

Table 3. *The least-squares plane through the S₂CNC₂ ligand section and atomic deviations (Å) expressed in orthogonal space*

Equation $0.2345X + 0.4084Y - 0.8821Z = -3.2385$

S(1)	0.006 (2)	N(1)	-0.022 (6)	Ni	0.137 (1)
S(2)	-0.002 (2)	C(2)	0.012 (9)	C(3)	-1.313 (10)
C(1)	0.003 (8)	C(5)	0.002 (8)	C(6)	1.428 (9)

As shown in Table 3, the S₂CNC₂ fragment of the ligand is substantially planar and conforms to the *mm* symmetry usually found in derivatives in which the ligand is symmetrically bidentate. The Ni atom is somewhat out of the ligand plane as a consequence of the folding of the ligand about the line through the two S atoms. However, the deviation of the metal atom from the ligand plane is much larger in some other dithiocarbamates (Kettmann, Garaj & Kúdela, 1978), and thus may be a measure of the steric crowding due to packing. This is also reflected in packing distances (Table 4) especially S...C which are rather elongated compared with those in most other dithiocarbamates.

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The Structure of Bis(2-aminothiazole)dichlorocobalt(II)

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Abstract. [Co(C₃H₄N₂S)₂Cl₂], C₆H₈Cl₂CoN₄S₂, orthorhombic, *M_r* = 330.13, *Pba*2, *a* = 11.528 (7), *b* = 7.818 (6), *c* = 6.639 (7) Å, *U* = 598.3 Å³, Mo *K*α, λ = 0.71069 Å, *Z* = 2, *D_m* = 1.81 (4), *D_c* = 1.82 Mg m⁻³, μ(Mo *K*α) = 2.09 mm⁻¹, *F*(000) = 326. Final *R* = 0.058 for 879 reflections. The Co atom lies on a twofold axis and is tetrahedrally coordinated to the Cl

atoms (Co–Cl 2.261 Å) and to the heterocyclic N atoms in the thiazole rings (Co–N 2.010 Å). The amino groups of the ligands form both intra- and intermolecular hydrogen bonds to the Cl atoms.

Introduction. The reaction between Co^{II} halides and 2-aminothiazole (2-amt) produces pseudo-tetrahedral

Table 4. *Shortest packing distances (<4.0 Å)*

E.s.d.'s are 0.01 Å.

S(1)···C(2) ^I	3.92	C(2)···C(6) ^{II}	3.73
S(2)···C(4) ^I	3.93	C(2)···C(7) ^{II}	3.64
S(2)···C(7) ^{II}	3.99	C(3)···C(6) ^{II}	3.94
C(1)···C(4) ^I	3.94	C(4)···C(5) ^{III}	3.93
C(1)···C(2) ^I	3.96	C(4)···C(7) ^{IV}	3.57

Symmetry code

(I)	$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$	(III)	$-x, -y, 1 - z$
(II)	$\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$	(IV)	$-\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$

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complexes of stoichiometry $[\text{Co}(2\text{-amt})_2X_2]$ ($X = \text{Cl}, \text{Br}$ and I) (Duff, Hughes & Rutt, 1972). Electronic spectra are indicative of Co–N rather than Co–S contacts for these complexes. There are, however, two types of N atom in the ligand which are capable of coordinating to Co^{II} . The distinction between amino N and heterocyclic N bonding to metals is difficult to make on the basis of $\nu(\text{Co}-\text{N})$ absorptions and a further complication is the fact that the amino $\nu(\text{N}-\text{H})$ absorptions show significant differences between the free and the complexed ligand. Such differences could be a result of either coordination or the formation of $\text{N}-\text{H}\cdots\text{Cl}$ contacts (Svatos, Curran & Quagliano, 1955).

This X-ray study has been undertaken in order to determine the coordination geometry of $[\text{Co}(2\text{-amt})\text{Cl}_2]$.

Blue crystals of $[\text{Co}(2\text{-amt})_2\text{Cl}_2]$ were prepared by a previously described method (Duff *et al.*, 1972). A crystal $0.25 \times 0.50 \times 0.62$ mm was mounted with c coincident with the rotation (ω) axis of a Stoe Stadi-2 two-circle diffractometer. Intensities were measured with monochromated $\text{Mo } K\alpha$ radiation and the background- ω -scan-background technique; 915 unique reflections were recorded of which 879 had $I > \sigma(I)$ and were considered to be observed. [The net intensity $I = T - B$, where $T = \text{scan count}$, $B = \text{mean background count over scan width}$; $\sigma(I) = (T + Bc/2t)^{1/2}$, where $c = \text{scan time}$, $t = \text{time for background measurement at each end of the scan}$.] Corrections for Lorentz, polarization and absorption effects were made.

Systematic absences do not distinguish between *Pba2* and *Pbam*. Subsequent analysis confirmed *Pba2* as correct with Co atoms lying on a twofold axis parallel to c . The Co atom was fixed at $0, \frac{1}{2}, 0$, and the remaining atoms were found from successive electron density maps. Scattering factors were calculated with an analytical approximation (*International Tables for X-ray Crystallography*, 1974). All H atoms were

located but their positions were not refined. Common isotropic temperature factors were applied to the amino and ethylenic H atoms and refined to final U values of 0.39 (2) and 0.38 (3) \AA^2 respectively. Full-matrix least-squares refinement gave a final $R = 0.058$. The weighting scheme was $w = 0.0036/[\sigma^2 F_o + 2.4127 \times$

Table 2. Bonding and non-bonding distances (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses

Symmetry code: None x, y, z ; (i) $\bar{x}, \bar{y}, \bar{z}$; (ii) $\frac{1}{2} - x, \frac{1}{2} + y, z$; (iii) $\frac{1}{2} + x, \frac{1}{2} - y, z$.

The coordination sphere

Co–Cl	2.261 (2)	N(3)–Co–Cl	110.1 (5)
Co–N(3)	2.010 (5)	Cl–Co–Cl ⁱ	111.9 (3)
Cl–N(3)	3.505 (4)	N(3)–Co–N(3) ^j	107.9 (7)
Cl–Cl ⁱ	3.748 (5)	Cl–Co–N(3) ^j	108.3 (6)
N(3)–N(3) ^j	3.251 (5)	Co–N(3)–C(2)	123.7 (5)
		Co–N(3)–C(4)	124.4 (5)

The ligands

S(1)–C(2)	1.713 (8)	C(2)–S(1)–C(5)	90.0 (0.5)
C(2)–N(3)	1.324 (10)	S(1)–C(5)–C(4)	111.6 (0.8)
N(3)–C(4)	1.400 (11)	C(5)–C(4)–N(3)	113.8 (0.8)
C(4)–C(5)	1.328 (14)	C(4)–N(3)–C(2)	111.6 (0.6)
C(5)–S(1)	1.713 (11)	N(3)–C(2)–S(1)	113.0 (0.6)
C(2)–N(2)	1.341 (11)	S(1)–C(2)–N(2)	123.6 (0.7)
N(2)–H(21)	1.006	N(3)–C(2)–N(2)	123.4 (0.7)
N(2)–H(22)	0.984	H(21)–N(2)–H(22)	101.5
C(4)–H(41)	1.198	C(2)–N(2)–H*	123.9
C(5)–H(51)	1.031	H(41)–C(4)–N(3)	105.3
		H(41)–C(4)–C(5)	121.2
		H(51)–C(5)–C(4)	128.6
		H(51)–C(5)–S(1)	119.6

Hydrogen-bonded contacts

N(2)–H(22) \cdots Cl ⁱⁱ	3.560	H \cdots Cl	2.635
N(2)–H(22) \cdots Cl ⁱⁱⁱ	3.375	H \cdots Cl	3.019
N(2)–H(21) \cdots Cl	3.322	H \cdots Cl	2.935

* Average value.

Table 3. Equations of least-squares planes referred to orthogonal axes with distances (\AA) of relevant atoms from the planes in square brackets

E.s.d.'s are given in parentheses.

Plane A: S(1), C(2), N(3), C(4), C(5)

$$-0.0135X + 0.9123Y - 0.4093Z - 3.7939 = 0$$

[S(1), -0.005 (2); C(2), 0.009 (5); N(3), -0.009 (5); C(4) 0.005 (8); C(5), 0.001 (9)]

Plane B: S(1), C(2), N(3), C(5), N(2)

$$-0.0145X + 0.9106Y - 0.4130Z - 3.7939 = 0$$

[S(1), -0.007 (2); C(2), 0.002 (5); N(3), -0.013 (5); C(4), 0.007 (8); C(5), 0.004 (9); N(2), 0.006 (9)]

Plane C: C(2), N(2), H(21), H(22)

$$0.4022X + 0.8450Y - 0.3526Z - 4.7277 = 0$$

[C(2), -0.045 (6); N(2), 0.127 (8); H(21), -0.062 ; H(22), -0.020]

Angle between plane A and plane C: 24.5 (1.5) $^\circ$.

Table 1. Final fractional coordinates ($\times 10^4$)

E.s.d.'s for the non-hydrogen atoms are in parentheses.

	x	y	z	B_{eq}^* (\AA^2)
Co	0	5000	0	3.31 (4)
Cl	231 (2)	7373 (2)	1906 (4)	4.22 (5)
S(1)	3480 (2)	4275 (3)	-2922 (5)	5.29 (7)
N(2)	2748 (6)	5630 (11)	592 (13)	5.15 (21)
N(3)	1391 (4)	4658 (6)	-1781 (9)	3.58 (12)
C(2)	2472 (7)	4932 (6)	-1190 (12)	3.71 (16)
C(4)	1350 (8)	3941 (10)	-3712 (15)	4.66 (21)
C(5)	2388 (9)	3653 (11)	-4512 (16)	5.63 (28)
H(21)	2590	5964	2029	
H(22)	3464	4956	736	
H(41)	628	4746	-4599	
H(51)	2589	3036	-5839	

* Defined according to Willis & Pryor (1975).

(F_o)²]; final positional parameters are listed in Table 1,* bond lengths and angles in Table 2 and mean planes in Table 3.

Discussion. The Co atom is tetrahedrally coordinated to Cl atoms and to the heterocyclic N atoms (Fig. 1); the angles about Co are close to the value for regular tetrahedral geometry, the maximum deviation being 2.5°. The Co–N and Co–Cl distances are within 0.01 Å of those found for related systems (Antti & Lundberg, 1972; Gadet, 1974). The thiazole ring is planar (plane *A*) with a maximum deviation of 0.009 Å [C(2), N(3)]. The exocyclic N atom is effectively coplanar with the thiazole ring (plane *B*) while the Co atom lies 0.23 Å from that plane. The bond lengths and angles within the heterocyclic molecule are in good agreement with those observed for other amino-thiazoles (Form, Raper & Downie, 1974; Mornon & Raveau, 1971). The C(4)–N(3) distance of 1.400 (11) Å is significantly longer than both C(2)–N(3) and C(2)–N(2), 1.324 (10) and 1.341 (11) Å respectively. The similarity of the exocyclic C–N distance to the C(2)–N(3) value suggests that the N(2) p_z electrons are conjugated to the π system of the heterocycle. This effectively eliminates N(2) as a possible donor atom and leaves N(3) with its favourably oriented lone pair of electrons as the preferred donor in the ligand. The amino H and the Cl atoms are involved in a complex network of hydrogen bonding (Fig. 2). The amino group (plane *C*) is twisted by 24.5° with respect to the heterocyclic ring, an arrangement which would appear to facilitate hydrogen bonding. The thiazole rings are oriented with respect to each other in the complex such that the dihedral angle is 48.3 (2.0)°. The N...Cl distances

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35775 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

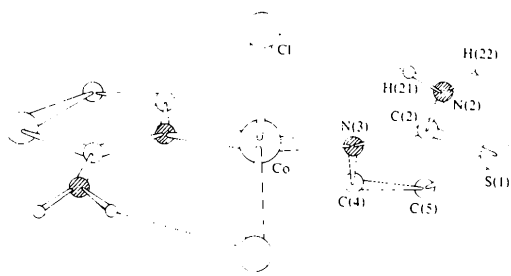


Fig. 1. Perspective diagram of the molecule with the atom labelling.

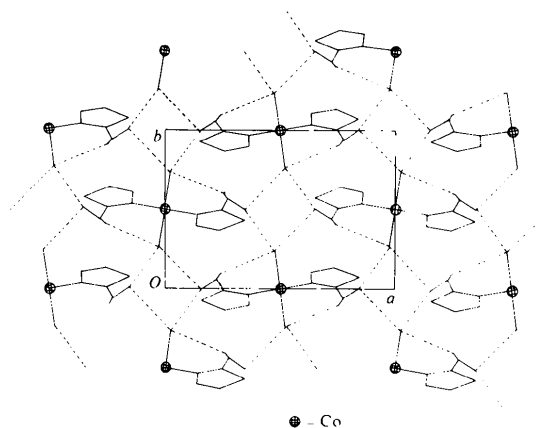


Fig. 2. Projection of the unit cell along *c*. The hydrogen bonds are represented by dashed lines.

are consistent with those of other hydrogen-bonded complexes, e.g. dichlorobis(thiabenzazole)cobalt(II) (Kowala & Wunderlich, 1973) and dichlorobis(imidazole)cobalt(II) (Antti & Lundberg, 1972), and fall within the range (3.22–3.59 Å) given by Olovsson (1960). The involvement of the amino H atoms in this hydrogen-bond network may explain the observation that the $\nu(\text{N–H})$ bands in the free ligand at 3400 (*s*) and 3290 (*m*) cm^{-1} are replaced by bands at 3900 (*s*), 3300 (*s*), 3200 (*m*), 3130 (*w*) and 3090 (*sh*) cm^{-1} in the complex (Abdullah-Noor, 1980).

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