

SHORT STRUCTURAL PAPERS

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Structure of Calcium Nitroprusside Tetrahydrate

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Abstract. $\text{Ca}[\text{Fe}(\text{CN})_5(\text{NO})] \cdot 4\text{H}_2\text{O}$, triclinic, $P\bar{1}$, $a = 7.68$ (3), $b = 9.02$ (2), $c = 10.33$ (3) Å, $\alpha = 78.17$ (1), $\beta = 68.28$ (1), $\gamma = 78.57$ (1)°, $V = 644.5$ (4.5) Å³, $Z = 2$, $D_x = 1.69$ (1), $D_m = 1.6$ Mg m⁻³, $\mu = 1.503$ mm⁻¹ (Mo $K\alpha$), $F(000) = 324$. The structure was solved by the heavy-atom method. A full-matrix least-squares refinement proceeded to $R = 0.041$ for 1966 unique reflections ($R_{\text{sym}} = 0.021$) measured by counter methods. An antiparallel alignment of the NC dipoles along **b** was observed as well as seven-coordinated Ca^{2+} ions.

Introduction. The determination of the structure of the title compound was undertaken as part of a series of chemical, spectroscopic, TGA–DTA and structural studies of alkaline-earth nitroprussides (Lanfranconi, Alvarez & Castellano, 1973; Alvarez, Aymonino, Baran, Gentil, Lanfranconi & Varetto, 1976; Castellano, Piro & Rivero, 1977a; Castellano, Piro, Podjarny, Rivero, Aymonino, Lesk & Varetto, 1978).

Crystals of the title compound obtained by slow evaporation from an aqueous solution at room temperature were supplied by Dr P. J. Aymonino and collaborators, Department of Chemistry, Universidad Nacional de La Plata, Argentina.

A crystal of irregular shape with maximum dimensions of about 0.4 and 0.3 mm was mounted on an Enraf–Nonius CAD-4 computer-controlled four-circle diffractometer. Accurate values for the lattice par-

ameters were calculated by least-squares analysis from setting angles of 22 high-angle reflections automatically centered on the diffractometer at room temperature (295 ± 2 K). Intensities were measured by the θ – 2θ scan technique at a rate of 1.33 – 20.0° min⁻¹ determined by a fast pre-scan of 20° min⁻¹. 2163 reflections were collected to a maximum $\sin \theta/\lambda$ of 0.58 Å⁻¹ using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å).

No systematic absences were observed and $\langle E^2 - 1 \rangle$ statistics together with the Laue symmetry indicated space group $P\bar{1}$. 1966 unique reflections ($R_{\text{sym}} = 0.0214$), corrected for Lorentz and polarization effects but not for absorption or extinction, were treated as observed in all subsequent calculations except for the last refinement stages, regardless of the $I/\sigma(I)$ ratio.

The coordinates of the Fe and Ca atoms derived from Patterson maps were used to phase an electron density map which revealed the remaining atoms of the nitroprusside ion. A difference Fourier map phased on the refined positional and isotropic thermal parameters of all the located atoms showed the four O atoms of the water molecules. At this stage the conventional R factor ($R = \sum |F_o| - |F_c| / \sum |F_o|$) was 0.238. Three cycles of isotropic full-matrix least-squares refinement of the non-hydrogen atoms reduced R to 0.0712. An anisotropic full-matrix least-squares refinement of the same atoms was performed to convergence yielding an $R = 0.0465$.

After introduction of the weighting scheme $w = 1/\sigma^2(F) + 0.0005F^2$ (which minimized the variation of $\langle w(F_o - F_c)^2 \rangle$ as a function of F_o) the H atoms were located from a further difference Fourier map. The H atoms were then refined, isotropically constraining the

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bond lengths within three of the water molecules and the bond lengths and angle within the fourth. The final R was 0.041; the final $R_w [= \sum(|F_o| - |F_c|)_w^{1/2} / \sum |F_o|_w^{1/2}]$ was 0.045 and for the 1872 reflections with $F > 2.5\sigma(F)$ it was 0.04.

All the calculations were performed with the *SHELX* program (Sheldrick, 1975). Atomic scattering factors for Fe and Ca were taken from Cromer & Mann (1968). Those for C, O, N and H were supplied internally by *SHELX*.

Final atomic positions are given in Table 1.* The atom numbering, bond lengths and angles in the nitroprusside ion are shown in Fig. 1. A stereoscopic view of the structure is given in Fig. 2, showing all possible hydrogen bonds.

Discussion. The NO dipoles of the nitroprusside ions have an antiparallel orientation and are stacked at an average distance of 4.7 Å along *b*. A similar geometrical disposition of the nitrosyl groups has been found in other alkaline-earth nitroprussides, such as

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34913 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters* ($\times 10^4$) *with e.s.d.'s in parentheses*

The water molecule formed by O_w(4), H(7) and H(8) was refined as a rigid body.

	<i>x</i>	<i>y</i>	<i>z</i>
Fe	3710 (1)	2049 (1)	1766 (1)
Ca	691 (1)	2515 (1)	-2671 (1)
C(1)	5185 (5)	3414 (4)	2017 (4)
C(2)	5706 (4)	407 (4)	1928 (3)
C(3)	2090 (4)	578 (4)	1902 (3)
C(4)	1651 (4)	3718 (4)	1944 (3)
C(5)	2740 (4)	1682 (3)	3800 (4)
N(1)	6071 (5)	4166 (4)	2204 (4)
N(2)	6913 (4)	-512 (3)	2043 (3)
N(3)	1143 (4)	-302 (3)	2020 (3)
N(4)	521 (4)	4775 (3)	2070 (3)
N(5)	2185 (4)	1494 (4)	5017 (3)
N(6)	4557 (4)	2381 (3)	13 (3)
O(6)	5152 (4)	2641 (3)	-1175 (3)
O _w (1)	6632 (4)	6174 (3)	3883 (3)
O _w (2)	8571 (4)	3640 (3)	6094 (3)
O _w (3)	-403 (5)	2390 (3)	-162 (3)
O _w (4)	7066 (4)	2156 (3)	4713 (4)
H(1)	6555 (74)	5483 (49)	3284 (49)
H(2)	5436 (58)	6773 (75)	4060 (77)
H(3)	8067 (76)	4656 (34)	6065 (61)
H(4)	8268 (73)	3162 (55)	5541 (49)
H(5)	-954 (81)	3220 (50)	271 (61)
H(6)	-480 (81)	1548 (45)	477 (48)
H(7)	7386 (4)	1042 (3)	4757 (4)
H(8)	7179 (4)	2521 (3)	3809 (4)

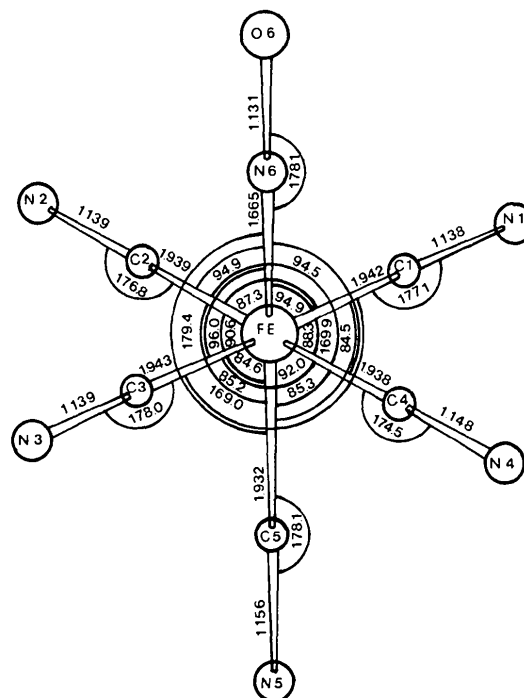


Fig. 1. Bond distances (Å) and angles (°) in the anion. E.s.d.'s are 0.003 Å and 0.1°.

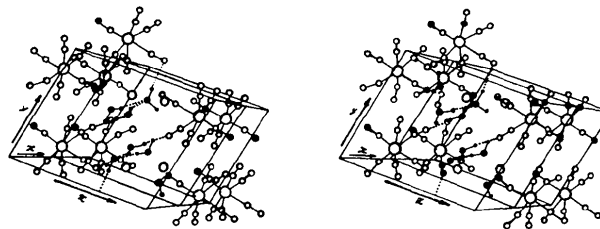


Fig. 2. Stereoscopic view of the structure.

$\text{Na}_2[\text{Fe}(\text{CN})_5(\text{NO})] \cdot 2\text{H}_2\text{O}$ (Manoharan & Hamilton, 1963), $\text{Ba}_2[\text{Fe}(\text{CN})_5(\text{NO})] \cdot 2\text{H}_2\text{O}$ (Lanfranconi, Alvarez & Castellano, 1973) and $\text{Sr}[\text{Fe}(\text{CN})_5(\text{NO})] \cdot 4\text{H}_2\text{O}$ (Castellano, Piro & Rivero, 1977a). The strong dipole-dipole interaction between the nitrosyl groups arising from the arrangement described above is probably responsible for the broadness of the NO band at about 1960 cm^{-1} (Alvarez *et al.*, 1976). A wide NO band also occurs for the other above-mentioned nitroprusside salts (Khanna, Brown & Jones, 1969; Varetto & Aymonino, 1973; Aymonino, Lesk, Varetto, Castellano, Piro, Podjarny & Rivero, 1980).

Fig. 1 shows the very distorted octahedral configuration of the nitroprusside ion. The equatorial CN groups lie on a conical surface with the axis along the Fe-C(5) direction and an apical angle of about 85°. The Fe atom is displaced towards the nitrosyl group, the Fe-N distance, 1.66 Å, is shorter than Fe-C distances (mean 1.94 Å), in agreement with determinations on the other nitroprussides (Manoharan &

Table 2. Coordination distances (Å) and angles (°) around the Ca²⁺ ion with e.s.d.'s in parentheses

Ca ¹ —N(5 ^{II})	2.513 (3)	N(5 ^{II})—Ca ¹ —N(2 ^{III})	81.8 (1)
Ca ¹ —N(2 ^{III})	2.480 (3)	N(5 ^{II})—Ca ¹ —N(3 ^{IV})	82.7 (1)
Ca ¹ —N(3 ^{IV})	2.507 (3)	N(5 ^{II})—Ca ¹ —O _w (1 ^V)	76.8 (1)
Ca ¹ —O _w (1 ^V)	2.367 (3)	N(5 ^{II})—Ca ¹ —O _w (2 ^{VI})	76.3 (1)
Ca ¹ —O _w (2 ^{VI})	2.380 (3)	N(5 ^{II})—Ca ¹ —O _w (3 ^{VI})	156.2 (1)
Ca ¹ —O _w (3 ^{VI})	2.395 (3)	N(2 ^{III})—Ca ¹ —N(3 ^{IV})	82.3 (1)
Ca ¹ —N(4 ^{VII})	2.552 (3)	N(2 ^{III})—Ca ¹ —O _w (1 ^V)	81.8 (1)
		N(2 ^{III})—Ca ¹ —O _w (2 ^{VI})	155.1 (1)
		N(2 ^{III})—Ca ¹ —O _w (3 ^{VI})	78.5 (1)
		N(3 ^{IV})—Ca ¹ —O _w (1 ^V)	155.7 (1)
		N(3 ^{IV})—Ca ¹ —O _w (3 ^{VI})	81.5 (1)
		N(3 ^{IV})—Ca ¹ —O _w (2 ^{VI})	83.3 (1)
		O _w (1 ^V)—Ca ¹ —O _w (2 ^{VI})	104.2 (1)
		O _w (1 ^V)—Ca ¹ —O _w (3 ^{VI})	113.0 (1)
		O _w (2 ^{VI})—Ca ¹ —O _w (3 ^{VI})	119.2 (1)
		N(4 ^{VII})—Ca ¹ —N(5 ^{II})	132.1 (1)
		N(4 ^{VII})—Ca ¹ —N(2 ^{III})	131.8 (1)
		N(4 ^{VII})—Ca ¹ —N(3 ^{IV})	127.9 (1)
		N(4 ^{VII})—Ca ¹ —O _w (3 ^{VI})	71.7 (1)
		N(4 ^{VII})—Ca ¹ —O _w (1 ^V)	76.2 (1)
		N(4 ^{VII})—Ca ¹ —O _w (2 ^{VI})	72.9 (1)

Symmetry code

- (i) x, y, z
- (ii) $x, y, z - 1$
- (iii) $1 - x, -y, \bar{z}$
- (iv) $\bar{x}, \bar{y}, \bar{z}$
- (v) $1 - x, 1 - y, \bar{z}$
- (vi) $x - 1, y, z - 1$
- (viii) $1 - x, 1 - y, 1 - z$
- (ix) $1 - x, \bar{y}, 1 - z$

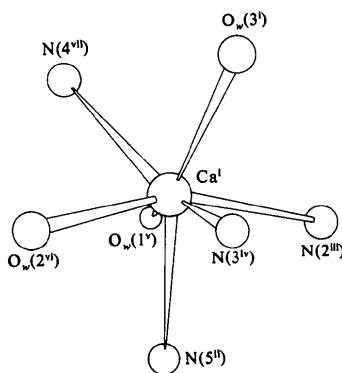


Fig. 3. Calcium coordination polyhedron.

Hamilton, 1963; Lanfranconi, Alvarez & Castellano, 1973; Castellano, Piro & Rivero, 1977*a,b*; Rigotti, Punte, Rivero & Castellano, 1980). This configuration supports the interpretation of Ballhausen & Gray (1963) and the MO calculations of Manoharan & Gray (1965) and Tullberg & Vannenberg (1967) concerning bonding in the nitroprusside ion.

Bond distances and angles around Ca²⁺ are given in Table 2. Fig. 3 shows the geometry of the Ca²⁺ ion environment. The seven atoms that are bound to the Ca²⁺ ion assume a distorted 7c coordination polyhedron (Wells, 1962). Each Ca²⁺ ion is bound to three O atoms of water molecules, with distances ranging from 2.36 to 2.5 Å, and to four N atoms of CN groups of different nitroprusside ions, with distances ranging from 2.48 to 2.56 Å. The Ca²⁺—N distances are similar to those previously reported in other Ca²⁺

Table 3. Hydrogen-bond distances (Å) and angles (°) with e.s.d.'s in parentheses

The water molecule O _w (4), H(7), H(8) was refined as a rigid body.			
D—H...A	D...A	H...A	∠D—H...A
O _w (1 ^{VIII})—H(2 ^{VIII})...O _w (4 ^I)	2.943 (3)	2.048 (28)	158.3 (3.7)
O _w (1 ^{VIII})—H(1 ^{VIII})...N(1 ^{II})	2.896 (4)	1.954 (25)	172.9 (4.3)
O _w (2 ^{VIII})—H(4 ^{VIII})...O _w (4 ^I)	2.789 (4)	1.908 (20)	166.6 (4.6)
O _w (4 ^I)—H(7 ^I)...N(5 ^{III})	3.200 (3)	2.222 (3)	174.5 (0.1)

compounds (Verdier, L'Haridon, Maunaye & Marchand, 1974; Einspahr & Bugg, 1974).

The shortest Ca²⁺—O and Ca²⁺—N distances are approximately equal to the sum of the ionic radius of Ca²⁺ and the van der Waals radii of the other atoms (2.39 Å for O and 2.44 Å for N). Therefore, the Ca²⁺ and the three O atoms of its coordination polyhedron are in quite close contact.

The four water molecules are crystallographically and stereochemically non-equivalent. One of the water molecules, *W*(3), is coordinated to the Ca²⁺ ion. The other three are interlinked by hydrogen bonds (see Fig. 2). *W*(4) is bound as an acceptor atom to the other water molecules and as a donor atom to a CN group, *W*(1) and *W*(2) are coordinated to the Ca²⁺ ion; *W*(1) is also bound as a donor atom to a CN group. Table 3 shows bond distances and angles for the hydrogen bonds. The different bond strengths suggested by the patterns and lengths of the various hydrogen bonds are in accordance with IR spectral results (Rigotti, Aymonino & Varetto, 1979).

As can be seen from Table 1 and Fig. 2, the packing in the [001] direction is characterized by successive layers of nitroprusside ions, confining the *W*(3) water molecules, Ca²⁺ ions and interlinked water molecules. These layers are centered at zero, $\frac{1}{4}$ and $\frac{1}{2}$ of the unit cell, respectively.

The relatively weak hydrogen and coordination bonds between water and the other layers suggest that three water molecules may be easily lost. This was observed in TGA and dehydration experiments (Rigotti, Aymonino & Varetto, 1979).

In accordance with their layer structure, crystals grow, by slow evaporation from a saturated solution, in the form of plates parallel to (001). Also the crystals present a cleavage plane along (001).

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Structure of Thallium Nitroprusside

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Abstract. $\text{Tl}_2[\text{Fe}(\text{CN})_5(\text{NO})]$, monoclinic, Cc , $a = 13.349$ (15), $b = 12.520$ (9), $c = 6.779$ (5) Å, $\beta = 66.180$ (1)°, $Z = 4$, $D_c = 4.003$ Mg m⁻³, $\mu = 32.802$ mm⁻¹ (Mo $K\alpha$), $F(000) = 1063$. The structure was solved by the heavy-atom method and refined, with constraints in the first stages, to an R of 0.067 for 738 unique reflections. The structure is tightly packed with a shortest Tl–Tl distance of 3.480 (2) Å. The nitrosyl groups of neighbouring nitroprusside ions form a staggered stack along the c axis with a mean separation of 4.8 Å; directions of consecutive groups form an angle of approximately 55°.

Introduction. The determination of the structure of thallium nitroprusside was undertaken as part of a series of chemical, spectroscopic, TGA–DTA and structural studies of nitroprusside compounds (Lanfranconi, Alvarez & Castellano, 1973; Alvarez,

Aymonino, Baran, Gentil, Lanfranconi & Varetti, 1976; Castellano, Piro & Rivero, 1977a,b; Rivero *et al.*, 1978; Castellano, Piro, Podjarny, Rivero, Aymonino, Lesk & Varetti, 1978; Punte, Rigotti, Rivero, Podjarny & Castellano, 1980).

Crystals were obtained by slow evaporation from an aqueous solution. A crystal of irregular shape (maximum and minimum linear dimensions of about 0.4 and 0.3 mm respectively) was mounted on an Enraf–Nonius CAD-4 diffractometer. Intensities were measured by the θ – 2θ scan technique at a rate of 1.33–20.0° min⁻¹, determined by a fast pre-scan of 20° min⁻¹. 738 unique reflections above background (3σ) were collected using graphite-monochromated Mo $K\alpha$ radiation in the range $1^\circ < 2\theta < 48^\circ$. Data were corrected for Lorentz and polarization effects but not for absorption or extinction.

The systematic absences (hkl : $h + k = 2n$; $h0l$: $l = 2n$) suggested space group Cc or $C2/c$. Statistical intensity tests and the cell content indicated the space group Cc .

The positions of the two Tl and Fe atoms were obtained from a Patterson map. A difference map

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