

## The Crystal and Molecular Structure of Strontium Nitroprusside Tetrahydrate

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$\text{Sr}[\text{Fe}(\text{CN})_5\text{NO}]\cdot 4\text{H}_2\text{O}$  crystallizes in the monoclinic system, space group  $C2/m$ , with  $a = 20.08(2)$ ,  $b = 7.51(4)$ ,  $c = 8.42(2)$  Å,  $\beta = 98.4(3)^\circ$ ,  $Z = 4$ . The structure was solved by the heavy-atom method and refined by least squares to  $R = 0.099$  for 1014 reflexions. The nitroprusside ion is in a special position with site symmetry  $m$ ; the water molecules can be grouped into three categories according to their chemical environments: in one category the molecule is at the van der Waals distance from its inversion-symmetry-related molecule and also strongly hydrogen-bonded to a molecule of the second category. The third type belongs to the octahedral environment of the Sr ion. The nitrosyl groups of neighbouring nitroprusside ions are approximately parallel to  $\mathbf{a}$  and are piled up along  $\mathbf{c}$  at intervals of about 4 Å, a distance short enough to allow a strong dipole-dipole interaction which is perhaps responsible for the broadness of the NO stretching band. The  $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$  ions are highly distorted octahedra with a mean Fe–C distance of 1.94 and Fe–N of 1.64 Å.

### Introduction

The determination of the structure of strontium nitroprusside tetrahydrate was undertaken as part of a series of chemical, spectroscopic, TGA–DTA and structural studies of the alkaline-earth nitroprussides (Lanfranconi, Alvarez & Castellano, 1973; Alvarez, Aymonino, Baran, Gentil, Lanfranconi & Varetto, 1976).

### Experimental

The crystals were obtained by slow evaporation from an aqueous solution at room temperature. A previous determination of cell dimensions and space group has been reported (Alvarez *et al.*, 1976). We confirmed the first but have found the space group to be  $C2/m$  rather than  $C2$ .

The crystal data of  $\text{Sr}[\text{Fe}(\text{CN})_5\text{NO}]\cdot 4\text{H}_2\text{O}$  are:  $a = 20.08(2)$ ,  $b = 7.51(4)$  and  $c = 8.42(2)$  Å;  $\beta = 98.4(3)^\circ$ ;  $\lambda = 1.5418$  Å;  $V = 1256.1$  Å<sup>3</sup>;  $M_r = 375.5$ ;  $\rho_m = 1.96$ ,  $\rho_c = 1.97$  g cm<sup>-3</sup>;  $Z = 4$ .

From a crystal mounted along  $\mathbf{b}$  1014 reflexions above background were visually estimated from equi-inclination Weissenberg photographs of the  $h0-6l$  layers. The intensities were corrected for Lorentz and polarization effects but not for absorption or extinction.

The Sr and Fe atoms were located from a Patterson map. A Fourier synthesis phased on these atoms showed all the non-hydrogen atoms of the asymmetric

unit. A block-diagonal anisotropic least-squares refinement was performed to convergence. The weighting

Table 1. Positional parameters ( $\times 10^4$ ) with estimated deviations in parentheses

	$x$	$y$	$z$
Sr(1)	1329 (1)	0 (0)	2945 (2)
Fe(1)	4103 (1)	0 (0)	2208 (3)
O(1)	5519 (9)	0 (0)	2596 (22)
O(2)	2851 (13)	5000 (0)	1723 (25)
O(3)	5057 (7)	5000 (0)	2440 (21)
N(1)	4929 (8)	0 (0)	2420 (21)
N(4)	2549 (9)	0 (0)	1836 (27)
C(4)	3113 (11)	0 (0)	2028 (32)
N(2)	3940 (8)	2851 (20)	-451 (18)
N(3)	4034 (8)	2859 (21)	4776 (18)
C(2)	3990 (7)	1790 (24)	548 (15)
C(3)	4059 (7)	1816 (23)	3813 (16)
O(4)	2051 (11)	2917 (35)	3556 (29)

Table 2. Coordination distances (in Å) and angles (in degrees) around the  $\text{Sr}^{2+}$  ion with estimated standard deviations in parentheses

$\text{Sr}^i\text{--N}(4^i)$	2.74 (2)	$\text{N}(4^i)\text{--Sr}^i\text{--O}(3^{\text{iii}})$	150.8 (5)
$\text{Sr}^i\text{--N}(2^{\text{iii}})$	2.64 (2)	$\text{N}(4^i)\text{--Sr}^i\text{--N}(2^{\text{iv}})$	79.6 (5)
$\text{Sr}^i\text{--N}(3^{\text{iv}})$	2.69 (2)	$\text{N}(4^i)\text{--Sr}^i\text{--N}(3^{\text{iv}})$	126.2 (5)
$\text{Sr}^i\text{--O}(3^{\text{iii}})$	2.53 (2)	$\text{O}(3^{\text{iii}})\text{--Sr}^i\text{--N}(2^{\text{iv}})$	77.4 (4)
$\text{Sr}^i\text{--O}(4^i)$	2.64 (3)	$\text{O}(3^{\text{iii}})\text{--Sr}^i\text{--N}(3^{\text{iv}})$	75.4 (4)
		$\text{N}(2^{\text{iii}})\text{--Sr}^i\text{--N}(3^{\text{iv}})$	99.0 (5)
		$\text{N}(4^i)\text{--Sr}^i\text{--O}(4^i)$	65.8 (6)
		$\text{O}(3^{\text{iii}})\text{--Sr}^i\text{--O}(4^i)$	123.1 (6)

Symmetry code

- (i)  $x, y, z$  (iii)  $x + \frac{1}{2}, y + \frac{1}{2}, z$   
 (ii)  $\bar{x}, \bar{y}, \bar{z}$  (iv)  $\bar{x} + \frac{1}{2}, \bar{y} + \frac{1}{2}, \bar{z}$

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## Description of the structure

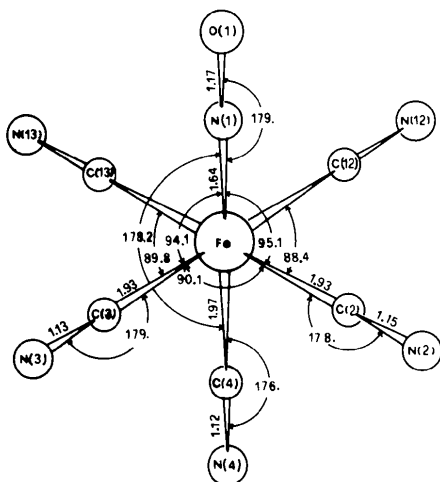


Fig. 1. Bond distances and angles in the anion. Standard deviations are 0.02 to 0.03 Å and 1–2°.

scheme  $w = 1$  if  $F_o < a$ ;  $w = 1/F_o$  if  $F_o \geq a$ , with  $a = 70$  on an absolute scale, was used. The final  $R$  was 0.099.

The final atomic coordinates are given in Table 1.\* Fig. 1 gives bond distances and angles in the nitroprusside ion. Table 2 gives the coordination distances and angles around Sr.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32313 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The nitroprusside ion is located in a special position of point symmetry  $m$  with the nitrosyl group pointing approximately along  $a$ . The presence of the twofold screw axis along  $b$  together with the small value of  $c$  forces a piling up of the nitrosyl groups along  $c$  in an alternating antiparallel fashion at a distance of about 4 Å (Fig. 2). This strong dipole–dipole interaction between the nitrosyl groups is probably responsible for the broadness of the NO bands at about 1960  $\text{cm}^{-1}$  (Aymonino, Lesk & Varetto, 1976). This characteristic wide NO band appears systematically in other compounds with similar geometrical arrangements of the nitrosyls, such as  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$  (Manoharan & Hamilton, 1963; Khanna, Brown & Jones, 1969) and  $\text{Ba}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$  (Lanfranco, Alvarez & Castellano, 1973; Varetto & Aymonino, 1973) and it is essentially different from the narrower NO stretching band corresponding to structures in which the geometrical arrangement makes the dipole–dipole interaction negligibly small, as in the isomorphous compounds  $[\text{As}(\text{C}_6\text{H}_5)_4]_2[\text{Fe}(\text{CN})_5\text{NO}]$  and  $[\text{P}(\text{C}_6\text{H}_5)_4]_2[\text{Fe}(\text{CN})_5\text{NO}]$  (Gentil & Aymonino, 1977; Castellano, Piro & Rivero, 1977). This particular arrangement is also responsible for the very strong dichroism of the NO stretching band observed in single-crystal IR spectra (Aymonino, Lesk & Varetto, 1976).

The nitroprusside ion shows a very distorted octahedral configuration with site symmetry  $m$ . The distances between the Fe atom and its ligands agree with

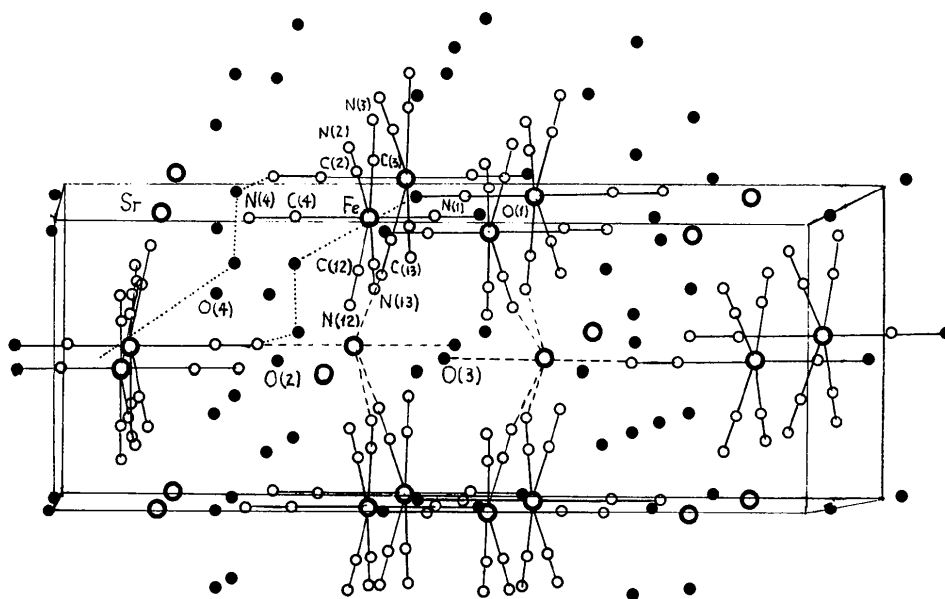


Fig. 2. Projection of the structure down  $c$ . O atoms are indicated by black dots. Dotted lines indicate the presumed hydrogen bonds in one asymmetric unit. Dashed lines indicate the coordination atoms around Sr.

other determinations on nitroprusside compounds (Manoharan & Hamilton, 1963; Lanfranconi, Alvarez & Castellano, 1973; Castellano, Piro & Rivero, 1977). In particular the short Fe–N distance supports the interpretation of Ballhausen & Gray (1963) and its further numerical verification by Manoharan & Gray (1965) that the strong Fe–NO bond dominates the electronic structure of the levels involved in the optical transitions and those of the near-UV region of the absorption spectrum.

The equatorial CN groups lie on a conical surface with an axis along the Fe–C (4) direction, with the Fe atom at its apex and an apical angle of about 85°. This configuration can be attributed to the weak anti-bonding rather than the non-bonding character of the  $2b_2(3d_{xy})$  orbital (Tullberg & Vannenberg, 1967).

The atoms closer to the  $\text{Sr}^{2+}$  ion form a very distorted octahedron. This probably minimizes the electrostatic interaction between the noble-gas-type cation and its environment. Fig. 3 shows the schematic arrangement of these octahedra in the crystal. It can be seen that the  $\text{Sr}^{2+}$  ions share one N of a CN group of each of five nitroprusside anions, completing the octahedron with the O atoms of a water molecule. This pattern of ion–ion interaction dominates the packing characteristics in the (100) plane. The unshared NO groups tend to stabilize the packing along the [100] direction through the dipole–dipole interactions (Fig. 2) while the monopolar contributions to the NO interaction are perhaps opposite to the dipolar ones, tending to destabilize the packing energy along the [100] direction (Vannenberg & Jagner, 1974; Folkesson, 1974). This is suggested by the presence of cleavage (100) planes and also because crystals grown from a saturated solution by slow evaporation occur mainly in the form of thin sheets parallel to the planes (100).

From the crystallographic and stereochemical points of view, the water molecules can be divided into three types. One type occupies a general position and the other two occupy the special position  $m$ . O(3) belongs

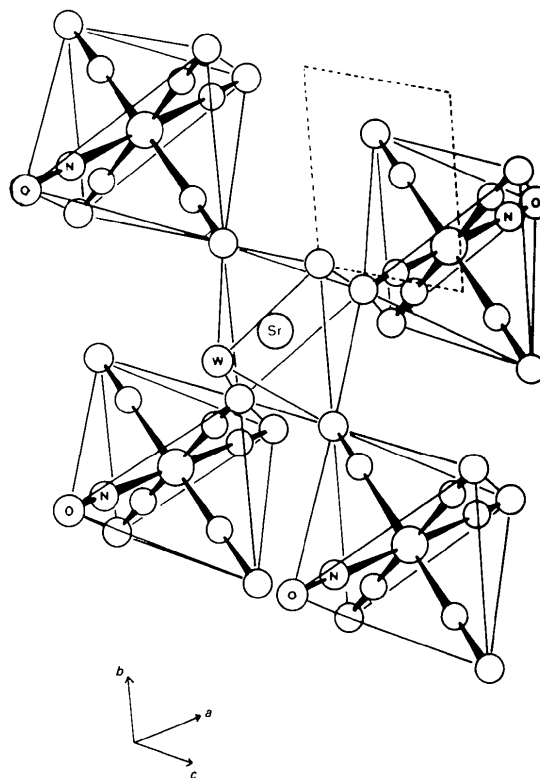


Fig. 3. Schematic diagram showing the Sr coordination octahedra throughout the structure. For the sake of clarity the top-right Sr coordinated nitroprusside ion and the hydrogen-bonded water molecules have been omitted.

Table 3. *Hydrogen bonds and short van der Waals contacts*

Symmetry code is given in Table 2.

(a) Hydrogen bonds involving O(4)

Donor atom	Acceptor atom X	Distance (Å)	Angle (°) $X-O(4^i)-Sr^i$	Angle (°) $O(2^i)-O(4^i)-O(1^{iii})$
O(4 <sup>i</sup> )	O(2 <sup>i</sup> )	2.85 (3)	133 (1)	100 (1)
	O(1 <sup>iii</sup> )	3.44 (3)	83.3 (7)	

(b) Hydrogen bonds involving O(2)

	Distance (Å)		Angle (°)
O(2 <sup>i</sup> )–N(4 <sup>iv</sup> )	2.85 (3)	O(4 <sup>i</sup> )–O(2 <sup>i</sup> )–N(4 <sup>iv</sup> )	116.9 (8)

(c) Short van der Waals contact

	Distance (Å)
O(4 <sup>i</sup> )–O(4 <sup>iv</sup> )	2.87 (3)

to the octahedral environment of the  $\text{Sr}^{2+}$  and is too far from other atoms to form hydrogen bonds. Table 3 gives the distances and angles between the O(2) and O(4) atoms of water molecules and the atoms to which hydrogen-bonding is presumed (Chidambaram, Sequeira & Sikka, 1964; Holzbecher, Knop & Falk, 1971).

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## The Crystal and Molecular Structure of Bis(tetraphenylarsonium) Nitroprusside

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$[\text{As}(\text{C}_6\text{H}_5)_4]_2[\text{Fe}(\text{CN})_5\text{NO}]$  is monoclinic, space group  $P2_1/c$ , with  $a = 9.09$  (1),  $b = 21.43$  (2),  $c = 24.51$  (1) Å,  $\beta = 104.3$  (3)°,  $Z = 4$ . 1607 visual data were used. The final  $R$  is 0.120. The nitroprusside anion has a somewhat distorted octahedral configuration with  $\text{Fe}-\text{N} = 1.61$  (5) and  $\text{Fe}-\text{C} = 1.92$  (2) Å (mean). The two independent cations differ in the orientation of the phenyl groups. The packing of the structure is such that the ions are all relatively distant from each other, the shortest  $\text{Fe}-\text{As}$  distance being 6.53 Å.

### Introduction

The structure determination of  $[\text{As}(\text{C}_6\text{H}_5)_4]_2[\text{Fe}(\text{CN})_5\text{NO}]$  was undertaken as part of a study of some nitroprusside compounds (Lanfranconi, Alvarez & Castellano, 1973; Varetti & Aymonino, 1973; Castellano, Piro & Rivero, 1977; Alvarez, Aymonino, Baran, Gentil, Lanfranconi & Varetti, 1976).

### Experimental

From a crystal mounted along a 1607 reflexions above background were visually estimated from equi-inclination Weissenberg photographs of the 0–6 $k$ l layers. The intensities were corrected for Lorentz and polarization effects but not for absorption or extinction. The As and Fe atoms were located from a Patterson map. A Fourier synthesis phased on these atoms showed all the non-hydrogen atoms of the asymmetric unit. A block-diagonal isotropic least-squares refine-

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