

Di- μ -azido-bis{[hydrotris(pyrazol-1-yl)-borato]copper(II)}

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Key indicators

Single-crystal X-ray study

T = 293 K

Mean $\sigma(\text{C}-\text{C}) = 0.006 \text{ \AA}$

R factor = 0.049

wR factor = 0.110

Data-to-parameter ratio = 14.4

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

The molecule of the title compound, $[\text{Cu}_2(\text{N}_3)_2(\text{C}_9\text{H}_{10}\text{BN}_6)_2]$, is located at a crystallographic inversion centre. The two Cu atoms have distorted square-pyramidal coordination and are bridged by two end-on azide groups. Weak $\text{C}-\text{H} \cdots \text{N}$ contacts result in a two-dimensional network with base vectors $[101]$ and $[010]$, parallel to the $(10\bar{1})$ plane.

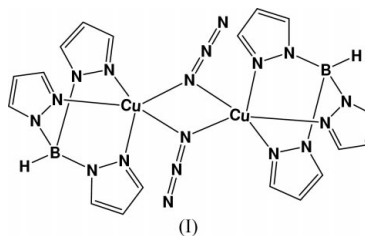
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Comment

Azide-bridged metal complexes have attracted much attention because of the structural diversity of the two bridging modes, end-on and end-to-end, which mediate ferro- and anti-ferromagnetic exchange interactions, respectively (Shen *et al.*, 2000; Wang *et al.*, 2003). Dinuclear copper(II) complexes bridged by an azide ion have been studied by many investigators with a view to understanding the relationship between their structures and magnetic properties (Cortes *et al.*, 1993; Tandon *et al.*, 1994). Ferromagnetic interactions have been found in some end-on bridged dinuclear compounds and have been extensively studied, from a theoretical point of view, by Kahn and co-workers, who have developed the concept of spin polarization induced by the in-plane π_g orbital of the azide anion (Charlot *et al.*, 1986; Kahn *et al.*, 1983). Trofimenko's hydrotris(pyrazolyl)borate ligand (Tp) has been widely used as a convenient tripod nitrogen ligand, which provides effective steric shielding of the metal centre (Trofimenko, 1993). Against this background, we report here the synthesis and crystal structure of the title compound, (I).



The structure of (I) consists of centrosymmetric $[\text{Cu}_2(\text{Tp})_2(\text{N}_3)_2]$ dimers formed by the union of two $\text{Cu}(\text{Tp})(\text{N}_3)$ fragments. The Cu^{II} ions in the dimer are linked by two end-on bridging azide groups. Each Cu^{II} cation exhibits a distorted square-pyramidal coordination geometry, with three N atoms of the Tp ligand (N2, N4 and N6) and two N atoms of the two bridging azide groups [N7 and N7ⁱⁱ; symmetry code: (ii) $2 - x, 2 - y, 1 - z$]. The average distance for $\text{Cu1}-\text{N2}$, $\text{Cu1}-\text{N4}$ and $\text{Cu1}-\text{N6}$ is 2.074 (3) \AA , and that for $\text{Cu1}-\text{N7}$ and $\text{Cu1}-\text{N7}^{\text{ii}}$ is 2.007 (3) \AA . In this dimeric unit, the Cu^{II} cations are separated from each other by 3.136 (2) \AA .

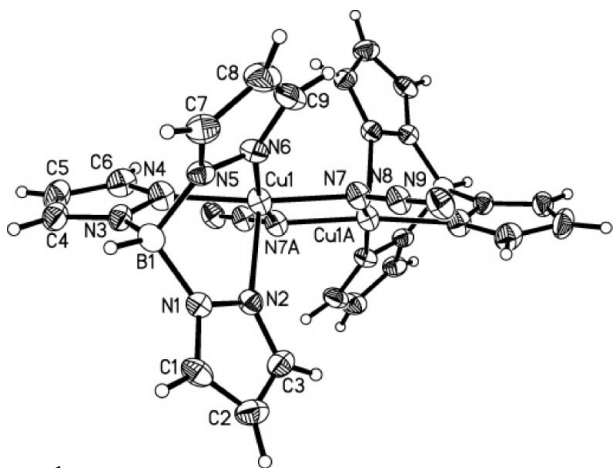


Figure 1

The molecular structure of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme. Atoms labelled with the suffix A are at the symmetry position $(2-x, 2-y, 1-z)$.

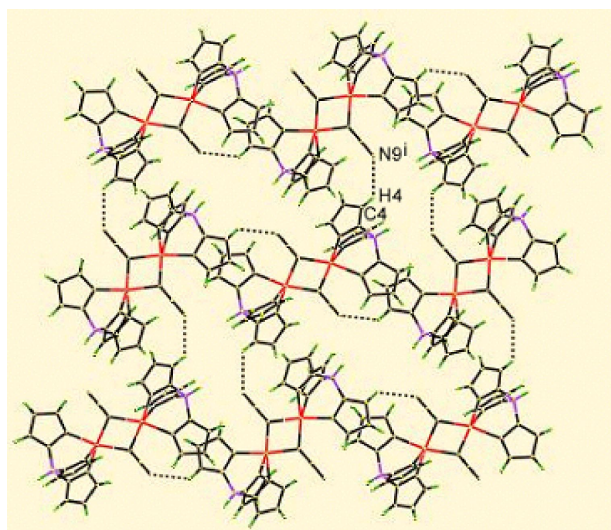


Figure 2

A view of a layer in (I). The broken lines show weak C—H...Nⁱ interactions [symmetry code: (i) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$].

The Cu1—N7—Cu1ⁱⁱ angle in the bridging azide is 102.74 (15)°.

There are weak intermolecular C—H...N interactions in the structure of (I), mediating the formation of layers. The weak C—H...N contacts result in a two-dimensional network with base vectors [101] and [010], parallel to the $(10\bar{1})$ plane. Each molecule participates as both donor and acceptor in such contacts (Fig. 2 and Table 1).

Experimental

A solution of CuCl₂·6H₂O (17.1 mg, 0.1 mmol) in methanol (2 ml) was added to a solution of NaN₃ (20 mg, 0.3 mmol) in H₂O (2 ml) and the mixture was stirred at room temperature for 2 min. An aqueous solution of KTp (25.2 mg, 0.1 mmol) was then added to the mixture and the resulting suspension was stirred for a further 2 min. After filtration, green microcrystals of (I) were obtained and recrystallized from acetonitrile. Spectroscopic analysis: IR (KBr pellet, ν): 2475 (B—H), 2068 (N₃) cm⁻¹.

Crystal data

[Cu₂(N₃)₂(C₉H₁₀BN₆)₂]
 $M_r = 637.22$
 Monoclinic, $P2_1/n$
 $a = 7.515$ (1) Å
 $b = 13.363$ (2) Å
 $c = 13.285$ (2) Å
 $\beta = 93.65$ (1)°
 $V = 1331.4$ (3) Å³
 $Z = 2$

$D_x = 1.590$ Mg m⁻³
 Mo K α radiation
 Cell parameters from 1028 reflections
 $\theta = 2.2$ – 19.8°
 $\mu = 1.64$ mm⁻¹
 $T = 293$ (2) K
 Block, green
 $0.3 \times 0.2 \times 0.2$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2000)
 $T_{\min} = 0.68$, $T_{\max} = 0.72$
 6976 measured reflections

2605 independent reflections
 2000 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.028$
 $\theta_{\max} = 26.0^\circ$
 $h = -4 \rightarrow 9$
 $k = -15 \rightarrow 16$
 $l = -16 \rightarrow 15$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.110$
 $S = 1.01$
 2605 reflections
 181 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.05P)^2 + 1.22P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.61$ e Å⁻³
 $\Delta\rho_{\min} = -0.76$ e Å⁻³

Table 1

Hydrogen-bonding geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
C4—H4...N9 ⁱ	0.93	2.51	3.176 (5)	128

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

All H atoms bonded to C atoms were placed in calculated positions, with C—H distances of 0.93 Å, and included in the refinement in a riding model approximation, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$ of the carrier atom. H atoms bonded to B atoms were found in difference Fourier maps and refined isotropically in a riding model, with B—H distances of 0.982 (2) Å.

Data collection: SMART (Bruker, 2000); cell refinement: SMART; data reduction: SAINT (Bruker, 2000); program(s) used to solve structure: SHELXTL (Bruker, 2000); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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