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catena-Poly[[[2,4-dichloro-6-(pyridin-2-ylmethyliminomethyl)phenolato]copper(II)]-μ-thiocyanato]

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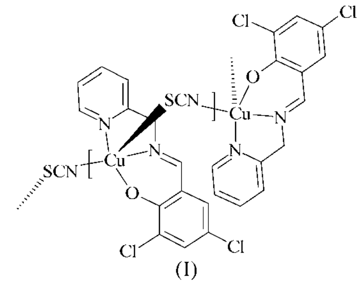
The title complex, $[Cu(C_{13}H_9Cl_2N_2O)(NCS)]_n$, is a novel thiocyanate-bridged polynuclear copper(II) compound. The Cu^{II} atom is five-coordinated in a square-pyramidal configuration, with one O and two N atoms of one Schiff base ligand and one terminal N atom of a bridging thiocyanate ligand defining the basal plane, and one terminal S atom of another bridging thiocyanate ligand occupying the axial position. The [2,4-dichloro-6-(pyridin-2-ylmethyliminomethyl)phenolato]copper(II) moieties are linked by the bridging thiocyanate ligands, forming polymeric chains running along the *a* axis.

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 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, 2005*a*). 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 not 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).



(I)

Our work is aimed at obtaining multidimensional polymetallic complexes. Based on the above considerations, we designed and synthesized a rigid tridentate ligand, namely 2,4-dichloro-6-(pyridin-2-ylmethyliminomethyl)phenol (DPMP). The reason we do not use a flexible ligand is that the rigid DPMP ligand could adopt an almost fixed coordination mode through its three donor atoms (You, Chen *et al.*, 2004; You & Zhu, 2004*a*,*b*). The second ligand, *viz*. thiocyanate, is a well known bridging group. It readily bridges different metal ions through its terminal donor atoms, forming polynuclear complexes (Kuang *et al.*, 2001). Copper(II) is a good candidate for square-pyramidal coordination geometry. We report here the formation of novel one-dimensional infinite chains in the structure of the title compound, (I), which was formed by the reaction of the DPMP ligand, thiocyanate and copper(II) acetate.

Complex (I) is a polynuclear copper(II) compound (Fig. 1). The smallest repeat unit contains two DPMP–Cu^{II} cations and two bridging thiocyanate anions. The Cu^{II} atom is in a square-pyramidal coordination environment and is five-coordinated by one O atom and two N atoms of one Schiff base ligand and one N atom of a thiocyanate anion defining the basal plane, and by a symmetry-related terminal S atom occupying the axial position. The Schiff base acts as a tridentate ligand and ligates to the metal *via* the three O and N donor atoms. The thiocyanate anion acts as a bridging ligand and ligates to two different but symmetry-related copper(II) atoms *via* the

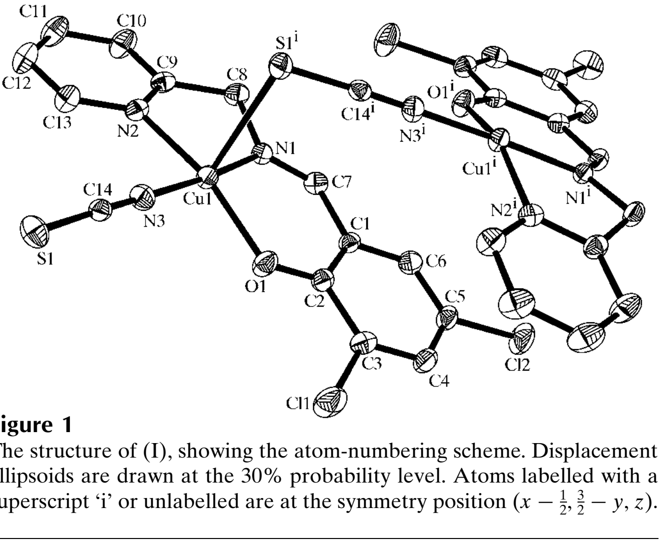


Figure 1
The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Atoms labelled with a superscript 'i' or unlabelled are at the symmetry position $(x - \frac{1}{2}, \frac{3}{2} - y, z)$.

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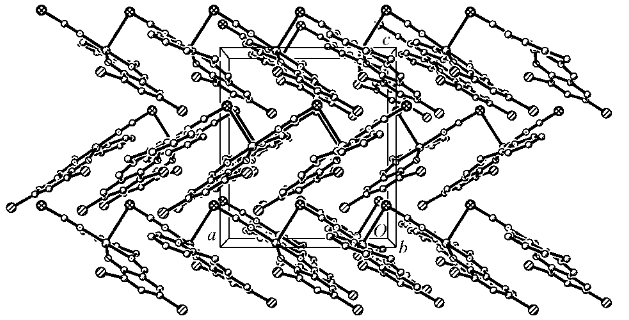

Figure 2
The crystal packing of (I), viewed along the *b* axis.

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 bond angle N1—Cu1—N2 deviates from 90° by 8.08 (13)°, which is due to the strain created by the five-membered chelate ring Cu1—N1—C8—C9—N2. The apical bond [Cu1—S1^{i}; symmetry code: (i) $x - \frac{1}{2}, \frac{3}{2} - y, z$] is 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 with the corresponding values observed in other Schiff base copper(II) complexes (You & Zhu, 2004*c*; You, Xiong & Zhu, 2004; Zhang *et al.*, 2001; Elmali *et al.*, 2000). The bridging NCS group is nearly linear and shows bent coordination modes with the metal atoms [the N3—C14—S1, Cu1—N3—C14 and Cu1—S1^{i}—C14^{i} angles are 177.8 (3), 179.6 (3) and 92.19 (14)°, respectively].

The basal least-square planes defined by the four donor atoms of two adjacent Cu^{II} centres are almost parallel and form a dihedral angle of 10.9 (3)°. The deviation of atom Cu1 from the best-fit square plane is 0.164 (3) Å. The CuN_3O basal plane forms dihedral angles of 7.6 (3) and 16.2 (3)° with the benzene and pyridine rings, respectively, which are inclined at 17.1 (3)° to each other. The two adjacent [2,4-dichloro-6-(pyridin-2-ylmethyliminomethyl)phenolato]copper(II) moieties are almost vertical to each other, which can decrease the steric effects between the molecules.

In (I), the C7═N1 bond length [1.274 (5) Å] conforms to the normal value for a double bond, while the C8—N1 bond length [1.456 (4) Å] conforms to the normal value for a single bond (You, 2005*b*).

In the title crystal structure, the [2,4-dichloro-6-(pyridin-2-ylmethyliminomethyl)phenolato]copper(II) moieties are linked by bridging thiocyanate ligands, forming polymeric chains running along the *a* axis (Fig. 2).

Experimental

3,5-Dichlorosalicylaldehyde (0.1 mmol, 19.1 mg) and pyridin-2-ylmethylamine (0.1 mmol, 10.8 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 MeOH solution (10 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 12 d, blue block-shaped crystals of (I) were formed.

Crystal data

$[Cu(C_{13}H_9Cl_2N_2O)(NCS)]$
$M_r = 401.74$
Orthorhombic, $Pna2_1$
$a = 10.499 (2)$ Å
$b = 12.208 (2)$ Å
$c = 11.886 (2)$ Å
$V = 1523.5 (5)$ Å^3
$Z = 4$
$D_x = 1.752$ Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 4105 reflections
$\theta = 2.4$–26.7°
$\mu = 1.92$ mm^{-1}
$T = 298 (2)$ K
Block, blue
0.16 × 0.15 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.748$, $T_{max} = 0.802$
12153 measured reflections
3431 independent reflections

3175 reflections with $I > 2\sigma(I)$
$R_{int} = 0.036$
$\theta_{max} = 27.5°$
$h = -13 \rightarrow 13$
$k = -15 \rightarrow 15$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.095$
$S = 1.10$
3431 reflections
199 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0484P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.66$ e Å^{-3}
$\Delta\rho_{min} = -0.37$ e Å^{-3}
Absolute structure: Flack (1983), with 1602 Friedel pairs
Flack parameter: 0.023 (16)

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.932 (3)	Cu1—S1^{i}	2.7923 (12)
Cu1—N3	1.944 (3)	N1—C7	1.274 (5)
Cu1—N1	1.952 (3)	N1—C8	1.456 (4)
Cu1—N2	2.030 (3)		
O1—Cu1—N3	92.23 (14)	N1—Cu1—N2	81.92 (13)
O1—Cu1—N1	91.68 (12)	O1—Cu1—S1^{i}	103.69 (10)
N3—Cu1—N1	176.00 (14)	N3—Cu1—S1^{i}	88.35 (10)
O1—Cu1—N2	159.93 (13)	N1—Cu1—S1^{i}	91.48 (9)
N3—Cu1—N2	94.12 (14)	N2—Cu1—S1^{i}	95.51 (9)

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

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 $U_{iso}(H) = 1.2U_{eq}(C)$.

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: AV1260). Services for accessing these data are described at the back of the journal.

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