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A cyano-bridged binuclear Cu–Fe complex based on nitroprusside

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The title compound, μ-cyano-1:2κ^2C:N-tetracyano-1κC-[3,7-bis(2-aminoethyl)-1,3,5,7-tetraazabicyclo[3,3,2]decane-2$\kappa^4N^{1,3,5,7}$]-nitrosyl-1κN-copper(II)iron(II) monohydrate, $[CuFe(CN)_5(C_{10}H_{24}N_6)(NO)]\cdot H_2O$, has been synthesized and structurally characterized; the Cu atom is five-coordinate and has a square pyramidal configuration. The $[Fe(CN)_5(NO)]^{2-}$ anion uses the CN^- ligand *cis* to the NO^+ ligand to link to the Cu atom. The Cu—N≡C—Fe linkage is nonlinear, similar to that in other cyano-bridged bimetallic complexes.

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.041
wR factor = 0.091
Data-to-parameter ratio = 22.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

It is well known that the cyanide ion may coordinate through the C atom, acting as a monodentate ligand, or through both the C and N atoms, acting as a bridging ligand. Recently, using $[Fe(CN)_5(NO)]^{2-}$ as a building block, some cyano-bridged polymeric complexes have been prepared for the investigation of the photo-functional (Bellouard *et al.*, 2001; Gu *et al.*, 2001) and semipermeable membrane properties (Mullica *et al.*, 1990) of nitroprusside. Also, there has been much interest in clarifying the structural correlation with the magnetic properties of nitroprusside-bridged complexes. Magnetic studies show that the nitroprusside anion transmits a very weak antiferromagnetic interaction. Tang and co-workers reported a two-dimensional cyano-bridged $[Cu_2(oxpn)Fe(CN)_5(NO)]_n$ [H_2oxpn = N,N'-bis(3-aminopropyl)oxamide] complex, in which an N atom of the cyano group in $[Fe(CN)_5(NO)]^{2-}$ is coordinated to one of the adjacent Cu^{II} ions in $[Cu_2(oxpn)]^{2+}$ (Chen *et al.*, 1995). The complexes $M(en)_2Fe(CN)_5$(-nH_2O (where en = ethylenediamine, M = Ni^{II} and Cu^{II}, n = 0 or 1) exhibit one-dimensional chain-like structures, in which weak antiferromagnetic coupling is present through the nitroprusside (Kou *et al.*, 1998; Shyu *et al.*, 1997), whereas $Cu(L^1)_2Fe(CN)_5(NO)\cdot nH_2O$ (where L^1 = 2-dimethylaminoethylamine, 1-dimethylamino-2-propylamine, 3,10-bis(2-hydroxyethyl)-1,3,5,8,10,12-hexaazacyclotetradecane and 1,2-diaminopropane) are cyano-bridged dinuclear complexes (Zhang *et al.*, 2002). We have been interested in this versatile building block, and recently we prepared a new tetraazabicyclo–Cu^{II} complex $[CuL^2](ClO_4)_2$ [L^2 = 3,7-bis(2-aminoethyl)-1,3,5,7-tetraazabicyclo[3,3,2]decane], in which the Cu^{II} ion exhibits 4 + 2 coordination geometry (He *et al.*, 2003). By reacting the precursor with $[Fe(CN)_5(NO)]^{2-}$ we expect to generate cyano-bridged species.

A displacement ellipsoid plot of the title compound, (I), is illustrated in Fig. 1. The central Cu atom is coordinated by five N atoms, leading to a distorted pyramidal structure with four N atoms from the L^2 ligand defining the equatorial plane and one N atom from the bridging CN^- ligand occupying the axial

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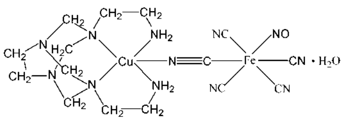
position. The Cu—N$_{\text{equatorial}}$ bond lengths [range 1.998 (2)–2.032 (2) Å] are shorter than the Cu—N$_{\text{axial}}$ bond length [2.303 (2) Å] due to the Jahn–Teller effect for the d^9 configuration of the Cu$^{\text{II}}$ ion in a pyramidal environment. The equatorial atoms (N7, N8, N11 and N12) show some deviation from coplanarity [largest deviation 0.129 (3) Å]. The coordination sphere of Cu$^{\text{II}}$ shows a distortion from square pyramidal (SP) towards trigonal bipyrimidal (TBP), which can be defined by a τ value (where τ = 1.0 for a regular TBP and τ = 0.0 for a regular SP stereochemistry; Brophy *et al.*, 1999). For the coordination environment of Cu in the present complex, a τ value of 0.19 is obtained, emphasizing that the metal centre geometry is much closer to SP than to TBP. The bridging cyanide coordinates to the Cu$^{\text{II}}$ ion in a bent fashion, with a C1—N1—Cu bond angle of 141.37 (19)°; this is similar to the values in related compounds (Kou *et al.*, 1998; Zhang *et al.*, 2002; Smekal *et al.*, 2000; Mondal *et al.*, 2000). The Fe···Cu distance through the cyano bridge is 5.027 (1) Å.



(I)

As usual, the $[Fe(CN)_5(NO)]^{2-}$ moiety exhibits a distorted octahedral structure (C_{4v}), with the four equatorial CN$^-$ ligands bent away from the NO$^+$ ligand. This is due to the greater electronegativity of the nitrosyl group compared to the cyanide groups. The C—Fe—NO angles are greater than 90°, and consequently the C—Fe—C5 angles are less than 90°. The mean Fe—C and C—N bond lengths are 1.938 (3) and 1.141 (3) Å, respectively. The Fe—N6 and N6—O11 bond distances are 1.657 (2) and 1.124 (3) Å. The Fe—C—N and Fe—N—O bonds are linear, with bond angles ranging from 174.8 (2) to 179.1 (3)°. These values are in good agreement with those of previous reports (Mondal *et al.*, 2000; Shyu *et al.*, 1997). As in other dinuclear bimetallic nitroprussides, the cyanide ligand *cis* to the NO$^+$ ligand serves as a bridging group to connect two metal ions with similar bridging bond angles (Ribas *et al.*, 1984; Zhang *et al.*, 2002).

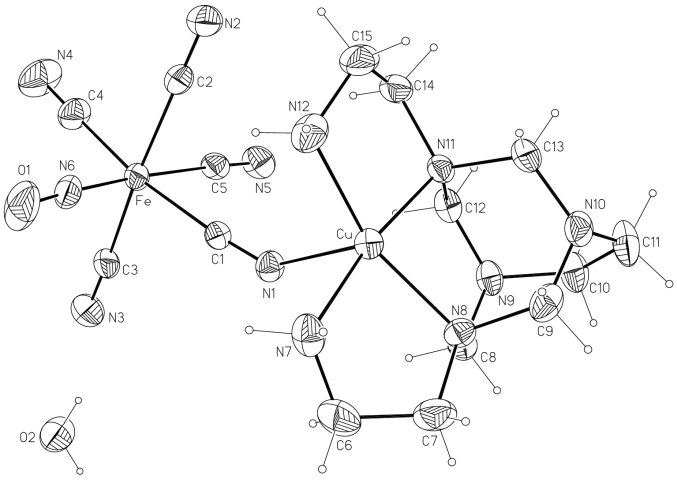


Figure 1
A view of the title compound (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level for non-H atoms.

The water molecules are hydrogen bonded to the non-bridging cyanide N atom and to the primary amine atoms to produce a hydrogen-bonded three-dimensional network; details are given in Table 2.

Experimental

Cu(L^2)(ClO$_4$)$_2$ was synthesized as described in the literature (He *et al.*, 2003). Slow evaporation of an aqueous solution of Cu(L^2)(ClO$_4$)$_2$ and Na$_2$[Fe(CN)$_5$(NO)]·2H$_2$O (molar ratio, 1:1) at room temperature resulted in red crystals of (I) suitable for single-crystal analysis.

Crystal data

$[CuFe(CN)_5(C_{10}H_{24}N_6)(NO)]\cdot H_2O$
M_r = 525.87
Triclinic, $P\overline{1}$
a = 9.3360 (19) Å
b = 11.013 (2) Å
c = 12.020 (2) Å
α = 71.36 (3)°
β = 81.26 (3)°
γ = 72.34 (3)°
V = 1113.8 (4) Å^3
Z = 2
D_x = 1.568 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4565 reflections
θ = 2.3–30°
μ = 1.65 mm^{-1}
T = 293 (2) K
Platelet, red
0.4 × 0.2 × 0.1 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{\min}$ = 0.566, $T_{\max}$ = 0.848
9026 measured reflections
6292 independent reflections
4956 reflections with $I > 2\sigma(I)$
R_{int} = 0.017
$\theta_{\max}$ = 30.0°
$h = -13 \rightarrow 8$
$k = -15 \rightarrow 15$
$l = -16 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.091
S = 0.91
6292 reflections
280 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.031P)^2 + 1P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.55 e Å^{-3}
$\Delta\rho_{\min}$ = −0.26 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu—N7	1.998 (2)	Fe—C2	1.944 (3)
Cu—N11	2.006 (2)	Fe—C5	1.945 (3)
Cu—N12	2.021 (2)	N1—C1	1.149 (3)
Cu—N8	2.032 (2)	N6—O1	1.124 (3)
Cu—N1	2.303 (2)	C2—N2	1.138 (4)
Fe—N6	1.657 (2)	C3—N3	1.139 (4)
Fe—C1	1.931 (2)	C4—N4	1.136 (4)
Fe—C3	1.933 (3)	C5—N5	1.146 (3)
Fe—C4	1.937 (3)		
N6—Fe—C1	91.91 (10)	N1—C1—Fe	174.8 (2)
N6—Fe—C3	94.37 (13)	O1—N6—Fe	175.3 (2)
N6—Fe—C4	97.24 (13)	N2—C2—Fe	178.8 (3)
N6—Fe—C2	94.77 (13)	N3—C3—Fe	177.4 (3)
N6—Fe—C5	175.86 (10)	N4—C4—Fe	179.1 (3)
C1—N1—Cu	141.37 (19)	N5—C5—Fe	178.0 (2)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N7-H7A\cdots N4^{i}$	0.90	2.25	3.092 (4)	156
$N7-H7D\cdots N3^{ii}$	0.90	2.42	3.295 (4)	163
$N12-H12D\cdots O2^{iii}$	0.90	2.06	2.947 (4)	169
$O2-H200\cdots N3$	0.86 (5)	2.02 (5)	2.838 (4)	158 (4)
$O2-H201\cdots N4^{iv}$	0.83 (5)	2.08 (5)	2.881 (4)	162 (5)
$N12-H12C\cdots O2^{ii}$	0.90	2.78	3.174 (4)	108

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

The H atoms of the water molecule were found in a difference Fourier map and refined isotropically. The H atoms bound to C and N atoms were also located in a difference map and were refined as riding atoms (C—H 0.97 Å and N—H 0.86 Å).

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2002); software used to prepare material for publication: *SHELXL*97.

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References

Bellouard, F., Clemente-Leon, M., Coronado, E., Galan-Mascaros, J. R., Gimenez-Saiz, C., Gomez-Garcia, C. J. & Woike, T. (2001). *Polyhedron*, **20**, 1615–1619.

Brophy, M., Murphy, G., O'Sullivan, C., Hathaway, B. & Murphy, B. (1999). *Polyhedron*, **18**, 611–613.

Bruker (2000). *SMART* (Version 5.6), *SAINT* (Version 5.6) and *SADABS* (Version 2.01). Bruker AXS Inc., Madison, Wisconsin, USA.

Chen, Z. N., Wang, J. L., Qiu, J., Miao, F. M. & Tang, W. X. (1995). *Inorg. Chem.* **34**, 220–225.

Gu, Z. Z., Sato, O., Einaga, Y., Kai, M., Iyoda, T., Fujishima, A. & Hashimoto, K. (2001). *Bull. Chem. Soc. Jpn*, **74**, 1617–1622.

He, Y., Kou, H.-Z., Li, Y., Zhou, B. C., Xiong, M. & Li, Y. D. (2003). *Inorg. Chem. Commun.* **6**, 38–42.

Kou, H.-Z., Wang, H.-M., Liao, D.-Z., Cheng, P., Jiang, Z.-H., Yan, S.-P., Huang, X. Z. & Wang, G.-L. (1998). *Aust. J. Chem.* **51**, 661–665.

Mondal, N., Saha, M. K., Mitra, S., Gramlich, V. & Fallah, M. S. E. (2000). *Polyhedron*, **19**, 1935–1939.

Mullica, D. F., Tippin, D. B. & Sappenfield, B. L. (1990). *Inorg. Chim. Acta*, **174**, 129–135.

Ribas, J., Julia, J. M., Aolans, X., Font-Altaba, M., Isalgué, A. & Tejada, X. (1984). *Transition Met. Chem.* **9**, 57–60.

Sheldrick, G. M. (1997). *SHELXL*97 and *SHELXS*97. University of Göttingen, Germany.

Shyu, H. L., Wei, H. H. & Wang, Y. (1997). *Inorg. Chim. Acta*, **258**, 81–86.

Smekal, Z., Travnicek, Z., Marek, J. & Nadvornik, M. (2000). *Aust. J. Chem.* **53**, 225–228.

Spek, A. L. (2002). *PLATON*. 2002 Version, University of Utrecht, The Netherlands.

Zhang, K. L., Xu, Y., Wang, Z., Jin, C. M. & You, X. Z. (2002). *Transition Met. Chem.* **27**, 95–99.