The Crystal Structure of Sodium Nitroprusside[1]

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The crystal structure of sodium nitroprusside, $Na_2Fe(CN)_5(NO)\cdot2H_2O$, has been determined by an analysis of three-dimensional X-ray diffraction data. The crystal is orthorhombic, space group Pnnm. The nitroprusside ion lies on the mirror plane and has approximate C_{4v} symmetry. The important distances are Fe–C, 1.90 ± 0.02 Å.; C–N, 1.16 ± 0.02 Å.; Fe–N, 1.63 ± 0.02 Å.; N–O, 1.13 ± 0.02 Å. The ligands are colinear with the metal atom, which is displaced slightly in the direction of the NO group from the plane of the four pseudo-equivalent CN groups. Each sodium ion lies at the center of a distorted octahedron composed of four CN groups and two water molecules. These octahedra share edges in such a way that each CN group is coordinated to two Na^+ ions, as is each water molecule; the Na^+–ligand distance is approximately 2.5 Å. in every case. The nitroso group is coordinated only to Fe^{+2}. The water molecules do not lie near enough to other electronegative atoms to permit significant hydrogen bonding.

Introduction

The coordination of the NO group to transition metals is of great theoretical interest,[3-6] but X-ray diffraction data on inorganic nitroso compounds are rather sparse. In particular, the linearity of the M–N–O linkage, which has important implications as to the nature of the metal–nitrogen bond, is open to question.

Johansson and Lipscomb[7] have carried out a structure determination of Roussin's black salt, $CsFe_4F_3(NO)_7\cdot H_2O$, and Thomas, Robertson, and Cox[8] have determined the structure of Roussin's red ethyl ester, $(NO)_4FeS_2(C_2H_5)_2$. The Fe–N distances in these compounds vary from 1.57 to 1.71 Å., suggesting a large amount of double-bond character for the Fe–N bond. Such double bonding would seem to force linearity on the Fe–N–O link. However, values of $167.7 \pm 3.5°$ and $167.2 \pm 3.5°$ are ascribed to the Fe–N–O angles in the ester, and a value as small as 160° may be calculated for one such angle in the black salt. Johansson and Lipscomb consider these deviations to be indicative of crystalline packing forces rather than of any unusual electronic structure.

Alderman, *et al.*,[9,10] have reported a rather more severe departure from linearity in the compound $Co(NO)[S_2CN(CH_3)_2]_2$. The Co atom lies above the plane of the four sulfur atoms, and the N–O bond is reported to make an angle of about 140° with the approximate fourfold axis of the FeS_4 configuration, with its mid-point approximately on this axis. This investigation was based on two-dimensional data only.

The three preceding compounds all involve rather unusual coordination about the metal atoms. Two octahedral complexes of ruthenium have been the subjects of two-dimensional X-ray diffraction investigations.[11,12] Values of 150 and 153° are found for the Ru–N–O angles in $[Ru(NH_3)_4(NO)(OH)]Cl_2$ and $[Ru(NH_4)_2(NO)(OH)]Cl_4$.

In view of the fact that these determinations are either of nontypical structures or are of limited accuracy, we decided to undertake a three-dimensional X-ray diffraction study of the geometrically simple and extensively studied sodium nitroprusside, $Na_2Fe(CN)_5$-$NO\cdot2H_2O$. A preliminary report[13] of the structure of the isostructural $Na_2Co(CN)_5NO\cdot2H_2O$ indicated a distorted octahedral arrangement about the Co atom but gave no further information regarding the linearity of Co–N–O. No further work on this structure has been published.

Preliminary results of a neutron diffraction investigation of another octahedral ruthenium salt, $Na_2[Ru(NO_2)_4(NO)(OH)]\cdot2H_2O$, indicate a linear Ru–N–O bond and a Ru–N bond length of about 1.67 Å.[14]

Crystallographic Data

Sodium nitroprusside is orthorhombic, space group D_{2h}^{12}-Pnnm. The cell constants were determined to be $a = 6.17 \pm 0.03$, $b = 11.84 \pm 0.06$, and $c = 15.43 \pm 0.08$ Å., in satisfactory agreement with those reported by Cooke[15]: 6.22, 11.8, and 15.52 Å. The X-ray density calculated for four formula weights per unit cell is 1.76 g. cm.$^{-3}$, in good agreement with the macroscopically observed value of 1.72 g. cm.$^{-3}$.

Experimental

Equi-inclination Weissenberg photographs of seven reciprocal lattice nets perpendicular to *a* were obtained from a needle-like crystal with approximate dimensions $0.5 \times 0.25 \times 0.25$ mm.[3] The observed absences, $(0kl)$ for $k + l$ odd and $(h0l)$ for $h + l$ odd, indicated that the probable space groups are the centro-

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(2) Participant in Brookhaven National Laboratory summer student program, 1962.

(3) H. B. Gray and C. J. Ballhausen, *J. Chem. Phys.*, **36**, 1151 (1962).

(4) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **2**, 426 (1963).

(5) H. B. Gray, I. Bernal, and E. Billig, *J. Am. Chem. Soc.*, **84**, 3404 (1962).

(6) J. Lewis, *Sci. Progr.*, **47**, 506 (1959).

(7) G. Johansson and W. N. Lipscomb, *Acta Cryst.*, **11**, 594 (1958).

(8) J. T. Thomas, J. H. Robertson, and E. G. Cox, *ibid.*, **11**, 599 (1958).

(9) P. R. H. Alderman and P. G. Owston, *Nature*, **178**, 1071 (1956).

(10) P. R. H. Alderman, P. G. Owston, and J. M. Rowe, *J. Chem. Soc.*, 668 (1962).

(11) G. B. Bokii and N. A. Parpiev, *Soviet Phys.-Cryst.*, **2**, 681 (1957).

(12) N. A. Parpiev and M. A. Porai-Koshits, *ibid.*, **4**, 26 (1959).

(13) Y. Okaya, R. Pepinsky, Y. Takeuchi, H. Kuroya, A. Shimada, P. Gallitelli, N. Stemple, and A. Beevers, *Acta Cryst.*, **10**, 798 (1957).

(14) S. H. Simonsen and M. H. Mueller, paper to be presented at meeting of International Union of Crystallography, Rome, September, 1963.

(15) P. W. Cooke, *Nature*, **157**, 518 (1946).

1044 P. T. MANOHARAN AND WALTER C. HAMILTON *Inorganic Chemistry*

TABLE I[a]

OBSERVED AND CALCULATED STRUCTURE FACTORS IN ELECTRONS/UNIT CELL FOR SODIUM NITROPRUSSIDE

***** H = 0 *****

K	L	F0	FC	
0	4	62	98	$
0	6	51	68	
0	8	104	213	$
0	10	50	64	
0	12	77	99	$
0	14	63	74	$
0	16	49	52	
0	18	22	19	
0	20	39	41	
0	22	44	46	
0	24	31	33	
0	26	20	21	
0	28	48	16	
1	5	29	33	
1	7	17	15	
1	9	16	-9	
1	11	30	33	
1	13	25	23	
2	4	57	-82	$
2	6	60	-79	$
2	8	0	-6	$
2	10	72	-90	$
2	12	52	-61	
2	14	50	-54	
2	16	12	-15	
2	18	38	-32	
2	20	29	-27	
2	22	33	-32	
2	24	21	-21	
3	1	35	-46	
3	3	41	-45	
3	7	49	-61	
3	9	29	-28	
3	11	40	-38	
3	15	45	-33	
3	17	21	-19	
3	19	24	-19	
4	0	59	-73	$
4	2	25	17	
4	4	41	45	
4	6	9	8	
4	8	28	29	
4	10	27	23	
4	12	12	10	
4	14	19	-12	
4	16	47	40	
4	18	28	25	
5	3	49	56	
5	5	66	96	$
5	7	19	18	
5	9	35	33	
5	11	15	12	
5	13	38	40	
5	15	17	16	
5	17	38	32	
5	19	15	19	
6	0	28	24	
6	2	37	-34	
6	4	24	-23	
6	6	69	-83	$
6	14	31	-31	
6	16	13	-8	
6	18	17	-17	
7	1	57	-77	$
7	3	28	-26	
7	5	51	-56	
7	7	65	-83	$
7	9	51	-55	
7	11	12	-11	
7	13	30	-28	
7	15	41	-41	
7	17	34	-34	
7	19	25	-24	
7	21	16	-17	
8	0	64	86	$
8	2	33	-33	
8	4	18	13	
8	6	12	-10	
8	8	49	52	
8	10	22	-19	
9	1	46	45	
9	3	55	66	
9	5	51	50	
9	7	34	32	
9	9	35	32	
9	11	52	53	
9	13	42	40	
9	15	24	24	
9	17	20	20	
9	19	27	24	
9	21	27	25	
10	0	46	56	
10	4	13	10	
10	8	42	43	
10	10	17	-6	
10	16	22	18	
11	1	52	-58	
11	3	47	-46	
11	5	16	-12	
11	7	27	-24	
11	9	43	-41	
11	11	56	-56	$
11	13	23	-25	
11	15	24	-24	
11	17	19	-17	
11	19	20	-20	
11	21	14	-18	
11	23	24	-26	
12	0	20	-15	
12	2	24	-24	
12	4	27	-27	
12	6	28	-28	
12	8	11	-13	
12	10	21	-19	
12	12	20	-16	
12	14	22	-23	
13	1	35	40	
13	3	27	27	
13	5	28	30	
13	7	24	21	
13	9	31	28	
13	11	22	25	
13	13	28	35	
13	15	24	16	
14	0	36	33	
14	2	22	21	
14	4	26	31	
14	6	20	16	
14	8	27	30	
14	10	20	21	
14	12	23	22	
14	14	20	13	
14	16	19	23	
15	5	18	-12	
15	7	20	-21	
16	2	28	-30	
16	4	24	-24	
16	6	29	-34	
16	10	20	-22	
16	12	21	-16	
16	14	19	-21	
16	16	20	-17	
16	18	22	-19	

***** H = 1 *****

K	L	F0	FC	
0	5	26	23	
0	7	39	44	
0	9	22	21	
0	11	67	79	$
0	13	50	52	
0	15	39	36	
0	17	0	5	$
0	19	32	29	
0	21	33	31	
0	23	30	30	
0	25	24	16	
1	4	24	-25	
1	5	17	11	
1	6	30	24	
1	7	19	-19	
1	8	13	12	
1	9	17	11	
1	10	40	36	
1	12	23	-18	
1	14	19	14	
1	18	22	17	
2	3	46	-61	
2	4	76	-175	$
2	5	40	-47	
2	6	17	-19	
2	7	54	-71	
2	8	27	-29	
2	9	62	-88	$
2	10	31	-30	
2	11	45	-46	
2	12	12	-14	
2	13	38	-44	
2	14	10	3	
2	15	36	-36	
2	16	22	-22	
2	17	37	-37	
2	18	28	-30	
2	19	22	-21	
2	21	29	-26	
2	23	26	-23	
2	25	25	-23	
3	0	46	-48	
3	3	34	-39	
3	4	69	-138	$
3	5	22	-17	
3	6	14	-14	
3	7	27	-27	
3	8	38	-41	
3	10	11	-11	
3	11	11	-13	
3	12	50	-55	
3	13	8	7	
3	14	10	-13	
3	15	8	-11	
3	16	26	-23	
3	17	9	-6	
3	18	17	-15	
3	20	26	-22	
4	1	34	31	
4	2	68	107	$
4	5	74	109	$
4	6	36	37	
4	7	41	40	
4	8	21	19	
4	9	33	37	
4	10	13	-13	
4	11	49	49	
4	13	39	40	
4	14	12	10	
4	15	30	27	
4	17	26	28	
4	19	30	29	
5	0	39	41	
5	2	63	90	$
5	6	69	99	$
5	7	30	28	
5	8	48	51	
5	10	49	49	
5	14	39	41	
5	16	30	33	
5	18	31	32	
6	1	24	-20	
6	4	54	63	
6	5	21	-18	
6	6	15	-11	
6	7	38	-36	
6	9	34	-28	
6	15	20	-17	
6	17	26	-25	
7	0	39	-38	
7	2	28	-28	
7	3	20	17	
7	4	63	-83	$
7	6	42	-43	
7	7	23	20	
7	8	44	-44	
7	10	20	-18	
7	12	45	-47	
7	14	28	-26	
7	16	32	-31	
7	18	20	-20	
7	20	31	-29	
8	1	18	-15	
8	3	7	10	
8	6	21	-21	
8	8	17	-12	
8	9	22	-19	
8	10	15	14	
9	0	54	59	
9	2	54	68	
9	4	27	26	
9	5	13	-12	
9	6	46	48	
9	7	33	-32	
9	8	41	41	
9	10	54	56	
9	12	27	28	
9	14	35	34	
9	15	18	-14	
9	16	25	25	
9	18	29	29	
10	3	16	16	
10	4	14	-13	
10	5	14	16	
11	0	55	-59	
11	2	35	-35	
11	4	56	-59	$
11	6	15	-15	
11	8	36	-34	
11	10	34	-34	
11	12	46	-51	
11	14	26	-23	
11	16	23	-18	
12	1	31	-30	
12	3	15	-14	
12	5	16	-17	
12	7	28	-30	
12	9	24	-23	
12	11	14	-11	
12	13	18	-13	
13	0	25	26	
13	2	33	32	
13	5	27	9	
13	6	18	23	
13	7	16	19	
13	9	25	-3	
13	14	24	20	
14	1	24	22	
14	3	29	34	
14	5	32	33	
14	7	25	25	
14	9	23	20	
14	11	27	25	
14	13	25	21	
14	15	20	20	
16	1	24	-25	
16	3	22	-24	
16	5	24	-27	
16	7	23	-25	
16	9	23	-26	

***** H = 2 *****

K	L	F0	FC	
0	4	67	80	$
0	6	16	15	
0	8	51	63	
0	10	45	50	
0	12	39	39	
0	14	0	6	$
0	16	49	45	
0	18	32	28	
0	20	22	20	
0	22	17	10	
0	24	28	24	
1	5	43	51	
1	7	28	-25	
1	8	19	-19	
1	13	22	20	
2	4	40	-46	
2	6	54	-86	$
2	8	13	-12	
2	9	32	31	
2	10	46	-54	
2	12	37	-38	
2	13	33	31	
2	14	48	-49	
2	16	16	-15	
2	17	14	-10	
2	18	27	-27	
2	19	12	-7	
2	20	25	-23	
2	21	13	12	
2	22	26	-25	
3	2	32	37	
3	3	14	-13	
3	4	7	-6	
3	5	30	-28	
3	7	42	-53	
3	8	20	-17	
3	9	42	-41	
3	10	18	20	
3	11	11	-7	
3	12	9	9	
3	13	10	-8	
3	15	30	-27	
3	17	27	-25	
3	19	18	-16	
4	0	77	184	$
4	2	16	14	
4	3	17	16	
4	4	36	43	
4	5	33	36	
4	6	29	28	
4	7	28	28	
4	8	73	104	$
4	10	15	15	
4	11	14	-10	
4	12	38	38	
4	14	34	31	
4	16	41	36	
4	18	38	14	
4	20	23	23	
4	22	22	20	
5	0	40	37	
5	1	48	57	
5	3	52	72	
5	4	22	18	
5	5	60	74	$
5	6	10	11	
5	7	48	55	
5	8	22	21	
5	9	34	33	
5	11	41	45	
5	13	48	48	
5	15	29	31	
5	17	20	23	
5	19	24	25	
5	21	28	27	
6	0	27	24	
6	1	29	-29	
6	2	54	-68	
6	4	47	-54	
6	5	14	-10	
6	6	44	-47	
6	8	14	8	
6	9	16	-14	
6	10	49	-48	
6	12	28	-26	
6	13	16	-15	
6	14	26	-24	
6	18	26	-23	
6	20	13	-12	
7	1	59	-77	$
7	2	28	-22	
7	3	56	-68	$
7	5	41	-40	
7	7	53	-59	
7	8	19	14	
7	9	50	-56	
7	10	18	-17	
7	11	52	-56	
7	13	25	-28	
7	15	40	-39	
7	17	32	-32	
7	19	31	-29	
7	21	19	-18	
7	23	23	-26	
8	0	23	16	
8	3	13	-10	
8	4	14	12	
8	5	20	-21	
8	7	19	-19	
8	8	26	24	
8	16	20	17	
9	1	39	37	
9	3	48	52	
9	4	23	-22	
9	5	49	54	
9	6	29	-24	
9	7	25	24	
9	8	17	-18	
9	9	38	36	
9	11	34	34	
9	13	37	40	
9	15	21	19	
9	17	25	23	
9	19	17	20	
9	21	22	24	
10	0	36	34	
10	4	23	22	
10	8	27	24	
11	0	18	-16	
11	1	36	-38	
11	5	17	-17	
11	7	34	-37	
11	9	26	-26	
11	15	23	-23	
12	2	37	-34	
12	4	21	-21	
12	6	36	-35	
12	10	24	-23	
12	14	20	-21	
13	3	21	24	
13	4	16	13	
13	5	22	22	
13	6	16	16	
13	12	16	-6	
14	0	35	36	
14	2	16	16	
14	4	23	25	
14	6	22	24	
14	8	31	35	
15	0	18	18	
16	0	21	-18	
16	2	27	-28	
16	4	25	-28	
16	6	26	-28	
16	8	17	-10	
16	10	20	-25	
16	12	21	-20	
18	0	28	30	

***** H = 3 *****

K	L	F0	FC	
0	3	52	112	
0	5	67	128	$
0	7	37	39	
0	9	43	49	
0	11	46	45	
0	13	39	42	
0	15	34	29	
0	17	44	42	
0	19	43	35	
1	3	14	15	
1	4	46	-63	
1	5	14	15	
1	6	50	60	
1	8	13	12	
1	10	22	19	
1	12	31	-24	
1	14	22	18	
2	3	28	-37	
2	4	11	11	
2	5	38	-46	
2	6	28	-28	
2	7	54	-63	
2	8	10	-12	
2	9	56	-60	$
2	10	20	18	
2	11	24	-23	
2	12	16	12	
2	13	29	-28	
2	15	36	-33	
2	17	45	-38	
2	19	22	-21	
2	21	20	-19	
3	0	17	-16	
3	2	14	-14	
3	3	23	24	
3	4	40	-51	
3	6	33	-33	
3	7	16	-12	
3	8	27	-26	
3	11	19	16	
3	12	38	-33	
3	14	15	-15	
3	16	18	-19	
3	20	23	-21	
4	0	43	-52	
4	1	42	51	
4	2	23	-24	
4	3	40	46	
4	5	23	22	
4	7	44	47	
4	8	17	-16	
4	9	11	8	
4	10	14	-13	
4	11	50	51	
4	12	17	-17	
4	13	35	33	
4	14	13	-13	
4	15	31	31	
4	19	29	21	
4	21	24	22	
4	23	23	21	
5	0	46	56	
5	2	50	59	
5	3	13	-9	
5	4	26	25	
5	5	14	-13	
5	6	33	32	
5	7	16	-15	
5	8	34	34	
5	10	51	57	
5	12	22	21	
5	14	27	28	
5	16	21	20	
5	18	33	28	
6	0	23	17	
6	1	50	-58	
6	2	12	10	
6	3	24	-22	
6	5	16	-13	
6	6	16	7	
6	7	25	-24	
6	9	41	-42	
6	11	23	-23	
6	13	22	-21	
6	15	19	-13	
6	17	18	-17	
7	0	59	-76	$
7	1	9	-10	
7	2	38	-39	
7	3	15	-15	
7	4	68	-94	$
7	6	21	-19	
7	7	17	10	
7	8	46	-46	
7	10	41	-40	
7	11	21	-19	
7	12	58	-63	$
7	14	26	-27	
7	16	30	-25	
7	18	18	-20	
7	20	24	-28	
7	22	25	-23	
7	24	19	-22	
8	0	29	29	
8	1	16	-16	
8	2	14	12	
8	3	20	21	
8	5	24	24	
8	6	13	11	
8	7	16	-14	
9	0	43	43	
9	1	29	26	
9	2	53	63	
9	3	12	7	
9	6	56	62	$
9	7	14	13	
9	8	37	39	
9	9	15	11	
9	10	39	38	
9	14	34	37	
9	16	24	27	
9	18	24	24	
10	0	12	-10	
10	1	15	14	
10	3	26	26	
10	5	20	17	
10	11	26	24	
10	13	17	15	
11	0	19	-15	
11	2	17	-16	
11	4	42	-41	
11	6	35	-34	
11	8	25	-27	
11	12	16	-21	
11	14	24	-17	
11	16	16	-24	
11	18	21	-17	
12	1	22	-20	
12	3	19	-19	
12	5	21	-22	
12	9	29	-27	
13	0	16	13	
13	1	18	-16	
13	2	23	22	
13	4	21	19	
13	6	24	23	
13	8	21	17	
14	1	19	17	
14	3	22	24	
14	5	25	27	
14	7	22	24	
15	0	20	-18	
16	1	26	-30	
16	3	21	-19	
16	5	20	-18	
16	7	22	-26	

***** H = 4 *****

K	L	F0	FC	
0	4	41	55	
0	6	46	61	
0	8	60	82	$
0	10	17	19	
0	12	30	25	
0	14	30	29	
0	16	55	52	
0	18	33	32	
0	20	30	26	
1	4	15	12	
1	5	24	23	
1	6	13	11	
1	8	19	15	
1	10	16	-16	
1	13	26	22	
2	2	45	-81	
2	3	27	30	
2	4	46	-71	
2	5	8	9	
2	6	54	-81	
2	7	11	9	
2	8	21	-24	
2	10	47	-54	
2	11	23	18	
2	12	34	-35	
2	14	42	-42	
2	16	25	-25	
2	18	36	-35	
2	20	23	-23	
2	22	22	-21	
3	0	21	21	
3	1	41	-54	
3	2	15	-16	
3	3	12	-12	
3	5	12	-11	
3	7	38	-41	
3	8	15	12	
3	9	32	-33	
3	10	16	-9	
3	11	19	-16	
3	13	17	-15	
3	15	25	-22	
4	0	57	94	$
4	1	11	-7	
4	2	26	28	
4	4	38	46	
4	6	10	9	
4	8	50	60	
4	10	31	30	
4	12	36	36	
4	14	18	17	
4	16	28	27	
4	18	17	14	
5	1	26	25	
5	2	11	13	
5	3	50	61	
5	4	15	-12	
5	5	37	40	
5	6	15	-12	
5	8	14	-13	
5	9	26	27	
5	11	49	47	
5	13	29	30	
6	1	11	11	
6	2	25	-25	
6	3	22	-20	
6	4	15	10	
6	5	13	-12	
6	6	16	-13	
6	7	14	-10	
6	8	19	13	
6	10	18	-16	
6	12	17	-13	
6	14	23	-18	
7	0	20	-20	
7	1	42	-49	
7	3	23	-23	
7	5	13	-12	
7	7	36	-36	
7	9	33	-31	
7	11	29	-30	
7	13	18	-19	
7	15	26	-26	
7	17	17	-16	
7	19	17	-18	
7	21	15	-15	
7	23	24	-19	
8	0	19	18	
8	2	11	-8	
8	6	18	-15	
8	8	14	10	
9	0	15	9	
9	1	36	36	
9	3	38	39	
9	5	51	51	
9	7	42	41	
9	9	31	30	
9	11	21	23	
9	13	37	36	
9	15	24	26	
9	17	25	24	
9	19	25	21	
9	21	26	23	
10	0	25	29	
10	8	21	20	
11	0	17	9	
11	1	31	-32	
11	3	41	-40	
11	5	43	-44	
11	7	44	-44	
11	9	33	-35	
11	11	23	-23	
11	13	23	-18	
11	15	28	-30	
11	17	29	-32	
11	19	26	-24	
12	2	28	-28	
12	4	23	-19	
12	6	22	-20	
12	10	24	-24	
13	3	24	25	
13	5	24	28	
13	7	15	18	
14	0	36	33	
14	2	20	20	
14	4	24	24	
14	6	15	16	
14	8	29	27	
14	10	16	19	
14	12	17	21	
16	0	22	-23	
16	2	24	-24	
16	4	17	-15	
16	6	20	-21	
18	0	21	23	

***** H = 5 *****

K	L	F0	FC	
0	3	52	74	
0	5	61	71	$
0	7	59	69	$
0	9	33	33	
0	11	48	47	
0	13	44	38	
0	15	48	43	
0	17	49	27	
0	19	35	33	
0	21	48	23	
1	6	16	9	
1	7	25	22	
1	10	28	24	
2	3	31	-35	
2	5	39	-41	
2	7	47	-48	
2	9	45	-45	
2	11	22	-22	
2	13	28	-25	
2	15	33	-29	
2	17	39	-33	
3	0	35	-43	
3	2	12	-13	
3	3	14	-12	
3	4	47	-51	
3	7	26	27	
3	8	24	-20	
3	10	22	-20	
3	12	44	-42	
4	0	23	22	
4	2	14	11	
4	3	29	33	
4	5	29	33	
4	11	27	23	
4	13	25	20	
5	0	42	40	
5	2	50	54	
5	6	38	39	
5	8	27	26	
5	10	39	38	
5	14	32	28	
6	1	34	-33	
6	7	17	-15	
6	8	29	-5	
7	0	42	-35	
7	2	29	-28	
7	4	48	-49	
7	6	32	-33	
7	8	34	-33	
7	10	22	-20	
7	12	38	-35	
7	14	26	-22	
8	0	26	-18	
8	3	20	10	
8	11	27	18	
9	0	30	25	
9	1	21	-16	
9	2	35	34	
9	4	32	27	
9	6	40	38	
9	8	32	29	
9	10	34	30	
11	0	27	-23	
11	4	41	-43	
11	6	24	-24	
11	8	28	-26	
12	1	27	-27	
13	2	26	25	
13	5	30	-1	

***** H = 6 *****

K	L	F0	FC
0	4	28	36
0	6	24	12
0	8	45	45
0	10	21	18
0	12	30	26
0	14	28	17
0	16	33	25
0	18	27	16
1	3	21	28
1	11	27	26
2	2	33	-42
2	4	31	-31
2	6	41	-44
2	10	33	-29
2	12	28	-22
2	14	33	-29
3	1	31	-38
3	3	24	-26
3	7	18	-15
3	9	30	-24
3	11	39	-36
4	0	32	34
4	2	28	28
4	4	33	32
4	6	31	32
4	8	40	38
4	10	22	20
4	12	22	20
4	14	32	14
5	1	34	37
5	3	26	22
5	5	32	33
5	7	33	29
5	9	27	26
5	11	21	17
5	13	41	35
6	2	29	-27
6	4	23	-21
6	6	27	-22
6	10	28	-24
6	12	26	-15
7	1	31	-33
7	3	26	-28
7	5	31	-34
7	7	39	-39
7	9	31	-32
7	11	23	-18
7	13	25	-19
7	15	26	-27
7	17	28	-26
7	19	29	-20
8	0	34	37
9	3	37	40
9	5	35	37

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[a] The X-ray scattering factors used in the calculated values are those for Na^{+}, Fe^{+2}, C, N, and O (International Tables for X-Ray Crystallography, Vol. 3, Birmingham, The Kynoch Press, 1952). The reflections denoted by \$, as well as 45 other reflections with |FC| greater than 50, were omitted from the least squares refinement.

TABLE II
ATOMIC PARAMETERS FOR SODIUM NITROPRUSSIDE FROM FINAL LEAST SQUARES REFINEMENT

Atom	x	y	z	B, Å.^{2}
Fe	0.5003 ± 0.0004	0.2797 ± 0.0001	$^1/_2$	0.62 ± 0.04
Na$_1$	$^1/_2$	0	0.2452 ± 0.0004	$2.03 \pm .09$
Na$_2$	0	0	$.3776 \pm .0004$	$2.36 \pm .10$
Nitroso N	0.7197 ± 0.0023	0.3566 ± 0.0010	$^1/_2$	$1.56 \pm .18$
Nitroso O	$.8747 \pm .0028$	$.4074 \pm .0012$	$^1/_2$	$3.26 \pm .25$
C$_1$	$.2556 \pm .0032$	$.1827 \pm .0012$	$^1/_2$	$1.64 \pm .20$
N$_1$	$.1056 \pm .0032$	$.1201 \pm .0013$	$^1/_2$	$2.79 \pm .26$
C$_2$	$.6038 \pm .0021$	$.1799 \pm .0007$	0.5884 ± 0.0005	$1.32 \pm .13$
N$_2$	$.6690 \pm .0019$	$.1203 \pm .0008$	$.6412 \pm .0006$	$2.31 \pm .16$
C$_3$	$.3407 \pm .0019$	$.3599 \pm .0008$	$.4121 \pm .0006$	$1.45 \pm .13$
N$_3$	$.2505 \pm .0023$	$.4044 \pm .0009$	$.3577 \pm .0006$	$2.70 \pm .17$
Water O	$.1737 \pm .0018$	$.1236 \pm .0009$	$.2680 \pm .0006$	$3.18 \pm .17$

symmetric Pnnm or the acentric Pnn2. The peak concentrations in the Patterson and the derived structure confirm the centrosymmetric space group assigned by Cooke,[15] Pnnm.

Structure amplitudes were derived in the usual way from the Weissenberg photographs, which were exposed with filtered Mo Kα radiation, using the multiple film technique. Approximate scale factors and an over-all temperature factor were obtained by performing Wilson plots.[16]

The positions of the Na and Fe atoms were determined unambiguously from the highest peaks in an unsharpened three-dimensional Patterson function calculated from the data. Difference electron density syntheses with coefficients $\Delta F = (F_{obsd} - F_{Na,Fe})$, with the sign of $F_{Na,Fe}$ being assigned to F_{obsd}, then led to approximate light atom positions. The positions of all atoms, separate isotropic temperature factors for all atoms, and the seven scale factors were refined by the usual full-matrix least squares technique. The refinement was carried out on the squares of the structure factors, omitting the reflections with highest intensity, which quite obviously suffered from extinction. A few other reflections were also given zero weight. The remainder were assigned weights proportional to $1/F^2$. Following the refinement, an additional electron-density difference synthesis confirmed the correctness of the structure. The largest peak in this map had a peak height of 2.0 electrons/Å.^{3}; the peak heights of the atoms in an electron density map calculated from F_{obsd} ranged from 9.7 electrons/Å.^{3} for the water molecules to 121 electrons/Å.^{3} for the iron atoms. The average noise-level in the difference synthesis was about 1.2 electrons/Å.^{3}; it thus did not appear to be reasonable to try to find the hydrogen atoms.

The goodness-of-fit parameter

$$R^G = \left[\frac{\Sigma w_i (F_{obsd}^2 - F_{calcd}^2)^2}{\Sigma w_i F_{obsd}^4} \right]^{1/2}$$

is 0.267 for the final parameter values. The conventional crystallographic R factor

$$R = \frac{\Sigma ||F_{obsd}| - |F_{calcd}||}{\Sigma |F_{obsd}|}$$

is 0.100 for the 787 reflections used in the refinement and 0.154 for the entire group of 876 reflections. The observed structure factors and those calculated from the final parameters are presented in Table I. Some of the 89 reflections omitted from the refinement and from the calculation of R are denoted by a $ sign.

The Structure

The metal atoms may be placed in the following positions of space group Pnnm[17]

4Fe in (g): $\pm(x,y,^1/_2)$; $\pm(^1/_2 + x,^1/_2 - y,0)$
4Na$_1$ in (f): $\pm(0,^1/_2,z)$; $\pm(^1/_2,0\,^1/_2 - z)$
4 Na$_2$ in (f)

(16) A. J. C. Wilson, *Nature*, **150**, 152 (1942).
(17) "International Tables for X-Ray Crystallography," Vol. 1, Birmingham, The Kynoch Press, 1952.

[The nitroso group and C$_1$–N$_1$ also are placed in positions on the mirror plane in positions (g).] All other atoms lie in the eightfold general positions

(h): $\pm(x,y,z)$; $\pm(x,y,-z)$;
$\pm(^1/_2 + x,^1/_2 - y,^1/_2 - z)$; $\pm(^1/_2 - x,^1/_2 + y,^1/_2 - z)$

The parameter values resulting from the final least squares refinement are given in Table II.

The nitroprusside ion has a crystallographic plane of symmetry, which contains the approximately linear ($\angle$ N$_1$–Fe–O = 177 $\pm$ 1°) N$_1$–C$_1$–Fe–N–O group. All Fe–C–N groups, as well as the Fe–N–O group, are linear within the limits of error of this investigation. The bond distances and angles for the nitroprusside ion are presented in Table III.

TABLE III
GEOMETRY OF THE Fe(CN)$_5$NO^{-2} OCTAHEDRON[a]

Distance	Value, Å.	Angle	Value
Fe–N	1.63 ± 0.02	Fe–N–O	$178.3 \pm 1.3°$
N–O	$1.13 \pm .02$		
Fe–C$_1$	$1.90 \pm .02$	Fe–C$_1$–N$_1$	$178.5 \pm 1.6°$
C$_1$–N$_1$	$1.19 \pm .03$		
Fe–C$_2$	$1.91 \pm .02$	Fe–C$_2$–N$_2$	$179.0 \pm 1.1°$
C$_2$–N$_2$	$1.15 \pm .02$		
Fe–C$_3$	$1.93 \pm .02$	Fe–C$_3$–N$_3$	$177.1 \pm 0.9°$
C$_3$–N$_3$	$1.14 \pm .02$		
		N–Fe–C$_2$	$93.9 \pm .7°$
		N–Fe–C$_3$	$98.6 \pm .7°$
		C$_1$–Fe–C$_2$	$83.8 \pm .7°$
		C$_1$–Fe–C$_3$	$83.8 \pm .7°$
		C$_2$–Fe–C$_2$ (m)	$90.9 \pm .9°$
		C$_3$–Fe–C$_3$ (m)	$89.5 \pm .9°$
		C$_2$–Fe–C$_3$ (m)	$88.5 \pm .8°$

[a] The errors quoted are estimated standard deviations from the least squares treatment of the data and should be multiplied by three to obtain conservative limits of error.

The departure from C$_{4v}$ symmetry is not significant; although there are significant distortions from the ideal 90° bond angles, these are generally such as to retain the C$_{4v}$ symmetry. The distortion from a configuration with 90° bond angles is such that the four C–N groups related by the pseudo-fourfold axis are bent down away from the N–O group toward the remaining CN group (see Fig. 1). The average N–Fe–C angle is 96°.

The five C–N distances and the five Fe–C distances are not significantly different. The N–O distance of 1.13 Å. and the short Fe–N distance of 1.63 Å. are in
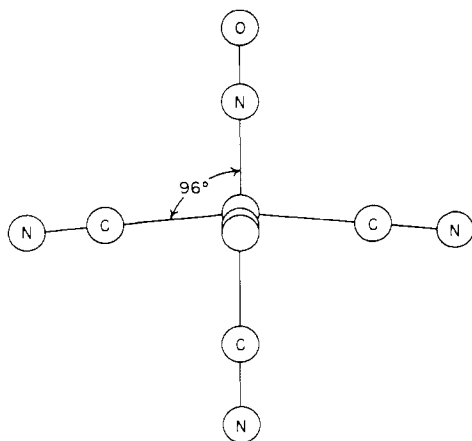
Fig. 1.—Idealized C_{4v} structure of the nitroprusside ion. The metal atom lies 0.2 Å. above the plane of the four carbon atoms.

Fig. 2.—The crystal structure of sodium nitroprusside: perspective view approximately in the a direction. Slightly more than one unit cell is shown. The large octahedra are the nitroprusside ions; the small octahedra represent the coordination of the sodium atoms, which are rendered with a tweedy appearance.

agreement with values found for the other compounds discussed above.

Each sodium ion lies in the interior of a very distorted octahedron composed of four nitrogens from CN groups and the oxygen atoms of two water molecules. The coordination distance of 2.5 Å. is remarkably constant, although the angles vary a great deal. The numerical values are given in Table IV.

TABLE IV
GEOMETRY OF THE COORDINATION OCTAHEDRA OF SODIUM IONS

	Coordination of Na₁				Coordination of Na₂		
Atom	x	y	z	Atom	x	y	z
Na_1	0.50	0.00	0.25	Na_2	0.00	0.00	0.38
W	.17	.12	.27	W	.17	.12	.27
W'	.83	− .12	.27	W'	− .17	− .12	.27
N_2	.67	.12	.36	N_2	.33	− .12	.36
N_2'	.33	− .12	.36	N_2'	− .33	.12	.36
N_3	.75	.10	.14	N_1	.11	.12	.50
N_3'	.25	− .10	.14	N_1'	− .11	− .12	.50

Angle	Value	Angle	Value
N_2–Na–N_2'	$90.4 \pm 0.8°$	W–Na–W'	$94.0 \pm 0.8°$
N_3–Na–N_3'	$100.7 \pm .8°$	N_1–Na–N_1'	$79.3 \pm .8°$
N_2–Na–N_3 N_2'–Na–N_3'	$85.9 \pm .7°$	W–Na–N_1 W'–Na–N_1'	$93.9 \pm .8°$
W–Na–N_2 W'–Na–N_2'	$84.5 \pm .7°$	N_2–Na–W N_2'–Na–W'	$84.5 \pm .7°$
W–Na–N_2' W'–Na–N_2	$84.2 \pm .7°$	N_2–Na–W' N_2'–Na–W	$86.4 \pm .7°$
W–Na–N_3 W'–Na–N_3'	$108.8 \pm .7°$	N_2–Na–N_1 N_2'–Na–N_1'	$101.7 \pm .8°$
W–Na–N_3' W'–Na–N_3	$81.8 \pm .7°$	N_2–Na–N_1' N_2'–Na–N_1	$88.6 \pm .8°$

Distance	Value, Å.	Distance	Value, Å.
Na–W	2.51 ± 0.02	Na–W	2.48 ± 0.02
Na–N_2	$2.49 \pm .02$	Na–N_1	$2.45 \pm .02$
Na–N_3	$2.49 \pm .02$	Na–N_2	$2.51 \pm .02$

The N–O groups are not coordinated to anything but Fe. The two N–O groups related by a symmetry center have an oxygen–oxygen contact distance of 2.68 Å. There are as well four nonbonded contacts between O and N_3 of the adjacent octahedron of 3.22 Å.

The water oxygen atoms do not lie near enough to any N in CN groups to permit hydrogen bonding at the distances typical for such bonds. The two shortest water–cyanide distances are 3.27 and 3.36 Å. between
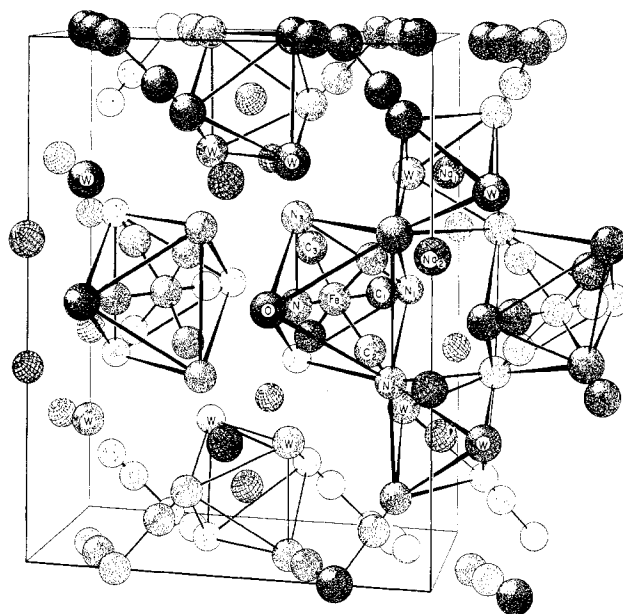
W (0.17, 0.12, 0.27) and N_2 (0.67, 0.12, 0.36) and the same W and N_3 (0.75, 0.20, 0.14). The N_2–W–N_3 angle is 63°, which is not an unfavorable angle for weak hydrogen bonding. The O–H$\cdots$N angles would be about 20°, and this is not uncommon.[18] One may postulate weak hydrogen bonds in these directions, but there are other water–CN distances not much longer, so that the evidence supporting any one assignment of hydrogen bonds must be very weak. The absence of strong hydrogen bonding is in good agreement with the interpretation of the infrared spectrum offered by Cotton, *et. al.*[19]

The structure is built to twin columns of edge-linked Na coordination octahedra running up the a direction of the crystal. These columns are linked together by the octahedral nitroprusside ions. The structural relationships are well illustrated in Fig. 2, which is a view of slightly more than one unit cell looking at a small angle to the a axis, and in Fig. 3, which shows the arrangement of the sodium coordination octahedra running along a. In the latter drawing, the full unit cell in the b direction is not shown, nor is a complete nitroprusside ion.

Conclusions

The nitroprusside ion in the crystal has, within experimental error, C_{4v} symmetry. The Fe=N=O portion of the ion is strictly linear, as are the Fe—C≡N groups. This, of course, does not imply linearity in other NO coordinated compounds, although the evidence for nonlinearity is for the most part rather weak.

(18) W. C. Hamilton, *Ann. Rev. Phys. Chem.*, **13**, 19 (1962).
(19) F. A. Cotton, R. R. Monchamp, R. J. M. Henry, and R. C. Young, *J. Inorg. Nucl. Chem.*, **10**, 28 (1959).
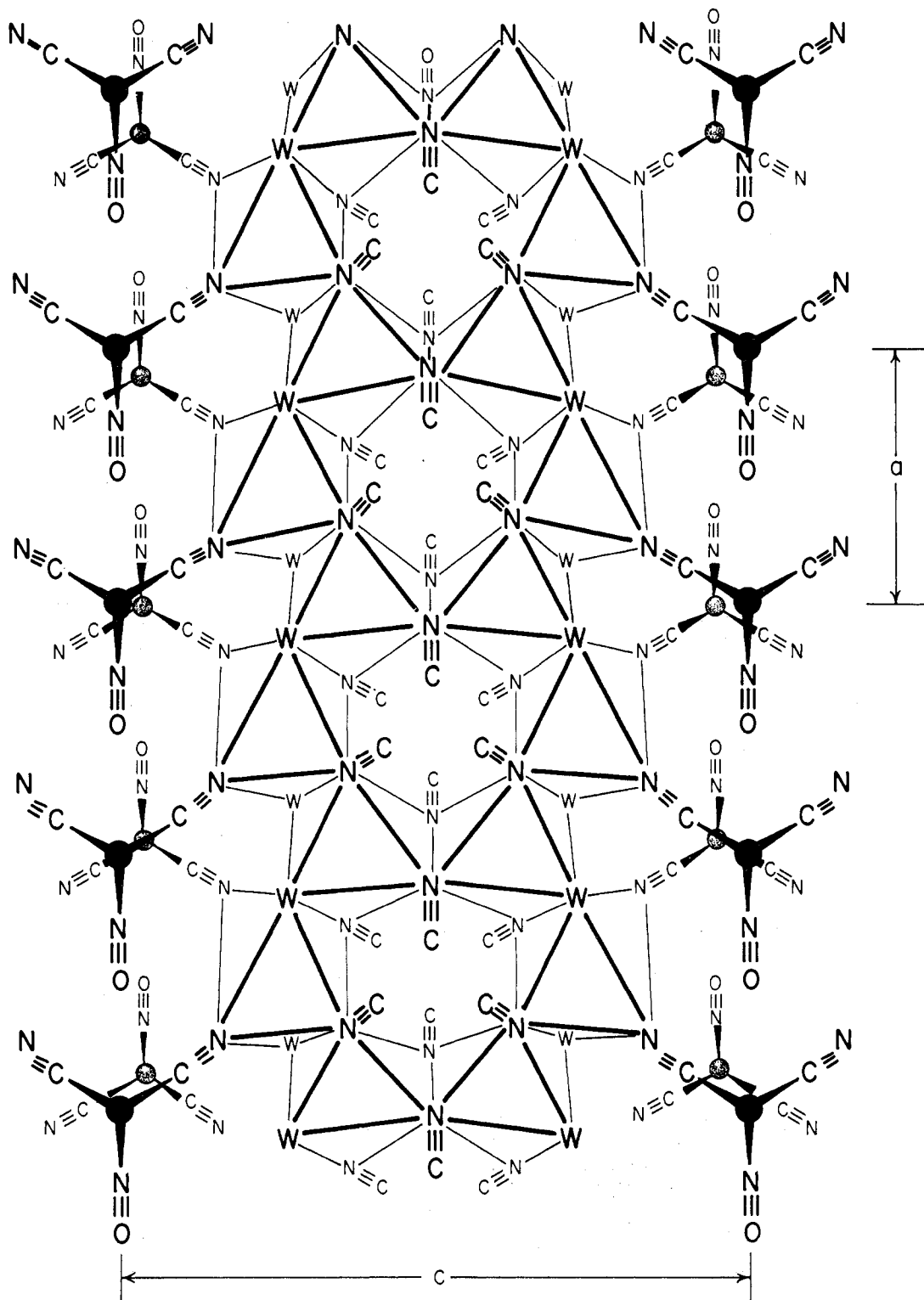
Fig. 3.—Perspective view along *b* of the twin column of sodium coordination octahedra.   Only a portion of the unit cell in the *b* direction is shown.   W indicates location of oxygen atom in water molecules.   The sodium atoms themselves are not shown.