Redetermination of the Structure of Disodium Pentacyanonitrosylferrate (Sodium Nitroprusside)

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Abstract. $Na_2[Fe(CN)_5(NO)].2H_2O$, orthorhombic, *Pnnm*, $a = 6.198$ (2), $b = 11.897$ (5), $c = 15.557$ (5) Å, $Z = 4$, $D_c = 1.71$ Mg m^{-3}. The structure was refined to $R_1 = 0.045$ for 1361 observed reflections, and is basically as described by Manoharan & Hamilton [*Inorg. Chem.* (1963). **2**, 1043–1047]. The $[Fe(CN)_5(NO)]^{2-}$ anion has effective 4*mm* symmetry, the Fe atom being displaced 0.183 (1) Å out of the plane of the *cis* C atoms towards the NO. The *cis* Fe—C distances are 1.929 (4) and 1.936 (4) Å. The *trans* Fe—C distance, 1.918 (6) Å, is not significantly different from the *cis* distances. This is in contrast to other $[M(CN)_5(NO)]^{n-}$ complexes where the *trans* M—C distances are longer than the *cis* M—C, and also to other $[ML_5(NO)]^{n+}$ complexes of Group VIII metals, where the *trans* M—L distances are shorter than the *cis* M—L. The Fe—N—O angle is 175.7 (5)° and the Fe—N distance 1.653 (5) Å.

Introduction. The structure of $Na_2[Fe(CN)_5-(NO)].2H_2O$ was previously investigated by Manoharan & Hamilton (1963). They used 787 visually estimated intensities and obtained a final R_1 of 0.10 with Fe—N or Fe—C e.s.d.'s of 0.02 Å. This structure is inaccurate by modern standards, and because of the pivotal position of $[Fe(CN)_5(NO)]^{2-}$ in

chemical, physical, and theoretical studies of nitrosyl complexes (Swinehart, 1967; Fenske & DeKock, 1972; Masĕk, 1969) and as a continuation of our programme on the *trans* influence in six-coordinate nitrosyls (Bottomley, 1975) we have reinvestigated it.

Examination of Weissenberg and precession photographs of a commercial sample of $Na_2[Fe(CN)_5-(NO)].2H_2O$ confirmed the possible space groups *Pnnm* or *Pnn2* found by Manoharan & Hamilton (1963). The crystal used for the intensity determination was of dimensions $0.09 \times 0.185 \times 0.335$ mm. Intensities of 1717 reflections ($2\theta < 60°$) were measured using graphite-monochromated Mo $K\alpha$ radiation on a Picker FACS 1 diffractometer. From the 1717 total, 1361 unique observed reflections $[I > 3\sigma(I)]$ were corrected for absorption ($\mu = 1.381$ mm^{-1}; transmission coefficients 0.612 to 0.756) and used for the refinement. The atomic coordinates given by Manoharan & Hamilton (1963) were used as starting parameters and gave an R_1 ($\sum |\Delta F|/\sum |F_o|$) of 0.097 on isotropic refinement. Scattering factors (including the real and imaginary parts of the anomalous-dispersion correction for all atoms except H) were taken from *International Tables for X-ray Crystallography* (1974). Anisotropic refinement with fixed positional and thermal parameters for the H atoms (observed in a difference synthesis) converged to $R_1 = 0.045$, $R_2 [= (\sum w|\Delta F|^2/\sum w|F_o|^2)^{1/2}] = 0.054$ and R' (as R_1, but including unobserved reflections) = 0.056. Refinement by minimizing $\sum w(\Delta F)^2$, with w based on counting statistics, was by block matrices using the program suite of Gabe, Larson, Lee, Wang & Le Page (1978). There were no significant trends in the data analysed as a function of $|F_o|$ and sin θ. The estimated error in an observation of unit weight was 2.06. A final difference map had a highest positive peak of

Table 1. *Atomic coordinates* ($\times 10^4$)

	x	y	z
Fe	4995 (1)	2795 (0)	5000 (0)
N(4)	7199 (8)	3577 (4)	5000 (0)
O(1)	8772 (8)	4048 (4)	5000 (0)
C(1)	2540 (10)	1814 (5)	5000 (0)
N(1)	1062 (10)	1230 (5)	5000 (0)
C(2)	6074 (6)	1796 (3)	5876 (2)
N(2)	6667 (6)	1207 (3)	6415 (2)
C(3)	3446 (6)	3606 (3)	4115 (2)
N(3)	2494 (7)	4039 (3)	3572 (2)
Na(1)	5000 (0)	0 (0)	2447 (1)
Na(2)	0 (0)	0 (0)	3779 (1)
O(2)	1743 (6)	1230 (3)	2688 (2)
H(1)	1726	1884	2926
H(2)	728	1348	2345

Table 2. *Bond lengths* (Å)

Fe—C(1)	1.918 (6)	C(1)—N(1)	1.150 (9)
Fe—C(2)	1.929 (4)	C(2)—N(2)	1.153 (5)
Fe—C(3)	1.936 (4)	C(3)—N(3)	1.152 (6)
Fe—N(4)	1.653 (5)	N(4)—O(1)	1.124 (7)

Table 3. Bond angles (°)

Fe—N(4)—O(1)	175·7 (5)	C(2)—Fe—C(2')	90·0 (2)
Fe—C(1)—N(1)	179·6 (6)	C(2)—Fe—C(3)	169·1 (2)
Fe—C(2)—N(2)	177·9 (4)	C(2)—Fe—C(3')	88·7 (2)
Fe—C(3)—N(3)	176·6 (4)	C(3)—Fe—C(3')	90·6 (2)
C(1)—Fe—N(4)	176·7 (3)	N(4)—Fe—C(2)	93·4 (2)
C(1)—Fe—C(2)	84·3 (2)	N(4)—Fe—C(3)	97·4 (2)
C(1)—Fe—C(3)	84·8 (2)		

Fig. 1. The $[Fe(CN)_5(NO)]^{2-}$ anion.

1·6 e $Å^{-3}$ and a lowest negative of $-0·6$ e $Å^{-3}$, both within 1·2 Å of the Fe atom. Complex scattering factors for the neutral atoms were used. The final atomic coordinates are given in Table 1 and bond lengths and angles within the $[Fe(CN)_5(NO)]^{2-}$ anion in Tables 2 and 3.*

Discussion. The geometry of the $[Fe(CN)_5(NO)]^{2-}$ anion is shown in Fig. 1. Two features of the co-ordination geometry are worthy of note. First, the symmetry of the cation is extremely close to the idealized C_{4v}, though crystallographically only C_s is required. The O atom of NO has the maximum deviation (0·06 Å) from the two vertical planes, these planes making an angle of 88·1° with one another; the maximum deviation from linearity is the Fe—N—O angle of 175·7 (5)°; and the cis Fe—C bond lengths are 1·929 (4) and 1·936 (4) Å. This unusually precise conformation to non-imposed ideal symmetry makes the deviation of the anion from pseudo-octahedral symmetry [by displacement of the Fe atom 0·183 (1) Å out of the plane of the cis C atoms towards NO] especially marked. The result is the C(2)—Fe—C(3) angle of 169·1 (2)°. The bending of the cis ligands away from NO seems to be a general feature of the structures of six-coordinate nitrosyls. There have been three previous explanations of similar displacements: (a) the antibonding character of the d_{xy} orbital (Tullberg & Vannerberg, 1967), (b) repulsions between the ligand atoms (Bright & Ibers, 1969), and (c) repulsions between electrons in the metal—ligand bonds (Schultz, Henry, Reed & Eisenberg, 1974). Molecular-orbital calculations indicate d_{xy} is in fact non-bonding (Manoharan & Gray, 1966; Fenske & DeKock, 1972; Bottomley & Grein, 1979) thus eliminating (a). Consideration of the structures of $[Cr(CN)_5(NO)]^{3-}$ (Enemark, Quinby, Reed, Steuk & Walthers, 1970), $[Mn(CN)_5(NO)]^{3-}$ (Tullberg & Vannerberg, 1967) and $[Fe(CN)_5(NO)]^{2-}$ shows that the displacement of the cis ligands away from NO decreases slightly as the

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* Lists of structure factors, anisotropic thermal parameters, distances and angles about the Na and H atoms, and equations of mean planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34471 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
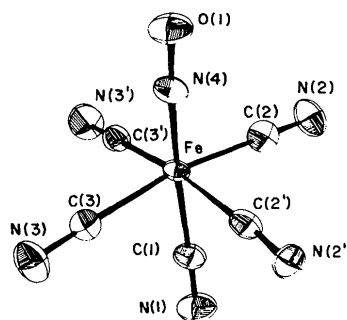
M—NO bond length increases, but is unaffected by large changes in the cis or trans M—CN bond lengths. Such behaviour is more easily interpreted if the primary effect on the geometry in these $[M(CN)_5(NO)]^{n-}$ complexes is (c), the repulsion of electrons in the M—CN bonds.

The second feature of note is the relative lengths of the trans and cis Fe—CN bonds, which are equal within experimental error. Previous structures of $[ML_5(NO)]^{n+}$ complexes with 18 valence electrons around a Group VIII metal show a marked shortening of the trans M—L bond (Bottomley, 1974, 1975; Veal & Hodgson, 1972). On the other hand both $[Cr(CN)_5(NO)]^{3-}$ (17 electrons, Group VI) and $[Mn(CN)_5(NO)]^{3-}$ (18 electrons, Group VII) show longer trans than cis M—CN bonds (Enemark et al., 1970; Tullberg & Vannerberg, 1967). In all of the complexes with short trans M—L bonds the L ligands are incapable of competing with NO as a π-electron-withdrawing group, which CN^- potentially can. In $[M(CN)_5(NO)]^{n-}$ complexes there may be therefore a delicate balance of electronic forces determining the relative bond lengths, and secondary effects such as packing forces may be important. This is being further investigated (Bottomley & Grein, 1979).

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Structure du Rhodostannite Synthétique

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Abstract. $Cu_2FeSn_3S_8$, tetragonal, $I4_1/a$, $a = 7\cdot305$ (2), $c = 10\cdot330$ (5) Å, $Z = 2$, $V = 551\cdot2$ Å^3, $d_c = 4\cdot79$ Mg m^{-3}, $\mu(Mo\,K\alpha) = 13\cdot34$ mm^{-1}. The structure, which is similar to Fe_2SnS_4, has been refined by least squares to a final R value of $0\cdot038$ (weighted R is $0\cdot049$) for the 623 observed data. $Cu_2FeSn_3S_8$ has a disordered spinel structure with the tetrahedral sites occupied by Cu^+ ions and the octahedral sites occupied by Sn^{4+} and Fe^{2+} ions in random distribution.

Introduction. Le rhodostannite $Cu_2FeSn_3S_8$, minéral naturel, a été décrit pour la première fois par Springer (1968) dans un article consacré aux composés de l'étain de type stannite Cu_2FeSnS_4 ou apparentés.

Cette phase a également été synthétisée par Wang (1975), au cours de l'étude du système $FeS–Cu_2Sn_{3,5}S_8$, qui en a déterminé les constantes cristallographiques: système quadratique, groupe d'espace $I4_1/a$, $a = 7,29$, $c = 10,31$ Å et $Z = 2$.

Ces dernières valeurs très comparables à celles caractérisant le composé Fe_2SnS_4 (Jumas, Philippot & Maurin, 1977) nous ont conduit à envisager une isotypie possible entre ces deux phases. Nous présentons ici les résultats de l'étude structurale de $Cu_2FeSn_3S_8$.

Ce composé a été préparé à partir des sulfures FeS, SnS_2 et des éléments Cu, S mélangés en quantité stoechiométrique par réaction dans l'état solide à 973 K en tube de quartz scellé sous vide. On obtient ainsi le produit sous forme de poudre microcristalline.

Pour préparer les cristaux nous avons réalisé une réaction de transport dans un tube de quartz de 200 mm de long scellé sous vide dans lequel nous avions introduit le produit sous forme de poudre et l'agent de transport (ici l'iode à une concentration de 5 Mg m^{-3}).

Les températures extrêmes du gradient de température utilisé dans cette réaction sont 1053 et 983 K. Les cristaux recueillis dans la partie froide du tube se présentent sous forme de petits octaèdres de couleur noire (Fig. 1).

L'analyse quantitative des éléments Cu, Fe, Sn et S effectuée à la microsonde de Castaing sur cristal confirme bien la formule $Cu_2FeSn_3S_8$ (Tableau 1). L'étude cristallographique préliminaire effectuée en chambres de Weissenberg et de précession de Buerger conduit aux résultats en bon accord avec ceux trouvés par Wang (1975).
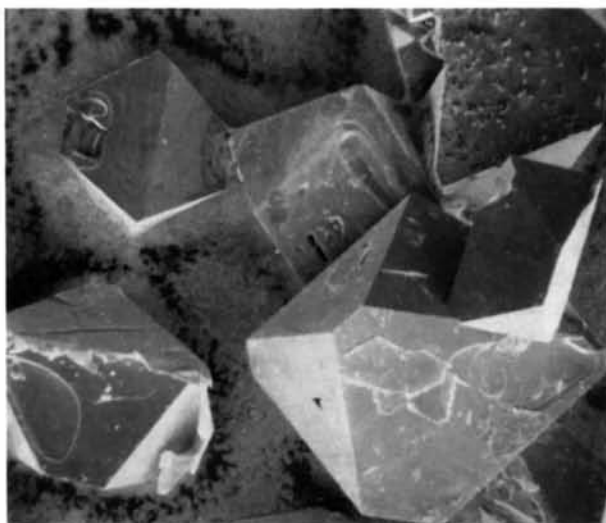

Fig. 1. Monocristaux de $Cu_2FeSn_3S_8$ photographiés sous microscope électronique à balayage ($G = 55$).