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trans-Dibromobis(phenazine)copper(II)

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Key indicators

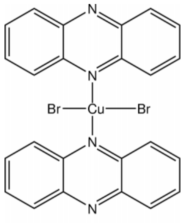
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.031
wR factor = 0.077
Data-to-parameter ratio = 17.2

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

In the title compound, $[CuBr_2(C_{12}H_8N_2)_2]$, the Cu^{II} ion lies on an inversion centre and exhibits a square planar coordination, with the two bromide ions and two N atoms of phenazine ligands in a *trans* configuration. The Cu—Br and Cu—N distances are 2.382 (1) and 2.020 (2) Å, respectively. The crystal structure consists of an assemblage of discrete molecules of the title complex. No unusual intermolecular contact distances are observed, so that the molecular packing may be attributed to normal van der Waals interactions.

Comment

The synthetic methods controlling the orientation of molecules in crystals is a rapidly growing subject of modern solid-state chemistry. A variety of bridging ligands and their transition metal complexes have attracted great interest due to their potential as building blocks for supramolecular assemblies. The planar electron-rich phenazine (phz) is known as a monodentate or bridging ligand as well as an electron donor which can form columnar stacks through π–π interactions. The electron-density distribution in phz is typical for diazo compounds. There is a greater accumulation of density in the more electronegative N atoms and depletion in the region of C atoms. An inspection of the Cambridge Structural Database (release April 2003; Allen, 2002) shows that only a few copper(I) complexes with phz have been structurally characterized so far. This short list includes copper(I) halide complex polymers having multilayered arrangements of phz (Munakata *et al.*, 1994), monomeric and dimeric non-halide copper(I) complexes with phz such as $[Cu(phz)_2(NO_3)]$ or $[\{Cu_2(phz)_3(MeOH)_2\}(phz)(PF_6)]$ (Munakata *et al.*, 1993), and non-halide copper(I) complexes with phz which have one- or two-dimensional polymeric structures together with π–π stacking of phz (Kuroda-Sowa *et al.*, 1995). We report here the synthesis and crystal structure of a new copper(II) halide complex with phz, (I), the first complex ever reported of copper(II) with phz.



(I)

The crystal structure consists of an assemblage of discrete molecules of the *trans*-dibromobis(phz)copper(II) complex (Fig. 1.); the molecule is centrosymmetric, the copper ions

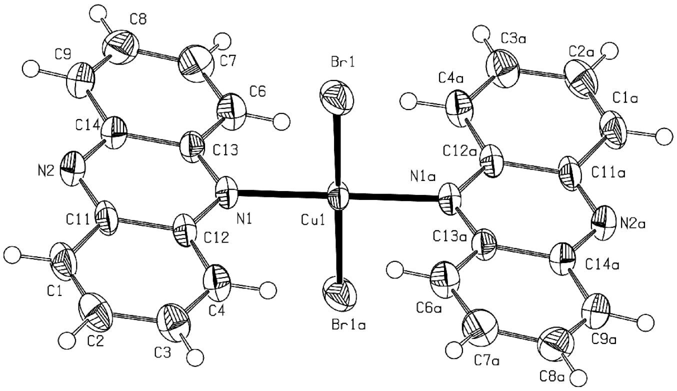


Figure 1
View of the title compound with the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level. Suffix *a* corresponds to symmetry code (i) in Table 1

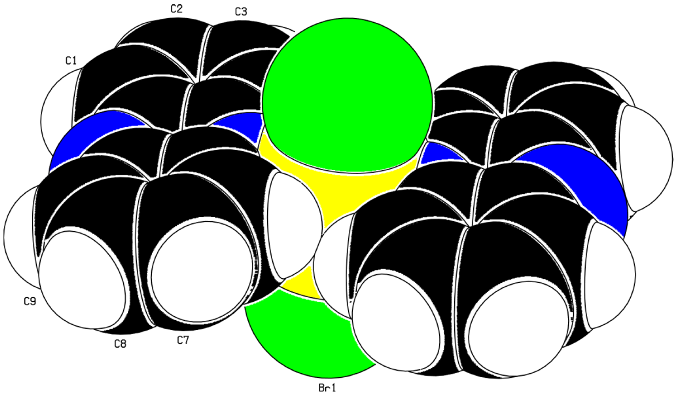


Figure 2
Space-filling plot of the title compound, illustrating the steric crowding around the copper center.

being located at inversion centers in the unit cell. The copper center is square-planar, coordinated by two bromide ions and two N atoms of phenazine ligands in a *trans* configuration with bond distances Cu—Br1 of 2.382 (1) Å and Cu—N1 of 2.020 (2) Å. This four-coordinate copper(II) stereochemistry may be attributed to steric (bulky halogen and ligand) requirements (Fig. 2). The bond lengths and angles in the phz ligand do not differ significantly from those reported previously for α- and β-phenazine (Herbstein & Schmidt, 1955; Woźniak *et al.*, 1991; Jankowski & Gdaniec, 2002). The phz ring system is approximately planar, the maximum deviation from the 14-atom least-squares plane being 0.123 (2) Å. Unexpectedly, no unusual intermolecular contact distances are observed, so that the molecular packing may be attributed to normal van der Waals interactions.

Experimental

The complex was prepared by addition of 0.001 mol of $\mathrm{CuBr_2{\cdot}2H_2O}$ to a warm solution containing 0.001 mol of phenazine in 50 ml of methanol. The resulting solution was filtered and allowed to cool. Slow evaporation deposited dark brown crystals analysed as $[\mathrm{CuBr_2(C_{12}H_8N_2)_2}]$ (m.p. 512.1–512.9 K). Analysis found: C 49.55, N 9.56, H 2.89%; calculated for $\mathrm{C_{24}H_{16}Br_2CuN_4}$: C 49.38, N 9.60, H 2.76%.

Crystal data

$[\mathrm{CuBr_2(C_{12}H_8N_2)_2}]$
$M_r = 583.76$
Monoclinic, $P2_1/c$
$a = 9.688$ (2) Å
$b = 9.331$ (2) Å
$c = 12.034$ (2) Å
$\beta = 102.04$ (3)°
$V = 1063.9$ (4) Å^3
$Z = 2$
$D_x = 1.822$ Mg m^{-3}
$D_m = 1.80$ (3) Mg m^{-3}
D_m measured by flotation in $\mathrm{CH_3I/CCl_4}$
Mo *Kα* radiation
Cell parameters from 1534 reflections
$\theta = 3.6$–24.5°
$\mu = 4.80$ mm^{-1}
$T = 293$ K
Block, dark brown
0.30 × 0.15 × 0.15 mm

Data collection

Kuma *KM*4 CCD diffractometer
ω scans
Absorption correction: numerical (*X-RED*; Stoe & Cie, 1999)
$T_{\min} = 0.236$, $T_{\max} = 0.497$
12944 measured reflections
2439 independent reflections
2138 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.048$
$\theta_{\max} = 27.5°$
$h = -12 \rightarrow 10$
$k = -12 \rightarrow 12$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.077$
$S = 1.12$
2439 reflections
142 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0405P)^2 + 0.2911P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.42$ e Å^{-3}
$\Delta\rho_{\min} = -0.55$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Br1—Cu1	2.3822 (6)	C3—C4	1.361 (4)
Cu1—N1	2.020 (2)	C4—C12	1.411 (4)
N1—C12	1.356 (3)	C6—C7	1.359 (4)
N1—C13	1.346 (3)	C6—C13	1.422 (4)
N2—C11	1.329 (3)	C7—C8	1.408 (4)
N2—C14	1.337 (3)	C8—C9	1.352 (4)
C1—C2	1.348 (4)	C9—C14	1.423 (4)
C1—C11	1.431 (4)	C11—C12	1.436 (3)
C2—C3	1.420 (4)	C13—C14	1.445 (3)
Br1—Cu1—N1	89.64 (6)	N2—C11—C12	122.5 (2)
Br1—Cu1—N1$^{\rm i}$	90.36 (6)	N1—C12—C4	121.0 (2)
Cu1—N1—C12	121.05 (16)	N1—C12—C11	119.6 (2)
Cu1—N1—C13	120.24 (15)	N1—C13—C6	121.4 (2)
C12—N1—C13	118.4 (2)	N1—C13—C14	120.2 (2)
C11—N2—C14	117.6 (2)	N2—C14—C9	120.0 (2)
N2—C11—C1	119.1 (2)	N2—C14—C13	121.4 (2)

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

All H atoms were included at calculated positions (C—H = 0.93 Å) and refined using a riding model, with $U_{\rm iso}$ equal to 1.2 times $U_{\rm eq}$ of the attached C atom.

Data collection: *CrysAlis CCD* (UNIL IC & Oxford Diffraction, 2001); cell refinement: *CrysAlis RED* (UNIL IC & Oxford Diffraction, 2001); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1990); software used to prepare material for publication: *SHELXL*97 and *PLATON*.

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