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catena-Poly[[{4-bromo-2-[2-(dimethylamino)ethyliminomethyl]phenolato}copper(II)]-μ-azido]

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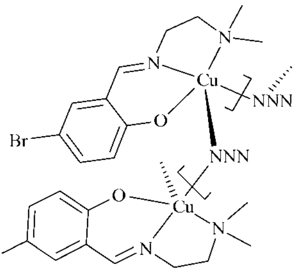
The title complex, $[Cu(C_{11}H_{14}BrN_2O)(N_3)]_n$, is an interesting azide-bridged polynuclear copper(II) compound. The Cu^{II} atom is five-coordinated in a square-pyramidal configuration, with one O and two N atoms of one Schiff base and one terminal N atom of a bridging azide ligand defining the basal plane, and another terminal N atom of another bridging azide ligand occupying the axial position. The {4-bromo-2-[2-(dimethylamino)ethyliminomethyl]phenolato}copper(II) moieties are linked by the bridging azide ligands, forming polymeric chains running along the *b* axis. Adjacent chains are further linked by weak Br···Br interactions into a sheet.

Comment

The magnetic properties of extended coordination compounds featuring exchange-coupled magnetic centres have become a fascinating subject in recent years (Dalai *et al.*, 2002; Bhaduri *et al.*, 2003). The prime strategy for designing these molecular materials is to use a suitable bridging ligand that determines the nature of the magnetic interactions (Koner *et al.*, 2003). Due to the versatile coordination modes of the ambidentate azide ligand and the wide range of magnetic coupling mediated by azide bridges, this pseudohalide ligand has become one of the most extensively studied building blocks in the field (Thompson & Tandon, 1996; Meyer & Pritzkow, 2001). Azide complexes of various dimensionalities have been obtained (Mukherjee *et al.*, 2001; Goher *et al.*, 2002). These also include some examples of the so-called alternating one-dimensional magnetic systems, which have two or more different structural bridges and which are of considerable interest in terms of their magnetic behaviour (Vicente *et al.*, 1992; Escuer *et al.*, 1994; Ribas *et al.*, 1995; Vicente & Escuer, 1995). A major obstacle to a more comprehensive study of such azide-based polymeric coordination compounds is the lack of rational synthetic procedures, since with the present state of knowledge it is hardly possible to determine which coordination mode will be adopted by the azide ligand and whether the sought-after alternating chain structure will finally be formed (Ribas *et al.*, 1999).

Our work is aimed at obtaining multidimensional polymetallic complexes. Based on the above considerations, we designed and synthesized a flexible tridentate ligand, 4-bromo-2-[2-(dimethylamino)ethyliminomethyl]phenol (BDMP). The reason we do not use a rigid ligand is that the flexible BDMP ligand can adopt a different coordination mode according to the geometric need of the transition metal ions and the coordination environment (Mondal *et al.*, 2001). The second ligand, *viz*. azide, is a well known bridging group. It readily bridges different metal ions through the terminal donor atoms, forming polynuclear complexes (Monfort *et al.*, 2001). Copper(II) is a good candidate for octahedral coordination geometry. We report here the novel one-dimensional infinite chains in the structure of the title compound, (I), formed by the reaction of BDMP, azide and copper(II) acetate.



(I)

Complex (I) is an azide-bridged polynuclear copper(II) compound (Fig. 1). The smallest repeat unit contains one BDMP–Cu^{II} cation and one bridging azide ligand. The Cu^{II} atom is in a square-pyramidal coordination environment, with the NNO donor set of one Schiff base and one terminal N atom of a bridging azide ligand defining the basal plane, and a different but symmetry-related terminal N atom occupying the axial position. The Schiff base acts as a tridentate ligand and

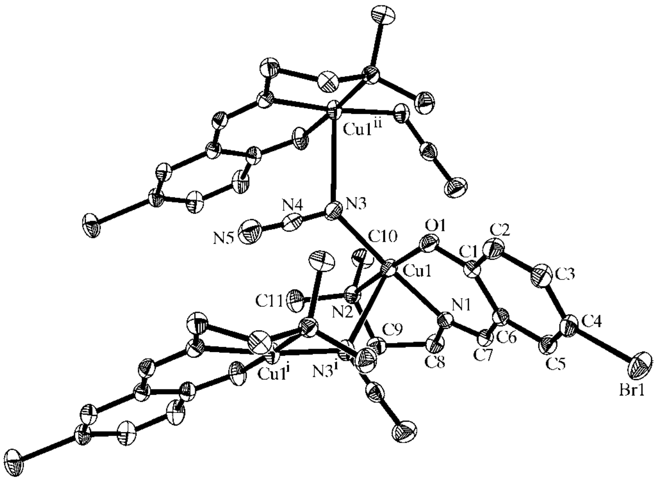


Figure 1
The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (i) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$; (ii) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$.]

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ligates to the metal atom *via* the three O- and N-donor atoms. It is very interesting that the azide anion acts as a bridging ligand and ligates to two different but symmetry-related Cu^{II} atoms *via* the terminal N atom. Atom N3 acts as a basal donor of the Cu1 moiety, while for the Cu1^{ii} moiety, it acts as the axial donor atom [symmetry code: (ii) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$]. The Cu1^{ii}—N3 bond [2.655 (2) Å] is much longer than the Cu1—N3 bond [1.981 (2) Å], which is probably due to the hindrance effects of the copper(II) moieties. The basal least-squares planes of the adjacent two Cu^{II} centres are not parallel and form a dihedral angle of 43.5 (2)°. The deviation of atom Cu1 from the best-fit square plane towards atom N3 is 0.054 (2) Å.

The bond lengths (Table 1) subtended at atom Cu1 in the basal plane are comparable with those observed in other Schiff base–copper(II) complexes (Zhang *et al.*, 2001; Elmali *et al.*, 2000) and, as expected, the bond involving amine atom N2 [2.070 (2) Å] is longer than that involving imine atom N1 [1.950 (2) Å] (Mondal *et al.*, 2001). The bridging azide group is nearly linear and shows bent coordination modes with the metal atoms [the angles N3—N4—N5, Cu1—N3—N4 and Cu1^{i}—N3—N4 are 177.7 (3), 117.8 (2) and 113.1 (2)°, respectively; symmetry code: (i) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$]. The N1—Cu1—N2 bond angle [84.90 (8)°] of the five-membered chelate ring is much smaller than 90°, which is due to the strain created by the five-membered chelate ring Cu1/N2/C9/C8/N1.

In the crystal structure, the {4-bromo-2-[2-(dimethylamino)-ethyliminomethyl]phenolato}copper(II) moieties are linked by the bridging azide ligands, forming polymeric chains running along the *b* axis. Adjacent chains are further linked by weak Br···Br interactions into a sheet (Fig. 2).

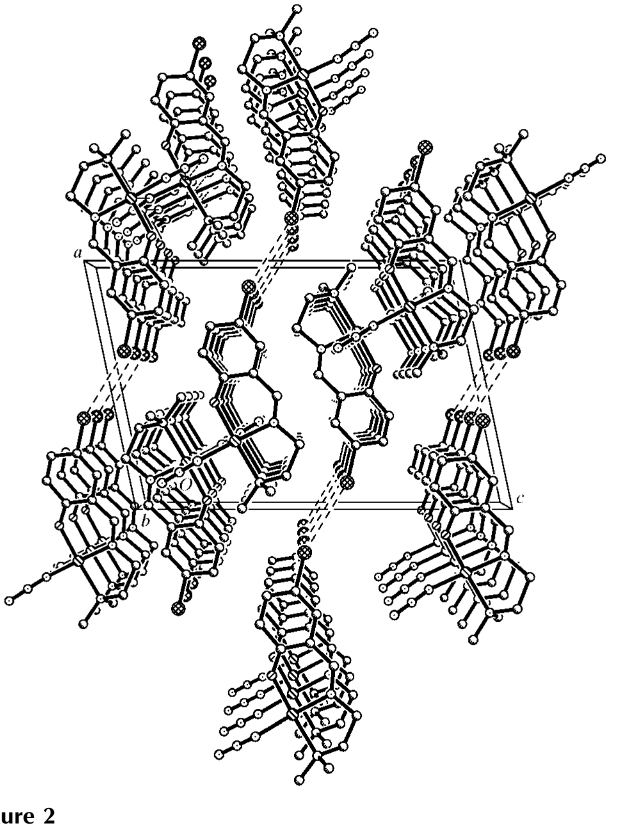

Figure 2
The crystal packing of (I), viewed along the *b* axis. Dashed lines indicate the Br···Br interactions.

Experimental

5-Bromosalicylaldehyde (0.1 mmol, 20.1 mg) and *N*,*N*-dimethylethane-1,2-diamine (0.1 mmol, 8.8 mg) were dissolved in MeOH (10 ml). The mixture was stirred at room temperature for 10 min to give a yellow solution. To this solution was added with stirring an aqueous solution (2 ml) of NaN_3 (0.1 mmol, 6.5 mg) and an MeOH solution (3 ml) of $Cu(CH_3COO)_2 \cdot H_2O$ (0.1 mmol, 19.9 mg). The mixture was stirred for another 10 min at room temperature. After keeping the filtrate in air for 7 d, blue block-shaped crystals of (I) were formed.

Crystal data

$[Cu(C_{11}H_{14}BrN_2O)(N_3)]$
$M_r = 375.72$
Monoclinic, $P2_1/n$
$a = 12.076$ (2) Å
$b = 6.757$ (2) Å
$c = 17.875$ (2) Å
$\beta = 101.88$ (1)°
$V = 1427.3$ (5) Å^3
$Z = 4$
$D_x = 1.748$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 5698 reflections
$\theta = 2.3$–27.0°
$\mu = 4.33$ mm^{-1}
$T = 298$ (2) K
Block, blue
0.18 × 0.14 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.510$, $T_{max} = 0.625$
15608 measured reflections

3258 independent reflections
2631 reflections with $I > 2\sigma(I)$
$R_{int} = 0.033$
$\theta_{max} = 27.5°$
$h = -15 \rightarrow 15$
$k = -8 \rightarrow 8$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.077$
$S = 1.05$
3258 reflections
174 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0336P)^2 + 0.7176P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.88$ e Å^{-3}
$\Delta\rho_{min} = -0.50$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.909 (2)	Cu1—N3	1.981 (2)
Cu1—N1	1.950 (2)	Cu1—N2	2.070 (2)
O1—Cu1—N1	92.63 (7)	O1—Cu1—N2	177.37 (8)
O1—Cu1—N3	89.18 (8)	N1—Cu1—N2	84.90 (8)
N1—Cu1—N3	174.47 (9)	N3—Cu1—N2	93.19 (9)

All H atoms were placed in geometrically idealized positions and allowed to ride on their parent atoms, with C—H distances in the range 0.93–0.97 Å and with $U_{iso}(H) = 1.2$ or $1.5U_{eq}(C)$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1843). Services for accessing these data are described at the back of the journal.

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