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Key indicators

Single-crystal X-ray study

$T = 173\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$

R factor = 0.054

wR factor = 0.128

Data-to-parameter ratio = 15.1

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

Bis(2,2-bipyridine N,N' -dioxide- κ^2O,O')-bis(dicyanamido- κN^1)copper(II)

In the crystal structure of the title compound, $[\text{Cu}(\text{C}_2\text{N}_3)_2(\text{C}_{10}\text{H}_8\text{N}_2\text{O}_2)_2]$, the Cu^{II} atom adopts a distorted octahedral geometry, with the basal plane formed by two O atoms of two chelating 2,2'-bipyridine N,N' -dioxide ligands and two N atoms of the two monodentate dicyanamido anions $[\text{Cu}-\text{N}/\text{O} 1.976(3)-2.000(2)\text{ \AA}]$. The apical positions are occupied by the two other O atoms $[\text{Cu}-\text{O} 2.288(2)-2.310(2)\text{ \AA}]$ of the chelating ligands.

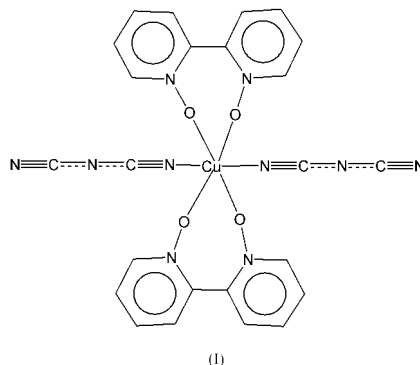
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Comment

In recent years, the dicyanamide anionic ligand has been the object of much interest, in forming complexes $M^{\text{II}}(\text{dca})_2$ [$M = \text{Ni}, \text{Co}, \text{Cu}$; $\text{dca} = \text{N}(\text{CN})_2$], as a new class of molecule-based magnetic materials (Batten *et al.*, 1998; Batten & Murray, 2001; Manson *et al.*, 1999). In the field of crystal engineering, the number of X-ray crystal structures with the dca molecule present in one-, two- and three-dimensional compounds has increased enormously over the last few years (Albada *et al.*, 2000; Kohout *et al.*, 2000; Vangdal *et al.*, 2002; Mohamadou *et al.*, 2003; Kooijman *et al.*, 2002; Shi *et al.*, 2003). Dicyanamide itself is a most interesting anionic bridging ligand, and can act as a monodentate, bidentate (two types of binding), or even a tridentate ligand (Mroziński *et al.*, 1997; Escuer *et al.*, 2000). Various coordination modes of the dicyanamide ligand and the metal can occur, *viz.* monodentate bonding *via* the nitrile atom, coordination *via* the amide atom (Marshall *et al.*, 2002; Mohamadou *et al.*, 2003) and even μ_4 coordination where one nitrile atom bridges two metal atoms (Vangdal *et al.*, 2002; Shi *et al.*, 2002, 2003). However, in most cases monodentate or bidentate coordination *via* the nitrile N atom is found.



Until now, only a few crystal structures of the other ligand used in this study, 2,2'-bipyridine N,N' -dioxide (bipyNO), with Cu^{II} have been published (Baran *et al.*, 1991, 1993; Koman *et al.*, 1991; Paulus *et al.*, 1992*a,b*).

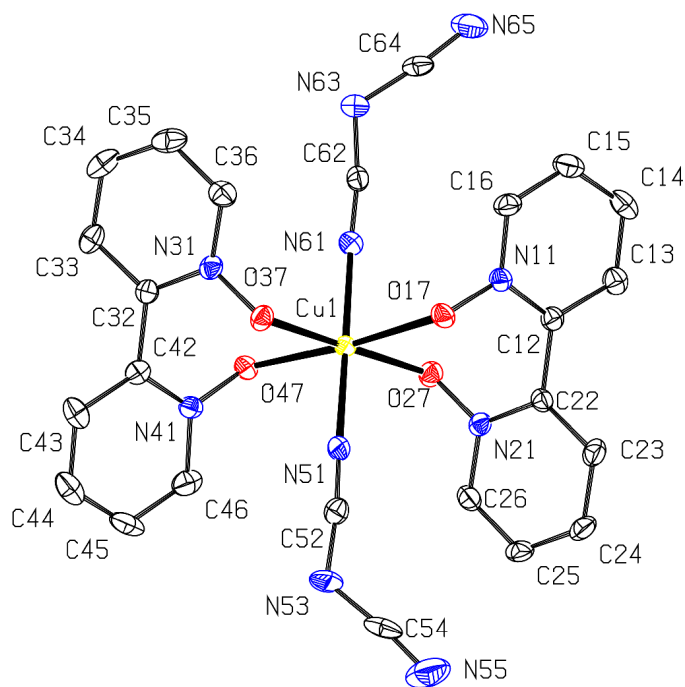


Figure 1
A view of the title structure, showing the atom-numbering scheme and displacement ellipsoids drawn at the 30% probability level. H atoms are omitted for clarity.

In the title compound, (I), the geometry around the copper(II) ion is distorted octahedral, with the basal plane formed by two O atoms of two different bipyNO molecules and two N atoms of two monodentate dca anions, with distances ranging from 1.976 (3) to 2.000 (2) Å. The *trans* angles are almost linear [178.49 (10) and 179.31 (13)°]. The apical positions are occupied by two O atoms of two different chelating bipyNO molecules, with distances of 2.288 (2) and 2.310 (2) Å. The crystal structure is stabilized by stacking of the pyridine rings, with distances of about 3.65 Å.

The electron paramagnetic resonance (EPR) spectrum, measured from a polycrystalline powder at room temperature, shows an axial $S = \frac{1}{2}$ signal, with $g_{\text{perp}} = 2.12$ and $g_{\text{par}} = 2.35$, consistent with a $\text{CuN}_2\text{O}_2(\text{O}_2)$ chromophore and in agreement with a $d(x^2 - y^2)$ ground state.

The characteristic infrared vibrations for the dicyanamide anion are found in the 2400–2100 cm^{-1} region (Kohout *et al.*, 2000). The $\nu_s + \nu_{\text{as}}(\text{C}-\text{N})$ are observed as two medium bands (one of them split) at 2361, 2344 and 2278 cm^{-1} , and the $\nu(\text{C}=\text{N})$ is observed as two medium-to-strong bands at 2232 and 2162 cm^{-1} . These vibrations occur in the range found for other copper(II) dicyanamide compounds (Kohout *et al.*, 2000; Riggio *et al.*, 2001; Albada *et al.*, 2000, Mohamadou *et al.*, 2003).

Experimental

Physical methods and synthesis of the compounds were performed as described in the literature (Riggio *et al.*, 2001). Yield 68%, elemental analysis [found (calculated)] for $\text{C}_{24}\text{H}_{16}\text{CuN}_{10}\text{O}_4$: 49.8 (50.4)% C, 2.6 (2.8)% H, 24.3 (24.5)% N. The crystal selected for the X-ray

measurements was mounted on a glass fiber using the oil-drop method (Kottke & Stalke, 1993).

Crystal data

[$\text{Cu}(\text{C}_2\text{N}_3)_2(\text{C}_{10}\text{H}_8\text{N}_2\text{O}_2)_2$]
 $M_r = 572.01$
 Monoclinic, $P2_1/c$
 $a = 6.8650$ (10) Å
 $b = 21.647$ (3) Å
 $c = 17.214$ (3) Å
 $\beta = 113.21$ (2)°
 $V = 2351.1$ (6) Å³
 $Z = 4$

$D_x = 1.616$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 20 133 reflections
 $\theta = 2.7\text{--}27.5^\circ$
 $\mu = 0.99$ mm⁻¹
 $T = 173$ (2) K
 Needle, green
 0.22 × 0.05 × 0.03 mm

Data collection

Nonius KappaCCD diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\text{min}} = 0.812$, $T_{\text{max}} = 0.971$
 20 133 measured reflections
 5330 independent reflections

3423 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.091$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -8 \rightarrow 8$
 $k = -28 \rightarrow 27$
 $l = -22 \rightarrow 22$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.054$
 $wR(F^2) = 0.128$
 $S = 1.03$
 5330 reflections
 352 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0494P)^2 + 0.5193P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.44$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.67$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cu1—N51	1.976 (3)	Cu1—O27	2.000 (2)
Cu1—N61	1.983 (3)	Cu1—O47	2.288 (2)
Cu1—O37	1.995 (2)	Cu1—O17	2.309 (2)
N51—Cu1—N61	179.31 (11)	O37—Cu1—O47	81.97 (8)
N51—Cu1—O37	86.24 (10)	O27—Cu1—O47	99.53 (9)
N61—Cu1—O37	93.07 (10)	N51—Cu1—O17	90.48 (11)
N51—Cu1—O27	93.52 (11)	N61—Cu1—O17	89.59 (10)
N61—Cu1—O27	87.17 (10)	O37—Cu1—O17	96.07 (8)
O37—Cu1—O27	178.49 (9)	O27—Cu1—O17	82.44 (9)
N51—Cu1—O47	92.89 (11)	O47—Cu1—O17	175.98 (9)
N61—Cu1—O47	87.01 (10)		

H atoms were introduced in calculated positions ($\text{C}-\text{H} = 0.95$ Å) and refined as riding, with $U_{\text{iso}} = 1.2U_{\text{eq}}$ of the parent atom.

Data collection: COLLECT (Nonius, 2002); cell refinement: DENZO (Otwinowski & Minor, 1997); data reduction: DENZO; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Sheldrick, 1990); software used to prepare material for publication: SHELXL97.

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