

Na₂Fe(CN)₅(NO)·2D₂O at 11 and 293 K by X-ray, and at 15 K by neutron diffraction

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The crystal structure of Na₂Fe(CN)₅(NO)·2D₂O, disodium pentacyanonitrosylferrate(III) bis(dideuterium oxide), has been determined by X-ray diffraction at 11 and 293 K, and by neutron diffraction at 15 K. The accurate and extensive data sets lead to more precise determinations than are available from earlier work. The agreement in atomic positional and displacement parameters between the determinations at low temperature is very good.

Comment

Disodium pentacyanonitrosylferrate(III) dihydrate, also known as sodium nitroprusside, Na₂Fe(CN)₅(NO)·2H₂O, has long been of interest in inorganic chemistry, as the interpretation of the interaction between the Fe atom and the odd-electron NO ligand presents difficulties to a simple formulation in terms of oxidation numbers. There are a number of structural studies of the complex available in the literature, most recently at ambient temperature by Navaza *et al.* (1989) and at 50 K, including multipole analysis, by Bolotovskiy *et al.* (1995). The remarkable photochemical behaviour of the compound at low temperatures has also received attention, at 80 K (Ruedlinger *et al.*, 1991), at 50 K (Carducci *et al.*, 1997) and at 138 K (Pressprich *et al.*, 1994), including studies of the deuterated substance at 80 K (Ruedlinger *et al.*, 1991) and hydrogenous at 60 K (Schefer *et al.*, 1997), where distinctly different structural parameters were found for the excited state.

It is our intention to pursue further charge-density analysis of the X–N type on this salt, and to this end, we have measured highly precise and extensive X-ray and neutron diffraction data on the deuterated compound, (I), at the lowest available temperatures, and we report the structural results here. In the process, we obtained ambient temperature data which are more accurate than those available for the hydro-

genous form, so we report the structural analysis of that data set also. The data sets will be referred to as (Irtx), (Iltx) and (IltN) for the room-temperature X-ray, the low-temperature X-ray and the low-temperature neutron determinations, respectively.

The structure of sodium nitroprusside has been well described in the literature, for example, by Bottomley & White (1979), and is outlined in Fig. 1. It consists of Na⁺ and octahedral [Fe(CN)₅(NO)]²⁻ ions, and separate lattice water molecules. The present studies do not change any of the major structural features, so we do not discuss its general features further. We retain the atom-numbering system used previously. Our 293 K structure presents s.u.'s significantly lower than have been reported previously for the hydrogenous compound at ambient temperature.

Selected bond lengths and angles are given in Table 1. The atomic displacements we obtained by X-ray diffraction at 11 K are illustrated for the [Fe(CN)₅(NO)]²⁻ ion and for the water molecules in Fig. 1. Lists of calculated and observed structure factors are given in the supplementary material.

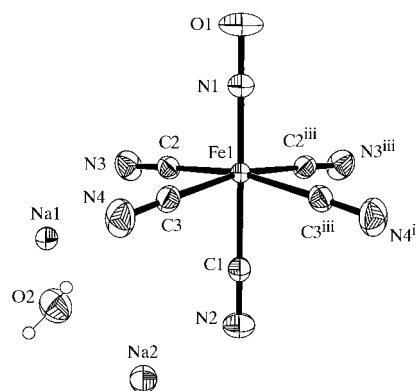


Figure 1

The environments of the atoms in Na₂[Fe(CN)₅(NO)]·2D₂O at 11 K. Displacement ellipsoids are shown at the 99% probability level. Equivalent atoms positions were generated by symmetry transformation (iii) of Table 1.

At 11 and 15 K, only zero-point thermal motion is expected to remain, so ideally the X-ray and neutron positional and atomic displacement parameters should be the same. At the very low temperatures used in this work, the agreement between the X-ray and neutron positional parameters is very good, with most differing by less than the sum of the s.u.'s and only one, *y* for O1, differing at the 3 σ level. The agreement for the atomic displacement parameters, while quite satisfactory, is not as good, with one disagreement at the 5 σ level [*U*₁₁(N1)] and several at the 3 σ level. The position is similar, if a little poorer, than we have obtained previously with other very low temperature X-ray and neutron structure studies, such as for (ND₄)₂Cu(SO₄)₂·6D₂O (Iversen *et al.*, 1994), Ni(ND₃)₄(NO₂)₂ (Iversen *et al.*, 1996) and (ND₄)₂Fe(SO₄)₂·6D₂O (Figgis *et al.*, 1998). It appears probable that, as pointed out by Abrahams (1997) after a detailed statistical analysis of our Ni(ND₃)₄(NO₂)₂ results, our s.u.'s are probably underestimated by a factor of perhaps two.

Experimental

Analytical reagent grade sodium nitroprusside was dissolved in ten times its weight of heavy water (99% D) and the solution was allowed to evaporate in a desiccator over several days. Small crystals were removed for X-ray data collection as they appeared, and larger ones were allowed to continue to grow for neutron diffraction purposes.

Data set (Irtx)

Crystal data

Na₂Fe(CN)₅(NO)·1.45D₂O·0.55H₂O
M_r = 300.87
 Orthorhombic, *Pnmm*
a = 6.207 (3) Å
b = 11.915 (5) Å
c = 15.583 (6) Å
V = 1152.5 (9) Å³
Z = 4
D_x = 1.734 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 14 reflections
 θ = 18.62–20.09°
 μ = 1.387 mm⁻¹
T = 293 (2) K
 Prism, dark red–brown
 0.62 × 0.47 × 0.41 mm

Data collection

Huber four-circle diffractometer
 $\omega/2\theta$ scans
 Absorption correction: Gaussian (*Xtal3.4*; Hall *et al.*, 1995)
T_{min} = 0.539, *T_{max}* = 0.608
 7566 measured reflections
 1067 independent reflections
R_{int} = 0.022
 θ_{\max} = 25.05°
h = -7 → 7
k = -14 → 14
l = -18 → 18
 3 standard reflections every 100 reflections
 intensity decay: 1%

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.019
wR(*F*²) = 0.051
S = 1.227
 1067 reflections
 95 parameters
 All D-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.0240P)^2 + 0.3324P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.23 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.28 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL97* (Sheldrick, 1997)
 Extinction coefficient: 0.134 (4)

Data set (Iltx)

Crystal data

Na₂Fe(CN)₅(NO)·1.45D₂O·0.55H₂O
M_r = 300.87
 Orthorhombic, *Pnmm*
a = 6.124 (2) Å
b = 11.837 (5) Å
c = 15.547 (6) Å
V = 1127.0 (7) Å³
Z = 4
D_x = 1.773 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 8 reflections
 θ = 34.5–34.5°
 μ = 1.419 mm⁻¹
T = 11 (1) K
 Prism, dark red–brown
 0.38 × 0.32 × 0.29 mm

Data collection

Huber four-circle diffractometer
 $\omega/2\theta$ scans
 Absorption correction: Gaussian (*Xtal3.4*; Hall *et al.*, 1995)
T_{min} = 0.641, *T_{max}* = 0.705
 44 955 measured reflections
 6020 independent reflections
R_{int} = 0.028
 θ_{\max} = 50.13°
h = -12 → 12
k = -25 → 25
l = -33 → 33
 3 standard reflections every 100 reflections
 intensity decay: 1%

Table 1

Selected bond lengths and angles (Å, °) for Na₂Fe(CN)₅(NO)·2D₂O at 293 K [X-ray, (Irtx)], 11 K [X-ray, (Iltx)] and 15 K [neutron, (Iltm)]

	(Irtx)	(Iltx)	(Iltm)
Fe1–N1	1.660 (2)	1.6652 (6)	1.666 (1)
Fe1–C1	1.928 (2)	1.9226 (7)	1.923 (1)
Fe1–C2	1.937 (1)	1.9281 (6)	1.9258 (9)
Fe1–C3	1.946 (1)	1.9380 (6)	1.9393 (9)
Na1–O2	2.524 (2)	2.5042 (7)	2.507 (1)
Na1–N3	2.510 (2)	2.4658 (7)	2.4660 (2)
Na1–N4 ⁱ	2.498 (1)	2.4661 (7)	2.467 (1)
Na2–O2	2.496 (2)	2.4705 (7)	2.473 (2)
Na2–N2	2.488 (2)	2.4710 (8)	2.470 (2)
Na2–N3 ⁱⁱ	2.536 (2)	2.5014 (7)	2.5003 (8)
O1–N1	1.129 (2)	1.1317 (7)	1.129 (1)
O2–D1	0.81 (3)	0.81 (1)	0.950 (2)
O2–D2	0.76 (3)	0.83 (2)	0.954 (2)
N2–C1	1.146 (3)	1.1591 (8)	1.157 (1)
N3–C2	1.145 (2)	1.1604 (6)	1.1621 (8)
N4–C3	1.148 (2)	1.1627 (6)	1.1616 (8)
N1–Fe1–C1	176.89 (7)	176.63 (2)	176.64 (5)
N1–Fe1–C2	93.48 (6)	93.38 (2)	93.35 (4)
N1–Fe1–C3	97.45 (6)	97.63 (3)	97.68 (4)
C1–Fe1–C2	84.33 (6)	84.25 (3)	84.29 (4)
C1–Fe1–C3	84.72 (6)	84.70 (3)	84.65 (4)
C2–Fe1–C3	88.45 (6)	88.12 (3)	88.13 (4)
C2–Fe1–C3 ⁱⁱⁱ	169.05 (5)	168.94 (2)	168.93 (4)
C3–Fe1–C3 ⁱⁱⁱ	90.71 (8)	91.35 (3)	91.31 (5)
D1–O2–D2	104 (3)	103 (1)	105.3 (2)
N2–C1–Fe1	179.7 (2)	179.72 (5)	179.623 (1)
N3–C2–Fe1	178.6 (1)	178.35 (4)	178.44 (6)
N4–C3–Fe1	176.9 (1)	176.36 (4)	176.34 (6)
O1–N1–Fe1	176.2 (2)	176.03 (5)	175.92 (8)

Symmetry codes: (i) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$; (ii) $x - 1, y, z$; (iii) $x, y, 1 - z$.

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.020
wR(*F*²) = 0.054
S = 1.081
 6020 reflections
 95 parameters
 All D-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.0230P)^2 + 0.2957P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 0.98 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -1.07 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL97* (Sheldrick, 1997)
 Extinction coefficient: 0.0096 (6)

Data set (Iltm)

Crystal data

Na₂Fe(CN)₅(NO)·1.45D₂O·0.55H₂O
M_r = 300.87
 Orthorhombic, *Pnmm*
a = 6.124 (2) Å
b = 11.837 (5) Å
c = 15.547 (6) Å
V = 1127.0 (7) Å³
Z = 4
D_x = 1.774 Mg m⁻³
 Pulsed neutron radiation
 $\lambda = 0.7\text{--}4.2 \text{ \AA}$
 $\mu = 0.0559 + 0.0029(\lambda) \text{ mm}^{-1}$
T = 11 K
 Prism, dark red–brown
 3.0 × 2.0 × 1.0 mm

Data collection

IPNS single-crystal diffractometer
 Laue time-of-flight scans
 Absorption correction: Gaussian (Schultz, 1993)
T_{min} = 0.879, *T_{max}* = 0.940
 8305 measured reflections
 8305 independent reflections
 6343 reflections with *I* > 3σ(*I*)
 $\theta = 34.5^\circ$
h = -1 → 13
k = -26 → 26
l = -7 → 34

Refinement

Refinement on F	$(\Delta/\sigma)_{\max} = 0.04$
$R = 0.058$	$\Delta\rho_{\max} = 0.563 \text{ e } \text{\AA}^{-3}$
$wR = 0.051$	$\Delta\rho_{\min} = -0.512 \text{ e } \text{\AA}^{-3}$
$S = 3.75$	Extinction correction: secondary
6343 reflections	Type I (Larson & Von Dreele, 1994)
131 parameters	Extinction coefficient: $8.4(1) \times 10^{-5}$
All D- and H-atom parameters refined	Scattering factors from <i>GSAS</i>
$w = (2F_o/\sigma F_o)^2$	(Larson & Von Dreele, 1994)

Data sets (Irtx) and (Iltx) were collected on a locally assembled Huber 512 goniometer equipped with a Displex 202D cryogenic refrigerator (Henriksen *et al.*, 1986; Larsen, 1995). For data set (Iltx), the correction for absorption by the Be shield was performed by *PROFIT* (Streltsov & Zavodnik, 1989). Data set (Iltx) was obtained at the Single Crystal Diffractometer (SCD) beamline of the Intense Pulsed Neutron Source (IPNS) of the Argonne National Laboratory (Schultz *et al.*, 1984). This instrument was also equipped with a Displex 202 cryo-refrigerator. One histogram of data was collected to check for crystal quality and to determine the initial orientation matrix using an auto-indexing routine. 25 time-of-flight histograms were collected with different χ and φ settings and covered approximately two octants of data ($\pm h, +k, +l$). Bragg reflections in each histogram were integrated and corrected for the Lorentz factor, the incident spectrum and the detector efficiency. A wavelength-dependent spherical absorption correction was applied but symmetry-related reflections were not averaged because of the wavelength dependence of extinction. The unit-cell parameters for the neutron diffraction experiment were taken from those of (Iltx). The two H/D positions were modelled by putting both an H and a D atom on the same site. The occupancies were constrained to be fully occupied and allowed to refine. As noted by Figgis *et al.* (1998), the zero-point motion of H should be a factor of $2^{1/2}$ greater than that for D. Therefore, the isotropic displacement parameters of the H atoms were allowed to vary, while those of D were constrained to be $2^{-1/2}$ of the H-atom displacement parameters. The occupancies of the H/D positions refined to $\sim 72\%$ D on both sites. The D and H atoms were refined isotropically. The large value of S from the neutron data relative to that from the X-ray structure determinations (3.75 versus ~ 1) arises because of the inclusion of many weak or unobserved reflections at high values of $(\sin\theta)/\lambda$.

For data sets (Irtx) and (Iltx), data collection: local software; cell refinement: local software; data reduction: *PROFIT* (Streltsov & Zavodnik, 1989); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1983); software used to prepare material for publication: *SHELXTL*.

For data set (Iltx), data collection: IPNS data acquisition software; cell refinement: values from (Iltx) used; data reduction: *ANVRED*

(Schultz, 1993) program(s) used to refine structure: *GSAS* (Larson & Von Dreele, 1994); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1292). Services for accessing these data are described at the back of the journal.

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