metal-organic papers

A three-dimensional polymeric mixed-valence copper complex: poly[tri-μ-azido-μ-di-2-pyridyl-diazene-dicopper(I,II)]

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The title complex, $[Cu_2(N_3)_3(C_{10}H_8N_4)]_n$, shows a three-dimensional poylmeric structure. Each Cu atom is surrounded by five N atoms from three bridging azide ligands and one di-2-pyridyldiazene ligand [Cu—N = 2.002 (5), 2.317 (6), 2.020 (4), 1.995 (5) and 1.985 (3) Å], forming a CuN_5 trigonal bipyramid. One $\mu_{1,1}$-azide bridges two Cu atoms and the other two $\mu_{1,1}$-azides bridge pairs of Cu atoms, forming a —Cu—N—Cu—N_2— chain. The di-2-pyridyldiazene bridges two Cu atoms of different —Cu—N—Cu—N_2— chains, forming a three-dimensional polymeric structure. On the basis of charge equilibrium, the presence of one Cu^{II} and one Cu^I ion are deduced and the two ions are disordered because of the occurrence of only one unique Cu atom in the structure.

Comment

μ-Azidocopper complexes have received intense attention due to their structural and magnetic diversity. The azide anion can bridge two copper ions either in an 'end-on' ($\mu_{1,1}$-N_3) fashion or an 'end-to-end' ($\mu_{1,3}$-N_3) fashion (Comarmond *et al.*, 1982; Sikorav *et al.*, 1984; Agnus *et al.*, 1979; Kahn *et al.*, 1983). Sometimes both bridging fashions are present in one complex (Felthouse & Hendrickson, 1978; Banci *et al.*, 1984). We report here the preparation and crystal structure of a three-dimensional azido mixed-valence copper complex, (I).

(I)
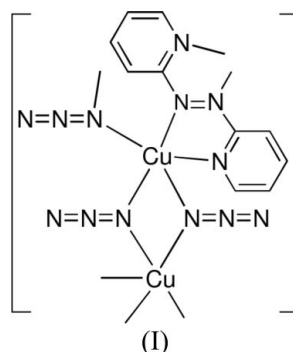
As shown in Fig. 1, each Cu atom in (I) is surrounded by five N atoms of three azide bridging ligands and one di-2-pyridyldiazene ligand, forming a CuN_5 trigonal bipyramid. A linear $\mu_{1,1}$-azide ligand bridges two Cu atoms, and two linear $\mu_{1,1}$-azide anions bridge two Cu atoms, forming a —Cu—N—Cu—N_2— chain; di-2-pyridyldiazene bridges two Cu atoms of different —Cu—N—Cu—N_2— chains, forming a three-dimensional structure. Charge equilibrium calculation suggests that there present one Cu^{II} and one Cu^I ion, which are disordered because of the existence of only one unique Cu atom in the structure. Therefore, the bond distances and the bond angles around the Cu^I ion should be the average values. One azide group (N6/N7/N8) lies along a twofold rotation axis.
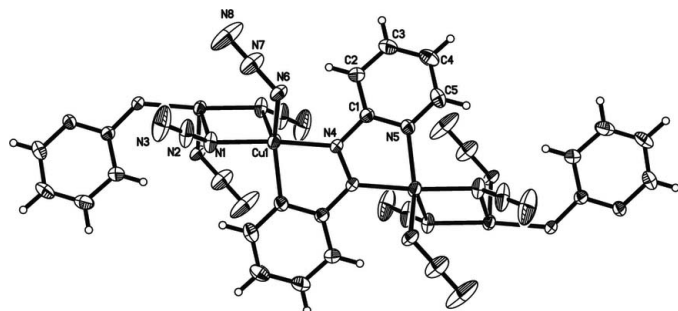
Figure 1
A view of the coordination environment in the title compound, shown with 30% probability displacement ellipsoids.
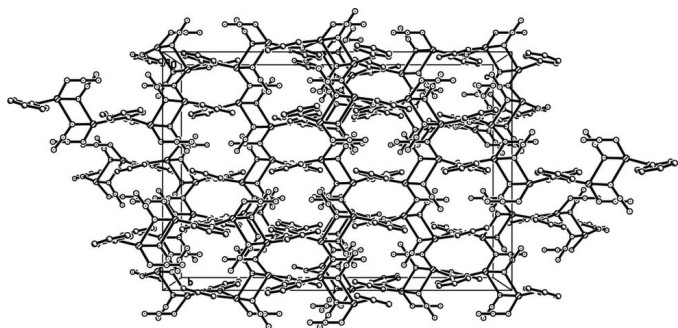

Figure 2
The crystal structure of the title compound, viewed along the *a* axis. H atoms have been omitted.

The Cu—N distances found in (I) are in accord with the Cu—N distances found in other copper complexes containing an azide bridging ligand (You, 2005; Ghoshal *et al.*, 2004). The coordinating azide anions are nearly linear and show bent coordination modes with the metal atoms (Table 1). The N—N bond of di-2-pyridyldiazene is longer than the N—N bonds of the azide ligand. The Cu···Cu distances, which are bridged by one azide bridging ligand, two azide bridging ligands and di-2-pyridyldiazene, are 3.492 (4), 3.342 (3) and 4.678 (4) Å, respectively. The dihedral angle between the two pyridine ring planes of di-2-pyridyldiazene is 29.8 (1)°.

Experimental

Crystals of (I) were prepared by the multilayer diffusion method. In a typical preparation, a solution of NaN_3 (19.5 mg, 0.3 mmol) in water (10 ml) was placed in a tube to which was added a buffer layer of ethanol/water (20 ml, 1:1 *v/v*) Finally, a solution of $CuNO_3$ (25.1 mg, 0.2 mmol) and di-2-pyridyldiazene (18.4 mg, 0.1 mmol) in ethanol (10 ml) was added to form a third layer. Black block-shaped crystals were formed on diffusion of the reactants over a period of two weeks. Analysis found: C 27.21, H 1.80, N 41.26%; calculated for $C_{10}H_8Cu_2N_{13}$: C 27.46, H 1.84, N 41.63%.

Crystal data

$[Cu_2(N_3)_3(C_{10}H_8N_4)]$	$Z = 16$
$M_r = 437.37$	$D_x = 1.789$ Mg m^{-3}
Orthorhombic, $Fddd$	Mo $K\alpha$ radiation
$a = 13.520$ (3) Å	$\mu = 2.64$ mm^{-1}
$b = 18.127$ (4) Å	$T = 292$ (3) K
$c = 26.501$ (5) Å	Block, black
$V = 6495$ (2) Å^3	$0.12 \times 0.08 \times 0.06$ mm

Data collection

Rigaku R-AXIS RAPID IP diffractometer	18086 measured reflections
ω scans	1876 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	1808 reflections with $I > 2\sigma(I)$
$T_{min} = 0.774$, $T_{max} = 0.852$	$R_{int} = 0.077$
	$\theta_{max} = 27.5°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0802P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.074$	$+ 91.4266P]$
$wR(F^2) = 0.189$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.24$	$(\Delta/\sigma)_{max} = 0.003$
1876 reflections	$\Delta\rho_{max} = 1.35$ e Å^{-3}
115 parameters	$\Delta\rho_{min} = -0.45$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	2.001 (5)	Cu1—N6	1.986 (3)
Cu1—N1^i	2.318 (6)	N1—N2	1.213 (9)
Cu1—N4^{ii}	2.020 (4)	N4—N4^{ii}	1.319 (8)
Cu1—N5	1.995 (5)	N6—N7	1.210 (10)
N1—Cu1—N4^{ii}	167.3 (2)	N4^{ii}—Cu1—N1^i	93.60 (19)
N1—Cu1—N1^i	78.8 (2)	N5—Cu1—N1	95.5 (2)
N2—N1—Cu1	123.7 (5)	N5—Cu1—N1^i	113.5 (2)
N2—N1—Cu1^i	116.9 (5)	N7—N6—Cu1^{iii}	118.44 (16)
N3—N2—N1	177.4 (10)	N8—N7—N6	180

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+\frac{5}{4}, y, -z+\frac{5}{4}$; (iii) $-x+\frac{5}{4}, -y+\frac{5}{4}, z$.

All H atoms were placed in idealized positions and constrained to ride on their parent C atoms, with C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. The highest residual density peak is 0.96 Å from the Cu1 atom.

Data collection: *CrystalStructure* (Rigaku/MSC, 2004); cell refinement: *CrystalStructure*; data reduction: *CrystalStructure*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 1998); software used to prepare material for publication: *SHELXTL*.

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