

The Structure of Bis(1,3-benzothiazole)dichlorocobalt(II)

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Abstract. $[\text{Co}(\text{C}_7\text{H}_5\text{NS})_2\text{Cl}_2]$, $\text{C}_{14}\text{H}_{10}\text{Cl}_2\text{CoN}_2\text{S}_2$, $M_r = 400.03$, monoclinic, $C2/c$, $a = 7.901(4)$, $b = 12.994(6)$, $c = 15.042(6)$ Å, $\beta = 90.58(5)$, $U = 1544.23$ Å³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $Z = 4$, $D_m = 1.70(4)$, $D_c = 1.72$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 1.62$ mm⁻¹, $F(000) = 796$. Final $R = 0.048$ for 1122 reflections having $I/\sigma(I) \geq 3.0$. The Co atom lies on a twofold axis, and is tetrahedrally coordinated to the Cl atoms [Co–Cl 2.234(2) Å] and to the heterocyclic N atoms in the benzothiazole rings [Co–N 2.057(5) Å]. The thiazole rings are planar and have a dihedral angle of 130.4(15)°.

Introduction. A variety of metal complexes of the S,N-containing heterocyclic molecule benzothiazole (bt) and its 2-substituted derivatives, $R = \text{NH}_2$, CH_3 and Cl, (Fig. 1) have been prepared and characterized. With first-row transition and related metals ($M = \text{Fe}$, Co, Ni, Cu and Zn) the ligand normally coordinates through its N atom (Chan, Goodgame & Weeks, 1968; Goodgame & Weeks, 1966; Duff, Hughes & Rutt, 1968; Campbell, Card, Grzeskowiak & Goldstein, 1970; Birchall & Morris, 1972). Coordination of bt by bidentate bridging, involving both hetero atoms, has been found in $\text{Ni}(\text{bt})\text{Br}_2$ (Duff *et al.*, 1968). While σ -donating processes dominate in the bonding of the ligand to transition metals, a π interaction involving the metal and the conjugated $\text{S}=\text{C}=\text{N}$ portion of the molecule has been suggested and supported by ³H NMR spectra for Rh^{I} complexes (Aresta, 1980). The gas-phase bond dissociation energy, \bar{D} , of the Co–bt bond in $\text{Co}(\text{bt})_2\text{Cl}_2$ is also indicative of π interaction (Mortimer & McNaughton, 1973), in addition to σ donation through the N atom (Duff, Hughes & Rutt, 1969). This X-ray study has been undertaken to determine the coordination geometry of $[\text{Co}(\text{bt})_2\text{Cl}_2]$.

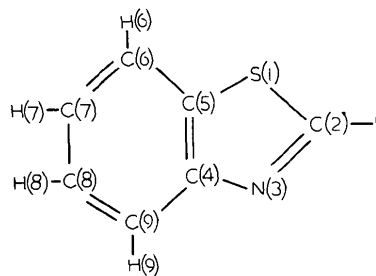


Fig. 1. Diagram of the benzothiazole molecule ($R = \text{H}$).

Blue crystals of $[\text{Co}(\text{bt})_2\text{Cl}_2]$ were prepared by a previously described method (Duff *et al.*, 1968). A crystal $0.2 \times 0.4 \times 0.5$ mm was mounted with **b** coincident with the rotation (ω) axis of a Stoe Stadi-2 two-circle diffractometer. Intensities were measured with monochromated Mo $K\alpha$ radiation using the background- ω -scan-background technique; 1647 unique reflections in the range $2\theta \leq 55^\circ$ were measured of which 1122 had $I \geq 3\sigma(I)$ and were considered to be observed. Corrections for Lorentz and polarization but not absorption effects were made. Systematic absences do not distinguish between space groups Cc and $C2/c$ but the latter, when $Z = 4$, requires the molecules to be located in special positions. Subsequent analysis confirms the centrosymmetric space group with the Co atoms located on a twofold axis. A Patterson map enabled the y coordinate of the Co atom to be determined; the remaining atoms were found from successive difference-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 parameters were not refined; those associated with the

six-membered rings were placed in calculated positions (C—H 1.08 Å). Full-matrix least-squares refinement with anisotropic thermal parameters gave a final $R = 0.048$, unit weights being used in the calculations. Final positional parameters for non-H atoms are listed in Table 1.* Bond lengths and angles are given in Table 2 and mean-planes' data in Table 3.

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36815 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final fractional coordinates ($\times 10^4$) and equivalent isotropic temperature factors defined according to Willis & Pryor (1975) with *e.s.d.*'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq} (Å ²)
Co	0	8561 (1)	7500	2.53 (5)
Cl	2382 (2)	9487 (1)	7539 (1)	3.77 (8)
S(1)	1237 (3)	6014 (1)	5536 (2)	4.24 (9)
N(3)	256 (6)	7580 (4)	6436 (4)	2.7 (2)
C(2)	978 (9)	6675 (5)	6494 (5)	3.5 (3)
C(4)	-119 (7)	7808 (4)	5554 (4)	2.5 (3)
C(5)	332 (8)	7028 (5)	4952 (4)	3.0 (3)
C(6)	27 (9)	7138 (6)	4056 (5)	4.1 (3)
C(7)	-738 (9)	8025 (7)	3762 (5)	4.6 (4)
C(8)	-1187 (9)	8813 (6)	4362 (5)	4.0 (3)
C(9)	-881 (8)	8710 (5)	5253 (4)	3.0 (3)

Table 2. Bond lengths (Å) and angles (°) with *e.s.d.*'s in parentheses

Symmetry code

None *x,y,z*; (i) $-x, y, 1.5 - z$

The coordination sphere

Co—Cl	2.234 (2)	Cl—Co—Cl ⁱ	114.8 (3)
Co—N(3)	2.057 (5)	Cl—Co—N(3)	105.3 (1)
		Cl—Co—N(3 ⁱ)	113.7 (2)
		N(3)—Co—N(3 ⁱ)	103.4 (3)

The ligands

S(1)—C(2)	1.692 (7)	C(2)—S(1)—C(5)	89.6 (3)
C(2)—N(3)	1.309 (7)	S(1)—C(5)—C(4)	109.1 (5)
N(3)—C(4)	1.389 (8)	C(5)—C(4)—N(3)	114.1 (5)
C(4)—C(5)	1.407 (8)	C(4)—N(3)—C(2)	110.1 (5)
C(5)—S(1)	1.734 (7)	N(3)—C(2)—S(1)	117.1 (5)
C(5)—C(6)	1.374 (10)	C(9)—C(4)—C(5)	120.6 (6)
C(6)—C(7)	1.373 (11)	C(4)—C(5)—C(6)	120.9 (6)
C(7)—C(8)	1.413 (11)	C(5)—C(6)—C(7)	118.4 (7)
C(8)—C(9)	1.365 (9)	C(6)—C(7)—C(8)	121.0 (7)
C(9)—C(4)	1.392 (8)	C(7)—C(8)—C(9)	120.8 (7)
C(2)—H(21)	0.917	C(8)—C(9)—C(4)	118.3 (6)
		S(1)—C(5)—C(6)	130.0 (5)
		C(9)—C(4)—N(3)	125.3 (5)
		Co—N(3)—C(2)	123.4 (4)
		Co—N(3)—C(4)	126.1 (4)
		H(21)—C(2)—S(1)	125.1
		H(21)—C(2)—N(3)	117.4

Table 3. Distances (Å) of relevant atoms from least-squares planes

The equations of the planes are referred to orthogonal axes.

Plane *A* S(1), C(2), N(3), C(4), C(5), C(6), C(7), C(8), C(9)

$$0.9016X + 0.4192Y - 0.1069Z - 3.1947 = 0.0000$$

|S(1), -0.005 (2); C(2), 0.004 (7); N(3), -0.008 (5); C(4), 0.003 (5); C(5), 0.005 (6); C(6), 0.004 (7); C(7), -0.006 (7); C(8), -0.002 (7); C(9), 0.004 (6); Co, 0.158 (1) Å|

Plane *B* Co, Cl, Clⁱ

$$0.0312X + 0.0000Y - 0.9995Z + 11.2790 = 0.0000$$

The angle between planes *A* and *B* is 82.2 (8)°.

Discussion. The Co atoms lie on twofold axes along **b** and are tetrahedrally coordinated to the Cl and N atoms of the heterocyclic molecule (Fig. 2). The angles about the Co atom are slightly distorted from those of a regular tetrahedron, the maximum deviation being 6.1°. The Co—Cl and Co—N bond lengths are in the range previously reported for related systems (Raper, Oughtred, Nowell & March, 1981; Antti & Lundberg, 1972; Manojlović-Muir & Muir, 1974). Both the five- and six-membered rings of the heterocyclic molecule are effectively coplanar (Table 3). The dihedral angle between the two heterocyclic molecules in the complex is 130.4 (15)°. Planar benzothiazole rings have been reported in both the free molecule (Chesick & Donohue, 1971) and metal complexes of its derivatives (Nardelli, Pelizzi & Pelizzi, 1975; Thompson, Ball & Trotter, 1980). Within the fused benzene ring the C—C bond lengths range from 1.413 (11) to 1.365 (9) Å; the latter value is just possibly significantly different from the standard C—C (benzene) value of 1.397 Å (Bacon, Curry & Wilson, 1964). Such differences are common, particularly in fused-ring systems (Stenson, 1970).

The C(2)—S(1)—C(5) angle [89.6 (3)°] is typical of S-containing five-membered heterocyclic molecules (Fehlmann, 1970; Stenson, 1970). The S(1)—C(2) and S(1)—C(5) bond lengths are significantly different and possess 50% [1.692 (7) Å] and 40% [1.734 (7) Å] SCF π character respectively (Trinajstić, 1968). In addition, significant differences exist between the C(2)—N(3) [1.309 (7) Å] and C(4)—N(3) [1.389 (8) Å] bonds. These observations suggest that localized π -electron density exists in the

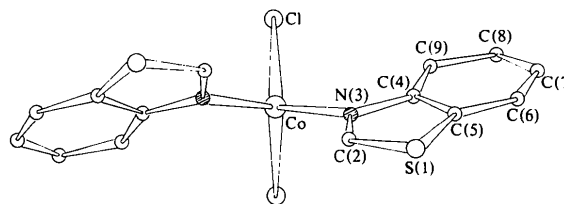


Fig. 2. Perspective view of the molecule with the atom labelling.

S(1)—C(2)—N(3) portion of the heterocyclic molecule in this complex. Within uncoordinated benzothiazole derivatives the C—S bonds range from 1.73 to 1.78 Å while the C—N distances are in the range 1.28 to 1.45 Å and are frequently significantly different from one another (Stenson, 1970). Similar trends have been observed among metal complexes of thiazole and benzothiazole derivatives (Caira & Nassimbeni, 1974; Raper *et al.*, 1981; Thompson *et al.*, 1980). Consequently, the localization of π density in the S(1)—C(2)—N(3) portion of the molecule appears to be significant in this structure.

A possible explanation for this localized π density may be that it is part of the process of optimizing the factors which are likely to favour a π interaction between the d orbitals of the Co^{II} ion and the heterocyclic portion of the ligand molecule. Localizing the π density in the N(3)—C(2)—S(1) region of the ligand molecule and narrowing the Co—N(3)—C(2) angle [123.4 (4)°] at the expense of the Co—N(3)—C(4) angle [126.1 (4)°] will favour such an interaction. However, since the Co—N(3) distance, 2.057 (5) Å, is normal for a σ bond and the Co...C(2)

distance, 2.985 (9) Å, is rather long, this suggests that a $d\pi$ - $p\pi$, metal-ligand interaction is likely to be weak and a minor component of the bonding scheme in this complex.

A projection of the unit cell along c^* is shown in Fig. 3.

References

- ANTTI, C. J. & LUNDBERG, B. K. S. (1972). *Acta Chem. Scand.* **26**, 3995–4000.
- ARESTA, M. (1980). *Inorg. Chim. Acta*, **44**, L3–L4.
- BACON, G. E., CURRY, N. A. & WILSON, S. A. (1964). *Proc. R. Soc. London Ser. A*, **279**, 98–110.
- BIRCHALL, T. & MORRIS, M. F. (1972). *Can. J. Chem.* **50**, 211–216.
- CAIRA, M. R. & NASSIMBENI, L. R. (1974). *Acta Cryst.* **B30**, 2332–2337.
- CAMPBELL, M. J. M., CARD, D. W., GRZESKOWIAK, R. & GOLDSTEIN, M. (1970). *J. Chem. Soc. A*, pp. 672–675.
- CHAN, N. N. Y., GOODGAME, M. & WEEKS, J. (1968). *J. Chem. Soc. A*, pp. 2499–2501.
- CHESICK, J. P. & DONOHUE, J. (1971). *Acta Cryst.* **B27**, 1441–1444.
- DUFF, E. J., HUGHES, M. & RUTT, K. J. (1968). *J. Chem. Soc. A*, pp. 2354–2357.
- DUFF, E. J., HUGHES, M. & RUTT, K. J. (1969). *J. Chem. Soc. A*, pp. 2101–2105.
- FEHLMANN, M. (1970). *Acta Cryst.* **B26**, 1736–1741.
- GOODGAME, M. & WEEKS, M. J. (1966). *J. Chem. Soc. A*, pp. 1156–1159.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- MANOJLOVIĆ-MUIR, L. J. & MUIR, K. W. (1974). *Molecular Structure by Diffraction Methods*, Vol. II, pp. 297–330. London: The Chemical Society.
- MORTIMER, C. T. & MCNAUGHTON, J. L. (1973). *Thermochim. Acta*, **6**, 269–274.
- NARDELLI, M., PELIZZI, C. & PELIZZI, G. (1975). *J. Chem. Soc. Dalton Trans.* pp. 1595–1597.
- RAPER, E. S., OUGHTRED, R. E., NOWELL, I. W. & MARCH, L. A. (1981). *Acta Cryst.* **B37**, 928–930.
- STENSON, P. (1970). *Acta Chem. Scand.* **24**, 3729–3738.
- THOMPSON, L. K., BALL, R. G. & TROTTER, J. (1980). *Can. J. Chem.* **58**, 1566–1576.
- TRINAJSTIĆ, N. (1968). *Tetrahedron Lett.* **12**, 1529–1532.
- WILLIS, B. T. M. & PRYOR, A. W. (1975). *Thermal Vibrations in Crystallography*, pp. 101–102. Cambridge Univ. Press.

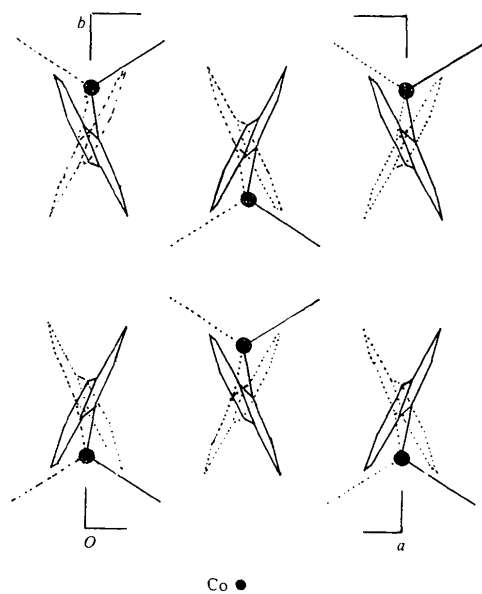


Fig. 3. Projection of the unit cell along c^* .