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Oxygen–Water Disorder in Strontium Pentacyanonitrosyl Ferrate(II) Tetrahydrate Crystals (Strontium Nitroprusside $4H_2O$)

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The crystal structure of strontium nitroprusside tetrahydrate ($Sr[Fe(CN)_5NO]\cdot 4H_2O$) has been determined with a better than standard precision by X-ray diffraction on single crystals at room temperature: monoclinic; space group *C2/m*; $a = 20.109(4)$, $b = 7.616(5)$, $c = 8.398(3)$ Å; $\beta = 98.7(5)°$; $V = 1271(2)$ Å^3; $Z = 4$; $M_r = 375.6$; $D_x = 1.96$ g cm^{-3}; final $R = 0.027$ for 1567 observed structure factors. The positions of three hydrogen atoms were found. The results show two different sites, with occupation factors of 2/3 and 1/3, for one oxygen–water atom located in a general position within the asymmetric unit. Analysis of distances between neighboring water oxygens and of possible hydrogen bonds indicates that different strontium coordination polyhedra exist in the crystal. These are connected in zig-zag chains along the [0 1 0] direction by short contacts between water oxygens, suggesting the existence of an infinite network of hydrogen bonds of periodicity three times the cell parameter *b*. © 1995 Academic Press, Inc.

INTRODUCTION

The structure of strontium nitroprusside tetrahydrate has been previously investigated by X-ray diffraction on single crystals using visually estimated reflections (1).[3] This crystallographic study permitted the authors to classify the water molecules in three types. The molecules of the first type (W3, its oxygen atom designated as O3) are coordinated to the strontium cation and are hydrogen bonded to water molecules of the second type, the only water molecules not coordinated to strontium cations. Oxygen atoms, O3, are located in a general position, while oxygen atoms of the second and third type molecules (W1, O1, and W2, O2, respectively) lie on the crystallographic mirror plane *m*. W2 molecules have only weak contacts with nitrogen atoms of CN groups. Subsequent spectroscopic results were interpreted using this structure (2).

Recently, the motion of water molecules in this hydrate has been analyzed by proton NMR relaxation measurements but the motions of individual molecules could not be discerned as expected (3). Furthermore, DTA experiments detected that strontium nitroprusside tetrahydrate crystals undergo four phase transitions between room temperature and 77 K (at 197, 192, 182, and 174K) (4). Lower hydrates (2) are produced by controlled thermal hydration, i.e.: the dihydrate at 72°C and the monohydrate at 138°C, and by controlled dehydration over P_4O_{10} as well. These substances have been studied by X-ray diffraction on a pseudo-single crystals (5) and a powder sample (2), respectively.

This behavior of the water molecules, also observed in the widely studied barium nitroprusside hydrates (6, 7, and references therein), led us, in an attempt to determine an accurate structure, to a new study of strontium nitroprusside tetrahydrate ($Sr[Fe(CN)_5NO]\cdot 4H_2O$: SrNP) by X-ray diffraction at room temperature.

EXPERIMENTAL

Crystals of SrNP were obtained by slow evaporation from an aqueous solution at 20°C. A complete diffraction data set was collected, at room temperature, from a brown crystal of the approximate dimensions 0.45 × 0.4 × 0.25 mm by employing the four-circle diffractometer Enraf-Nonius CAD4 (graphite-monochromated Mo$K\alpha$ = 0.71073 Å). Unit cell parameters and orientation matrix for data collection were determined from the refinement of setting angles of 25 centered reflections in the range $16° < 2\theta < 24°$. Reflection intensities were measured using the $\omega/2\theta$-scan mode for $3° < 2\theta < 60°$, covering the Miller index ranges $-28 \leq h \leq 0$, $-10 \leq k \leq 10$, $-11 \leq l \leq 11$. Systematic extinctions corresponding to the space group *C2/m* were controlled ($4° < 2\theta < 50°$).

Intensities of three reference reflections monitored every hour were essentially constant throughout the data

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[3] The equivalent between the name of the atoms of the precedent structure (1) and those used in this work is: N1 ⇒ N; N2 ⇒ N1; N3 ⇒ N2; N4 ⇒ N3; O1 ⇒ O; C2 ⇒ C1; C3 ⇒ C2; C4 ⇒ C3; O2 ⇒ O1; O3 ⇒ O2; O4 ⇒ O3.

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collection period. Of 3823 measured reflections, 2797 were independent ($R_{sym} = \Sigma||F_O| - |F_{Oav}||/\Sigma|F_O| = 0.017$) and 1567 (having $|F|^2 > 3\,\sigma(|F|^2)$ were used in the refinement of 103 parameters. Absorption corrections were applied by empirical methods ($\mu = 52.33$ cm^{-1}).

Starting parameters for the full matrix least-squares refinement based on $|F|$ values were taken from Castellano *et al.* (1). The very high thermal parameter of one water oxygen atom led us to calculate a difference Fourier map phased with the refined positions and isotropic thermal parameters of strontium and nitroprusside atoms only. Four independent positions of water oxygen atoms (O1, O2, O3, O4) were so obtained; the occupation factors of the O3 and O4 water oxygens were refined to the values 2/3 and 1/3, respectively. On the last difference map only three positive peaks could be assigned to hydrogen positions (H11, H21, and H31); they were introduced in the calculations with fixed thermal and positional parameters. The absolute value of the other residual peaks was smaller than 0.3 $e/\text{Å}^3$. The final anisotropic refinement, with weights $\omega = 1/(\sigma^2(|F_O|) + 0.02|F_O|^2)$, converged to $R = \Sigma||F_O| - |F_C||/\Sigma|F_O| = 0.027$, $R_W = [\Sigma_\omega(|F_O| - |F_C|)^2/\Sigma\omega|F_O|^2]^{0.5} = 0.034$, and $R = 0.05$ for all reflections ($s = [(\Sigma\omega(|F_O| - |F_C|)^2/(N_O - N_V)]^{0.5} = 1.7$). There were no significant trends in the data analyzed as a function of $|F_O|$ and sin θ. Scattering factors (including the real and imaginary parts of the anomalous-dispersion correction) were taken from the International Tables for X-Ray Crystallography (8). The final positional and equivalent isotropic thermal parameters are listed in Table 1.[4,5]

TABLE 1

Final Atomic Coordinates, Equivalent Isotropic Thermal Parameters with Their Estimated Standard Deviations and Occupation Factors

Atom	x	y	z	B_{iso}/B_{eq}	s.o.f
Sr	0.13294(2)	0.000	0.29469(4)	1.397(5)	0.5
Fe	0.41030(2)	0.000	0.22103(5)	1.316(9)	0.5
O	0.5502(2)	0.000	0.2584	3.84(8)	0.5
N	0.4938(2)	0.000	0.2427(4)	1.89(6)	0.5
N(1)	0.3938(1)	0.2841(4)	−0.0427(3)	3.54(6)	1.0
N(2)	0.4033(2)	0.2856(4)	0.4761(3)	3.97(6)	1.0
N(3)	0.2555(2)	0.000	0.1866(5)	4.0(1)	0.5
C(1)	0.3995(1)	0.1777(4)	0.0557(3)	2.12(5)	1.0
C(2)	0.4059(1)	0.1792(4)	0.3813(3)	2.18(5)	1.0
C(3)	0.3132(2)	0.000	0.1980(5)	2.56(8)	0.5
O(1)	0.2869(2)	0.500	0.1751(4)	5.6(1)	0.5
O(2)	0.5034(2)	0.500	0.2408(4)	3.64(7)	0.5
O(3)	0.7047(2)	0.2083(6)	0.3554(4)	5.02(9)	0.66
O(4)	0.2664(3)	0.415(1)	0.4775(7)	5.08(2)	0.34
H(11)*	0.290	0.500	0.062	7.0	0.5
H(21)*	0.482	0.500	0.125	5.0	0.5
H(31)*	0.732	0.250	0.250	7.0	0.66

Note. Atoms with asterisks were kept fixed in the refinements. $B_{eq} = 4/3\ \Sigma_i\ \Sigma_j\ \beta_{ij}a_ia_j$.

DISCUSSION

The two cations (Fe and Sr) occupy sites of symmetry *m*. Distances and angles concerning their environment are given in Table 2. The pseudo-octahedral molecular geometry and packing of the nitroprusside anions (NP) have been described by Castellano *et al.* (1); the NP anions pile up along the *c* crystallographic axis, forming double chains where the anions are intercalated in an antiparallel fashion with the NO groups facing up (Fig. 1). This characteristic packing is responsible for the very strong dichroism of the NO stretching band observed in single-crystal IR spectra (2, 13). It is an excellent system to study the origin and magnitude of correlation effects due to the coupling between strongly polar vibrations of neighboring NP anions in the crystal (Davydov splitting) (14, 15).

Figure 2a shows the strontium cation with its neighboring atoms and some of the distances between them. Certainly, the positions of the water oxygens O3 and O4 cannot be occupied at the same time. Study of the possible chemical contacts leads to the pattern of Fig. 2a, where the space group symmetry disappears. The occupied sites are repeated with a periodicity of three times the cell parameter *b*, thus giving a proportion of atoms in the unit cell of 2/3 for O3 and 1/3 for O4, values which are also obtained from refinement of the occupation factors. So, in the crystal, the strontium atoms coordinate five CN groups of different NPs and two water oxygens in different distorted bicapped trigonal prisms; one contains two symmetrically related O3 atoms and the others (two enantimorphic polyhedra) contain O3 and O4 oxygen atoms (Fig. 2c). The different polyhedra are connected along the [0 1 0] direction by chains of water oxygens (Fig. 2b). These chains could be a consequence of an infinite network of hydrogen bonds of periodicity 3*b*. [*h* *k*/3 1] reflections were searched but all were found absent; this means

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[4] Computer used: MicroVAX II. Programs: cell refinements and data collection, Enraf-Nonius CAD-4 software. Data reduction, structure resolution and refinements: SDP software (9). Absorption correction: on Ψ scans (10) and DIFABS (11). Molecular graphics: ORTEP (12).

[5] Lists of observed and calculated structure factors and anisotropic thermal parameters have been deposited as supplementary material (nine pages). See NAPS document No. 00000 for 9 pages of supplementary material. Order from ASIS/NAPS Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance $4.00 for microfiche copy or for photocopy, $7.75 up to 20 pages plus $0.30 for each additional page. All orders must be prepaid. Institutions and organizations may order by purchase order. However, there is a billing and handling charge for this service of $15. Foreign orders add $4.50 for postage and handling, for the first 20 pages, and $1.00 for additional 10 pages of material, $1.50 for postage of any microfiche orders.

TABLE 2

Cations Environment

(a) Fe coordination

Atom 1	Atom 2	Distance (Å)	Atom 1	Atom 2	Distance (Å)
Fe	N	1.661(4)	N	O	1.122(6)
Fe	**C(1)**	**1.927(3)**	**C(1)**	**N(1)**	**1.151(4)**
Fe	**C(2)**	**1.928(3)**	**C(2)**	**N(2)**	**1.143(4)**
Fe	C(3)	1.933(4)	C(3)	N(3)	1.150(6)

Atom 1	Atom 2	Atom 3	Angle (°)	Atom 1	Atom 2	Atom 3	Angle (°)
N	Fe	C(3)	179.5(2)	**N**	**Fe**	**C(1)**	**94.6(1)**
C(1)	Fe	C(1)^a	89.2(1)	**N**	**Fe**	**C(2)**	**94.4(1)**
C(2)	Fe	C(2)^a	90.1(1)	**C(1)**	**Fe**	**C(2)**	**89.6(1)**
C(1)	**Fe**	**C(3)**	**85.8(1)**	**C(2)**	**Fe**	**C(3)**	**85.3(1)**
C(1)	**Fe**	**C(2)^a**	**171.0(1)**	**N(1)**	**C(1)**	**Fe**	**179.3(2)**
O	N	Fe	179.5(4)	**N(2)**	**C(2)**	**Fe**	**180.0(4)**
N(3)	C(3)	Fe	179.4(4)				

(b) Sr coordination

Atom 1	Atom 2	Distance (Å)	Atom 1	Atom 2	Distance (Å)
Sr	N(3)	2.753(4)	Sr	O(2)^d	2.575(4)
Sr	**N(2)^c**	**2.707(3)**	**Sr**	**N(1)^b**	**2.753(4)**
Sr	**O(3)^d**	**2.656(4)**	**Sr**	**O(4)^c**	**2.646(6)**

Note. Distances (Å) and angles (°) occurring twice due to the *m* crystallographic plane are printed in bold type.

[a] $x, \bar{y}, z$.

[b] $z + 1/2, \bar{y} + 1/2, \bar{z}$.

[c] $z + 1/2, \bar{y} + 1/2, \bar{z} + 1$.

[d] $x - 1/2, y - 1/2, z$.

that the infinite oxygen chains are randomly dispersed in the crystal studied.

Table 3 presents selected distances and angles concerning the water molecules W1, W2, W3, and W4.

W3 and W4 are coordinated to the strontium cation. W3 has two different environments according to the site occupied in the crystal (Fig. 2).

W2 is coordinated to the strontium atom. The environment of this water molecule is similar to that of W2 of barium nitroprusside trihydrate at room temperature (16), which is a molecule with trigonal coordination. H21 is directed to N1 and N1′ (N1′ is related by the symmetry plane *m* to N1). The three strontium nitroprusside hydrates have in common this water molecule.

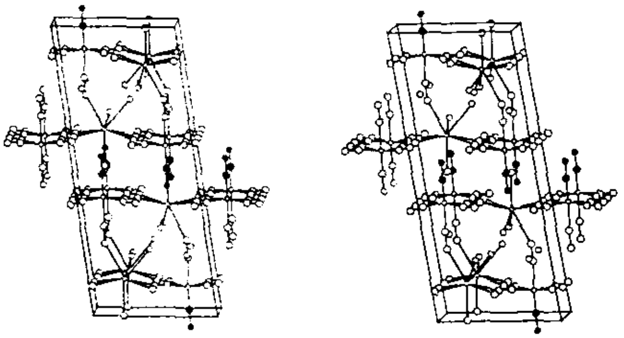

FIG. 1. Stereoscopic ORTEP view of the structure along the [0 1 0] direction. Atoms of the NO groups are represented in black.

W1 is the other water molecule retained by strontium nitroprusside dihydrate (2); this molecule is not coordinated to any cation. There are two possible environments of W1; in one environment, it is close to two W3 molecules, whereas in the other, its nearest neighbors are W3 and W4. Vibrational studies on crystals of SrNP (2) showed that W1 has one hydrogen atom that appears to be free and that its oxygen accepts a hydrogen bond. W1 is a hydrogen bond donor for N3^i via H11 and it could be a hydrogen bond acceptor or donor for W3 and W4. Different hydrogen bond systems are then possible according to this acceptor or donor character of W1. Assuming the results of the vibrational studies, and analyzing the distances and angles presented in Table 3, the hydrogen bonds presented in Fig. 2b are the most likely. A neutron diffraction study is in progress in order to confirm this assumption.

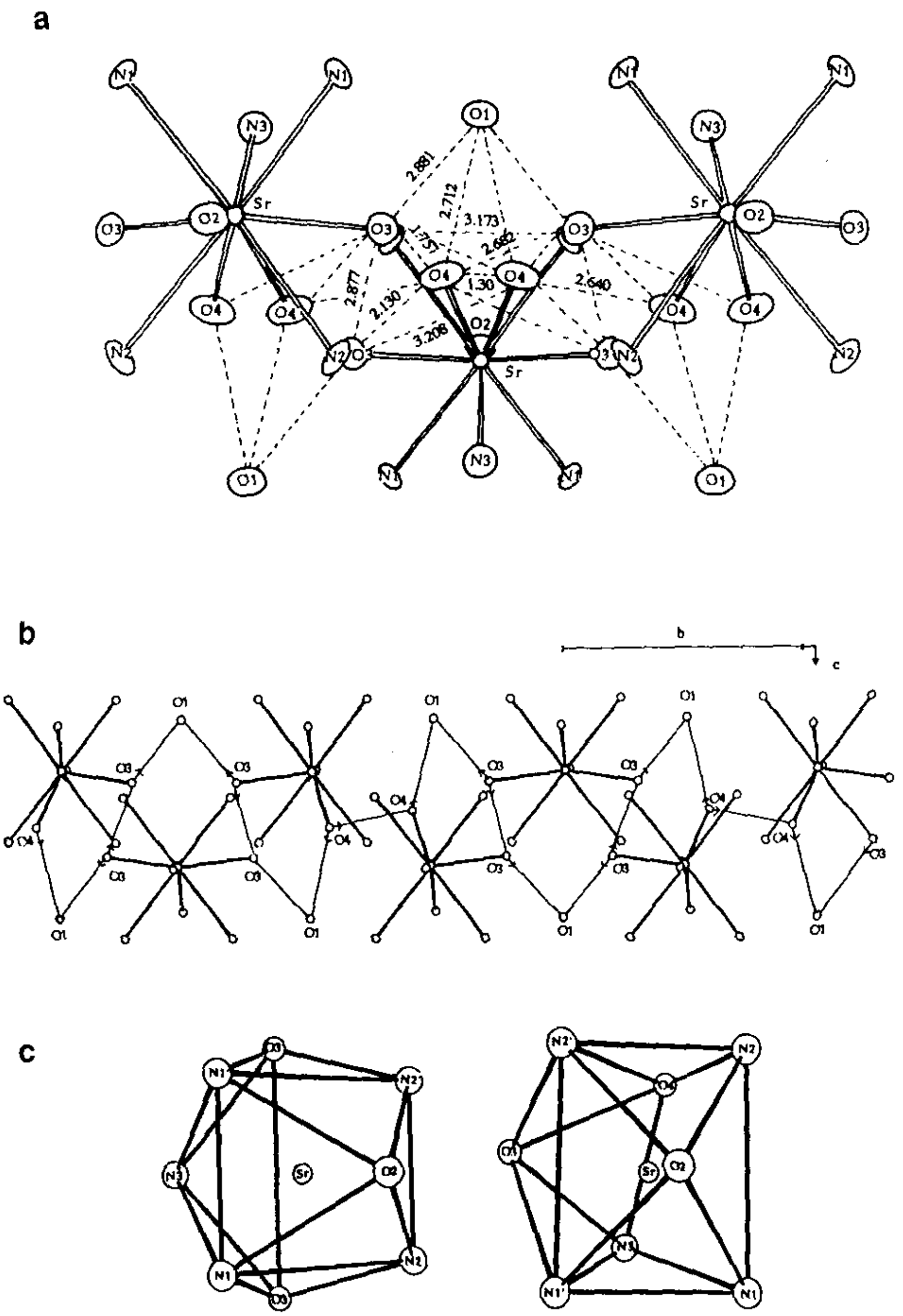

FIG. 2. (a) Strontium environment with relevant distances (Å). (Some positions cannot be simultaneously occupied). (b) Ordered infinite chains of water oxygens along the [0 1 0] direction. (c) Strontium coordination polyhedra.

TABLE 3
Water Oxygen Environment

(a) W(1)					
Atom 1	Atom 2	Distance (Å)	Atom 1	Atom 2	Distance (Å)
O(1)	H(11)	0.961(4)	O(1)	N(3)[a]	3.028(5)
O(1)	N(1)	3.444(5)	O(1)	N(2)	3.569(4)
O(1)	O(3)[b]	2.881(5)	O(1)	O(4)	2.712(7)
O(1)	H(31)	2.335(2)	H(11)	N(3)[a]	2.149(4)

TABLE 3—*Continued*

Water Oxygen Environment

Atom 1	Atom 2	Atom 3	Angle (°)	Atom 1	Atom 2	Atom 3	Angle (°)
O(1)	H(11)	N(3)[a]	151.4(3)	O(3)[b]	O(1)	O(4)	57.2(2)
O(3)[b]	O(1)	O(3)[c]	66.8(2)	**N(1)**	**O(1)**	**N(2)**	**76.3(1)**
N(3)[a]	**O(1)**	**O(3)[b]**	**115.5(1)**	**N(3)[a]**	**O(1)**	**O(4)**	**151.6(2)**
N(3)[a]	**O(1)**	**N(1)**	**64.6(1)**	**N(3)[a]**	**O(1)**	**N(2)**	**139.9(1)**
N(1)	**O(1)**	**N(2)[d]**	**101.5(1)**				

(b) W(2)

Atom 1	Atom 2	Distance (Å)	Atom 1	Atom 2	Distance (Å)
O(2)	H(21)	1.002(3)	**O(2)**	**N(2)**	**3.439(5)**
O(2)	Sr[e]	2.575(4)	**O(2)**	**N(1)**	**3.411(4)**
O(2)	**N(1)[f]**	**3.285(4)**	**O(2)**	**N(2)**	**3.238(4)**
H(21)	**N(1)**	**2.700(3)**			

Atom 1	Atom 2	Atom 3	Angle (°)	Atom 1	Atom 2	Atom 3	Angle (°)
Sr[e]	O(2)	H(21)	116.4(2)	**N(1)**	**O(2)**	**N(2)**	**78.4(1)**
O(2)	**H(21)**	**N(1)**	**131.9(2)**	**O(2)**	**H(22)**	**N(2)**	**140.0(1)**
Sr[e]	**O(2)**	**N(1)**	**130.7(1)**	**Sr[e]**	**O(2)**	**N(2)**	**124.3(1)**

(c) W(3)

Atom 1	Atom 2	Distance (Å)	Atom 1	Atom 2	Distance (Å)
O(3)	Sr[e]	2.646(6)	O(3)	O(4)[h]	2.682(8)
O(3)	N(3)[e]	2.903(5)	O(3)	N(2)[i]	2.828(7)
O(3)	O(3)[j]	2.877(5)	O(3)	O(1)[h]	2.881(5)
O(3)	O(3)[k]	3.173(7)	O(3)	H(31)	1.159(4)

Atom 1	Atom 2	Atom 3	Angle (°)	Atom 1	Atom 2	Atom 3	Angle (°)
Sr[e]	O(3)	O(3)[j]	103.(2)	Sr[e]	O(3)	O(1)[h]	134.3(2)
Sr[e]	O(3)	O(3)[k]	146.8(2)	O(2)[h]	O(3)	O(3)[j]	103.0(2)
O(2)[h]	O(3)	O(3)[k]	56.6(1)	O(4)[j]	O(3)	O(3)[k]	102.8(2)
Sr[e]	O(3)	O(4)[h]	167.5(2)	O(5)[h]	O(3)	O(1)[h]	58.2(2)
O(5)[h]	O(3)	O(3)[j]	70.4(2)				

(d) W(4)

Atom 1	Atom 2	Distance (Å)	Atom 1	Atom 2	Distance (Å)
O(4)	Sr[l]	2.646(6)	O(4)	O(4)[l]	2.640(10)
O(4)	N(3)[l]	2.991(8)	O(4)	N(2)	2.926(7)
O(4)	O(3)[b]	2.682(8)	O(4)	O(1)	2.712(7)
O(4)	O(3)[g]	3.208(9)			

Atom 1	Atom 2	Atom 3	Angle (°)	Atom 1	Atom 2	Atom 3	Angle (°)
Sr[l]	O(4)	O(4)[l]	108.1(3)	Sr[l]	O(4)	O(1)	114.2(3)
Sr[l]	O(4)	O(3)[b]	109.4(3)	O(1)	O(4)	O(4)[b]	64.6(2)
O(1)	O(4)	O(4)[l]	116.0(3)	O(3)[b]	O(4)	O(5)[l]	137.4(3)

Note. Distances (Å) and angles (°) occurring twice due to the *m* crystallographic plane are printed in bold type.

[a] $\bar{x} + 1/2, \bar{y} + 1/2, \bar{z}$.
[b] $x - 1/2, y + 1/2, z$.
[c] $x - 1/2, \bar{y} + 1/2, z$.
[d] $x, \bar{y} + 1, z$.
[e] $x + 1/2, y + 1/2, z$.
[f] $\bar{x} + 1, \bar{y} + 1, \bar{z}$.
[g] $\bar{x} + 1, \bar{y} + 1, \bar{z} + 1$.
[h] $x + 1/2, y - 1/2, z$.
[i] $\bar{x} + 1, y, \bar{z} + 1$.
[j] $\bar{x} + 3/2, \bar{y} + 1/2, \bar{z} + 1$.
[k] $x, \bar{y}, z$.
[l] $\bar{x} + 1/2, \bar{y} + 1/2, \bar{z} + 1$.

CONCLUSION

The disorder observed in the crystal of SrNP was solved on the basis of chemical criteria. The structure shows the existence of short contacts between water oxygens linking the different strontium polyhedra in zig-zag chains along the [0 1 0] direction. This fact suggests the existence of a possible infinite network of hydrogen bonds in the same direction, and of periodicity three times the cell parameter *b*. The hydrogen bond O1–H11..N3 joins the chains in the [001] direction.

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REFERENCES

1. E. E. Castellano, O. E. Piro, and B. E. Rivero, *Acta Crystallogr. B* **33,** 1725 (1977).
2. C. O. Della Vedova, J. H. Lesk, E. L. Varetti, and P. J. Aymonino, O. E. Piro, B. E. Rivero, and E. E. Castellano, *J. Mol. Struct.* **70,** 241 (1981).
3. J. Tritt-Goc and N. Pislewski, *J. Phys. Chem. Solids* **54,** 123 (1993).
4. M. J. Zuriaga, G. A. Monti, C. A. Martin, J. A. Güida, O. E. Piro, and P. J. Aymonino, to be published.
5. E. E. Castellano, O. E. Piro, A. D. Podjarny, and B. E. Rivero, P. J. Aymonino, J. H. Lesk, and E. L. Varetti, *Acta Crystallogr. B* **34,** 2673 (1978).
6. A. Navaza, G. Chevrier, P. Schweiss, and G. Rigotti, *J. Solid State Chem.* **99,** 158 (1992).
7. A. Navaza, G. Chevrier, and J. A. Güida, *J. Solid State Chem.* **114,** 102–107 (1995).
8. International Tables for X-Ray Crystallography, Vol. IV, p. 270. Kynoch Press, Birmingham, England, 1974.
9. B. A. Frenz, "Enraf-Nonius, Structure Determination Package, V3.0." Enraf-Nonius, Delft, The Netherlands, 1985.
10. A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr. A* **24,** 351 (1968).
11. N. Walker and D. Stuart, *Acta Crystallogr. A* **39,** 158 (1983).
12. C. K. Johnson, "ORTEPII," Report ORNL—5138 (Third Revision). Oak Ridge National Laboratory, Tennessee, 1976.
13. P. J. Aymonino, *Pure Appl. Chem.* **60,** 1257 (1988).
14. S. R. Gonzalez, P. J. Aymonino, and O. E. Piro, *J. Chem. Phys.* **81,** 625 (1984).
15. S. R. Gonzalez, O. E. Piro, P. J. Aymonino, and E. E. Castellano, *Phys. Rev. B* **33,** 5818 (1986).
16. A. Navaza, P. Schweiss, P. M. Alzari, G. Chevrier, G. Heger, and J. A. Güida, *J. Solid State Chem.* **89,** 23 (1990).