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Di-μ-azido-bis[azido(4,7-dimethyl-1,10-phenanthroline)copper(II)]

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The title complex, $[Cu(Me_2phen)(N_3)_2]_2$, is disposed about an inversion centre; Me_2phen is 4,7-dimethyl-1,10-phenanthroline ($C_{14}H_{12}N_2$). The structure features μ_2-bridging and terminal azide ligands, chelating Me_2phen and the Cu atom in a distorted square pyramidal geometry.

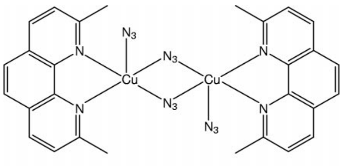
Key indicators

Single-crystal X-ray study
T = 223 K
Mean σ(C–C) = 0.003 Å
R factor = 0.037
wR factor = 0.101
Data-to-parameter ratio = 20.3

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

Comment

Azide-bridged copper(II) complexes involving combinations of chelating 1,10-phenanthroline (phen) ligands with end-on (μ1,1) and/or end-to-end (μ1,3) azides have been structurally determined. For example, $[Cu(phen)(N_3)_2]_n$ adopts a chain motif (Li *et al.*, 2000) and $[Cu(phen)(N_3)_3]_2{\cdot}2N_3{\cdot}4H_2O$ is dimeric and features uncoordinated azide (Cheng *et al.*, 2002). In order to determine the affect of steric hindrance in the phen ligand by introducing methyl groups at the 4- and 7-positions, so as to generate Me_2phen, we synthesized the complex $[Cu(Me_2phen)(N_3)_2]_2$, (I).



(I)

The dinuclear structure of $[Cu(Me_2phen)(N_3)_2]_2$ (Fig. 1) is situated about an inversion centre and features μ_2-bridging and terminal azides as well as chelating Me_2phen ligands. The bridges are effectively symmetric (Table 1) and, as expected, the bridging $Cu-N_{azide}$ distances are longer than the terminal $Cu-N_{azide}$ distance. The $Cu\cdots Cu^i$ separation within the dimer is 3.1616 (3) Å [symmetry code: (i) $\frac{1}{2}-x$, $\frac{1}{2}-y$, $-z$]. The coordination geometry for Cu is based on a square pyramid. Thus, azide atoms N1, N4 and $N1^i$ and the Me_2phen N7 atom define the basal plane and have deviations of 0.040 (2), 0.022 (3), −0.015 (3) and −0.060 (2) Å, respectively, from their least-squares plane. The Cu atom lies 0.2449 (3) Å out of this plane in the direction of atom N8. This arrangement introduces some of the disparity in the $Cu-N_{chelate}$ bond distances, with the axial Cu—N8 distance being significantly longer than the basal Cu—N distance. Within the molecule, the disposition of the Me_2phen methyl groups are such as to place one of the methyl-H atoms directly above the N1 atom, with $C14-H\cdots N1^i$ = 2.55 Å, $C14\cdots N1^i$ = 3.494 (3) Å and the angle subtended at H = 164°. The most significant contact in the crystal structure is also of the type C—H⋯N, so that $C3-H\cdots N6^{ii}$ = 2.42 Å, $C3\cdots N6^{ii}$ = 3.305 (3) Å and the angle at H

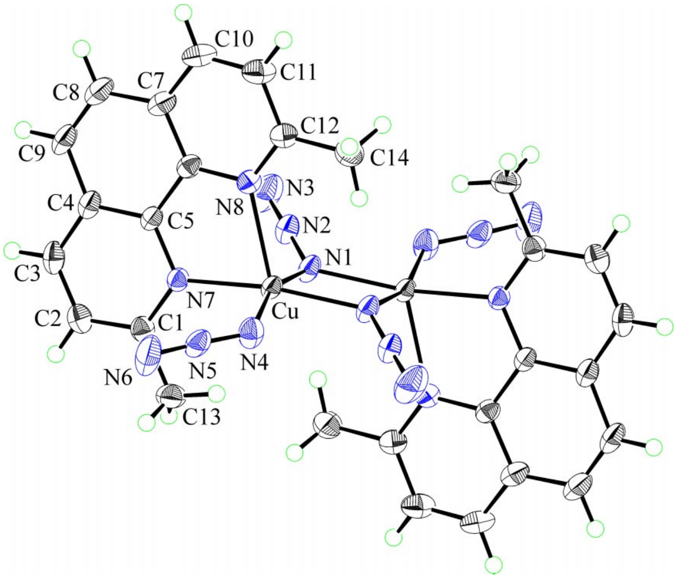


Figure 1
The molecular structure and crystallographic numbering scheme for (I). The unlabelled half of the molecule is generated by the symmetry operation ($\frac{1}{2} - x$, $\frac{1}{2} - y$, $-z$). Displacement ellipsoids are drawn at the 50% probability level.

= 157° [symmetry code: (ii) $-x$, y, $\frac{1}{2} - z$]. Such associations, as described, lead to the formation of weakly associated chains comprising complex molecules.

There is one closely related structure available in the literature for comparison, namely that of di-μ_2-azido-bis[-azido(*N*,*N*-diethylethylenediamine)copper(II)] (Casagrande *et al.*, 1989). This is centrosymmetric, like the title complex, and features essentially the same pattern of bond distances.

Experimental

A single-crystal of (I) was grown in aqueous solution by slow diffusion using an H-double-tube glass vessel. Methanol solutions of Cu(Me$_2$phen)(NO$_3$)$_2$ (0.01 *M*) and NaN$_3$ (0.02 *M*) were placed in separate arms. Brown crystals separated after two months.

Crystal data

[Cu$_2$(N$_3$)$_4$(C$_{14}$H$_{12}$N$_2$)$_2$]
M_r = 711.72
Monoclinic, $C2/c$
a = 13.3691 (5) Å
b = 11.2648 (5) Å
c = 19.5792 (9) Å
β = 95.565 (2)°
V = 2934.7 (2) Å^3
Z = 4
D_x = 1.611 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3661 reflections
θ = 2.4–30.0°
μ = 1.50 mm^{-1}
T = 223 (2) K
Block, brown
0.49 × 0.16 × 0.16 mm

Data collection

Bruker AXS SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000; Blessing, 1995)
$T_{\min}$ = 0.750, $T_{\max}$ = 0.787
11979 measured reflections
4259 independent reflections
3450 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.032
$\theta_{\max}$ = 30.0°
h = −18 → 18
k = −14 → 15
l = −27 → 19

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.101
S = 1.04
4259 reflections
210 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0584P)^2 + 0.0245P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.62 e Å^{-3}
$\Delta\rho_{\min}$ = −0.33 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu—N1	2.0285 (17)	N1—N2	1.212 (2)
Cu—N4	1.9499 (17)	N2—N3	1.137 (2)
Cu—N7	2.0316 (15)	N4—N5	1.187 (2)
Cu—N8	2.2554 (15)	N5—N6	1.149 (2)
Cu—N1$^{\rm i}$	2.0240 (17)		
N1—Cu—N4	160.67 (7)	N7—Cu—N1$^{\rm i}$	165.60 (6)
N1—Cu—N7	92.67 (6)	N8—Cu—N1$^{\rm i}$	112.53 (6)
N1—Cu—N8	94.60 (6)	Cu—N1—N2	125.03 (14)
N1—Cu—N1$^{\rm i}$	77.45 (7)	Cu$^{\rm i}$—N1—N2	125.47 (14)
N4—Cu—N7	96.31 (7)	Cu—N1—Cu$^{\rm i}$	102.55 (7)
N4—Cu—N8	103.95 (7)	N1—N2—N3	178.8 (2)
N4—Cu—N1$^{\rm i}$	90.27 (7)	Cu—N4—N5	126.15 (14)
N7—Cu—N8	78.34 (6)	N4—N5—N6	175.6 (2)

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

The carbon-bound H atoms were included in the riding-model approximation, with C—H distances of 0.94 Å (0.97 Å for methyl), $U_{\rm iso}$(phenyl–H) = 1.2$U_{\rm eq}$(C) and $U_{\rm iso}$(methyl–H) = 1.5$U_{\rm eq}$(C).

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT* and *SHELXTL* (Bruker, 2000); program(s) used to solve structure: *PATTY* in *DIRDIF*92 (Beurskens *et al.*, 1992); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXTL*.

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