Dichloro[2,2'-(methylenedithio)bi-1,3-thiazole-$\kappa^2 N,N'$]cobalt(II)

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.036
wR factor = 0.090
Data-to-parameter ratio = 18.9

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

In the title complex, [CoCl$_2$(C$_7$H$_6$N$_2$S$_4$)], 2,2'-(methylenedithio)bi-1,3-thiazole acts as a bidentate ligand and chelates one Co^{II} ion through the two N atoms to give an eight-membered symmetric unit. The Co^{II} ion is located on a twofold axis and displays a slightly distorted tetrahedral coordination environment, where the two Cl$^-$ anions occupy the remaining coordination sites. The N—Co—N and Cl—Co—Cl planes are nearly perpendicular, with a dihedral angle of 88.0 (3)°.

Comment

In recent years, a wide variety of fascinating structures generated by thioether ligands and transition metal ions have been obtained and some of them have been reported to exhibit interesting properties; examples are a neutral nanometre-sized cubic cage (Hong *et al.*, 2000) and semiconductivity (Su *et al.*, 2000). Heterocyclic thioether ligands containing flexible or rigid bridging spacers are widely used in constructing coordination frameworks, which yield many metal–organic polymers with structures ranging from one- to three-dimensional (Zou *et al.*, 2004; Zheng *et al.*, 2003; Bu *et al.*, 2003, 2002; Wei *et al.*, 2003; Xie & Bu, 2003; Song *et al.*, 2003; Liao *et al.*, 2002). However, among these polymers the metal ions are mainly restricted to the Ag^{I} ion (Liu *et al.*, 2005), with only limited examples for other transition metal ions (Addison *et al.*, 1984; Xie *et al.*, 2004). In contrast, as the activities of many enzymes rely on the interactions of the thiazole or imidazole group with certain metal ions (Kaim & Schwederski, 1994), the coordination behaviour of thiazole and its derivatives has been widely investigated (Liu & Xu, 2004; Liu *et al.*, 2001; Tian *et al.*, 1996). In this paper, a new bisthiazolyl thioether ligand, 2,2'-(methylenedithio)bi-1,3-thiazole (DTM), has been synthesized and the structure of its cobalt complex, (I), is presented.

(I)
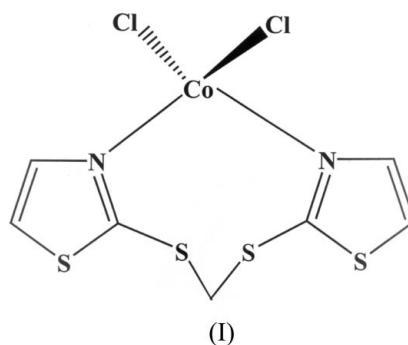
In the structure of (I), the Co^{II} ion is in a tetrahedral coordination geometry, consisting of two Cl$^-$ anions and two
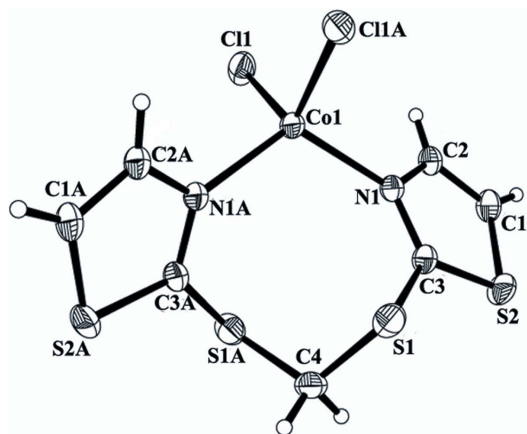
Figure 1
The molecular structure of (I), showing 30% probability displacement ellipsoids. The suffix A corresponds to symmetry code i in Table 1.
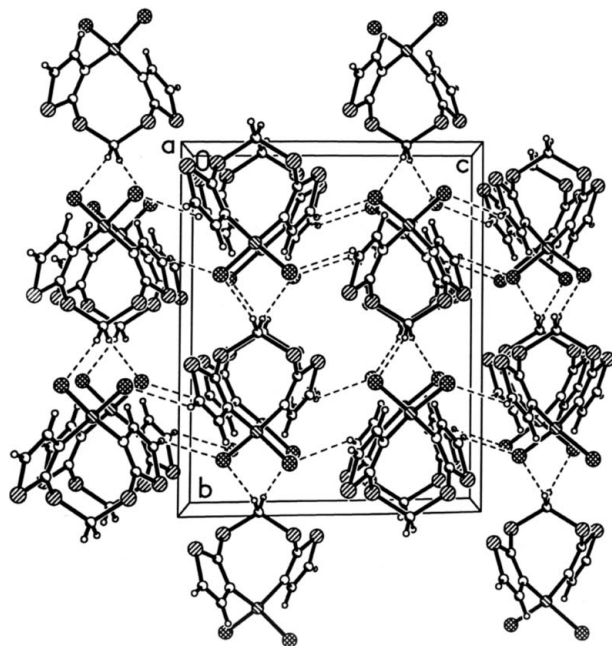

Figure 2
A packing diagram for (I), viewed down the *a* axis. Dashed lines represent intermolecular C—H···Cl hydrogen bonds.

thiazolyl N atoms. Each DTM ligand chelates one Co^{II} ion through two N atoms, forming an eight-membered centro-symmetric mononuclear unit (Fig. 1). In this eight-membered unit, the Co^{II} and C4 atoms lie on a twofold rotation axis and the distance between them is 4.110 (3) Å. Atoms Co1, C4, N1 and N1^i [symmetry code: (i) $-x, y, -z + \frac{3}{2}$] are coplanar, with atoms S1 and C3 deviating by 1.366 (4) and 0.511 (4) Å from this plane. The two thiazole rings form a dihedral angle of 50.1 (4)°.

The two Cl$^-$ anions are situated *syn* with respect to the eight-membered mononuclear unit. The dihedral angle between the N1—Co1—N1^i and Cl1—Co1—Cl1^i planes is 88.0 (3)°. The bond distances of Co—Cl [2.247 (1) Å] and Co—N [2.037 (2) Å] are close to those reported for the four-coordinated thiazole complex [Co(2-at)$_2$Cl$_2$], where 2-at is 2-aminothiazole [2.261 (2) and 2.010 (5) Å; Raper *et al.*, 1981],

but are evidently shorter than those for Co—Cl [2.499 (1) and 2.500 (1) Å] and Co—N [range 2.128 (3)–2.188 (3) Å] found in the six-coordinated bisthiazole complex [Co(DABT)$_2$Cl$_2$] (Liu *et al.*, 2003), due to the larger number of coordinated atoms.

In the crystal packing of (I), each Cl atom acts as a double H-atom acceptor, forming intermolecular C—H···Cl hydrogen bonds with atoms C4 and C1 (Table 2). These interactions connect the molecules into a three-dimensional network.

Experimental

Crystal data

[CoCl$_2$(C$_7$H$_6$N$_2$S$_4$)]	$Z = 4$
$M_r = 376.21$	$D_x = 1.839$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 7.026$ (2) Å	$\mu = 2.24$ mm^{-1}
$b = 15.408$ (5) Å	$T = 293$ (2) K
$c = 12.624$ (4) Å	Block, blue
$\beta = 96.146$ (5)°	$0.22 \times 0.14 \times 0.10$ mm
$V = 1358.8$ (7) Å^3	

Data collection

Bruker SMART CCD area-detector diffractometer	3860 measured reflections
φ and ω scans	1395 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	1080 reflections with $I > 2\sigma(I)$
$T_{min} = 0.607$, $T_{max} = 0.799$	$R_{int} = 0.086$
	$\theta_{max} = 26.4°$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.036$	$w = 1/[\sigma^2(F_o^2) + (0.0404P)^2]$
$wR(F^2) = 0.090$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{max} = 0.001$
1395 reflections	$\Delta\rho_{max} = 0.49$ e Å^{-3}
74 parameters	$\Delta\rho_{min} = -0.49$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co1—N1	2.037 (2)	S2—C1	1.703 (3)
Co1—Cl1	2.247 (1)	S2—C3	1.711 (3)
S1—C3	1.748 (3)	N1—C3	1.318 (4)
S1—C4	1.812 (2)	N1—C2	1.375 (4)
N1^i—Co1—N1	117.11 (13)	N1—Co1—Cl1	104.90 (7)
N1^i—Co1—Cl1	107.88 (8)	Cl1^i—Co1—Cl1	114.53 (6)

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4A···Cl1[ii]	0.97	2.64	3.560 (3)	158
C4—H4B···Cl1[iii]	0.97	2.64	3.560 (3)	158
C1—H1···Cl1[iv]	0.93	2.89	3.509 (3)	125

Symmetry codes: (ii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (iii) $x - \frac{1}{2}, y + \frac{1}{2}, z$; (iv) $x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$.

H atoms were placed in calculated positions (C—H = 0.93–0.97 Å) and allowed to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$.

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

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