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catena-Poly[[dicyanamidobis(3-hydroxypyridine-*N*)-copper(II)]-μ-dicyanamido]

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Key indicators

Single-crystal X-ray study
T = 193 K
Mean σ(C–C) = 0.005 Å
Disorder in main residue
R factor = 0.041
wR factor = 0.120
Data-to-parameter ratio = 11.6

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

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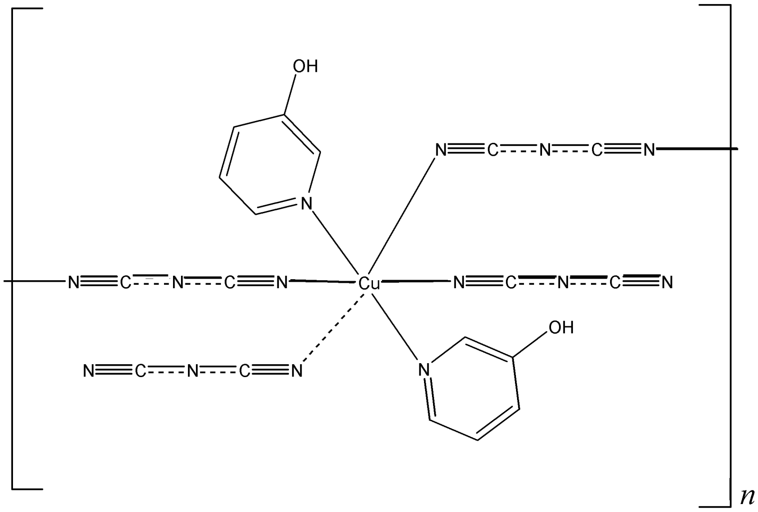
In the crystal structure of the title compound, $[Cu^{II}\{N(CN)_2\}_2(C_5H_5NO)_2]$, the geometry around the copper(II) ion is distorted square pyramidal, with the basal plane formed by the N atoms of two 3-hydroxypyridine molecules, one N atom of a bidentate dicyanamide anion and one N atom of a monodentate dicyanamide anion. The apical position is occupied by an N atom of a bidentate dicyanamide anion, forming a one-dimensional polymeric chain.

Comment

Dicyanamide has gained much interest in recent years, especially in the form of $M^{II}[N(CN)_2]_2$ (M = Ni, Co, Cu, Zn), as a new class of magnetic materials (Batten *et al.*, 1998; Jensen, Batten, Fallon, Moubaraki *et al.*, 1999; Kohout *et al.*, 2000; Manson *et al.*, 1998, 1999). The X-ray structures of a number of compounds of copper(II) containing the dicyanamide anion have been reported (Potočňák *et al.*, 2001; Riggio *et al.*, 2001, Martín *et al.*, 2001). Dicyanamide itself is a most interesting anionic bridging ligand and can act as a monodentate, bidentate (two types of binding) or even tridentate ligand (Mroziński *et al.*, 1997; Escuer *et al.*, 2000).



(I)

With the ligand used in this study, 3-hydroxypyridine, so far only five structures with Cu^{II} are known, *i.e.* two polymeric structures (Castillo *et al.*, 2000; Kawata *et al.*, 1997) and three structures in which this ligand is used as a coligand (Breeze & Wang, 1993; Castillo *et al.*, 2001).

X-ray structures of polymeric compounds with Cu^{II} and dicyanamide having the general formula $[Cu^{II}\{N(CN)_2\}_2(L)_y]_n$

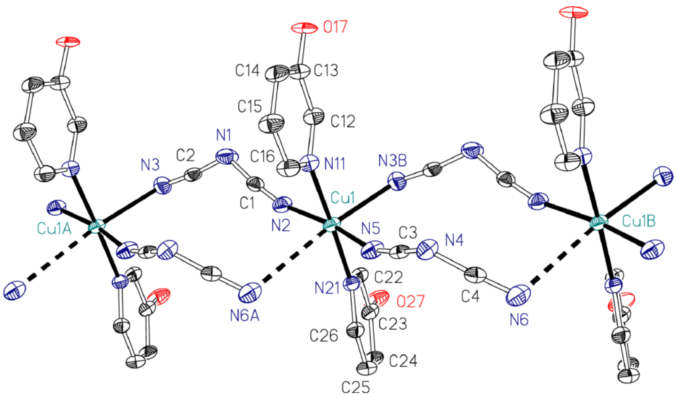


Figure 1
Ellipsoid plot (*SHELXTL*/*PC*; Sheldrick, 1994) of the title compound with the atom-labelling scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level. H atoms have been omitted for clarity. Atoms marked with an '*A*' are generated by an inversion centre.

(y = 1 or 2, L = coordinating organic molecule) are, however, very rare. Up to now, six compounds with different polymeric networks are known. The compound $[Cu^{II}\{N(CN)_2\}_2(2\text{-aminopyrimidine})_2]_n$ forms a one-dimensional network of two bridging dicyanamide anions to the same Cu atom (van Albada *et al.*, 2000); β-$[Cu^{II}\{N(CN)_2\}_2(\text{pyrazine})_2]_n$ forms a two-dimensional network of which the one-dimensional structure is obtained by bridging of the two dicyanamide anions to the same Cu atom and the two-dimensional structure by bridging of the pyrazine ligand to a different Cu atom (Jensen, Batten, Fallon, Hockless *et al.*, 1999). Compounds α-$[Cu^{II}\{N(CN)_2\}_2(\text{pyrazine})_2]_n$, $[Cu^{II}\{N(CN)_2\}_2(\text{pyrimidine})_2]_n$ and $[Cu^{II}\{N(CN)_2\}_2(\text{bipyrimidine})]_n$ form a two-dimensional network of dicyanamide anions which are bridging to different Cu atoms to form $[Cu(\text{dicyanamide})]_n$ sheets and the third dimension is obtained by bridging of the ligand (Jensen, Batten, Fallon, Hockless *et al.*, 1999; Riggio *et al.*, 2001; Martín *et al.*, 2001). The last group is of compounds of the type $[Cu^{II}\{N(CN)_2\}_2(1,10\text{-phenantroline})_2]_n$ (Wang *et al.*, 2000) and $[Cu^{II}\{N(CN)_2\}_2(5,5'\text{-dimethyl-}2,2'\text{-bipyridine})]_n$ (Kooijman *et al.*, 2001); these form a one-dimensional polymeric network of only one bridging dicyanamide anion, while the second dicyanamide is monodentate. The title compound, (I), belongs to this last class of these polymeric compounds.

The geometry around the Cu^{II} ion is distorted square pyramidal, with the basal plane formed by two N atoms of two different 3-hydroxypyridine molecules (N11 and N21), one N atom of the monodentate dicyanamide anion (N5) and one N atom of the bridging dicyanamide anion (N2). The Cu—N distances vary from 1.983 (3) to 2.023 (3) Å. The apical position is occupied by an N atom of the bridging dicyanamide anion (N3) at a distance of 2.313 (3) Å. The N atom at the other apical site (N6*A*) is at a very long distance [2.967 (3) Å]. The distortion from square pyramidal can be best described by the structural parameter τ (τ describes the relative amount of trigonality; τ = 0 for a square pyramid and τ = 1 for a trigonal bipyramid), which is, in this case, 0.16 (Addison *et al.*, 1984). The lattice is stabilized by stacking of the pyridine rings, with a distance of 3.743 Å, and by hydrogen bonding between the pyridine OH group and the N4 and N6 atoms of neighboring dicyanamide anions, with distances of 2.867 and 2.846 Å, respectively. All these structural parameters can be best compared with the compound $[Cu^{II}\{N(CN)_2\}_2(5,5'\text{-dimethyl-}2,2'\text{-bipyridine})]_n$ (Kooijman *et al.*, 2001), which has a similar type of structure.

The ligand field spectrum of the copper(II) compound shows a broad *d*–*d* transition band centered around 15.5 × 10^3 cm^{-1}, with a shoulder at the low-energy side. The characteristic IR vibrations for the dicyanamide anion are the $\nu_s + \nu_{as(CN)}$ vibration. These vibrations are found as a split band at 2303 and 2287 cm^{-1}, a medium strong band at 2243 cm^{-1} and a broad very strong band at 2169 cm^{-1}, with a shoulder at 2158 cm^{-1}.

Experimental

Physical methods and the synthesis of the compound were carried out as described in the literature (Riggio *et al.*, 2001). Yield 72%; elemental analysis [found% (calculated%)] for $C_{14}H_{10}CuN_8O_2$: 43.4 (43.6) C, 2.3 (2.6) H, 28.8 (29.0) N. A crystal was selected for the X-ray measurements and mounted on the glass fiber using the oil-drop method (Kottke & Stalke, 1993) and data were collected at 193 K.

Crystal data

$[Cu(C_2N_3)_2(C_5H_5NO)_2]$
M_r = 385.84
Orthorhombic, *Pbca*
a = 7.266 (2) Å
b = 13.925 (3) Å
c = 30.327 (6) Å
V = 3068.5 (12) Å^3
Z = 8
D_x = 1.670 Mg m^{-3}

Cu $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 12–27°
μ = 2.28 mm^{-1}
T = 193 (2) K
Prismatic, green
0.50 × 0.20 × 0.08 mm

Data collection

Enraf-Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.755, T_{max} = 1.000
2780 measured reflections
2723 independent reflections
2241 reflections with $I > 2\sigma(I)$

R_{int} = 0.100
θ_{max} = 66.9°
$h = -8 \rightarrow 0$
$k = -16 \rightarrow 0$
$l = -36 \rightarrow 11$
3 standard reflections every 200 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.120
S = 0.81
2723 reflections
235 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0878P)^2 + 8.7618P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.96 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N2	1.983 (3)	Cu1—N11	2.023 (3)
Cu1—N5	1.988 (3)	Cu1—N3^i	2.313 (3)
Cu1—N21	2.008 (3)		
N2—Cu1—N5	168.50 (12)	N21—Cu1—N11	178.38 (11)
N2—Cu1—N21	91.54 (11)	N2—Cu1—N3^i	96.10 (11)
N5—Cu1—N21	91.83 (10)	N5—Cu1—N3^i	94.96 (11)
N2—Cu1—N11	87.64 (11)	N21—Cu1—N3^i	88.91 (10)
N5—Cu1—N11	88.71 (11)	N11—Cu1—N3^i	92.56 (10)

Symmetry code: (i) $1 + x, y, z$.

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The O17 atom was disordered and was refined in the two positions with population parameters 0.75 and 0.25. The H atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1985); cell refinement: *CAD*-4 *Software*; data reduction: *XCAD*4 (Harms, 1996); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*/*PC* (Sheldrick, 1994); software used to prepare material for publication: *SHELXL*97.

References

Addison, A. W., Rao, T. N., Reedijk, J., van Rijn, J. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.

Albada, G. A. van, Quiroz-Castro, M. E., Mutikainen, I., Turpeinen, U. & Reedijk, J. (2000). *Inorg. Chim. Acta*, **298**, 221–225.

Batten, S. R., Jensen, P., Moubaraki, B., Murray, K. S. & Robson, R. (1998). *Chem. Commun.* pp. 439–440.

Breeze, S. R. & Wang, S. (1993). *Inorg. Chem.* **32**, 5981–5989.

Castillo, O., Luque, A., Iglesias, S., Vitoria, P. & Román, P. (2000). *New J. Chem.* **24**, 771–775.

Castillo, O., Luque, A., Julve, M., Lloret, F. & Román, P. (2001). *Inorg. Chim. Acta*, **315**, 9–17.

Enraf–Nonius (1985). *CAD*-4 *Software* (Updated 1998, Linux version). Enraf–Nonius, Delft, The Netherlands.

Escuer, A., Mautner, F. A., Sanz, N. & Vincente, R. (2000). *Inorg. Chem.* **39**, 1668–1673.

Harms, K. (1996). *XCAD*4. University of Marburg, Germany.

Jensen, P., Batten, S. R., Fallon, G. D., Moubaraki, B., Murray, K. S. & Price, D. J. (1999). *Chem. Commun.* pp. 177–178.

Jensen, P., Batten, S. R., Fallon, G. D., Hockless, D. C. R., Moubaraki, B., Murray, K. S. & Robson, R. (1999). *J. Solid State Chem.* **145**, 387–393.

Kawata, S., Breeze, S. R., Wang, S., Greedan, J. E. & Raju, N. P. (1997). *Chem. Commun.* pp. 717–718.

Kohout, J., Jäger, L., Hvastijová, M. & Kožíšek, J. (2000). *J. Coord. Chem.* **51**, 169–218.

Kooijman, H., van Albada, G. A. & Spek, A. L. (2001) *Acta Cryst.* C**57**. In preparation.

Kottke, T. & Stalke, D. (1993). *J. Appl. Cryst.* **26**, 615–619.

Manson, J. L., Kmety, C. R., Huang, Q.-Z., Lynn, J. W., Bendele, G. M., Pagola, S., Stephens, P. W., Liable-Sands, L. M., Rheingold, A. L., Epstein, A. J. & Miller, J. S. (1998). *Chem. Mater.* **10**, 2552–2560.

Manson, J. L., Incarvito, C. D., Arif, A. M., Rheingold, A. L. & Miller, J. S. (1999). *Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. A*, **334**, 605–613, and references therein.

Martín, S., Barandika, M. G., Ruiz de Larramendi, I., Cortés, R., Font-Bardia, M., Lezama, L., Serna, Z. E., Solans, X. & Rojo, T. (2001). *Inorg. Chem.* **40**, 3687–3692.

Mroziński, J., Kohout, J. & Hvastijová, M. (1997). *Pol. J. Chem.* **71**, 883–888.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Potočňák, I., Dunaj-Jurčo, M., Mikloš, D., Massa, W. & Jäger, L. (2001). *Acta Cryst.* C**57**, 363–365.

Riggio, I., van Albada, G. A., Ellis, D. D., Spek, A. L. & Reedijk, J. (2001). *Inorg. Chim. Acta*, **313**, 120–124, and references therein.

Sheldrick, G. M. (1994). *SHELXTL*/*PC*. Release 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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

Wang, Z.-M., Luo, J., Sun, B.-W., Yan, C.-H., Gao, S. & Liao, C.-S. (2000). *Acta Cryst.* C**56**, 786–788.

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