Table 3. *Contacts less than* 4·0 Å

Symmetry code: (ii) $\bar{x}, y - \frac{1}{2}, \frac{1}{2} - z$; (iii) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$.

| | | | |
|---|---|---|---|
| N(5)···I(2$^{ii}$) | 3·63 (4) Å | I(1)···N(5) | 3·56 (3) Å |
| N(1)···I(2$^{iii}$) | 3·62 (4) | I(2)···I(3) | 3·353 (4) |
| I(1)···N(1) | 3·64 (5) | | |

1975). The I(3)—I(3)—I(2) angle in the $^-$I(2)—I(3)—I(3)—I(2)$^-$ ion is 173·4°, similar to that in $I_3^-$ ions.

The pyridine ring and the two five-membered chelate rings are planar, but not coplanar, within the limits of the accuracy.

The cohesion between the layers is due to N(1)···I(2$^{iii}$) bonds (3·62 Å). Contacts less than 4·0 Å are listed in Table 3.

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*Acta Cryst.* (1981). B**37**, 926–928

# Structure of Bis(diallyldithiocarbamato)nickel(II)

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(*Received* 22 *September* 1980; *accepted* 8 *December* 1980)

**Abstract.** $[Ni(C_7H_{10}NS_2)_2]$, $C_{14}H_{20}N_2NiS_4$, $M_r$ = 403·3, monoclinic, $P2_1/n$, $a$ = 7·980 (3), $b$ = 9·069 (4), $c$ = 13·076 (3) Å, $\beta$ = 95·55 (3)°, $U$ = 941·9 Å$^3$, $Z$ = 2, $D_m$ = 1·40, $D_c$ = 1·42 Mg m$^{-3}$, Mo $K\alpha$ ($\lambda$ = 0·71069 Å), $\mu$ = 1·44 mm$^{-1}$. Final $R$ = 0·07 for 877 independent observed reflections. The Ni atom is coordinated by four S atoms in a plane. The ligand fragment $S_2CNC_2$ is nearly planar.

**Introduction.** As part of a study of dithiocarbamate complexes by X-ray diffraction (Kettmann, Garaj & Kúdela, 1977, 1978) we have examined bis(diallyldithiocarbamato)nickel(II).

The crystals are needles with approximate dimensions 0·225 × 0·27 × 0·15 mm. The diffraction intensities were collected on a Syntex $P2_1$ diffractometer by the $\theta$–$2\theta$ scan technique with a take-off angle

0567-7408/81/040926-03$01.00

Table 1. *Final atomic coordinates* ($\times 10^4$) *for non-hydrogen atoms*

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

| | $x$ | $y$ | $z$ | $B_{eq}$ (Å$^2$)* |
|---|---|---|---|---|
| Ni(1) | 5000 | 5000 | 5000 | 3·37 |
| S(1) | 2278 (3) | 4741 (2) | 4597 (2) | 5·21 |
| S(2) | 4896 (3) | 2727 (3) | 4388 (2) | 5·46 |
| C(1) | 2756 (10) | 3038 (9) | 4140 (6) | 4·67 |
| N(1) | 1678 (9) | 2125 (7) | 3703 (5) | 5·10 |
| C(2) | 2230 (12) | 637 (9) | 3294 (7) | 6·08 |
| C(3) | 1664 (14) | −551 (11) | 3956 (8) | 7·36 |
| C(4) | 619 (14) | −1620 (11) | 3599 (8) | 7·37 |
| C(5) | −149 (9) | 2511 (9) | 3513 (6) | 5·08 |
| C(6) | −565 (12) | 3034 (12) | 2401 (7) | 6·91 |
| C(7) | −1369 (14) | 4331 (13) | 2244 (10) | 9·38 |

* $B_{eq} = \frac{4}{3}\sum_i \sum_j \beta_{ij}\,\mathbf{a}_i\cdot\mathbf{a}_j$.

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

| | | | |
|---|---|---|---|
| Ni–S(1) | 2·198 (2) | C(2)–C(3) | 1·48 (1) |
| Ni–S(2) | 2·210 (2) | C(3)–C(4) | 1·33 (1) |
| S(1)–C(1) | 1·712 (8) | N(1)–C(5) | 1·50 (1) |
| S(2)–C(1) | 1·731 (8) | C(5)–C(6) | 1·54 (1) |
| C(1)–N(1) | 1·29 (1) | C(6)–C(7) | 1·35 (1) |
| N(1)–C(2) | 1·53 (1) | | |
| S(1)–Ni–S(2) | 79·2 (1) | C(1)–N(1)–C(5) | 121·4 (7) |
| Ni–S(1)–C(1) | 86·1 (3) | C(2)–N(1)–C(5) | 117·2 (6) |
| Ni–S(2)–C(1) | 85·3 (3) | N(1)–C(2)–C(3) | 108·8 (7) |
| S(1)–C(1)–S(2) | 109·3 (4) | C(2)–C(3)–C(4) | 122·7 (9) |
| S(1)–C(1)–N(1) | 125·0 (6) | N(1)–C(5)–C(6) | 110·3 (7) |
| S(2)–C(1)–N(1) | 125·6 (6) | C(5)–C(6)–C(7) | 118·1 (9) |
| C(1)–N(1)–C(2) | 121·3 (7) | | |

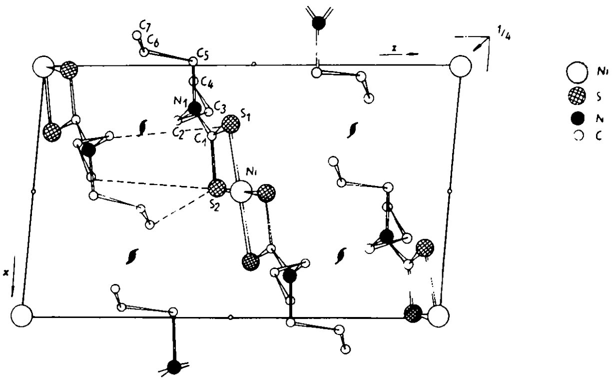

Fig. 1. Cell contents viewed down *b* showing the molecular packing and numbering of the atoms.

of 1·5°. The scan rate was variable and was determined by a fast (20° min$^{-1}$) 2 s prescan. If more than 20 net counts were found, a slow scan was carried out; if not, the reflections were considered as unobserved. Calculated speeds for the slow scan based on the net intensity gathered in the prescan ranged from 28 to 4·5 min$^{-1}$. Background counts were measured for half the total scan time at each end of the scan range. Two standard reflections were measured periodically; no significant fluctuation in the intensities was noticed. The intensities were corrected for Lorentz and polarization factors but not for absorption or extinction. The structure was solved from Patterson and electron density syntheses. H atoms were not located. The function $\sum w(|F_o| - |F_c|)^2$ was minimized; a weighting scheme $w^{-1} = \sigma^2(|F_o|) + (C|F_o|)^2$, where $\sigma(|F_o|)$ is derived from counting statistics and $C = 0{\cdot}05$, was employed. $C$ was adjusted so that constant values of $\sum w(|F_o| - |F_c|)^2$ were obtained in different $|F_o|$ intervals. The final $R = \sum \Delta F/\sum |F_o|$ was 0·070 for the observed reflections used in the refinement. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). All crystallographic calculations were performed with the NRC program package (Ahmed, 1970) on a Siemens 4004/150 computer. Atomic coordinates are listed in Table 1, bond distances and angles in Table 2.* A projection of the unit-cell contents down *b* and the numbering of the atoms are shown in Fig. 1.

**Discussion.** The crystal structure consists of discrete centrosymmetric [Ni{$S_2CN(C_3H_5)_2$}$_2$] molecules, with Ni atoms lying at centres of symmetry. The Ni atom is coordinated by two pairs of S atoms from two ligands; the geometry of the $NiS_4$ core is thus planar and the two pairs of Ni–S distances (2·198 and 2·210 Å) are almost identical. These distances are in good agreement with the correlation observed previously between Ni–S length and electron-donating effects of the N substituents as a consequence of $\pi$ delocalization in the $S_2CN$ ligand fragment (Newman & White, 1972). However, the statement that this correlation is due to Ni–S $\pi$ bonding is probably incorrect. From a comparison of subtle structural characteristics, various physical and chemical properties, and the electronic structures of 1,1-dithiolates (such as dithiocarbamates, xanthates, dithiophosphates and dithiophosphinates) with those of 1,2-dithiolenes (McCleverty, 1968; Eisenberg, 1970; Willemse, Cras, Steggerda & Keijzers, 1976), it follows that 1,1-dithiolate ligands, in general, are unable to $\pi$-bond with metal $d_\pi$ orbitals. Instead, the shortening of the Ni–S bond as the electron-donating effect of the *N* substituents increases should be rationalized in terms of the parallel increase of electron-donating strength of the dithiocarbamate ligand through the $\sigma$ orbitals of S donors. Similar covalent ligand→metal electron transfer is also operative in oxidized dithiocarbamates and is a dominant factor that expresses the exceptional ability of the dithiocarbamate ligand to stabilize transition-metal ions in unusually high oxidation states.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35760 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *The least-squares plane through the* $S_2CNC_2$ *ligand section and atomic deviations* (Å) *expressed in orthogonal space*

Equation $0{\cdot}2345X + 0{\cdot}4084Y - 0{\cdot}8821Z = -3{\cdot}2385$

| | | | | | |
|---|---|---|---|---|---|
| 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 $S_2CNC_2$ 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.

All calculations were performed on a Siemens 4004/150 computer at the Research Computing Centre of Comenius University. We thank Dr F. R. Ahmed for supplying us with the NRC program package, and Dr J. Soldanová for measuring the intensities.

Table 4. *Shortest packing distances* (<4·0 Å)

E.s.d.'s are 0·01 Å.

| | | | |
|---|---|---|---|
| $S(1)\cdots C(2)^{I}$ | 3·92 | $C(2)\cdots C(6)^{II}$ | 3·73 |
| $S(2)\cdots C(4)^{I}$ | 3·93 | $C(2)\cdots C(7)^{II}$ | 3·64 |
| $S(2)\cdots C(7)^{II}$ | 3·99 | $C(3)\cdots C(6)^{II}$ | 3·94 |
| $C(1)\cdots C(4)^{I}$ | 3·94 | $C(4)\cdots C(5)^{III}$ | 3·93 |
| $C(1)\cdots C(2)^{I}$ | 3·96 | $C(4)\cdots C(7)^{IV}$ | 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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*Acta Cryst.* (1981). B**37**, 928–930

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

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(*Received* 30 *September* 1980; *accepted* 22 *December* 1980)

**Abstract.** $[Co(C_3H_4N_2S)_2Cl_2]$, $C_6H_8Cl_2CoN_4S_2$, orthorhombic, $M_r = 330{\cdot}13$, $Pba2$, $a = 11{\cdot}528\,(7)$, $b = 7{\cdot}818\,(6)$, $c = 6{\cdot}639\,(7)$ Å, $U = 598{\cdot}3$ Å$^3$, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $Z = 2$, $D_m = 1{\cdot}81\,(4)$, $D_c = 1{\cdot}82$ Mg m$^{-3}$, $\mu$(Mo $K\alpha$) = 2·09 mm$^{-1}$, $F(000) = 326$. Final $R = 0{\cdot}058$ 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

0567-7408/81/040928-03$01.00