5), 0.95(1)	2.11(5), 2.05(2)	2.55(3), 2.54(1)			112(2), 109(2)
W4	8 O4		Sr[k]				2.65(3), 2.61(2)	108(5), 112(3)	
			H321[c]				2.09(2), 2.05(3)		
		H41	O1	0.89(5), 0.94(4)	1.82(4), 1.77(3)	2.67(3), 2.65(2)			159(2), 156(2)
		H422	O4[k]	0.80(9), 1.02(4)	2.24(6), 2.22(2)	2.75(6), 2.90(1)			124(4), 123(3)
	9 O4		Sr[k]				2.65(3), 2.61(2)	117(5), 116(4)	
			H422[k]				2.24(1), 2.22(1)		
		H41	O1	0.89(5), 0.94(4)	1.82(4), 1.77(3)	2.67(3), 2.65(2)			159(2), 156(2)
		H421	O3[c]	0.92(8), 0.76(4)	1.92(5), 1.96(3)	2.54(3), 2.54(2)			123(5), 133(5)

[a] Acceptor atom.
[b] Coordinated atom.
[c] $x - 0.5, y + 0.5, z$.
[d] $-x + 0.5, -y + 0.5, -z$.
[e] $x - 0.5, -y + 0.5, z$.
[f] $-x + 1, -y, z + 0.5$.
[g] $x, -y + 1, z$.
[h] $x, -y, z$.
[i] $x + 0.5, y - 0.5, z$.
[j] $-x + 1.5, -y + 0.5, -z + 1$.
[k] $-x + 0.5, -y + 0.5, -z$.

It is to be noted that cooling brings about the well-known improvement of definition and the general shift of bands towards higher wavenumbers, with the exception of H-bonded HO stretchings, which, in general, shift contrariwise. This happens also with the deformation bands of water molecules not coordinated to cations but bonded to H atoms of other water molecules.[15]
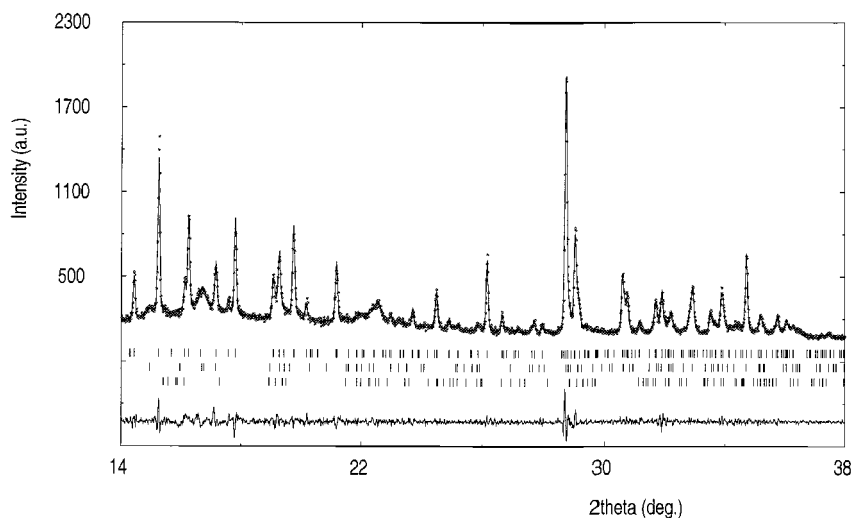
Fig. 3. Observed ($\cdots$), calculated (—) and difference (– at the bottom) diffractograms of a powdered sample at 146.4 K (tetrahydrate: space group $P2/m$, pseudo-Voigt profile 0.33(2), $u = -0.08(3)$, $v = 0.03(1)$, $w = 0.004(1)$; dihydrate: space group $Pcmm$, pseudo-Voigt profile 0.21(9), $u = 1.2(8)$, $v = -0.8(3)$, $w = 0.16(4)$; monohydrate: space group $Pmmm$, gaussian profile $w = 0.034(2)$). The three series of ticks correspond to tetra-, di-, and monohydrate theorical position reflections.

This behavior could be explained by the tightening of the H-bonds received by W1 from W3 and W4 and the concomitant polarisation towards the oxygen nucleus of the electron pairs that bond the own hydrogen atoms, increasing therefore the repulsion between them and lowering the δH_2O force constant. This force constant, in fact, seems to be the lowest of all, while those corresponding to W3 and W4 (the tightest H-bonded molecules, as donors to W1) are the highest. An-

other exception to this rule seems to be the behavior of one of the librational bands, possibly due to W1, which wavenumber lowers by cooling. This phenomenon has been previously found by Grodzicki and Piszczek but without paying attention to it.[15]

When cooling gradually the sample (*first series*), steady spectroscopical changes characteristic of the cooling effect take place increasing the definition and complexity of bands

a)　　　　　　　　　　　　　　　　　**b)**
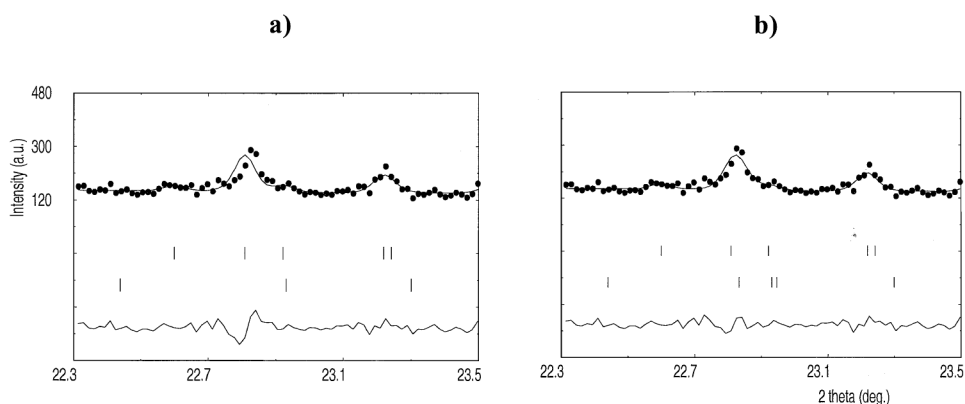
Fig. 4. Profile fit of the peak which appears at 22.83° in the NP300 diffractogram with (a) the (510) reflection of the tetrahydrate (space group $C2/m$) and the null contribution of the (501) reflection of the dihydrate (space group $Ccmm$); (b) the (510) reflection of the tetrahydrate (space group $C2/m$) and the (501) reflection of the dihydrate (space group $Pcmm$).
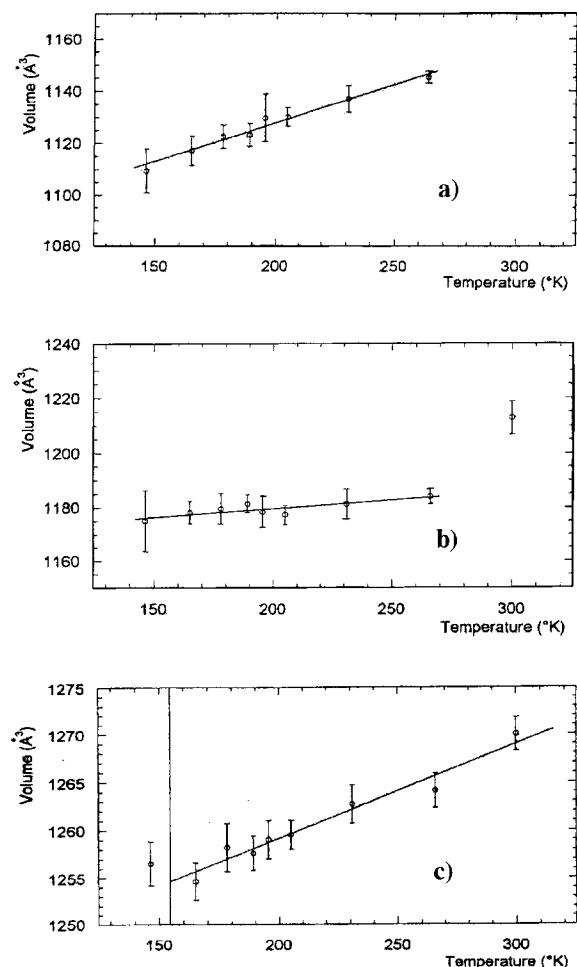
Fig. 5. Variations of the cells volumes as a function of the temperature: (a) monohydrate; (b) dihydrate; (c) tetrahydrate.

assignable to water, specially in the HO stretching region, in accordance with the presence of nine crystallographically different kinds of water molecules (Table 4). At 170–160 K, the fine structure of the broad and complex band begins to be noticeable and at about 100 K, the maximal resolution is attained. Well defined peaks of different intensities appear in the free HO (not hydrogen bonded) stretching region at 3644, 3631, 3610, 3584, 3561, 3553, 3545, and 3541 cm^{-1} while broad peaks and a shoulder are seen in the H-bonded HO stretching region at 3513, 3502, 3463, 3354, 3310, 3211, and 3130 cm^{-1} (wavenumbers were measured at 77 K).

In the δH_2O region, a broad band at 1649 cm^{-1} assignable to the H-bonded water molecules acting as donors—W3 and W4—gains in definition and shifts finally to ca. 1669 cm^{-1} (77 K). The band at 1613 cm^{-1} seems to suffer no shift. The barely seen shoulder at 1604 cm^{-1} (room temperature) clearly develops into a band located at 1598 cm^{-1} assignable to the W1 water molecules, which accept either one hydrogen atom each from W3 and W4 (W1, Site 1), or only from W3 (two) water molecules (W1, Site 2). They act also as weak H-donors to N3 atoms. The librational band at 557 cm^{-1} (room temperature) splits by cooling into a peak at 607 and a broad feature at 578 cm^{-1}, as expected from the more tightly bonded W3 and W4 molecules. The shoulder at ca. 465 cm^{-1} develops into a band at 486 cm^{-1} assignable to W2. New features of unknown origin appear at 468 cm^{-1} and 458 cm^{-1}. The shoulder at 385 cm^{-1} (room temperature) turns into a well-defined band in 368 cm^{-1}, seemingly due to the most mobile molecule, W1.[7] The decrease of the feature's wavenumber seems to confirm such assignment (see above).

Bands of the anion also experience progressive splitting (definition of shoulders and appearance of new shoulders). Shoulders of the room temperature bands at 2152 cm^{-1} (CN stretchings) and 1969 cm^{-1} (νNO), change into well-defined peaks located at 2178, 2164, and 1949 cm^{-1} (77 K). Shoulders develop, at the same time, at 2172 and 1943 cm^{-1}. It is to be noted that the shoulder at 2172 cm^{-1} (77 K) appears, in fact, as a very weak peak between about 155 and 140 K, which is preceded by a shoulder seen already but barely, at room temperature. This temperature region includes the first phase transition. The growth of the peak at 1949 cm^{-1} is accompanied by the definition of a shoulder which turns into a peak of 3867 cm^{-1} wavenumber (77 K) in the 2νNO region, where the wavenumber of the strongest band is 3887 cm^{-1} (77 K). Bands of 1969 and 3887 cm^{-1} wavenumbers should be assigned to the fundamental and the first overtone band, respectively, of the $^{14}N^{16}O$ stretching, the pair of bands at 3867 and 1949 cm^{-1} to the

$^{15}N^{16}O$ species, and the shoulder at 1943 cm^{-1} to $^{14}N^{18}O$.[16]

The spectra below room temperature of the *second series* (increasing temperatures after fast cooling to 77 K) show some differences with respect to the corresponding spectra of the other series, both in the water and anion regions. The fine structure of the H-bonded HO stretching complex band is still seen but barely at 120–130 K. At 150 K, the fine structure has practically disappeared, a distinction from the first series of spectra where this structure begins to be seen already at 170 K. At room temperature this broad band peaks at 3435 cm^{-1}.

Water bands in the other spectral regions also show continuous changes.

Concerning the anion bands, the thermal behavior is similar as in the first series, but the temperature interval of appearance of the very weak peak at 2170 cm^{-1} in the CN stretching region seems to be somewhat higher, ca. 150–160 K.

Summary and conclusions

DTA shows phase transition at 152.7 ± 3.3 K (exothermic), 174.3 ± 0.4 K, 183.0 ± 0.5 K, 193.0 ± 1.0 K, and 199.5 ± 0.6 K (all these endothermic). PMR results are in very good accordance with these results (transitions reported at 174, 182, 192, and 197 K.[6,7] Heat amounts involved in the transitions, referred to the last (199.5 K), are $Q_1/Q_5 = -0.82 \pm 0.04$, $Q_2/Q_5 = 1.57 \pm 0.08$, $Q_3/Q_5 = 1.98 \pm 0.10$, $Q_4/Q_5 = 1.10 \pm 0.05$, $Q_5 = 1$.

XRD confirms the phase transition found by DTA via the change of the space group from $C2/m$ to $P2/m$ in agreement with ND130 results.[4] A new neutron diffraction study, performed now at 60 K (ND60), shows that the structure does not suffer other structural changes when going from 130 to 60 K. IR spectra performed in steps (both when cooling samples from room temperature and when heating rapidly precooled samples) show a suggestive change in the CN stretching region between 155–140 K (first series) and between 150–160 K (second series). Both temperature intervals include the first phase transition.

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