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**The crystal and molecular structure of barium nitroprusside dihydrate.** By A. H. LANFRANCONI,\* A. G. ALVAREZ† and E. E. CASTELLANO,† *Departamento de Física, Universidad Nacional de La Plata, La Plata, Argentina*

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Barium nitroprusside dihydrate crystallizes in space group  $Pca2_1$  with  $a=19.471(20)$ ,  $b=7.631(20)$ ,  $c=8.609(20)$  Å,  $Z=4$ . The structure was solved by the heavy-atom method and refined by least squares. The  $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$  ions are highly distorted octahedra with  $\text{Fe}-\text{N}=1.705$  Å and  $\text{Fe}-\text{C}=1.91$  Å (mean value).

The crystal and molecular structure of barium nitroprusside dihydrate,  $\text{Ba}[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$ , has been determined to assist in the interpretation of its single-crystal infrared spectrum (Varetti & Aymonino, 1973).

The crystals, which were obtained by evaporation from aqueous solution at ambient temperature, are orthorhombic with the following crystallographic constants:

$$\begin{aligned} a &= 19.471(20) \text{ \AA} & d_0 &= 2.03 \text{ g cm}^{-3} \\ b &= 7.631(20) & d_c &= 2.04 \\ c &= 8.609(20) & Z &= 4 \\ \text{Cu } K\alpha_1 \lambda &= 1.5405 \text{ \AA} & \text{Space group} &: Pca2_1 \end{aligned}$$

1029 reflexions were assigned non-zero intensities by visual estimation of equi-inclination Weissenberg photographs of the  $hk0-8$  layers. The intensities were corrected for Lorentz and polarization effects, but not for absorption or extinction. The barium and iron atoms were located from a Patterson map. Three successive Fourier synthesis showed reasonable positions for the cation and for the atoms of the anion, and also two ill-defined further peaks. A difference map in which these peaks were not included showed them clearly to be the two water molecules of crystallization.

Seven cycles of least-squares refinement with isotropic thermal factors gave a final  $R$  of 0.141. The final atomic coordinates and temperature factors are given in Table 1, the distances and angles in the nitroprusside ion in Table 2, and the coordination distances in Table 3. Table 4 lists the observed and calculated structure factors. The contents of the unit cell are shown in projection down  $c$  in Fig. 1.

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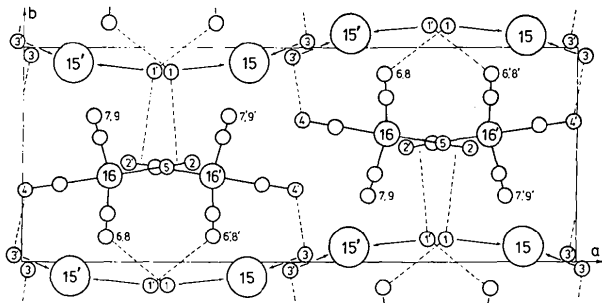


Fig. 1. Projection of the structure down  $c$ . Primed numbers denote atoms with coordinates  $z = \frac{1}{2}$ . Broken lines represent presumed hydrogen bonds, and arrows the coordination of water molecules.

Table 1. Final atomic parameters  
Positional parameters are  $\times 10^4$ .

	$x/a$	$y/b$	$z/c$	$B(\text{\AA}^2)$
O(1)	2581 (11)	8900 (27)	1637 (54)	1.15 (4)
O(2)	3018 (16)	4634 (27)	1643 (75)	2.70 (9)
O(3)	93 (26)	-250 (73)	-352 (56)	4.27 (43)
N(4)	53 (18)	3299 (49)	1636 (99)	2.93 (10)
N(5)	2454 (17)	4540 (36)	1529 (40)	1.14 (5)
N(6)	1583 (18)	1466 (51)	-898 (49)	1.76 (5)
N(7)	1323 (20)	6781 (49)	-654 (50)	3.57 (30)
N(8)	1567 (17)	1124 (47)	4121 (48)	1.69 (4)
N(9)	1279 (19)	6912 (50)	4211 (52)	3.87 (40)
C(10)	627 (16)	3647 (44)	1667 (52)	1.50 (9)
C(11)	1596 (21)	2440 (61)	73 (56)	1.49 (8)
C(12)	1411 (19)	5926 (47)	261 (48)	1.50 (8)
C(13)	1589 (22)	2243 (62)	3139 (61)	2.12 (22)
C(14)	1378 (24)	6088 (59)	3251 (60)	2.66 (21)
Ba	3975 (1)	9284 (7)	1721 (15)	1.57 (8)
Fe	1597 (1)	4147 (7)	1764 (24)	1.61 (3)

Table 2. Distances and angles in the nitroprusside ion

Fe—N(5)	1.71 (4) Å
Fe—C(10)	1.92 (3)
Fe—C(11)	1.95 (4)
Fe—C(12)	1.88 (4)
Fe—C(13)	1.88 (6)
Fe—C(14)	1.96 (6)
N(5)—O(2)	1.11 (5)
N(4)—C(10)	1.17 (5)
N(6)—C(11)	1.13 (5)
N(7)—C(12)	1.09 (6)
N(8)—C(13)	1.21 (7)
N(9)—C(14)	1.13 (9)
Fe—N(5)—O(2)	166 (4)°
Fe—C(10)—N(4)	176 (5)
Fe—C(11)—N(6)	176 (3)
Fe—C(12)—N(7)	174 (4)
Fe—C(13)—N(8)	172 (5)
Fe—C(14)—N(9)	170 (6)
C(10)—Fe—C(11)	80 (2)
C(10)—Fe—C(12)	85 (2)
C(10)—Fe—C(13)	83 (2)
C(10)—Fe—C(14)	89 (2)

Table 3. Coordination distances of the barium ion

Ba—O(1)	2.73 (2) Å
Ba—O(3)	2.90 (5)
Ba—N(6)	2.85 (4)
Ba—N(7)	2.99 (5)
Ba—N(8)	2.84 (4)
Ba—N(9)	2.83 (7)

Table 4. Observed and calculated structure factors  
Columns from left to right give  $k, l, 10F_o$ , and  $10F_c$ .

$k$	$l$	$10F_o$	$10F_c$
0	0	100	100
0	1	100	100
0	2	100	100
0	3	100	100
0	4	100	100
0	5	100	100
0	6	100	100
0	7	100	100
0	8	100	100
0	9	100	100
0	10	100	100
0	11	100	100
0	12	100	100
0	13	100	100
0	14	100	100
0	15	100	100
0	16	100	100
0	17	100	100
0	18	100	100
0	19	100	100
0	20	100	100
0	21	100	100
0	22	100	100
0	23	100	100
0	24	100	100
0	25	100	100
0	26	100	100
0	27	100	100
0	28	100	100
0	29	100	100
0	30	100	100
0	31	100	100
0	32	100	100
0	33	100	100
0	34	100	100
0	35	100	100
0	36	100	100
0	37	100	100
0	38	100	100
0	39	100	100
0	40	100	100
0	41	100	100
0	42	100	100
0	43	100	100
0	44	100	100
0	45	100	100
0	46	100	100
0	47	100	100
0	48	100	100
0	49	100	100
0	50	100	100
0	51	100	100
0	52	100	100
0	53	100	100
0	54	100	100
0	55	100	100
0	56	100	100
0	57	100	100
0	58	100	100
0	59	100	100
0	60	100	100
0	61	100	100
0	62	100	100
0	63	100	100
0	64	100	100
0	65	100	100
0	66	100	100
0	67	100	100
0	68	100	100
0	69	100	100
0	70	100	100
0	71	100	100
0	72	100	100
0	73	100	100
0	74	100	100
0	75	100	100
0	76	100	100
0	77	100	100
0	78	100	100
0	79	100	100
0	80	100	100
0	81	100	100
0	82	100	100
0	83	100	100
0	84	100	100
0	85	100	100
0	86	100	100
0	87	100	100
0	88	100	100
0	89	100	100
0	90	100	100
0	91	100	100
0	92	100	100
0	93	100	100
0	94	100	100
0	95	100	100
0	96	100	100
0	97	100	100
0	98	100	100
0	99	100	100
0	100	100	100

Table 5. Principal distances and angles involving the oxygen atoms of the water molecules

N(5)-O(1)	3.34 (4) Å
N(8)-O(1)	3.19 (5)
N(4)-O(3)	3.20 (7)
N(7)-O(3)	3.27 (7)
N(8)-O(1)-N(5)	118 (2)°
N(8)-O(1)-Ba	120 (1)
N(5)-O(1)-Ba	101 (1)
N(4)-O(3)-N(7)	130 (2)
N(4)-O(3)-Ba	123 (2)
N(7)-O(3)-Ba	141 (2)

The anion is in the form of a distorted octahedron elongated in the direction of the nitrosyl group. The iron atom is displaced from the best least-squares plane through C(11) to C(14) giving N(5)-Fe-C( $j$ ) angles ( $j = 11$  to 14) greater than 90°, as has been found in Na<sub>2</sub>Fe(CN)<sub>5</sub>NO·2H<sub>2</sub>O (Manoharan & Hamilton, 1963) and for the Mn atom in K<sub>3</sub>Mn(CN)<sub>5</sub>NO·2H<sub>2</sub>O (Tullberg & Vannerberg, 1967). The observed deviation from the ideal point group C<sub>4v</sub> is insignificant, and a non-crystallographic fourfold axis passes through O(2), N(5), Fe, C(10) and N(4).

Each nitroprusside ion is coordinated to four barium ions through the nitrogens of the equatorial plane of the anion. Each barium ion is located at the centre of a very distorted octahedron formed by the oxygen atoms of the water molecules and the nitrogens of the neighbouring anions.

The configuration of the anion agrees with the model proposed by Ballhausen & Gray (1963) in which the distorted octahedral complexes with tetragonal symmetry have strongly  $\pi$ -bonded axial substituents. The distances between the oxygen atoms of the water molecules and their neighbouring nitrogen atoms suggest the presence of weak hydrogen bonds (Table 5). The very high temperature factor found for O(3) is consistent with the abnormal N(7)-O(3)-Ba angle and with the infrared spectrum which shows the two weak hydrogen bonds to be non-equivalent.

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