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μ-Cyano-1:2κ^2C:N-tetracyano-1κ^4C-(5-methyl-5-nitro-3,7-diazanonane-1,9-diamine-2$\kappa^4N^{1,3,7,9}$)-nitrosyl-1κN-copper(II)iron(II) dihydrate

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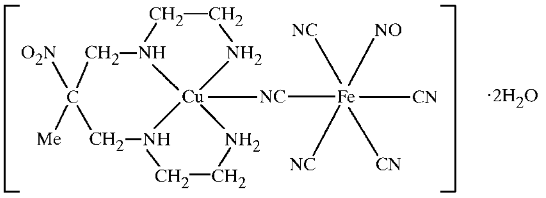
The title binuclear complex, $[CuFe(CN)_5(C_8H_{21}N_5O_2)(NO)]\cdot 2H_2O$ or $[CuFe(nelin)(CN)_5(NO)]\cdot 2H_2O$ (nelin is 5-methyl-5-nitro-3,7-diazanonane-1,9-diamine) consists of discrete binuclear mixed-metal species, with a Cu centre linked to an Fe centre through a cyano bridge, and two water molecules of crystallization. In the complex, the Cu^{II} ion is coordinated by five N atoms and has a distorted square-pyramidal geometry. The Fe^{II} centre is in a distorted octahedral environment.

Comment

It is well known that the cyanide ion may coordinate either through the C atom, acting as a monodentate ligand, or through both the C and N atoms, acting as a bridging ligand (Cromer *et al.*, 1965). The preparation and study of polynuclear cyanide-bridged metal complexes, especially ferro- and ferricyanide complexes, have been of great interest in recent years due to the unusual electronic state, magnetic behaviour and photochemical properties of these compounds (Alcock *et al.*, 1993; Entley & Giroloni, 1994; Clemente-Leon *et al.*, 2001). Several studies have been made of the $[Fe(CN)_5(NO)]^{2-}$ anion (Olabe *et al.*, 1984; Zhan *et al.*, 1999). Attempts have been made to clarify the correlation between the structure and the photochemical or magnetic properties of polynuclear complexes with the nitroprusside. We report here the preparation and structure of a new cyano-bridged Cu–Fe complex, namely $[Cu(nelin)Fe(CN)_5(NO)]\cdot 2H_2O$ (where nelin is 5-methyl-5-nitro-3,7-diazanonane-1,9-diamine), (I).



(I)

The dinuclear unit of (I) comprises one $[Fe(CN)_5(NO)]^{2-}$ anion linked to one $[Cu(nelin)]^{2+}$ cation through a CN^- ligand. As shown in Fig. 1, the coordination environment of the Cu atom can be described as distorted square-based pyramidal. The basal plane is constructed by the coordination of the four N atoms of the tetradentate nelin ligand, and the N atom of the cyanide group occupies the axial position. The Cu—N distances reveal a small tetragonal distortion of the Cu–N_4 plane, with the Cu—N bonds to the secondary amines being slightly longer than the Cu—N bonds to the primary amines; this may be a consequence of steric differences between the N atoms. Within the CuN_4 plane, the N2—Cu—N3 angle of 92.11 (7)° is about 3.6° smaller than the N1—Cu—N4 angle because of the steric difference. This is different from the similar structure, namely {3-[(2-aminoethyl)amino]-2-[(2-aminoethyl)aminomethyl]propionato}copper(II) perchlorate, studied by Bernhardt *et al.* (1990), in which the *trans* angles are almost the same. The axial Cu—N6 bond is elongated, as in the case of $[Cu_2(oxpn)Fe(CN)_5(NO)]_n$ [oxpn is N,N'-bis(3-aminopropyl)oxamide; Chen *et al.*, 1995] and $[Cu(dmen)_2\text{-}Fe(CN)_5(NO)]$ (dmen is 2-dimethylaminoethylamine; Mondal *et al.*, 2000).

The Fe^{II} atom is in a deformed octahedral arrangement. The equatorial plane is defined by four cyano C atoms and the two axial sites are occupied by a cyanide C atom and the N atom of the nitrosyl group. The Fe—C, Fe—N, C—N and N—O bond lengths in the $[Fe(CN)_5(NO)]$ moiety are comparable with those reported for other multinuclear complexes of $[Fe(CN)_5(NO)]^{2-}$ (Shyu *et al.*, 1997; Zhan *et al.*, 1999). The Fe—N distance [1.651 (2) Å] is much shorter than the five Fe—C distances, which lie between 1.939 (3) and 1.948 (2) Å. Hence, the NO ligand is perfectly localized in the structure.

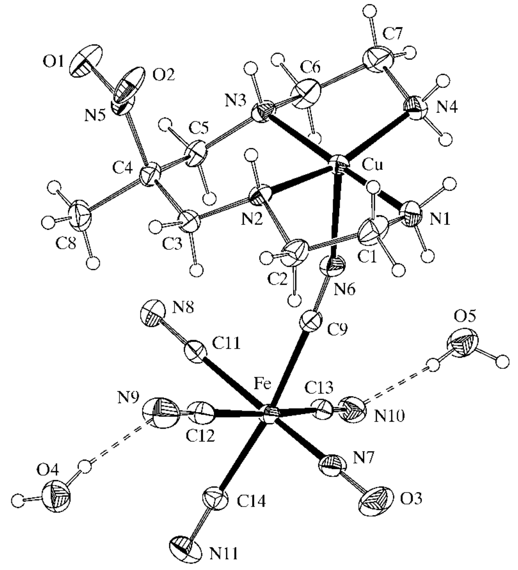


Figure 1
A view of the coordination environment in (I), shown with 35% probability displacement ellipsoids. Hydrogen bonds are illustrated as dotted lines.

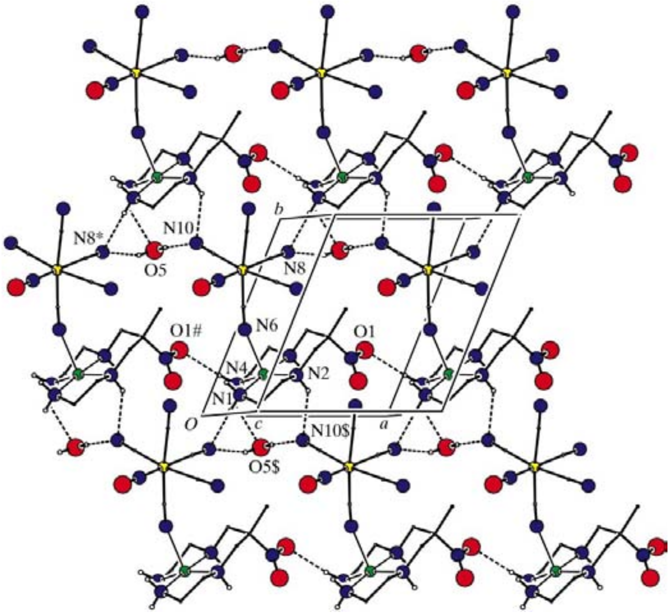


Figure 2
The molecular packing diagram for (I). Atoms labelled with an asterisk (*), hash sign (#) or dollar sign ($) are at symmetry positions ($x - 1, y, z$), ($x, y - 1, z$) or ($1 + x, y - 1, z$), respectively.

According to molecular orbital theory, M—NO$^+$ will be nearly linear, which is proved in (I) by the Fe—N—O bond angle of 179.1 (2)°. The Fe—C—N bond angles [in the range 176.7 (2)–179.2 (2)°] are also nearly linear. The Cu—N6—C9 bond angle is 157.1 (2)°, indicating a non-linear linkage between the N atom of the cyanide ligand and the Cu^{II} atom.

Hydrogen-bonding interactions play an important role in the solid-state structure of (I), as shown in Fig. 2. In the unit cell, the complex is linked by hydrogen bonds to form sheets which lie in the domain $0 < z < \frac{1}{2}$, and these sheets are then linked by the two water molecules *via* O—H···N hydrogen bonds to give a three-dimensional network (Table 2).

Experimental

To an aqueous solution (15 ml) of [Cu(nelin)(ClO$_4$)$_2$] (0.48 g, 1 mmol), an aqueous solution (15 ml) containing Na$_2$[Fe(CN)$_5$(NO)]·2H$_2$O (0.29 g, 1 mmol) was added dropwise. After stirring for 30 min at room temperature, the resulting precipitate was collected by suction filtration. Dark-purple single crystals of (I) were obtained by recrystallization from water in the dark.

Crystal data

[CuFe(CN)$_5$(C$_8$H$_{21}$N$_5$O$_2$)(NO)]·2H$_2$O
M_r = 534.83
Triclinic, $P\overline{1}$
a = 8.470 (2) Å
b = 9.702 (2) Å
c = 14.648 (3) Å
α = 85.55 (1)°
β = 80.11 (2)°
γ = 68.20 (1)°
V = 1100.9 (4) Å^3
Z = 2
D_x = 1.613 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 31 reflections
θ = 2.6–15.9°
μ = 1.67 mm^{-1}
T = 291 (2) K
Prism, dark purple
0.58 × 0.54 × 0.40 mm

Table 1
Selected geometric parameters (Å, °).

Cu—N1	2.0019 (19)	Fe—C14	1.940 (2)
Cu—N4	2.0076 (19)	Fe—C12	1.941 (3)
Cu—N2	2.0093 (17)	Fe—C9	1.944 (2)
Cu—N3	2.0322 (18)	Fe—C11	1.948 (2)
Cu—N6	2.2915 (19)	N6—C9	1.141 (3)
Fe—N7	1.651 (2)	O3—N7	1.135 (3)
Fe—C13	1.939 (3)		
N1—Cu—N4	95.69 (8)	C9—N6—Cu	157.02 (18)
N4—Cu—N2	163.66 (7)	N6—C9—Fe	176.73 (19)
N1—Cu—N3	176.38 (8)	O3—N7—Fe	179.1 (2)
N2—Cu—N3	92.11 (7)	N8—C11—Fe	177.8 (2)
C13—Fe—C12	169.74 (10)	N9—C12—Fe	179.2 (2)
C14—Fe—C9	171.53 (9)	N10—C13—Fe	177.0 (2)
N7—Fe—C11	178.87 (9)	N11—C14—Fe	177.4 (2)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4OA···N9	0.83 (3)	2.09 (3)	2.905 (4)	167 (4)
O4—H4OB···N11^{i}	0.84 (3)	2.03 (2)	2.847 (3)	165 (3)
O5—H5OA···N10	0.81 (3)	2.07 (3)	2.879 (3)	173 (3)
O5—H5OB···N8^{ii}	0.82 (3)	2.26 (3)	3.014 (4)	153 (3)
N1—H1NA···O4^{iii}	0.90	2.15	3.023 (3)	162
N1—H1NB···N8^{iv}	0.90	2.38	3.278 (3)	172
N2—H2N···N10^{v}	0.91	2.52	3.251 (3)	138
N3—H3N···O5^{vi}	0.91	2.20	2.996 (3)	145
N4—H4NA···O5^{v}	0.90	2.41	3.147 (3)	140
N4—H4NB···O1^{ii}	0.90	2.17	3.058 (3)	170

Symmetry codes: (i) $-x, 2 - y, 1 - z$; (ii) $x - 1, y, z$; (iii) $-x, 1 - y, 1 - z$; (iv) $x, y - 1, z$; (v) $1 + x, y - 1, z$; (vi) $-x, 1 - y, -z$.

Data collection

Siemens P4 diffractometer
ω scans
Absorption correction: empirical (North *et al.*, 1968)
$T_{\min}$ = 0.380, $T_{\max}$ = 0.512
4302 measured reflections
3874 independent reflections
3436 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.008
$\theta_{\max}$ = 25°
$h = 0 \rightarrow 10$
$k = -10 \rightarrow 11$
$l = -17 \rightarrow 17$
3 standard reflections every 97 reflections intensity decay: 0.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.067
S = 1.05
3874 reflections
307 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0379P)^2 + 0.3921P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.33 e Å^{-3}
$\Delta\rho_{\min}$ = −0.27 e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0042 (7)

All H atoms were visible in difference maps. The water H atoms were refined using *DFIX* restraints (*SHELXL*97; Sheldrick, 1997), with O—H = 0.82 (3) Å and H···H = 1.37 (3) Å. All other H atoms were allowed for as riding atoms, with C—H = 0.96 and 0.97 Å, and N—H = 0.90 and 0.91 Å. The nitro group (N5/O1/O2) showed some signs of disorder (one O atom was markedly anisotropic), and this was allowed for by refining atom O2 over two closely adjacent sites with 0.5 occupancy and with the N5—O2 and N5—O2′ distances restrained to be 1.22 (1) Å.

Acta Cryst. (2002). C**58**, m382–m384 Liang Shen *et al.* • [CuFe(CN)$_5$(C$_8$H$_{21}$N$_5$O$_2$)(NO)]·2H$_2$O **m383**

Data collection: *XSCANS* (Siemens, 1991); cell refinement: *XSCANS*; data reduction: *SHELXTL-Plus* (Sheldrick, 1990); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXTL-Plus*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1643). Services for accessing these data are described at the back of the journal.

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