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Bis(μ-azido-κ^2N:N)bis[azido(N,N-dimethyl-1,3-propylenediamine-κ^2N,N)copper(II)]

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Key indicators

Single-crystal X-ray study
T = 273 K
Mean σ(C–C) = 0.004 Å
R factor = 0.025
wR factor = 0.066
Data-to-parameter ratio = 19.3

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

The title complex, $[Cu_2(N_3)_4(C_5H_{14}N_2)_2]$, is a centrosymmetric dimer in which each Cu atom is coordinated by five N atoms from three azide anions and one N,N-dimethyl-1,3-propylenediamine molecule in a distorted square-pyramidal geometry; the Cu$\cdots$Cu distance is 3.416 (1) Å.

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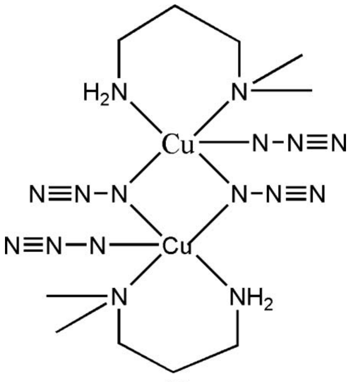
Comment

Research into transition metal azide complexes has expanded rapidly because of their fascinating structural diversity (Ribas *et al.*, 1993; Mukherjee, Dalai, Zangrando *et al.*, 2001; Ribas *et al.*, 1996; Escuer *et al.*, 1994; Mondal *et al.*, 2001). The azide ligand is an efficient superexchange pathway for propagating magnetic interaction between paramagnetic centres such as Cu^{II}, giving dinuclear or tetranuclear one-, two- or three-dimensional complexes (Lin *et al.*, 2005; Mukherjee *et al.*, 2002; Mukherjee, Dalai, Mostafa *et al.*, 2001). It can bridge two metal centres in two different fashions, end-on (μ-1,1) or end-to-end (μ-1,3). In this paper, we report the synthesis and X-ray crystal structure of a dinuclear Cu^{II} complex with end-on azide bridging ligands.



(I)

The structure of complex (I) is shown in Fig. 1. It is a centrosymmetric dimer, with two terminal azide anions in *trans* positions. The Cu$\cdots$Cu distance is 3.416 (1) Å. In the dimer, each Cu atom is five-coordinate in a distorted square-pyramidal environment. The basal coordination positions are occupied by four N atoms, two from N,N-dimethyl-1,3-propylenediamine, one from a terminal azide anion and one from a μ-1,1-bridging azide anion. The apical coordination position is occupied by an N atom from the other centrosymmetrically related μ-1,1-bridging azide anion. From a least-squares plane calculation, the four coordinated atoms, N1, N2, N3 and N6, in the basal positions deviate from the plane by −0.315, 0.309, 0.320 and −0.314 Å, respectively. The

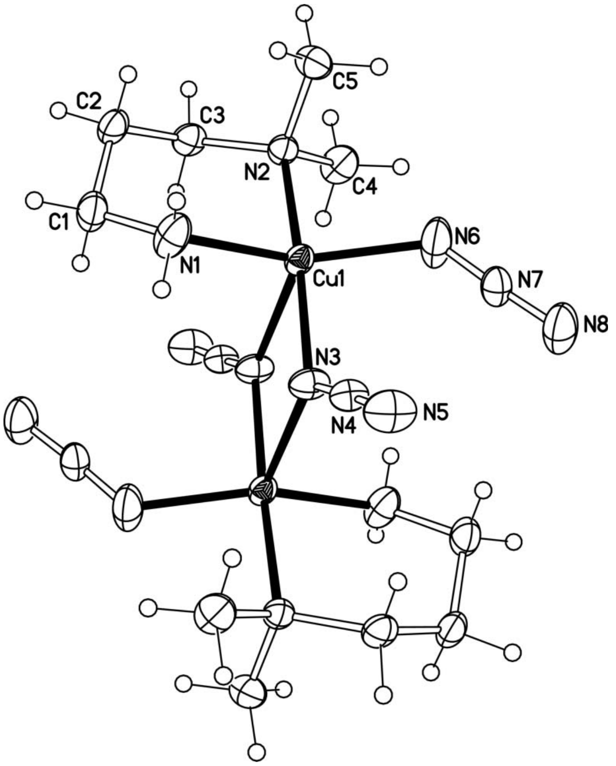


Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as spheres of arbitrary radius.

Cu—N bonds of the basal plane, in the range 1.967 (2)–2.071 (2) Å, are similar, except for the Cu1—N3^{i} bond of 2.351 (2) Å [symmetry code: (i) $-x + 2$, $-y$, $-z + 1$]. In general, these Cu—N distances are comparable with those in other five-coordinate Cu^{II} complexes (Zukerman-Schpector *et al.*, 1991; Luo *et al.*, 2004). The azide anions around the Cu atom are nearly linear, with angles of N5—N4—N3 = 177.4 (2)° and N8—N7—N6 = 176.5 (2)°.

Experimental

An aqueous solution (10 ml) of 3-dimethylamino-1-propylamine (0.10 g, 1.0 mmol) was added to a stirred solution of $Cu(OAc)_2\cdot H_2O$ (0.20 g, 1.0 mmol) in water (10 ml). A deep-blue precipitate quickly formed and this was dissolved in methanol (20 ml). To this solution, sodium azide (0.13 g, 2 mmol) in a minimum amount of water was added. After stirring for about 30 min, the deep-green solution was filtered, and the filtrate was left to stand undisturbed. Upon slow evaporation at room temperature for a few weeks, black crystals of (I) suitable for X-ray diffraction were collected.

Crystal data

$[Cu_2(N_3)_4(C_5H_{14}N_2)_2]$
$M_r = 499.56$
Monoclinic, $P2_1/c$
$a = 9.445$ (2) Å
$b = 11.164$ (2) Å
$c = 12.0678$ (18) Å
$\beta = 124.877$ (11)°
$V = 1043.9$ (4) Å^3
$Z = 2$
$D_x = 1.589$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 2.07$ mm^{-1}
$T = 273$ (2) K
Block, black
0.21 × 0.16 × 0.11 mm

Data collection

Bruker APEXII area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.682$, $T_{max} = 0.798$
6943 measured reflections
2489 independent reflections
2002 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 28.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.066$
$S = 1.02$
2489 reflections
129 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0381P)^2 + 0.0173P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N6	1.9671 (18)	Cu1—N2	2.0711 (15)
Cu1—N1	2.0102 (17)	Cu1—N3^{i}	2.3512 (16)
Cu1—N3	2.0334 (16)		
N6—Cu1—N1	149.96 (9)	N3—Cu1—N2	173.48 (6)
N6—Cu1—N3	93.41 (8)	N6—Cu1—N3^{i}	109.90 (9)
N1—Cu1—N3	87.63 (7)	N1—Cu1—N3^{i}	99.69 (7)
N6—Cu1—N2	89.62 (7)	N3—Cu1—N3^{i}	77.89 (7)
N1—Cu1—N2	92.62 (7)	N2—Cu1—N3^{i}	95.65 (6)

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

H atoms bonded to C atoms were positioned geometrically and refined using a riding model, with C—H = 0.97 Å and $U_{iso}(H) = 1.2U_{eq}(C)$, or C—H = 0.96 Å and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms. Methyl groups were allowed to rotate to fit the electron density. H atoms bonded to N atoms were located in a difference Fourier map and were refined with N—H distance restraints of 0.91 (2) Å and with $U_{iso}(H) = 1.2U_{eq}(N)$.

Data collection: *SMART* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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