

## catena-Poly[[[1,8-bis(2-hydroxyethyl)-1,3,6,8,10,13-hexaazacyclotetradecane]copper(II)]- $\mu$ -cyano-[tricyano-nitrosoiron(III)]- $\mu$ -cyano]

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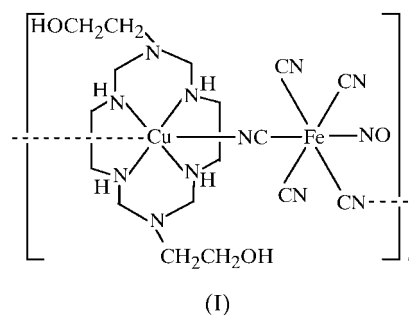
The bimetallic title complex,  $[\text{CuFe}(\text{CN})_5(\text{C}_{12}\text{H}_{30}\text{N}_6\text{O}_2)(\text{NO})]$  or  $[\text{Cu}(L)\text{Fe}(\text{CN})_5(\text{NO})]$  [where  $L$  is 1,8-bis(2-hydroxyethyl)-1,3,6,8,10,13-hexaazacyclotetradecane], has a one-dimensional zigzag polymeric  $-\text{Cu}(L)-\text{NC}-\text{Fe}(\text{NO})(\text{CN})_3-\text{CN}-\text{Cu}(L)-$  chain, in which the  $\text{Cu}^{\text{II}}$  and  $\text{Fe}^{\text{II}}$  centres are linked by two CN groups. In the complex, the  $\text{Cu}^{\text{II}}$  ion is coordinated by four N atoms from the  $L$  ligand [ $\text{Cu}-\text{N}(L) = 1.999(2)-2.016(2) \text{ \AA}$ ] and two cyanide N atoms [ $\text{Cu}-\text{N} = 2.383(2)$  and  $2.902(3) \text{ \AA}$ ], and has an elongated octahedral geometry. The  $\text{Fe}^{\text{II}}$  centre is in a distorted octahedral environment, with  $\text{Fe}-\text{N}(\text{nitroso}) = 1.656(2) \text{ \AA}$  and  $\text{Fe}-\text{C}(\text{CN}) = 1.938(3)-1.948(3) \text{ \AA}$ . The one-dimensional zigzag chains are linked to form a three-dimensional network *via*  $\text{N}-\text{H}\cdots\text{N}$  and  $\text{O}-\text{H}\cdots\text{N}$  hydrogen bonds.

### Comment

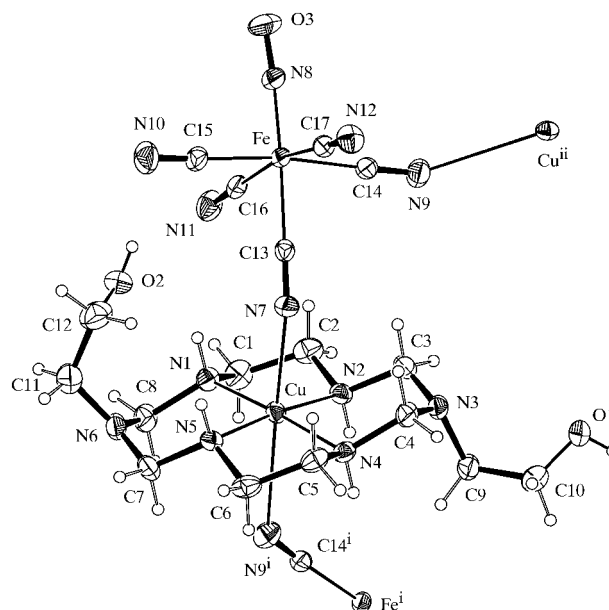
The coordination chemistry of cyanide-bridged metal complexes, especially ferro- and ferricyanides, has become of great interest in recent years due to their unusual electronic states, magnetic behaviour and photochemical properties (Alcock *et al.*, 1993; Entley & Giroloni, 1994; Clemente-Leon *et al.*, 2001). Several studies have been carried out with the  $[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$  anion (Olabe *et al.*, 1984; Zhan *et al.*, 1999), but the interesting cyanide-bridged polymeric complexes based on azamacrocyclic nickel(II) or copper(II) and nitroprusside have only been developed very recently (Kou *et al.*, 2000; Lu *et al.*, 2000). We report here the preparation and structure of a new cyano-bridged Cu–Fe complex, (I).

The asymmetric unit of (I) consists of one  $[\text{Cu}(L)]^{2+}$  cation [ $L$  is 1,8-bis(2-hydroxyethyl)-1,3,6,8,10,13-hexaazacyclotetradecane] linked to an  $[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$  anion. As shown in Fig. 1, two cyano N atoms in a *cis* arrangement coordinate to the adjacent Cu atoms, forming a one-dimensional zigzag chain

which extends in the  $b$  direction. The coordination environment of the Cu atom can be described as elongated octahedral. The basal plane is constructed by the coordination of four secondary N atoms of the tetradentate azamacrocyclic ligand ( $L$ ), with two N atoms of cyanide groups occupying the axial positions. The  $\text{Cu}-\text{N}(\text{azamacrocyclic})$  bond distances range from 1.999 (2) to 2.016 (2)  $\text{ \AA}$ , close to the values of 2.002 and 2.018  $\text{ \AA}$  in  $[\text{Cu}L(\text{H}_2\text{O})]_n[(\text{Cu}L)\text{Fe}(\text{CN})_6]_{2n}$  (Lu *et al.*, 2000). The axial  $\text{Cu}-\text{N}7$  and  $\text{Cu}-\text{N}9^i$  bonds [Table 1; symmetry code: (i)  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$ ] are elongated significantly, owing to the Jahn–Teller effect of the  $d^9$  electronic configuration of  $\text{Cu}^{\text{II}}$ . This was also present in  $[\text{Cu}L(\text{H}_2\text{O})]_n-[(\text{Cu}L)\text{Fe}(\text{CN})_6]_{2n}$  (Lu *et al.*, 2000) and  $[\text{Cu}(\text{en})_2\{\text{Fe}(\text{CN})_5(\text{NO})\}]_2[\text{Cu}(\text{en})_2]$  (en is ethylenediamine; Zhan *et al.*, 1999).

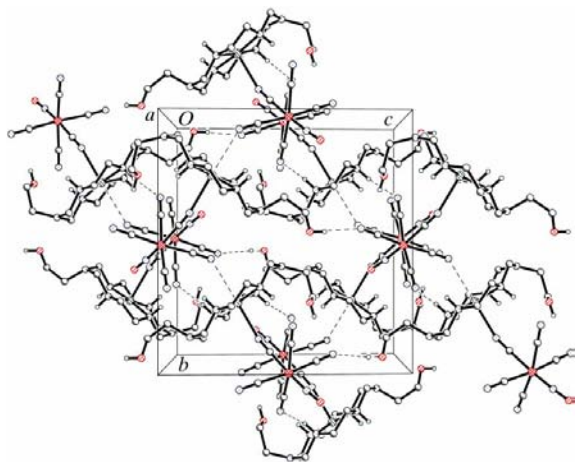


The average bite distances of the five- and six-membered chelate rings are 2.736 (3) and 2.939 (3)  $\text{ \AA}$ , respectively, and the average bite angles of the five- and six-membered chelate rings are 85.80 (9) and 92.47 (9) $^\circ$ , respectively. These values are similar to those in  $[\text{Cu}(L)(\text{SCN})_2]$  (Shen, 2002). The six-membered chelate rings adopt a chair conformation and the



**Figure 1**

A view of the asymmetric unit of (I) and some immediately adjacent atoms which generate the polymeric chain. The minor-occupancy disordered hydroxy groups are not shown. Displacement ellipsoids are drawn at the 30% probability level [symmetry codes: (i)  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$ ; (ii)  $\frac{1}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$ ].



**Figure 2**  
A packing diagram for (I), viewed along the *a* axis.

alkyl chains on the bridgehead N atoms are axial. The five-membered chelate rings assume a *gauche* conformation. The average N—C bond distance on the azamacrocycle is 1.46 (3) Å.

The Fe<sup>II</sup> atom in (I) is in a slightly deformed octahedral arrangement. The equatorial plane is defined by four cyanide C atoms, and the two axial sites are occupied by a cyanide C atom and the nitrosyl N atom. The Fe—C, Fe—N, C—N and N—O bond lengths in the [Fe(CN)<sub>5</sub>(NO)] moiety are comparable with those found in previously reported multinuclear [Fe(CN)<sub>5</sub>(NO)]<sup>2-</sup> complexes (Zhan *et al.*, 1999; Shen *et al.*, 2002). The Fe—N distance [1.656 (2) Å] is much shorter than the five Fe—C distances, which are in the range 1.938 (3)–1.948 (2) Å. Hence, the NO ligand is perfectly localized in the structure.

According to molecular orbital theory, *M*—NO<sup>+</sup> should be nearly linear: the observed Fe—N—O bond angle in (I) is 175.9 (2)°. The Fe—C—N bond angles [in the range 176.3 (2)–178.5 (3)°] are also essentially linear. The Cu—N7—C13 and Cu—N9<sup>i</sup>—C14<sup>i</sup> bond angles are 147.2 (2) and 133.9 (2)°, respectively, resulting in a one-dimensional zigzag chain being formed.

Hydrogen-bonding interactions (Table 2) play an important role in the solid-state structure of (I). As shown in Fig. 2, the one-dimensional zigzag chains are linked to form a three-dimensional network *via* N—H...N and O—H...N hydrogen bonds. In addition, there are some weak C—H...O interactions (Table 2).

## Experimental

The starting material, Cu(L)(ClO<sub>4</sub>)<sub>2</sub>, was prepared according to the literature method of Shen (2002). To an aqueous solution (15 ml) of Cu(L)(ClO<sub>4</sub>)<sub>2</sub> (0.48 g, 1 mmol), an aqueous solution (15 ml) of Na<sub>2</sub>[Fe(CN)<sub>5</sub>(NO)]·2H<sub>2</sub>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)<sub>5</sub>(C<sub>12</sub>H<sub>30</sub>N<sub>6</sub>O<sub>2</sub>)(NO)]  
*M<sub>r</sub>* = 569.92  
 Monoclinic, *P*2<sub>1</sub>/*n*  
*a* = 12.885 (2) Å  
*b* = 14.089 (2) Å  
*c* = 13.519 (3) Å  
 $\beta$  = 93.35 (1)°  
*V* = 2450.0 (7) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 1.545 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 28 reflections  
 $\theta$  = 2.7–15.1°  
 $\mu$  = 1.51 mm<sup>-1</sup>  
*T* = 296 (2) K  
 Prism, purple  
 0.40 × 0.36 × 0.36 mm

## Data collection

Siemens *P4* diffractometer  
 $\omega$  scans  
 Absorption correction: empirical (North *et al.*, 1968)  
 $T_{\min}$  = 0.549,  $T_{\max}$  = 0.582  
 4892 measured reflections  
 4324 independent reflections  
 3303 reflections with *I* > 2σ(*I*)

*R*<sub>int</sub> = 0.015  
 $\theta_{\max}$  = 25.0°  
*h* = 0 → 15  
*k* = 0 → 16  
*l* = -16 → 16  
 3 standard reflections every 97 reflections  
 intensity decay: 5.2%

## Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.032  
*wR*(*F*<sup>2</sup>) = 0.076  
*S* = 0.97  
 4324 reflections  
 332 parameters  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0405P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

( $\Delta/\sigma$ )<sub>max</sub> = 0.001  
 $\Delta\rho_{\max} = 0.42 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.31 \text{ e \AA}^{-3}$   
 Extinction correction: *SHELXL97* (Sheldrick, 1997)  
 Extinction coefficient: 0.0010 (3)

**Table 1**

Selected geometric parameters (Å, °).

Cu—N4	1.999 (2)	Fe—C17	1.946 (3)
Cu—N1	2.009 (2)	Fe—C16	1.947 (3)
Cu—N2	2.013 (2)	Fe—C14	1.948 (3)
Cu—N5	2.016 (2)	O3—N8	1.131 (3)
Cu—N7	2.383 (2)	N7—C13	1.152 (3)
Cu—N9 <sup>i</sup>	2.902 (3)	N9—C14	1.145 (3)
Fe—N8	1.656 (2)	N10—C15	1.138 (4)
Fe—C15	1.938 (3)	N11—C16	1.134 (4)
Fe—C13	1.942 (3)	N12—C17	1.144 (4)
N4—Cu—N1	175.33 (9)	C14—N9—Cu <sup>ii</sup>	133.9 (2)
N4—Cu—N2	92.65 (9)	C13—N7—Cu	147.2 (2)
N1—Cu—N2	85.91 (9)	O3—N8—Fe	175.9 (2)
N4—Cu—N5	85.69 (9)	N7—C13—Fe	176.3 (2)
N1—Cu—N5	95.31 (9)	N9—C14—Fe	177.0 (3)
N2—Cu—N5	174.37 (9)	N10—C15—Fe	176.7 (3)
N8—Fe—C13	177.34 (11)	N11—C16—Fe	176.7 (3)
C17—Fe—C16	168.68 (12)	N12—C17—Fe	178.5 (3)
C15—Fe—C14	172.16 (12)		

Symmetry codes: (i)  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$ ; (ii)  $\frac{1}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$ .

**Table 2**

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...O2	0.91	2.20	2.958 (5)	141
N4—H4...N11 <sup>i</sup>	0.91	2.25	3.103 (3)	156
N5—H5...N12 <sup>ii</sup>	0.91	2.38	3.139 (3)	141
O1—H11...N10 <sup>iii</sup>	0.82	2.03	2.836 (4)	170
O2—H12...N10	0.82	2.44	3.202 (4)	155
C5—H5B...O2 <sup>i</sup>	0.97	2.51	3.370 (5)	148
C8—H8A...O1 <sup>iv</sup>	0.97	2.44	3.376 (4)	162
C9—H9A...N12 <sup>iv</sup>	0.97	2.62	3.517 (4)	155

Symmetry codes: (i)  $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$ ; (ii)  $1 - x, -y, 1 - z$ ; (iii)  $x, y, 1 + z$ ; (iv)  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$ .

The H atoms were located geometrically and allowed to ride on their parent atoms, with C—H distances of 0.97 Å, N—H distances of 0.91 Å and O—H distances of 0.82 Å, and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent})$ . There is some disorder of the terminal O1—H11 and O2—H12 hydroxy groups, the disorder being over two orientations in each case. This was allowed for by appropriate occupancy refinement and resulted in occupancies of 0.724 (5)/0.276 (5) and 0.636 (4)/0.364 (4) for the O1/O1' and O2/O2' sites, respectively.

Data collection: *XSCANS* (Siemens, 1991); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Sheldrick, 1990); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1736). Services for accessing these data are described at the back of the journal.

## References

- Alcock, N. W., Samatus, A. & Szklarzewicz, J. (1993). *J. Chem. Soc. Dalton Trans.* pp. 885–889.
- Clemente-Leon, M., Coronado, E., Galan-Mascaros, J. R., Gomez-Garcia, C. J., Woike, Th. & Clemente-Juan, J. M. (2001). *Inorg. Chem.* **40**, 87–94.
- Entley, W. R. & Giroloni, G. S. (1994). *Inorg. Chem.* **33**, 5165–5168.
- Kou, H. Z., Bu, W. M., Gao, S., Liao, D. Z., Jiang, Z. H., Yan, S. P., Fan, Y. G. & Wang, G. L. (2000). *J. Chem. Soc. Dalton Trans.* pp. 2996–3000.
- Lu, T. B., Xiang, H., Li, X. Y., Su, C. Y., Mao, Z. W. & Ji, L. N. (2000). *Chem. J. Chin. Univ.* **21**, 187–189.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Olabe, J. A., Gentil, L. A., Rigotti, G. & Navaza, A. (1984). *Inorg. Chem.* **23**, 4297–4302.
- Sheldrick, G. M. (1990). *SHELXTL-Plus*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Shen, L. (2002). *Acta Cryst.* **C58**, m588–m590.
- Shen, L., Zhang, Y. J., Sheng, G. D. & Wang, W. T. (2002). *Acta Cryst.* **C58**, m382–m384.
- Siemens (1991). *XSCANS User's Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Zhan, S. Z., Chen, X. Y., Vij, A., Guo, D. & Meng, Q. (1999). *Inorg. Chim. Acta*, **292**, 157–162.