

## Single-Crystal Neutron Diffraction Structure of Sodium Pentacyanonitrosylferrate(2–) (Sodium Nitroprusside) Dihydrate

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**Abstract.**  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$ ,  $M_r = 297.973$ , orthorhombic,  $Pnmm$  (No. 58),  $a = 6.219$  (8),  $b = 11.947$  (11),  $c = 15.587$  (12) Å,  $V = 1158$  (4) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.69$  g cm<sup>-3</sup>,  $\lambda = 0.831$  (1) Å,  $\mu = 0.585$  cm<sup>-1</sup> (evaluated),  $F(000) = 43.2$ , room temperature, final  $R$  factor 0.046 for 1557 observed reflections,  $wR = 0.015$ . The structure is essentially the same as that determined by X-ray diffraction: the nitroprusside anion presents the usual distorted octahedral geometry with the Fe atom 0.261 (1) Å out of the equatorial least-squares mean plane (defined with *cis* CN ligands). The Fe–C and C–N bond lengths are in the ranges 1.929 (2)–1.945 (1) and 1.155 (1)–1.158 (1) Å respectively, the Fe–N distance is 1.667 (1) Å and the Fe–N–O angle is 176.2 (1)°. The water molecules are tetrahedrally coordinated, the H(1)–O(2)–H(2) angle is 105.4 (4)° and the O(2)–H distances [0.925 (4) and 0.939 (4) Å] are slightly shorter than the average value [0.945 Å] found for N-acceptors.

**Introduction.** The stable configuration of sodium nitroprusside can be transformed into an extremely long-lived metastable form when irradiated with laser light in the 400–530 nm spectral range below 160 K (Hauser, Oestreich & Rohrweck, 1977, 1978; Woike, Krasser, Bechthold & Haussuhl, 1983*a,b*; Guida, Piro & Aymonino, 1986). This transition is supposed to be optically induced by a charge transfer process which should produce noticeable structural modifications, particularly affecting the Fe–N–O bond angle (Woike, Krasser, Bechthold & Haussuhl, 1984).

$\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$  was studied by X-ray diffraction (Manoharan & Hamilton, 1963; Bottomley &

White, 1979) and preliminarily by neutron diffraction (Stockli, Fischer, Hurlimann, Furrer & Gudel, 1987). Significant changes were observed in some Bragg-peak intensities between the ground and metastable states, which led Stockli *et al.* (1987) to conclude the existence of a structural rearrangement.

The high-resolution neutron diffraction study of this compound in its ground state was undertaken as part of a research program on structural and vibrational properties of hydrated nitroprusside salts (Rigotti, Aymonino & Varetti, 1984, and references therein).

**Experimental.** Dark red prismatic crystal (2 × 2.62 × 6 mm); four-circle diffractometer P110 at the Orphee reactor; copper (220) monochromator; temperature 295 K; cell parameters and orienting matrix were determined by a centering of 20 reflections (30 ≤ 2θ ≤ 60°); data collection: 3 ≤ 2θ ≤ 75° ω-step scans, and 75 ≤ 2θ ≤ 89° ω–2θ step scans (35 steps, ~2 s per step); the ω-width was adjusted to the resolution as a function of 2θ(10–27tan2θ + 50tan<sup>2</sup>2θ); two standard reflections, 370 and 0,0,12 repeated every 100 reflections, absolutely stable over eight days; collected-data index range  $h: 0$  to 9,  $k: 0$  to 21,  $l: -27$  to 27; 5454 reflections measured, 2715 unique reflections ( $R_{\text{int}} = 0.006$ ) of which 1557 considered as observed with  $F^2 \geq 5\sigma(F^2)$ ; no absorption correction, anisotropic extinction correction by Coppens & Hamilton's (1970) method (for mosaic-spread-dominated extinction):  $Z(1,1) = 0.029$  (5),  $Z(2,2) = 0.016$  (4),  $Z(3,3) = 0.022$  (1),  $Z(1,2) = 0.010$  (3),  $Z(1,3) = 0.017$  (2),  $Z(2,3) = -0.030$  (3); full-matrix least-squares refinement based on  $F^2$ 's, weighting scheme  $w = 1/[\sigma^2(F^2)]$ ; factors:  $R = 0.046$ ,  $wR = 0.015$ ,  $S = 1.996$  for 110 parameters;  $(\Delta/\sigma)_{\text{max}} = 0.036$ .

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Table 1. Atomic and isotropic thermal parameters with estimated standard deviations in parentheses

	x	y	z	$U_{iso}^*(\text{\AA}^2)$
O(1)	0.8768 (3)	0.4056 (2)	0.5	0.0478 (11)
N(1)	0.1059 (2)	0.1227 (1)	0.5	0.0366 (6)
N(2)	0.6671 (1)	0.1203 (1)	0.6413 (1)	0.0351 (4)
N(3)	0.2490 (1)	0.4042 (1)	0.3572 (1)	0.0392 (4)
N(4)	0.7215 (1)	0.3580 (1)	0.5	0.0208 (4)
Na(1)	0.5	0.0	0.2449 (1)	0.0269 (11)
Na(2)	0.0	0.0	0.3780 (2)	0.0332 (12)
Fe(1)	0.4997 (1)	0.2797 (1)	0.5	0.0132 (3)
C(1)	0.2532 (2)	0.1817 (1)	0.5	0.0216 (5)
C(2)	0.6068 (1)	0.1797 (1)	0.5878 (1)	0.0216 (4)
C(3)	0.3442 (1)	0.3606 (1)	0.4113 (1)	0.0217 (4)
O(2)	0.1736 (2)	0.1236 (1)	0.2683 (1)	0.0429 (7)
H(1)	0.1915 (7)	0.1971 (3)	0.2856 (3)	0.091 (2)
H(2)	0.0700 (6)	0.1260 (4)	0.2245 (2)	0.090 (2)

\* The equivalent  $U_{iso}$  is defined as:  $\frac{1}{3}[U(1,1) + U(2,2) + U(3,3)]$ .

Table 2. Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) with estimated standard deviations in parentheses

Estimated standard deviations are in the ranges 0.001–0.003  $\text{\AA}$  and 0.1–0.4 $^\circ$ .

C(1)–N(1)	1.156 (1)	H(1)–O(2)	0.925 (4)
C(2)–N(2)	1.158 (1)	H(2)–O(2)	0.939 (4)
C(3)–N(3)	1.155 (1)	H(1)–H(2)	1.483 (5)
C(1)–Fe(1)	1.929 (2)	N(4)–O(1)	1.126 (2)
C(2)–Fe(1)	1.935 (1)		
C(3)–Fe(1)	1.945 (1)		
N(4)–Fe(1)	1.667 (1)		

C(1)–Fe(1)–N(4)	176.8 (1)	H(1)–O(2)–H(2)	105.4 (4)
C(2)–Fe(1)–N(4)	93.5 (1)	Fe(1)–C(1)–N(1)	179.8 (1)
C(2)–Fe(1)–C(1)	84.2 (1)	Fe(1)–C(2)–N(2)	178.6 (1)
C(3)–Fe(1)–N(4)	97.6 (1)	Fe(1)–C(3)–N(3)	177.0 (1)
C(3)–Fe(1)–C(1)	84.6 (1)	Fe(1)–N(4)–O(1)	176.2 (1)
C(3)–Fe(1)–C(2)	168.8 (1)		
C(3)–Fe(1)–C(2')	88.6 (1)		
C(3)–Fe(1)–C(3')	90.6 (1)		

N(1)···Na(2)···O(2)	93.5 (1)	N(2)···Na(1)···N(3)	86.0 (1)
N(1)···Na(2)···N(2)	102.0 (1)	N(2)···Na(1)···O(2)	84.1 (1)
N(1)···Na(2)···N(2')	88.5 (1)	N(2)···Na(1)···N(2')	90.0 (1)
N(1)···Na(2)···N(1')	80.4 (1)	N(2)···Na(1)···O(2')	84.3 (1)
N(1)···Na(2)···O(2')	169.4 (1)	N(2)···Na(1)···N(3')	165.9 (1)
O(2)···Na(2)···N(2)	84.3 (1)	N(3)···Na(1)···O(2)	108.7 (1)
O(2)···Na(2)···N(2')	86.4 (1)	N(3)···Na(1)···N(3')	100.9 (1)
O(2)···Na(2)···O(2')	93.9 (1)	N(3)···Na(1)···O(2')	82.1 (1)
N(2)···Na(2)···N(2')	166.4 (1)	O(2)···Na(1)···O(2')	163.5 (1)

Integrated intensities were determined from resolution-adapted profile measurements of the peaks: for  $3 \leq 2\theta \leq 50^\circ$ , background was determined with an average of the first and the last six steps of each side; for  $50 \leq 2\theta \leq 89^\circ$ , it was estimated with a special treatment, only a variable number of minimum counting rates (five to nine) was selected for the evaluation of the background.

The resolution conditions of the four circles (especially for the  $\chi$ -circle) imply some superposition of intensities of neighboring reflections  $hkl$  and  $h,k,l \pm 1$  due to a rather large  $c$  parameter of 15.587  $\text{\AA}$ . This effect gives rise to some problem in defining the background of peaks at large  $\sin\theta/\lambda$  values. Even a

careful study of the profiles cannot yield precise integrated intensities for weak reflections at large scattering angles. It is for this reason that we obtained, at an early stage of the refinement, an important deviation of the reliability factors  $wR$  and  $R$  (0.021 and 0.085 respectively), when retaining, as usual, all intensities for which  $F^2 \geq 3\sigma(F^2)$ . The reduced significance of the intensities of weak reflections due to the problematic background correction led us to increase this limit to  $F^2 \geq 5\sigma(F^2)$  for the final refinement. The resulting structure parameters presented here are not at all affected by this modification.

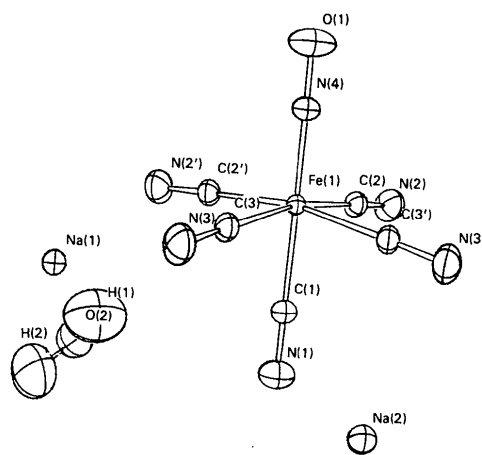


Fig. 1. ORTEP drawing (Johnson, 1976) showing atom labeling. Thermal ellipsoids are drawn at the 50% probability level.

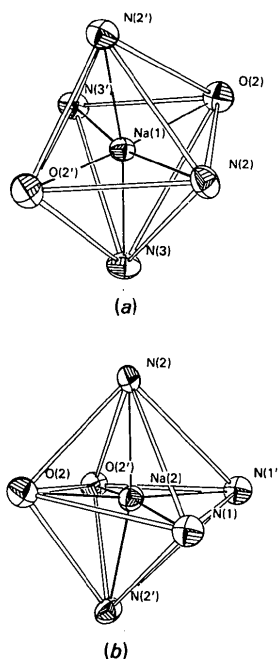


Fig. 2. Coordination geometry of Na atoms: (a) Na(1), (b) Na(2).

Computer programs used in refinement: *SHELX76* (Sheldrick, 1976) and *XFLS* (Busing, Martin & Levy, 1977). Computers used: MicroVAXII and CONVEX C1-XP. Scattering factors from *International Tables for X-ray Crystallography* (1974).

**Discussion.** Our structure analysis of  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$  based on neutron data completes the information concerning the light atoms, *i.e.* hydrogen. The atomic positions and equivalent isotropic thermal parameters are given in Table 1, bond lengths and angles in Table 2.\*

The structure (Fig. 1) is in reasonable agreement with that determined by Bottomley & White, (1979) from X-ray data. As expected there are some discrepancies between the atomic positions of the water molecule and of the NO group where the largest thermal parameters of the nitroprusside anion are also found. The Fe–N–O angle ( $176.2^\circ$ ) is slightly closer to  $180^\circ$  than that ( $175.7^\circ$ ) found from X-ray diffraction, whilst the distance from the Fe atom to the least-squares mean plane of the *cis* C atoms ( $0.189 \text{ \AA}$ , as opposed to  $0.182 \text{ \AA}$ ) is slightly greater.

The water oxygen atoms are tetrahedrally coordinated [ $\text{Na}(1)\cdots\text{O}(2) = 2.536(2)$ ,  $\text{Na}(2)\cdots\text{O}(2) = 2.504(2) \text{ \AA}$ ]; the corresponding angles centered at O(2) are:  $\text{Na}(1)\cdots\text{O}(2)\cdots\text{Na}(2) = 95.7(1)$ ,  $\text{Na}(1)\cdots\text{O}(2)\cdots\text{H}(1) = 119.9(3)$ ,  $\text{Na}(1)\cdots\text{O}(2)\cdots\text{H}(2) = 117.5(3)$ ,  $\text{Na}(2)\cdots\text{O}(2)\cdots\text{H}(1) = 114.3(2)$  and  $\text{Na}(2)\cdots\text{O}(2)\cdots\text{H}(2) = 102.6(2)^\circ$ .

Both cations are in a similar environment; Na(1) is coordinated to O(2), N(2) and N(3) [ $\text{Na}(1)\cdots\text{N}(2) = 2.508(2)$ ,  $\text{Na}(1)\cdots\text{N}(3) = 2.498(2) \text{ \AA}$ ] and Na(2)

to O(2), N(1) and N(2) [ $\text{Na}(2)\cdots\text{N}(1) = 2.490(2)$ ,  $\text{Na}(2)\cdots\text{N}(2) = 2.538(2) \text{ \AA}$ ] (Fig. 2).

The polar axis of the nitroprusside anion [N(1)–C(1)–Fe(1)–N(4)–O(1)] (almost parallel to the –N=O direction) lies on the crystallographic mirror plane (Manoharan & Hamilton, 1963), making an angle of  $30.3(2)^\circ$  with the *a* axis of the cell.

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## Structure of Tetramethylammonium Tetrabromomanganate at Room Temperature

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**Abstract.**  $[\text{N}(\text{CH}_3)_4]_2\text{MnBr}_4$ ,  $M_r = 522.8$ , orthorhombic, *Pmcn*,  $a = 9.301(1)$ ,  $b = 16.182(3)$ ,  $c = 12.750(3) \text{ \AA}$ ,  $V = 1919(1) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_x =$

$1.810 \text{ g cm}^{-3}$ ,  $\lambda(\text{Mo K}\alpha) = 0.7107 \text{ \AA}$ ,  $\mu = 95.20 \text{ cm}^{-1}$ ,  $F(000) = 1028$ ,  $T = 297 \text{ K}$ , final  $R = 0.060$  for 741 independent reflections. The  $\text{MnBr}_4$  is slightly distort-

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