

## The Crystal and Molecular Structure of Strontium Nitroprusside Dihydrate

BY E. E. CASTELLANO,\* O. E. PIRO, A. D. PODJARNY\* AND B. E. RIVERO

Physics Department, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 47 esq. 115,  
1900 La Plata, Argentina

AND P. J. AYMONINO,\* J. H. LESK AND E. L. VARETTI\*

Chemistry Department, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 47 esq. 115,  
1900 La Plata, Argentina

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Sr[Fe(CN)<sub>5</sub>NO].2H<sub>2</sub>O, obtained by dehydration of a single crystal of the tetrahydrate, crystallizes in the orthorhombic system, space group *Ccmm*, with  $a = 19.4$  (3),  $b = 7.5$  (1),  $c = 8.3$  (1) Å,  $Z = 4$ . The sample showed disorder around  $b$  and only an  $h0l$  layer of reflections was collected. The structure was solved by the heavy-atom method and refined by constrained least-squares calculations in projection to  $R = 13.2\%$  for 43 reflections. Ions and water molecules are in special positions *mm*. Comparison with the tetrahydrate shows the lack of the two equivalent water molecules which are presumed to form strong hydrogen bonds in this last compound. It shows also the relocation of the ions into *mm* sites which causes the change from monoclinic to orthorhombic symmetry. The proposed structure gives support to TGA–DTA and infrared data, which will be published elsewhere.

### Introduction

The structure of Sr[Fe(CN)<sub>5</sub>NO].4H<sub>2</sub>O was recently solved by X-ray techniques (Castellano, Piro & Rivero, 1977). In Table 1 we summarize the relevant structural data.

\* Member of the Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina.

TGA–DTA data and vibrational analysis, as well as the change of weight experienced by the tetrahydrate in a desiccator over P<sub>4</sub>O<sub>10</sub> at atmospheric pressure, show that dehydration proceeds in three distinct stages, the first one leading to the dihydrate. The vibrational analysis of the partially deuterated dihydrate in the water-bands region suggests that the two water molecules are crystallographically non-equivalent, symmetric and not strongly hydrogen-bonded. Further

Table 1. Structural data of Sr[Fe(CN)<sub>5</sub>NO].2H<sub>2</sub>O compared with those of Sr[Fe(CN)<sub>5</sub>NO].4H<sub>2</sub>O (in square brackets)

Tetrahydrate crystallographic parameters: space group *C2/m*,  $a = 20.08$  (2),  $b = 7.51$  (4),  $c = 8.42$  (2) Å,  $\beta = 98.4$  (3)°,  $Z = 4$ .

		Equipoint	Site symmetry	Positional parameters ( $\times 10^4$ ) with e.s.d.'s in parentheses					
				x	y	z			
Sr	[Sr(1)]	4(c) [4(i)]	<i>mm</i> [ <i>m</i> ]	1361 (10)	[1329 (1)]	0 (0)	[0 (0)]	2500 (0)	[2945 (2)]
Fe	[Fe(1)]	4(c) [4(i)]	<i>mm</i> [ <i>m</i> ]	4062 (18)	[4103 (1)]	0 (0)	[0 (0)]	2500 (0)	[2208 (3)]
O(1)	[O(1)]	4(c) [4(i)]	<i>mm</i> [ <i>m</i> ]	5505 (23)	[5519 (9)]	0 (0)	[0 (0)]	2500 (0)	[2596 (22)]
O <sub>w</sub> (2)	[O(2)]	4(c) [4(i)]	<i>mm</i> [ <i>m</i> ]	2326 (94)	[2851 (13)]	5000 (0)	[5000 (0)]	2500 (0)	[1723 (25)]
O <sub>w</sub> (3)	[O(3)]	4(c) [4(i)]	<i>mm</i> [ <i>m</i> ]	43 (83)	[57 (7)]	0 (0)	[0 (0)]	2500 (0)	[2440 (21)]
O <sub>w</sub> (4)	[O(4)]	— [8(j)]	— [1]	—	[2051 (11)]	—	[2917 (35)]	—	[3556 (29)]
N(1)	[N(1)]	4(c) [4(i)]	<i>mm</i> [ <i>m</i> ]	4904 (21)	[4929 (8)]	0 (0)	[0 (0)]	2500 (0)	[2420 (21)]
N(2)	[N(2)]	16(h) [8(j)]	1 [1]	*	[3940 (8)]	*	[2851 (20)]	*	[−451 (18)]
N(3)	[N(3)]	16(h) [8(j)]	1 [1]	3975 (38)	[4034 (8)]	2860 (*)	[2859 (21)]	5078 (45)	[4776 (18)]
N(4)	[N(4)]	4(c) [4(i)]	<i>mm</i> [ <i>m</i> ]	2469 (23)	[2549 (9)]	0 (0)	[0 (0)]	2500 (0)	[1836 (27)]
C(2)	[C(2)]	16(h) [8(j)]	1 [1]	*	[3990 (7)]	*	[1790 (24)]	*	[548 (15)]
C(3)	[C(3)]	16(h) [8(j)]	1 [1]	3937 (36)	[4059 (7)]	1820 (*)	[1816 (23)]	4113 (33)	[3813 (16)]
C(4)	[C(4)]	4(c) [4(i)]	<i>mm</i> [ <i>m</i> ]	3049 (21)	[3113 (11)]	0 (0)	[0 (0)]	2500 (0)	[2028 (32)]

\* N(2) and N(3) and also C(2) and C(3) are symmetry-related through an *m* plane in the dihydrate and therefore the positional parameters of N(2) and C(2) are not given. The  $y$  coordinates of N(3) and C(3) could not be refined in the  $XZ$  projection of the dihydrate; the values shown are obtained from stereochemical considerations. The positional parameters of O<sub>w</sub>(3) correspond to the water molecule coordinated to the Sr<sup>2+</sup>, while in the tetrahydrate they correspond to another asymmetric unit (Castellano, Piro & Rivero, 1977).

dehydration of the dihydrate allows the isolation of the monohydrate and finally of the anhydrous substance (Aymonino *et al.*, 1978).

To ascertain the structural effects of the drying process, a crystallographic study by X-ray, single-crystal methods was undertaken.

#### Data collection and structure determination

A small crystal of strontium nitroprusside tetrahydrate obtained by slow evaporation of an aqueous solution was mounted along  $b$ . The sample was sealed in a glass capillary together with  $P_4O_{10}$ . The Weissenberg photographs of the  $h0l$  layer obtained the following day showed a change of the crystal system from monoclinic to orthorhombic and a decrease of 3.39% in the length of the longer axis and of  $8^\circ$  in  $\beta$ .

The diffraction spots appeared as streaks parallel to the axial line due, probably, to a mosaic structure of small monocrystals oriented with  $b$  along the rotation axis but with a spread of  $a$  and  $c$  of about  $8^\circ$  (Fig. 1).

The crystal parameters are:  $a = 19.4(3)$ ,  $b = 7.5(1)$ ,  $c = 8.3(1)$  Å,  $\lambda = 1.5418$  Å,  $V = 1208$  Å<sup>3</sup>,  $M_r = 339.6$ ,  $Z = 4$ ,  $\rho_c = 1.88$ ,  $\rho_m = 1.92$  g cm<sup>-3</sup> (measured pycnometrically with benzene).

The higher layers showed very poor resolution. From the  $h0l$  and  $h1l$  layers, the following extinction rules were deduced:\*

$$\begin{array}{ll} hkl: h + k = 2n + 1 & hk0: (h + k = 2n + 1) \\ Okl: l = 2n + 1; (k = 2n + 1) & h00: (h = 2n + 1) \\ h0l: (h = 2n + 1) & 0k0: (k = 2n + 1). \\ 00l: (l = 2n + 1) \end{array}$$

These rules are shared by the space groups  $Ccm2_1$  and  $Ccmm = C2/c2/m2_1/m$ . We assumed the latter for the following reasons:

(1) It contains the space group  $C12/m1$  of  $Sr[Fe(CN)_5NO].4H_2O$  as a subgroup and only involves small changes in the positions of all the atoms with the exception of the two equivalent  $O_w(4)$  water molecules (Table 1).

\* To obtain these rules from those in *International Tables for X-ray Crystallography* (1969), we changed  $h \rightarrow k$ ,  $k \rightarrow h$ ,  $l \rightarrow \bar{l}$ ,  $x \rightarrow y$ ,  $y \rightarrow x$ ,  $z \rightarrow \bar{z}$ .

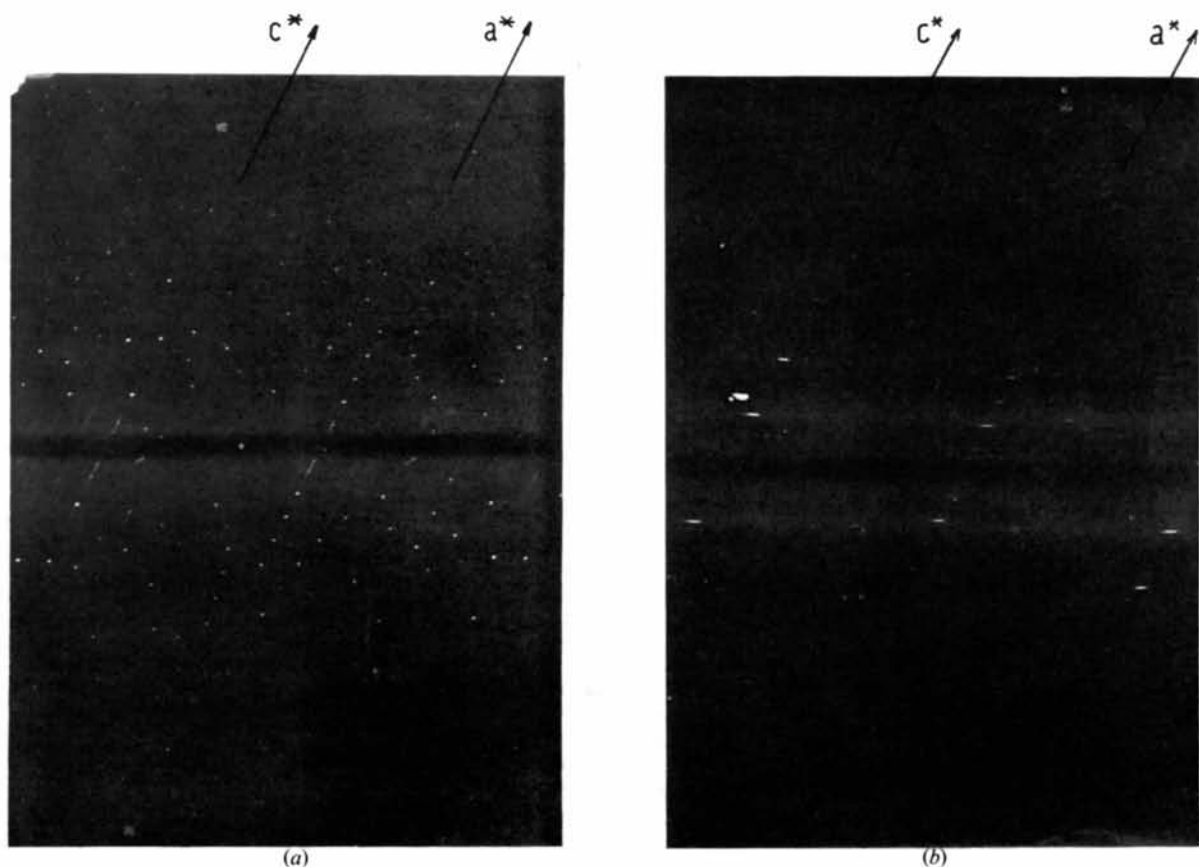


Fig. 1. (a) Weissenberg photograph of the  $h0l$  layer of the tetrahydrate. Note that  $\beta^* = 81.6^\circ$ , corresponding to the monoclinic system. (b) Weissenberg photograph of the  $h0l$  layer of the dihydrate.  $\beta^*$  is now  $90^\circ$ , corresponding to the orthorhombic system. Note the similarity of the intensity pattern compared with (a).

(2) Harker sections of the  $XZ$  projection of the Patterson map could be interpreted only in terms of  $Ccmm$ .

43 independent reflections were visually estimated from Weissenberg photographs of the  $h0l$  layer. The intensities were corrected for Lorentz and polarization effects but not for absorption or extinction. A projection of a sharpened Patterson map was then calculated. The locations of the Fe and Sr atoms were easily determined by comparison with the related map of  $Sr[Fe(CN)_5NO] \cdot 4H_2O$ . A Fourier synthesis phased on these atoms showed the NO and the equatorial CN groups well resolved. At this stage  $R$  was 39.1%,

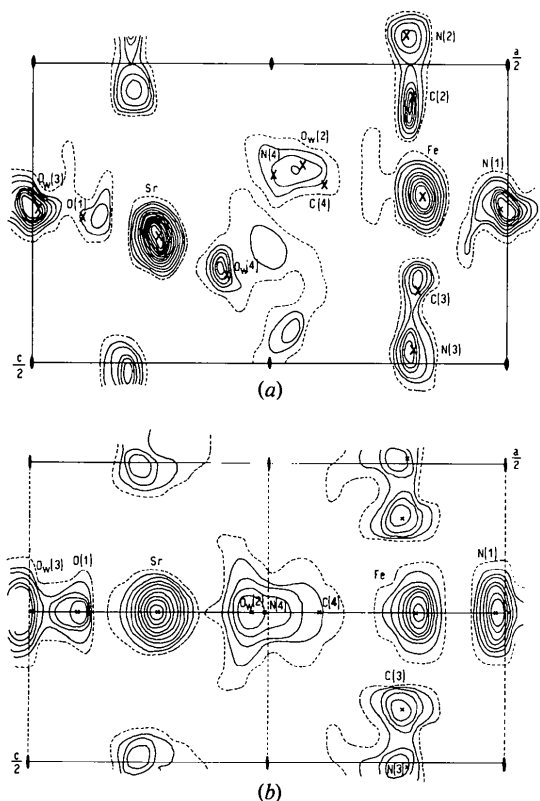


Fig. 2. (a) Distorted projection of the electron density along  $b$  of the tetrahydrate. Note the position of  $O_w(4)$ . 146 non-equivalent reflections phased only with the positions of the Fe and Sr atoms were used to calculate this map. The crosses show the final positions of the atoms, after least-squares refinement. The map is contoured each  $3 \text{ e } \text{\AA}^{-2}$  for light atoms and each  $10 \text{ e } \text{\AA}^{-2}$  for heavy atoms. The dashed lines correspond to null electron density. (b) Undistorted projection of the electron density along  $b$  of the dihydrate. Note the absence of  $O_w(4)$  and the shift in the position of the  $O_w(2)$  water molecule, which eliminates the strong hydrogen bonds. The strontium and nitroprusside ions are now in special positions  $mm$ . 43 non-equivalent reflections phased with the positions of the Fe and Sr atoms were used to calculate this map. The crosses show the final positions of the atoms, after least-squares constrained refinement. For comparison with (a), two asymmetric units are shown. The contour levels are the same as in (a).

Table 2. Crystallographic tests for the presence of water molecules  $O_w(2)$  and  $O_w(3)$

The molecules were omitted alternately, and a least-squares refinement was attempted which consistently refined to the  $R$  values shown below; these are systematically higher than the final  $R$  of 13.2%.

$O_w(2)$	$O_w(3)$	$R$
without	without	16.7%
with	without	15.8
without	with	13.9
with	with	13.2

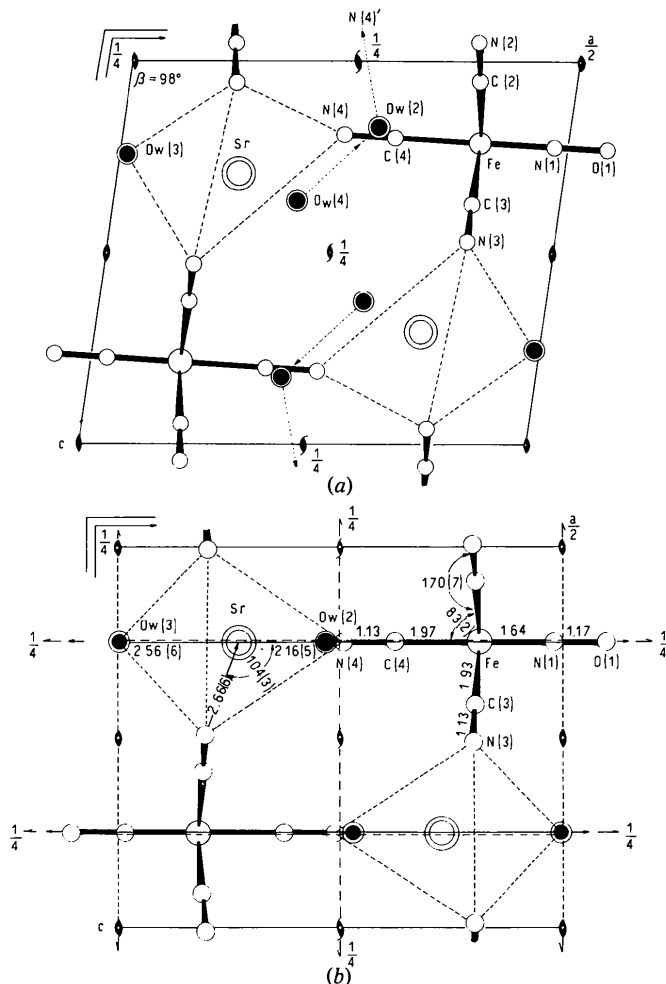


Fig. 3. (a) Undistorted projection of the tetrahydrate along  $b$ . The dotted lines involving  $O_w(4)$  and  $O_w(2)$  indicate the presumed hydrogen bonds.  $N(4)'$  which is hydrogen-bonded to the  $O_w(2)$  water molecule is symmetry-related to  $N(4)$  through the 2, screw axis at  $(\frac{1}{2}, 0, 0)$ . The coordination octahedra around the Sr atom (dashed lines) are very distorted. (b) Undistorted projection of the dihydrate along  $b$ . Note that  $O_w(2)$  is now too far from  $N(4)'$  to form a hydrogen bond. Note the alignment of the whole structure along the  $m$  planes (001) passing through  $(0, 0, \frac{1}{4})$  and  $(0, 0, \frac{3}{4})$ , and the less distorted coordination octahedra around the Sr atom. The bond distances within the nitroprusside ion were fixed (see text). The angles shown, as well as the distances involving the Sr atom and the water molecules, were obtained from the constrained refinement.

compared with 41.8% obtained for the tetrahydrate, calculated in the same way (146 reflections in the  $h0l$  layer).

Fig. 2 shows the electron density projection down  $b$  of both hydrates for comparison. Neither has the axial CN group resolved. An  $R$  of 31.2% was obtained after full-matrix isotropic least-squares refinement, with thermal parameters fixed and including all atoms in the asymmetric unit except the water O atoms. A difference map phased on the refined positions showed the location of the two water molecules. These were included in a further isotropic full-matrix refinement which failed to converge. As this was probably caused by the strong overlap in projection of unresolved atoms, and the poor ratio of number of data to number of parameters, a constrained refinement was performed. All the covalent bonds in the nitroprusside ion were fixed in length but not in direction. The refinement then converged smoothly to  $R = 13.2\%$ . The bond lengths were taken from Castellano, Piro & Rivero (1977). In view of the low accuracy of the measured intensities, the thermal parameters were taken as those of the corresponding atoms in  $\text{Sr}[\text{Fe}(\text{CN})_5\text{NO}] \cdot 4\text{H}_2\text{O}$ .\*

Several crystallographic tests were performed in order to confirm the presence of the two water molecules per unit formula of the compound. These tests consisted in omitting one or both of the water molecules and performing full-matrix isotropic least-squares refinements with the remaining atoms, calculating  $R$  and synthesizing a difference map each time. These maps always showed the missing water molecule(s). Table 2 summarizes the results of these calculations.

In Table 1 the final fractional coordinates of the dihydrate are given. A schematic perspective drawing of the structure as viewed along  $b$  is shown in Fig. 3.

### Discussion

Strontium nitroprusside tetrahydrate and dihydrate have closely related structures. Two of the water

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33472 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

molecules of the tetrahydrate [denoted by  $\text{O}_w(4)$ ], which are not present in the dihydrate, are related by an inversion center and are located at a van der Waals distance of 2.87 Å from each other, with no hydrogen-bonding between them. This implies an unfavorable location of the lone-pair electrons and provides an explanation for the relatively high lability of these molecules, in spite of each of them being hydrogen-bonded to an  $\text{O}_w(2)$  molecule [the  $\text{O}_w(4)$ – $\text{O}_w(2)$  distance is 2.85 Å]. The elimination of the two  $\text{O}_w(4)$  molecules gives place to the alignment of both the strontium and nitroprusside ions along the new  $m$  plane (Figs. 2 and 3), which causes the change of the spatial symmetry  $C 1 2/m 1$  of the tetrahydrate to the higher  $C 2/c 2/m 2_1/m$  of the dihydrate. Of the two remaining water molecules,  $\text{O}_w(3)$  remains electrostatically coordinated to  $\text{Sr}^{2+}$  at the van der Waals contact distance, as in the tetrahydrate. A shift occurs in the position of the other water molecule,  $\text{O}_w(2)$ . None of them is at an appropriate distance from acceptor atoms to form definite hydrogen bonds.

From the crystallographic point of view, the molecules  $\text{O}_w(2)$  and  $\text{O}_w(3)$  are not equivalent and are located in sites of symmetry  $mm$ . Thus the pair of H atoms belonging to each one are interchangeable, as confirmed by the results of the infrared study (Aymonino *et al.*, 1978). The axes of the nitroprusside ions lie on the intersection of the  $m$  planes, *i.e.* along the crystallographic  $a$  axis. The equatorial cyanide groups are at 45° to the symmetry planes.

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