

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

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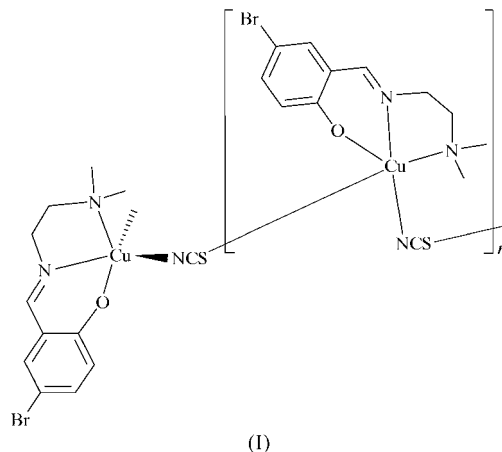
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The title complex, $[\text{Cu}(\text{C}_{11}\text{H}_{14}\text{BrN}_2\text{O})(\text{NCS})]_n$, is an interesting thiocyanate-bridged polynuclear copper(II) compound, which crystallizes with two independent molecules in the asymmetric unit. Each Cu^{II} atom is five-coordinate in a square-pyramidal configuration, with one O and two N atoms of one Schiff base ligand and one terminal N atom of a bridging thiocyanate ligand defining the basal plane, and one terminal S atom of another bridging thiocyanate ligand occupying the apical position. The {4-bromo-2-[2-(dimethylamino)ethyliminomethyl]phenolato}copper(II) units are linked by the bridging thiocyanate ligands, forming polymeric chains running along the *a* axis. There are weak intermolecular C—H...O and C—H...S hydrogen bonds between the chains in the crystal structure.

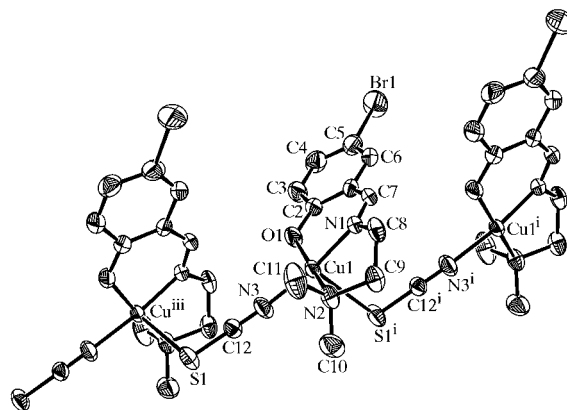
Comment

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). Owing to the versatile coordination modes of the ambidentate thiocyanate ligand and the wide range of magnetic coupling mediated by thiocyanate bridges, this pseudohalide ligand has become one of the most extensively studied building blocks in the field (Sailaja *et al.*, 2003; Dey *et al.*, 2004). Thiocyanate complexes of various dimensionalities have been obtained (Zurowska *et al.*, 2002; Zhang *et al.*, 2003; You, 2005a). 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 thiocyanate-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 thiocyanate ligand and whether the sought-after alternating chain structure will finally be formed (Tercero *et al.*, 2002; Ribas *et al.*, 1999; Liu *et al.*, 2003).



Our work is aimed at obtaining multidimensional poly-metallic complexes. Based on the above considerations, we designed and synthesized the 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 needs of the transition metal ion and the coordination environment (Mondal *et al.*, 2001). The second ligand, *viz.* thiocyanate, is a well known bridging group. It readily bridges different metal ions through the terminal donor atoms, forming polynuclear complexes (Kuang *et al.*, 2001). Copper(II) is a good candidate for octahedral coordination geometry. We report here a new one-dimensional infinite-chain complex, (I), formed by the reaction of BDMP, ammonium thiocyanate and copper(II) acetate.


Figure 1

The structure of molecule *A* of (I), showing the atom-numbering scheme and the formation of the polymeric chain. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. [Symmetry codes: (i) $x - \frac{1}{2}, -y, z$; (iii) $x + \frac{1}{2}, -y, z$.]

The title complex is a thiocyanate-bridged polynuclear copper(II) compound. The asymmetric unit contains two independent molecules, *A* (Fig. 1) and *B* (Fig. 2). Each of the molecules contains two BDMP–Cu^{II} cations and two bridging thiocyanate anions. The Cu^{II} atom is in a square-pyramidal coordination configuration and is five-coordinated by the NNO donor set of one Schiff base and by one terminal N atom of a bridging thiocyanate ligand, which define the basal plane, and by one terminal N atom of another bridging thiocyanate ligand, which occupies the apical position. The Schiff base acts as a tridentate ligand and ligates to the metal *via* the three O and N donor atoms. The bridging thiocyanate anion ligates to two different but symmetry-related Cu^{II} atoms *via* the terminal N and S atoms. The significant distortion of the square pyramid is revealed by the bond angles between the apical and basal donor atoms (Table 1). The N1–Cu1–N2 and N4–Cu2–N5 bond angles deviate from 90° by 6.10 (14) and

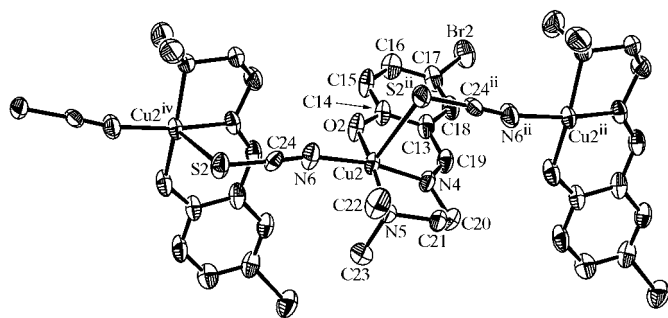


Figure 2
The structure of molecule *B* of (I), showing the atom-numbering scheme and the formation of the polymeric chain. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. [Symmetry codes: (ii) $x - \frac{1}{2}, -y + 1, z$; (iv) $x + \frac{1}{2}, 1 - y, z$.]

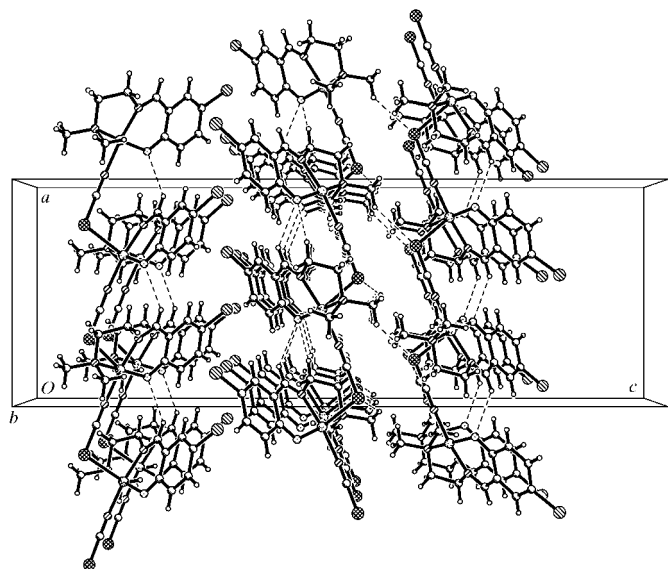


Figure 3
The crystal packing of (I), viewed along the *b* axis. Dashed lines show the weak intermolecular C–H···O and C–H···S hydrogen bonds.

4.65 (14)°, respectively, as a result of the strain created by the five-membered chelate rings Cu1/N1/C8/C9/N2 and Cu2/N4/C20/C21/N5. The apical bonds [Cu1–S1ⁱ and Cu2–S2ⁱⁱ; symmetry codes: (i) $x - \frac{1}{2}, -y, z$; (ii) $x - \frac{1}{2}, -y + 1, z$] are much longer than the basal bonds, indicating that the Cu–S bond is not very strong. The Cu–O and Cu–N bond lengths are comparable to the corresponding values observed in other Schiff base–copper(II) complexes (You & Zhu, 2004; You *et al.*, 2004; Zhang *et al.*, 2001; Elmali *et al.*, 2000) and, as expected, the bonds involving amine atoms N2 [2.068 (3) Å] and N5 [2.067 (3) Å] are longer than those involving imine atoms N1 [1.943 (3) Å] and N4 [1.948 (3) Å] (Mondal *et al.*, 2001). The bridging NCS groups are nearly linear and show bent coordination modes with the metal atoms [N3–C12–S1 = 179.9 (5)°, Cu1–N3–C12 = 169.7 (4)°, Cu1ⁱⁱ–S1–C12 = 102.12 (4)°, N6–C24–S2 = 177.7 (4)°, Cu2–N6–C24 = 166.8 (4)° and Cu2^{iv}–S2–C24 = 101.98 (4)°; symmetry code: (iv) $x + \frac{1}{2}, 1 - y, z$].

The basal least-square planes defined by the four donor atoms of the adjacent two Cu^{II} centres are not parallel and form a dihedral angle of 74.1 (2)° for the Cu1 moiety and 75.0 (2)° for the Cu2 moiety; this configuration can decrease the steric effects among the molecules. The deviation of atom Cu1 from the least-squares plane is 0.180 (2) Å, and the corresponding value for Cu2 is 0.176 (2) Å.

The C7=N1 [1.283 (5) Å] and C19=N4 bond lengths [1.264 (6) Å] conform to the values for double bonds, while the C8–N1 [1.452 (5) Å] and C20–N4 bond lengths [1.487 (6) Å] conform to the values for single bonds (You, 2005*b*).

In the crystal structure, the {4-bromo-2-[2-(dimethylamino)ethyliminomethyl]phenolato}copper(II) moieties are linked by the bridging thiocyanate ligands, forming polymeric chains running along the *a* axis; adjacent chains are further linked by weak intermolecular C–H···O and C–H···S hydrogen bonds, forming dimeric chains running along the *a* axis (Table 2 and Fig. 3).

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 an aqueous solution (2 ml) of NH₄NCS (0.1 mmol, 6.5 mg) and an MeOH solution (3 ml) of Cu(CH₃COO)₂·H₂O (0.1 mmol, 19.9 mg), with stirring. The mixture was stirred for another 10 min at room temperature. The filtrate was kept in air for 12 d, during which time blue block-shaped crystals were formed.

Crystal data

[Cu(C₁₁H₁₄BrN₂O)(NCS)]
M_r = 391.77
 Orthorhombic, *Pca*2₁
a = 11.767 (2) Å
b = 7.4180 (15) Å
c = 33.870 (7) Å
V = 2956.4 (10) Å³
Z = 8
D_x = 1.760 Mg m⁻³

Mo Kα radiation
 Cell parameters from 12201 reflections
 θ = 2.4–28.0°
 μ = 4.32 mm⁻¹
T = 298 (2) K
 Block, blue
 0.24 × 0.15 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer	6447 independent reflections
ω scans	5729 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.039$
$T_{\text{min}} = 0.424$, $T_{\text{max}} = 0.625$	$\theta_{\text{max}} = 27.0^\circ$
30513 measured reflections	$h = -15 \rightarrow 14$
	$k = -9 \rightarrow 9$
	$l = -43 \rightarrow 43$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0554P)^2 + 0.0383P]$
$R[F^2 > 2\sigma(F^2)] = 0.036$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.092$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.06$	$\Delta\rho_{\text{max}} = 1.09 \text{ e } \text{\AA}^{-3}$
6447 reflections	$\Delta\rho_{\text{min}} = -0.65 \text{ e } \text{\AA}^{-3}$
347 parameters	Absolute structure: Flack (1983),
H-atom parameters constrained	3160 Friedel pairs
	Flack parameter: 0.083 (9)

Table 1

Selected geometric parameters (\AA , $^\circ$).

Cu1—O1	1.922 (3)	Cu2—N6	1.969 (3)
Cu1—N1	1.943 (3)	Cu2—N5	2.067 (3)
Cu1—N3	1.953 (3)	Cu2—S2 ⁱⁱ	2.8332 (14)
Cu1—N2	2.068 (3)	N1—C7	1.283 (5)
Cu1—S1 ⁱ	2.8300 (14)	N1—C8	1.452 (5)
Cu2—O2	1.922 (3)	N4—C19	1.264 (6)
Cu2—N4	1.948 (3)	N4—C20	1.487 (6)
O1—Cu1—N1	92.34 (13)	O2—Cu2—N4	91.63 (13)
O1—Cu1—N3	90.21 (14)	O2—Cu2—N6	89.85 (14)
N1—Cu1—N3	167.79 (16)	N4—Cu2—N6	168.63 (16)
O1—Cu1—N2	170.22 (15)	O2—Cu2—N5	170.39 (15)
N1—Cu1—N2	83.90 (14)	N4—Cu2—N5	85.35 (14)
N3—Cu1—N2	91.65 (13)	N6—Cu2—N5	91.36 (14)
O1—Cu1—S1 ⁱ	97.67 (15)	O2—Cu2—S2 ⁱⁱ	97.89 (15)
N1—Cu1—S1 ⁱ	90.39 (15)	N4—Cu2—S2 ⁱⁱ	89.52 (15)
N3—Cu1—S1 ⁱ	101.10 (15)	N6—Cu2—S2 ⁱⁱ	101.44 (15)
N2—Cu1—S1 ⁱ	91.40 (15)	N5—Cu2—S2 ⁱⁱ	91.22 (15)

Symmetry codes: (i) $x - \frac{1}{2}, -y, z$; (ii) $x - \frac{1}{2}, -y + 1, z$.

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C7—H7 \cdots O1 ⁱ	0.93	2.51	3.285 (7)	141
C19—H19 \cdots O2 ⁱⁱ	0.93	2.55	3.316 (4)	139
C20—H20A \cdots O2 ⁱⁱ	0.97	2.58	3.468 (7)	153

Symmetry codes: (i) $x - \frac{1}{2}, -y, z$; (ii) $x - \frac{1}{2}, -y + 1, z$.

All H atoms were placed in geometrically idealized positions and allowed to ride on their parent atoms, with C—H = 0.93–0.97 \AA and $U_{\text{iso}}(\text{H}) = 1.2$ or 1.5 times $U_{\text{eq}}(\text{C})$. An unassigned maximum residual density was observed 0.81 \AA from atom Br1.

Data collection: SMART (Bruker, 1998); cell refinement: SMART; data reduction: SAINT (Bruker, 1998); program(s) used to solve

structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Sheldrick, 2000); 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: DN1095). Services for accessing these data are described at the back of the journal.

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