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Dichlorobis(1-propylimidazolidine-2-thione-κS)cobalt(II)

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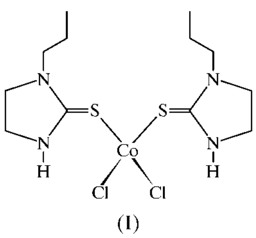
The crystal structure of the title compound, [$CoCl_2(C_6H_{12}N_2S)_2$], consists of monomer units of a Co^{II} atom coordinated to two 1-propylimidazolidine-2-thione ligands and to two chloride ions. The heterocyclic thione ligand is monodentate and coordinated to the metal through the thione S atom. The environment around the Co^{II} atom is a slightly distorted tetrahedron. The Co—S bond lengths are 2.341 (2) and 2.330 (2) Å, and the Co—Cl bond lengths are 2.234 (2) and 2.238 (2) Å. The most important point of distortion is the S—Co—S bond angle of only 97.83 (8)°. Intramolecular classical hydrogen bonds are found between the chloride ions and the N—H groups. Additionally, intra- and intermolecular non-classical hydrogen bonds are found.

Comment

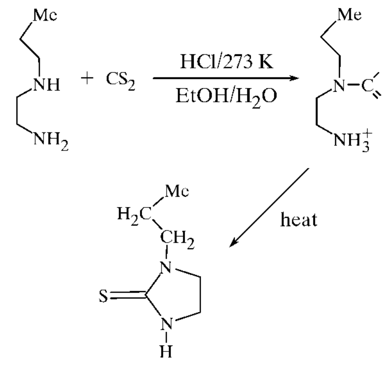
Heterocyclic thiones, and especially heterocyclic molecules containing the thioamide group, –C(S)—NH–, form a class of coordination compounds which are interesting because of the thione–thiol equilibrium, and the study of this equilibrium has been one of our objectives (García-Vázquez *et al.*, 1999). In addition, these compounds have a wide range of applications as analytical reagents, metal corrosion inhibitors and in the pharmaceutical field (Hussain *et al.*, 1990).



(I)

Furthermore, heterocyclic thione complexes of cobalt have been used to analyse the redox properties of the metal, studies which could be relevant to understanding the interaction of the cobalt ion with DNA (Tran Qui & Bagieu, 1990), but there have been relatively few reports of its complexation behaviour with this type of ligand.

We therefore synthesized a cobalt(II) complex incorporating a heterocyclic thionate ligand, namely dichlorobis(1-propylimidazolidine-2-thione-κS)cobalt(II), (I), the structure of which consists of monomeric units, although weak interactions between molecules through non-classical hydrogen bonds are found (Table 2). The heterocyclic thione ligand is monodentate and bonded to the metal through the S atom (Fig. 1). The environment around the Co^{II} atom is that of a slightly distorted tetrahedron, where the dihedral angle between the $CoCl_2$ and CoS_2 moieties is 88.35 (6)°. The main point of distortion is the S—Co—S angle of only 97.83 (8)°, which deviates greatly from the ideal tetrahedral value (within experimental error) seen for Cl—Co—Cl in (I). Intramolecular hydrogen bonds between the N—H groups and the Cl atoms are also found (see Table 2), where the two amine H atoms coordinate to different Cl atoms (clinal geometry, see below). Hence, the dihedral angle between the mean planes of the two five-membered rings in (I) is 52.5 (2)°.



(II)

Looking to explain the value of the S—Co—S angle, a search was made for $CoCl_2S_2$ complexes in the Cambridge Structural Database (CSD; Version 5.22 of October 2001; Allen & Kennard, 1993), which returned only 9 hits and 7 compounds, one being trinuclear and therefore not considered

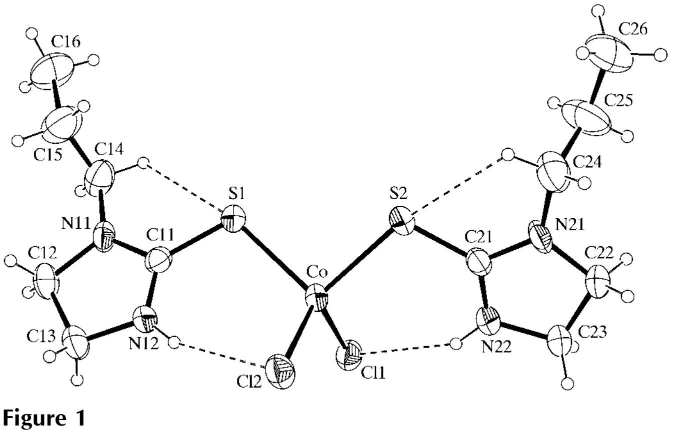


Figure 1
The asymmetric unit of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented by circles of arbitrary radii.

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further. There are three thiourea derivatives; one of them, dichlorobis(*N,N*′-di-*o*-tolylthiourea-*S*)cobalt(II) (Prisyazhnyuk *et al.*, 1986), has a very distorted tetrahedral core, with a Cl—Co—Cl angle close to 120° and an S—Co—S angle close to 111°. The remaining thiourea (Hall & Horrocks, 1969; Domiano & Tiripicchio, 1972) and *N,N*′-diethylthiourea (Bonamico *et al.*, 1973; Abbati *et al.*, 1999) derivatives both appear twice and both compounds are geometrically similar to (I). Hydrogen bonds are also found in these two compounds. It is noteworthy that there are two possibilities for intramolecular interactions involving the Cl atoms. The first is a periplanar geometry, where the two amine H atoms coordinate to the same Cl atom, and the second is a clinal geometry, where the two amine H atoms coordinate to different Cl atoms. It is interesting to note that both geometries are found in dichlorobis(*N,N*′-diethylthiourea)cobalt(II), as there are two molecules in the asymmetric unit (Abbati *et al.*, 1999). Still, the geometrical parameters around the Co atom are quite similar, the S—Co—S angles being 97.27 (5) and 98.57 (4)°, respectively.

In the other three compounds found in the CSD search, the S atom is connected to a ring and, in two of them, connects to a five-membered ring, as in (I). In the first of the latter two compounds, dinuclear bis{[*μ*-*N,N*′-ethylenebis(pyrrolidine-2-thione-*S,S*′)]dichlorocobalt(II)} (Atherton *et al.*, 1998), the dithione ligands bridge the two Co^{II} atoms and the larger S—Co—S angle of 121.38 (8)° can be understood as being a result of this bridging. The second compound, dichlorobis(2-mercaptobenzimidazole)cobalt(II) (Ravikumar *et al.*, 1995), is the most chemically similar to (I), and both display a clinal geometry. Still, the S—Co—S angle is 108.9 (1)° compared with the value of 97.38 (8)° in (I). Classical intramolecular hydrogen bonds between the amine H and the Cl atoms are found in both complexes, but the *N*-propyl groups in (I) prevent the occurrence of intermolecular hydrogen bonds and this is probably one of the reasons for the differences found between the two complexes.

The hybridization of the S atom has been discussed extensively by Raper & Nowell (1979) on the basis of the Co—S—C angle and the dihedral angle between the Co—S—C plane and the mean plane of the ligand. When the Co—S—C angle is close to 104°, an sp^3 hybridization is proposed, and values of about 108–110° are consistent with an sp^2 character. The corresponding values in (I), 106.7 (2) and 107.1 (3)°, do not allow us to distinguish between the two possibilities. The dihedral angles between the Co—S—C and SC(N)$_2$ planes found in (I) are 15.2 (3) and 10.2 (3)°, which are consistent with sp^2 hybridization.

Furthermore, the ring bond lengths are consistent with a considerable delocalization of the charge in the SC(N)$_2$ moiety, with the values for the C—N bond [average 1.318 (8) Å] being shorter than that expected for a single bond (Allen *et al.*, 1987). The C—S bonds [average 1.696 (7) Å] are only slightly longer than in the uncoordinated *N,N*′-dimethyl-1,3-imidazolidine-2-thione ligand [1.673 (5) Å; Chieh & Cheung, 1983], suggesting that the ligand is coordinated in the thione rather than the thionate form. The Co—S distances of 2.330 (2) and 2.341 (2) Å are slightly longer than in other complexes where a thionate form is suggested (Raper & Nowell, 1979). The Co—Cl bond lengths agree with the corresponding lengths of other tetrahedral cobalt(II) complexes (Tran Qui & Bagieu, 1990; Abbati *et al.*, 1999).

The geometrical parameters found in dichlorobis(2-mercaptobenzimidazole)cobalt(II) (Ravikumar *et al.*, 1995) are also consistent with a thione rather than a thionate form [C—S bond lengths of 1.701 (6) and 1.724 (7) Å, and Co—S—C bond angles of 105.6 (2) and 108.4 (2)°]. The C—S bond lengths found in dichlorobis(*N,N*′-diethylthiourea)cobalt(II) (Abbati *et al.*, 1999) are longer, whereas the average S—Co—S angle is 97.92 (5)°, similar to that found in (I). Hence, the value of the S—Co—S angle does not depend on the *sp* character of the S atom.

Thus, the value of the S—Co—S angle, together with the differences found in the Co—S and Co—Cl bond lengths, is probably a consequence of the different properties of the donor atoms. The Cl- and S-atom covalent radii differ by only 0.03 Å (Huheey *et al.*, 1993). However, the Co—S and Co—Cl bond lengths differ by about 0.1 Å in all the compounds found

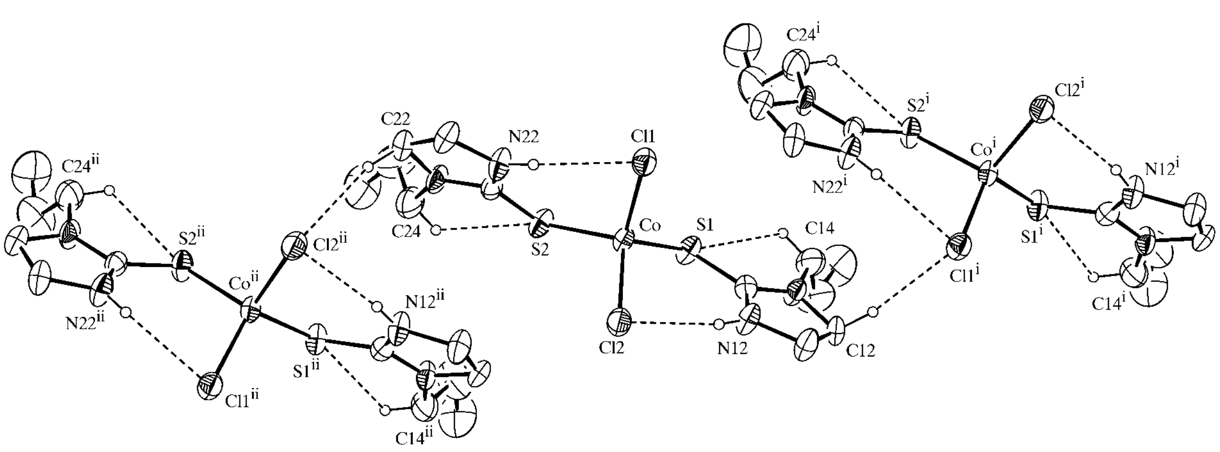

Figure 2
The hydrogen bonding in (I). [Symmetry codes: (i) $x, 2 - y, z - \frac{1}{2}$; (ii) $x, 1 - y, z + \frac{1}{2}$.]

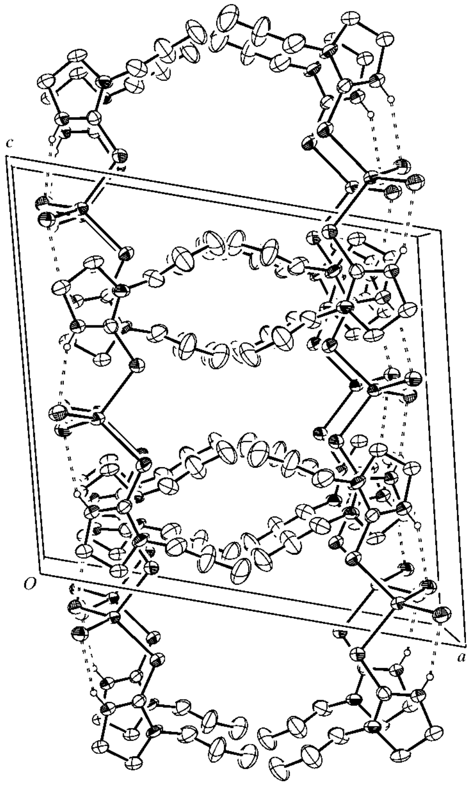

Figure 3
The crystal packing in (I) viewed along the *b* axis.

in the CSD search, except in dichlorobis(2-mercaptobenzimidazole)cobalt(II) (Ravikumar *et al.*, 1995), which again deviates by an average of 0.07 Å (maximum 0.098 Å and minimum 0.037 Å). This, together with the intermolecular hydrogen bonds and the crystal packing, results in the differences found for this compound, where the orientation of the ligands allows similar bond lengths and a regular geometry around the Co^{II} atom. The different orientation present in (I) (Fig. 3) is probably due to the propyl groups and the lack of classical intermolecular hydrogen bonds between the N atom and the Cl atoms of neighbouring molecules.

The thione ligands (excluding the *n*-propyl group) are essentially planar, with a maximum deviation from the least-squares mean planes of 0.053 (5) Å for atom C13. The Co^{II} atom deviates by 0.508 (9) and 0.363 (9) Å from these planes.

Experimental

The ligand 1-propylimidazolidine-2-thione, (II), was prepared and characterized following a modification of the procedure of Allen *et al.* (1959) (see reaction *Scheme* in *Comment*). *N*-Propylethylenediamine (3.64 g, 0.36 mmol) was dissolved in EtOH/H_2O (10 + 10 ml) and cooled in an ice bath. An excess of carbon disulfide (0.6 ml, 9.9 mmol) was added dropwise (0.01 ml min^{-1}) and the temperature raised to 333 K. A second portion of carbon disulfide (3.0 ml, 49.7 mmol) was added dropwise (0.02 ml min^{-1}). When the addition was complete, the temperature was raised to 383 K and reflux continued for 1 h. After this, 0.5 ml of hydrochloric acid was added and reflux continued for a further 10 h. The mixture was cooled and the 2.78 g of solid which was collected was washed with chilled acetone. The solid was identified as 1-propylimidazolidine-2-thione, (II). Elemental analysis, found: C 49.8, H 8.1, N 19.3, S 22.0%; calculated for $C_6H_{12}N_2S$: C 50.0, H 8.4, N 19.4, S 22.2%. Relevant spectroscopic data, IR spectrum (KBr mulls, cm^{-1}): 3192 ν(N—H), 1498 ν(C—N) + δ(N—H), 612 Δ(N—H), 510 ν(C—S); ^{1}H NMR (300 MHz, $CDCl_3$, p.p.m.): δ 6.57 (*bs*, 3H, N—H), 3.65–3.44 (*m*, 8H, CH_2), 1.65 (*m*, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, p.p.m.): δ 183.6, 48.9, 48.8, 41.8, 20.81, 11.5. For the preparation of (I), $CoCl_2$ hexahydrate (2 g, 8.4 mmol) was dried with refluxing Cl_2SO. After 2 h, the excess Cl_2SO was removed under vacuum. After this, all further reactions were carried out under an argon atmosphere. Anhydrous $CoCl_2$ (0.13 g, 1.0 mmol) was dissolved in 20 ml of dry MeOH and an excess of 1-propylimidazolidine-2-thione (0.43 g, 3.0 mmol) was added. After 12 h of reaction, the MeOH was removed under vacuum and the oily product obtained was recrystallized from toluene. Elemental analysis, found: C 35.3, H 5.7, N 13.6, S 15.6%; calculated for $C_{12}H_{24}Cl_2CoN_4S_2$: C 34.5, H 5.8, N 13.4, S 15.3%.

Crystal data

$[CoCl_2(C_6H_{12}N_2S)_2]$
$M_r = 418.30$
Monoclinic, $P2/c$
$a = 15.684$ (4) Å
$b = 8.640$ (2) Å
$c = 14.916$ (4) Å
$\beta = 104.528$ (5)°
$V = 1956.7$ (9) Å^3
$Z = 4$

$D_x = 1.420$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 926 reflections
$\theta = 2.7$–24.0°
$\mu = 1.36$ mm^{-1}
$T = 293$ (2) K
Prism, blue
0.39 × 0.20 × 0.09 mm

Data collection

Bruker SMART 1000 CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.619$, $T_{max} = 0.887$
11 320 measured reflections

4015 independent reflections
1464 reflections with $I > 2\sigma(I)$
$R_{int} = 0.092$
$\theta_{max} = 26.4°$
$h = -19 \rightarrow 18$
$k = -8 \rightarrow 10$
$l = -18 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.173$
$S = 0.86$
4015 reflections
192 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0728P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.47$ e Å^{-3}
$\Delta\rho_{min} = -0.43$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co—Cl1	2.234 (2)	N11—C14	1.454 (9)
Co—Cl2	2.238 (2)	N12—C11	1.319 (8)
Co—S1	2.341 (2)	N12—C13	1.464 (8)
Co—S2	2.330 (2)	N21—C21	1.329 (8)
S1—C11	1.696 (7)	N21—C22	1.458 (9)
S2—C21	1.697 (7)	N21—C24	1.462 (9)
N11—C11	1.318 (8)	N22—C21	1.306 (8)
N11—C12	1.464 (9)	N22—C23	1.441 (8)
Cl1—Co—Cl2	109.59 (9)	Cl2—Co—S1	110.99 (8)
Cl1—Co—S2	111.34 (8)	S2—Co—S1	97.83 (8)
Cl2—Co—S2	113.67 (8)	C11—S1—Co	106.7 (2)
Cl1—Co—S1	113.07 (8)	C21—S2—Co	107.1 (3)
N11—C14—C15—C16	−173.0 (8)	N21—C24—C25—C26	−172.0 (8)

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

D—H···A	D—H	H···A	D···A	D—H···A
N12—H12···Cl2	0.86	2.39	3.217 (6)	160
N22—H22···Cl1	0.86	2.50	3.291 (6)	154
C14—H14A···S1	0.97	2.69	3.163 (8)	110
C24—H24A···S2	0.97	2.67	3.148 (9)	111
C12—H12A···Cl1^{i}	0.97	2.68	3.618 (8)	161
C22—H22A···Cl2^{ii}	0.97	2.80	3.729 (8)	160

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

H atoms of CH_2 and CH_3 groups were placed in calculated positions and refined using a riding model (C—H = 0.97 and 0.96 Å, and 1.00 Å for CH_3 groups C15 and C16) and U_{iso} values were set at $1.2U_{eq}$ and $1.5U_{eq}$, respectively, of the C atoms to which they are attached. The H atoms of the N—H groups were also placed in calculated positions and refined with a riding model (N—H = 0.86 Å) and U_{iso} values were set at $1.2U_{eq}$ of the N atoms to which they are attached.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1998); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR1016). Services for accessing these data are described at the back of the journal.

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