

catena-Poly[[*trans*-dichloro-copper(II)]- μ -1,4,7,10,13,16-hexathia-cyclooctadecane- $S^1:S^{10}$]

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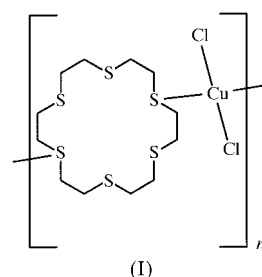
In the title complex, $[\text{CuCl}_2(\text{C}_{12}\text{H}_{24}\text{S}_6)]_n$, the CuCl_2 unit and the ligand lie on and about inversion centres, respectively. The coordination geometry at Cu^{II} is a tetragonally elongated octahedron with the equatorial positions occupied by two chlorides, $\text{Cu}-\text{Cl}$ 2.2786 (12) Å, and two S donors, $\text{Cu}-\text{S}$ 2.3710 (13) Å. The apical positions of the octahedron are defined by two S donors at distances of 2.8261 (14) Å from the metal. The macrocyclic ligand adopts a very puckered and distorted conformation. Eight of the 18 torsion angles are less than 90° and all S-donors are oriented *exo* to the ring.

Comment

Over the last decade, the coordination chemistry of cyclic thioether ligands has assumed great interest as a consequence

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of the observation that they can bind a wide range of soft second and third row transition metal ions, forming stable metal complexes in many of which the metal centre is forced to adopt unusual coordination geometries or oxidation states (Blake & Schröder, 1990). As free ligands, thioether macrocycles tend to adopt conformations in which the lone pairs on the S donors are in exodentate positions – pointing out of the ring cavity – and the number of *gauche* placements of the C–S bonds is maximized (Wolf *et al.*, 1987). For an in-cavity coordination, a reorganisational energy needs to be expended; this accounts for the diminished thermodynamic macrocyclic effect observed for some thioether crowns compared with their open-chain analogues. Generally, long reflux periods are necessary to facilitate these conformational changes. However, a few examples are known in which the thioether



donors bind *exo* to the ring, allowing bridging between two metal centres. Crystal structure determinations on $[\text{CuCl}_2([\text{12}]aneS_3)]$, $[(\text{NbCl}_5)_2([\text{14}]aneS_4)]$, $[\text{ReBr}(\text{CO})_3([\text{15}]aneS_5)]$ and $[(\text{HgCl}_2)_2([\text{14}]aneS_4)]$, where $[\text{12}]aneS_3$ is 1,5,9-trithiacyclododecane, $[\text{14}]aneS_4$ is 1,4,8,11-tetrathia-cyclo-tetradecane and $[\text{15}]aneS_5$ is 1,4,7,10,13-pentathia-cyclopenta-decane (Blake & Schröder, 1990), clearly exemplify this aspect of the coordination chemistry of thioether crowns and support the general observation that the kinetic product involves *exo* coordination of the thioether donors to the metal centre. We report herein the X-ray crystal structure of the polymeric complex $[\text{CuCl}_2([\text{18}]aneS_6)]_\infty$, (I), obtained by reacting $[\text{18}]aneS_6$ and CuCl_2 in $\text{MeCN}/\text{CH}_2\text{Cl}_2$ at room temperature ($[\text{18}]aneS_6$ is 1,4,7,10,13,16-hexathia-cyclooctadecane).

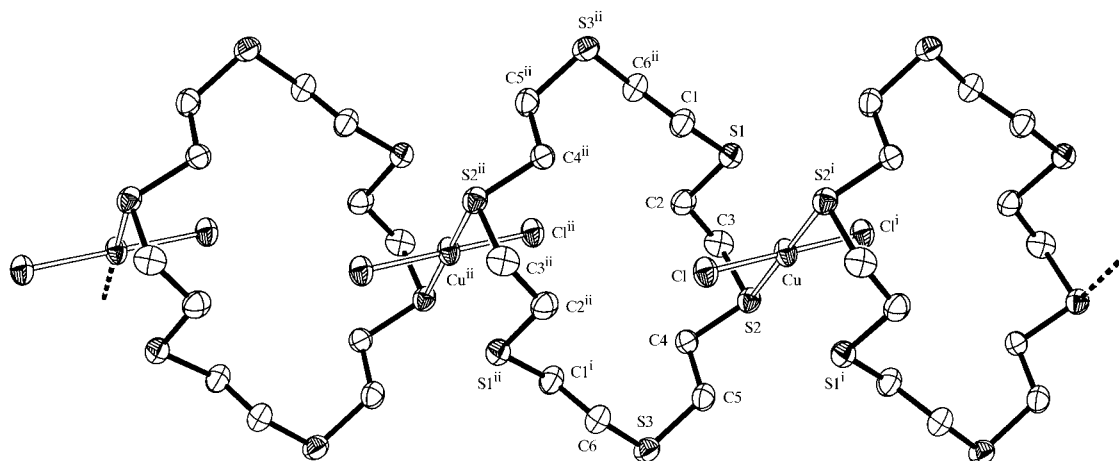


Figure 1

A view of (I) showing the atom-numbering scheme and 50% probability displacement ellipsoids. H atoms have been omitted for clarity, as have the long $\text{Cu}\cdots\text{S}$ axial contacts. The one-dimensional polymer, part of which is shown here, runs parallel to the *c* axis. [Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $1-x, 1-y, 2-z$.]

In the title compound, CuCl_2 units alternate with $[\text{18}]_{\text{aneS}}\text{S}_6$ ligand molecules to form infinite polymeric chains which run along the $[001]$ direction (see Fig. 1). The CuCl_2 units lie on, while the ligand molecules are disposed about, inversion centres: both therefore have crystallographically imposed C_i symmetry. The coordination geometry around the Cu^{II} metal centre can be viewed as a tetragonally distorted octahedron with the equatorial positions occupied by two *trans*-symmetry-equivalent chlorides, $\text{Cu}-\text{Cl}$ 2.2786 (12) Å, and two *trans*-symmetry-equivalent S donors, $\text{Cu}-\text{S}$ 2.3710 (13) Å, from two symmetry-related macrocyclic ligands. Another two symmetry-equivalent S donors from the same molecules of $[\text{18}]_{\text{aneS}}\text{S}_6$ occupy the apical positions of the octahedron with long-range $\text{Cu}-\text{S}$ distances of 2.8261 (14) Å. The macrocyclic ligand adopts a very puckered and distorted conformation. Eight torsion angles are less than 90° and all S-donors are *exo*-oriented with respect to the ring cavity.

It is noteworthy that the complex $[\text{Cu}([\text{18}]_{\text{aneS}}\text{S}_6)](\text{picrate})_2$, obtained by reacting the thioether ligand with copper(II) picrate at 323 K, is monomeric and the metal centre is disposed within the ring cavity of the ligand and coordinated to all six S donors in a tetragonally distorted octahedral geometry (Hartman & Cooper, 1986). In the case of the title compound, the very mild experimental conditions used in the synthesis appear to have prevented the macrocyclic ligand from encapsulating the metal centre by displacement of the two chloride ions, resulting in the preferential formation of the kinetic product with out-of-cavity coordination instead of the thermodynamic one with in-cavity coordination.

Experimental

A mixture of $[\text{18}]_{\text{aneS}}\text{S}_6$ (50 mg, 0.139 mmol) and CuCl_2 (18.95 mg, 0.139 mmol) in $\text{MeCN}/\text{CH}_2\text{Cl}_2$ (30 ml, 1:1 *v/v*) was stirred at room temperature for 3 h. A dark-green solid was formed and collected by filtration. Diffusion of Et_2O vapour into a solution of the green solid in *N,N'*-dimethylformamide gave deep-green crystals (66 mg, 95.7% yield, m.p. 415–417 K) suitable for X-ray diffraction studies. Found (calculated for $\text{C}_{12}\text{H}_{24}\text{Cl}_2\text{CuS}_6$, %): C 28.75 (29.12), H 4.45 (4.89). FAB mass spectrum (3-NOBA matrix): found, *m/z* 460; calculated for $[\text{CuCl}([\text{18}]_{\text{aneS}}\text{S}_6)]^+$, 460. IR spectrum (KBr pellet): ν (cm^{-1}) 2968 (*m*), 2923 (*m*), 1427 (*s*), 1408 (*s*), 1267 (*m*), 1203 (*m*), 924 (*w*), 849 (*w*), 830 (*w*), 694 (*w*).

Table 1
Selected geometric parameters (Å, °).

$\text{Cu}-\text{Cl}$	2.2786 (12)	$\text{Cu}-\text{S1}$	2.8261 (14)
$\text{Cu}-\text{S2}$	2.3710 (13)		
$\text{Cl}-\text{Cu}-\text{S2}$	95.28 (4)	$\text{Cl}-\text{Cu}-\text{S1}$	91.93 (4)
$\text{Cl}^{\text{i}}-\text{Cu}-\text{S2}$	84.72 (4)	$\text{S2}-\text{Cu}-\text{S1}$	84.16 (4)
$\text{S1}-\text{C2}-\text{C3}-\text{S2}$	75.1 (4)	$\text{C5}-\text{S3}-\text{C6}-\text{C1}^{\text{ii}}$	91.6 (4)
$\text{C2}-\text{C3}-\text{S2}-\text{C4}$	71.6 (4)	$\text{S3}^{\text{ii}}-\text{C6}^{\text{ii}}-\text{C1}-\text{S1}$	-176.5 (3)
$\text{C3}-\text{S2}-\text{C4}-\text{C5}$	175.9 (4)	$\text{C6}^{\text{ii}}-\text{C1}-\text{S1}-\text{C2}$	-63.3 (5)
$\text{S2}-\text{C4}-\text{C5}-\text{S3}$	-170.6 (3)	$\text{C1}-\text{S1}-\text{C2}-\text{C3}$	-161.8 (4)
$\text{C4}-\text{C5}-\text{S3}-\text{C6}$	-72.5 (4)		

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $1-x, 1-y, 2-z$.

Crystal data

$[\text{CuCl}_2(\text{C}_{12}\text{H}_{24}\text{S}_6)]$
 $M_r = 495.18$
 Monoclinic, $P2_1/c$
 $a = 8.9499$ (9) Å
 $b = 14.500$ (2) Å
 $c = 7.7348$ (11) Å
 $\beta = 101.630$ (10) $^\circ$
 $V = 983.2$ (2) Å 3
 $Z = 2$

$D_x = 1.672$ Mg m $^{-3}$
 Cu $K\alpha$ radiation
 Cell parameters from 46 reflections
 $\theta = 20-22^\circ$
 $\mu = 9.940$ mm $^{-1}$
 $T = 220$ (2) K
 Plate, brown
 $0.23 \times 0.12 \times 0.04$ mm

Data collection

Stoe Stadi-4 four-circle diffractometer
 ω/θ scans with on-line profile fitting (Clegg, 1981)
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\text{min}} = 0.336$, $T_{\text{max}} = 0.672$
 1518 measured reflections
 1255 independent reflections

1047 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.032$
 $\theta_{\text{max}} = 60.14^\circ$
 $h = -8 \rightarrow 10$
 $k = -16 \rightarrow 14$
 $l = -8 \rightarrow 8$
 3 standard reflections
 frequency: 60 min
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.107$
 $S = 1.03$
 1251 reflections
 97 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.054P)^2 + 1.712P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.002$
 $\Delta\rho_{\text{max}} = 0.44$ e Å $^{-3}$
 $\Delta\rho_{\text{min}} = -0.44$ e Å $^{-3}$

The presence of the low-temperature device (Cosier & Glazer, 1986) imposed an upper limit on θ of 60° during data collection. Furthermore, the ω circle obscured a number of reflections in the range $47 < \theta < 60^\circ$.

Data collection: *STADIA* (Stoe & Cie, 1997); cell refinement: *STADIA*; data reduction: *X-RED* (Stoe & Cie, 1997); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1994); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2000).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1153). Services for accessing these data are described at the back of the journal.

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