Crystal Structure of *cis*-Bis-(*N*-isopropyldithiocarbamato)nickel(II)

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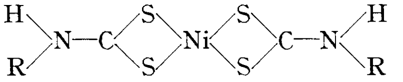
The crystal structure of the title compound, has been established by Patterson and Fourier methods from single-crystal photographic *X*-ray diffraction data, and was refined by full-matrix least-squares to *R* 0·09 (673 reflections). Crystals are trigonal, space group $R\bar{3}c$, *a* = 22·13(1), *c* = 15·06(3) Å, *Z* = 18.

The structure is the first example of a square-planar bis(dithiocarbamato) complex with different ligand substituents to adopt the *cis*-conformation in the solid; this imposes a marked distortion on the NiS_4 molecular core and is due to strong hydrogen bonding forces between the –NH– hydrogen and sulphur atoms of adjoining molecules, the overall molecular packing being a cylindrical array down *c*.

FOLLOWING earlier structural studies on a number of bis-(*NN*-disubstituted-dithiocarbamato)nickel(II) derivatives,[1-3] anomalies observed in the magnetic [4] and n.m.r. spectral properties [5] of certain other transition-metal derivatives of the ligands provoked further selected structural studies.[6-9] Among these, the study of the di-isopropyl derivative [8] was of particular interest because the nonequivalence of the ligand substituents accounted for the anomalous temperature-dependence of the n.m.r. spectrum.[5] Because of the desirability of obtaining information about the disposition of an individual isopropyl substituent, a preliminary study was made on the present compound. Preliminary Weissenberg data indicated from space-group symmetry and intensity distribution that the molecule was present in the hitherto unreported *cis*-configuration (I); because


(I)

of this and of the foregoing desirability, a structure determination was proceeded with.

TABLE 1

Final atomic fractional cell (× 10^4) and thermal parameters, with least squares estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	10^3U_{11}	10^3U_{22}	10^3U_{33}	10^3U_{12}	10^3U_{13}	10^3U_{23}
Ni	1613(2)	1613(2)	7500(—)	59(2)	55(—)	54(2)	27(1)	0(1)	–1(—)
S(1)	0971(3)	1026(2)	6335(3)	78(4)	62(3)	69(3)	38(3)	7(3)	0(2)
S(2)	2207(3)	2326(3)	6407(3)	93(4)	71(4)	53(2)	50(3)	3(3)	6(2)
N	1607(7)	1737(7)	4833(8)	71(5) *					
C(1)	1606(9)	1722(9)	5747(9)	65(4) *					
C(2)	2166(10)	2327(10)	4353(10)	77(6) *					
C(3)	2436(12)	2007(12)	3652(12)	114(8) *					
C(4)	1812(10)	2713(10)	3914(10)	92(7) *					
H(1)	1235(—)	1354(—)	4468(—)						
H(2)	2600(—)	2696(—)	4752(—)						

* Isotropic.

EXPERIMENTAL

The complex, prepared by the usual methods,[6] was obtained as well formed hexagonal crystals by the slow evaporation of chloroform solution. The crystal system was identified as trigonal and data collection and structure solution and refinement were carried out in terms of the hexagonal cell, as is the following discussion. Photographic multiple-film equi-inclination Weissenberg data were collected on a single crystal about both axes for the layers *h*0—5*l*, *hk*0—6, the crystal dimensions being 0·18 mm along all axes. Cell calibration was effected by the superposition of aluminium powder lines on zero-layer photographs (a_{298} = 4·0494 Å)

Crystal Data.—$C_8H_{16}N_2NiS_4$, *M* = 327·1, Trigonal, *a* = 22·13(1), *c* = 15·06(3) Å, *U* = 6387 Å^3, D_m (flotation) = 1·38(2), *Z* = 18, D_c = 1·38 g cm^{-3}, *F*(000) = 2720. Cu-K_α radiation, λ = 1·5418 Å, μ(Cu-K_α) = 62·4 cm^{-1}; μ*R* range 0·38—0·47. Space group $R\bar{3}c$ [D_{2d} (ref. 6), No. 167].

The data were measured, corrected for absorption, and processed, and the structure solved by Patterson and Fourier methods as described in our previous papers.[7] The structure was refined by full-matrix least-squares methods [10] to *R* 0·094 and *R'* 0·099, $\{R' = [\Sigma(|F_o| - |F_c|)^2/|\Sigma F_o|^2]^{\frac{1}{2}}\}$ with unit weights, the function minimized being $\Sigma(|F_o| - |F_c|)^2$, and anisotropic thermal parameters being of the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$, for the heavy atoms. The hydrogen atoms were fixed geometrically, assuming N–H 1·00 Å, C(2)–N–H(1) 117° (H in

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[5] R. M. Golding, P. C. Healy, P. W. G. Newman, E. Sinn, and A. H. White, *Inorg. Chem.*, 1972, **11**, 2435.

[6] P. W. G. Newman and A. H. White, *J.C.S. Dalton*, 1972, 1460.

[7] J. M. Martin, P. W. G. Newman, B. W. Robinson, and A. H. White, *J.C.S. Dalton*, 1972, 2233.

[8] P. W. G. Newman and A. H. White, *J.C.S. Dalton*, 1972, 2239.

[9] P. W. G. Newman, C. L. Raston, and A. H. White, *J.C.S. Dalton*, 1973, 1332.

[10] *X*-Ray System of Programs, version of June 1972, Technical Report TR 192, Computer Science Centre, University of Maryland, U.S.A.

the ligand plane), C–H 1·08 Å, and C(3,4)–C(2)–H 109°. Final parameter shifts in refinement were all $<0·02\sigma$; a final difference map showed no significant features. Scattering factors were for the neutral atoms,[11] those for nickel and sulphur being corrected for the effects of anomalous dispersion ($\Delta f', \Delta f''$).[12]

Computations were carried out on our PDP 10 and CDC 6200 machines. Structure factors are listed in Supplementary Publication No. SUP 21030 (5 pp., 1 microfiche); ‡ five reflections were deleted from the final data set because of apparent extinction effects. Results are listed in Tables 1—3; Figure 1 shows a diagram of the molecule and the atomic numbering system used in the analysis.

TABLE 2

Interatomic distances (<3 Å) and angles (°)

(*a*) Distances

Ni–S(1)	2·222(4)	C(2)–C(4)	1·56(4)
Ni–S(2)	2·202(4)	S(1) · · · H(1)	2·89
S(1) · · · S(2)	2·810(6)	S(1) · · · H(1$^{\mathrm{I}}$)	2·81 *
C(1)–S(1)	1·721(15)	S(1) · · · H(1$^{\mathrm{II}}$)	2·93 †
C(1)–S(2)	1·664(15)	S(2) · · · H(2)	2·63
C(1)–N	1·38(2)	S(1) · · · S(1$^{\mathrm{III}}$)	3·515(7)
N–C(2)	1·46(2)	S(2) · · · S(2$^{\mathrm{III}}$)	3·322(5)
C(2)–C(3)	1·55(4)		

(*b*) Angles

S(1)–Ni–S(2)	78·9(1)	C(2)–N–C(1)	120·4(12)
Ni–S(1)–C(1)	83·5(5)	N–C(2)–C(3)	106·0(16)
Ni–S(2)–C(1)	85·4(5)	N–C(2)–C(4)	105·4(14)
S(1)–C(1)–S(2)	112·2(9)	C(3)–C(2)–C(4)	112·1(16)
S(1)–C(1)–N	121·8(11)	S(1)–Ni–S(1$^{\mathrm{III}}$)	104·6(2)
S(2)–C(1)–N	126·0(11)	S(2)–Ni–S(2$^{\mathrm{III}}$)	97·9(2)

Roman numeral superscripts refer to the following transformations of the asymmetric unit (x, y, z):

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

* S(1) · · · N$^{\mathrm{I}}$ 3·64(1) Å, S(1) · · · H(1$^{\mathrm{I}}$)–N$^{\mathrm{I}}$ 141(1)°.
† S(1) · · · N$^{\mathrm{II}}$ 3·72(1) Å, S(1) · · · H(1$^{\mathrm{II}}$)–N$^{\mathrm{II}}$ 136(1)°

TABLE 3

Equations of best least-squares planes in the form $lX + mY + nZ = p$,* with atomic deviations (Å). Atoms defining the plane are italicised; their standard deviation from the plane is σ (Å)

	l	m	n	p	σ
Plane (i): The ligand					
	0·8858	−0·4632	−0·0289	−0·3003	0·01

S(1) 0·01, S(2) 0·00, N 0·00, C(1) −0·02, C(2) 0·01, Ni, 0·12, C(3) 1·17, C(4) −1·39, H(2) 0·15

	l	m	n	p	σ
Plane (ii): NiS_4 molecular core					
	0·8620	−0·4977	−0·0964	−1·0888	0·07

Ni 0·00, S(1) 0·06, S(1^{III}) −0·06, S(2) −0·07, S(2^{III}) 0·07, C(1) 0·03, C(2) 0·14

* X, Y, Z are orthogonal co-ordinates in Å, related to x, y, z by the transformation:

$$[X,Y,Z] = \begin{bmatrix} a & -0·5a & 0 \\ 0 & \sqrt{3}/2a & 0 \\ 0 & 0 & c \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

DISCUSSION

The structure consists of discrete molecules of the complex; the asymmetric unit is one half of the molecule. In all other bisdithiocarbamate complexes of nickel(II) hitherto studied {except the parent $[Ni(CS_2NH_2)_2]$ (ref. 1)}, the nickel atoms of the centrosymmetric molecules lie on inversion centres, implying in these cases of non-equivalent nitrogen substituents, the adoption of the *trans*-configuration. In the present complex, the second half of the molecule is generated by a two-fold axis through the nickel atom in the molecular plane so that the molecule adopts the *cis*-configuration. Figure 2 shows that within the cell the molecules are packed in two tiers up the c axis, the nickel atoms being centred on Wyckoff e positions at $z = 0·25, 0·75$. The molecules lie almost vertically within the cell, the long axis being almost parallel to c and the two-fold axis lying radially to the three-fold axis at $(1/3,2/3,z)$, $(2/3,1/3,z)$; the NH hydrogen atoms and the sulphur atoms S(1) are directed toward the three-fold axes. It has been shown elsewhere [1-3,6-9] that sulphur–hydrogen hydrogen bonds dominate the molecular interactions in these derivatives, particularly when the hydrogen atom substitutes the nitrogen. This is also the case in the present structure. The stacking of the three-fold tiers of molecules at intervals of half a cell along z is accompanied by the $c/2$ glide planes so that adjoining tiers are rotated by 60° to each other. The lower NH hydrogen atoms of one tier are hydrogen bonded to the upper sulphur atoms of the two adjoining molecules in the lower tier, their hydrogen atoms being likewise bonded to the lower sulphur atom S(1) of the upper tier, *i.e.* S(1) · · · H(1$^{\mathrm{I}}$),H(1$^{\mathrm{II}}$), 2·81 and 2·93 Å.

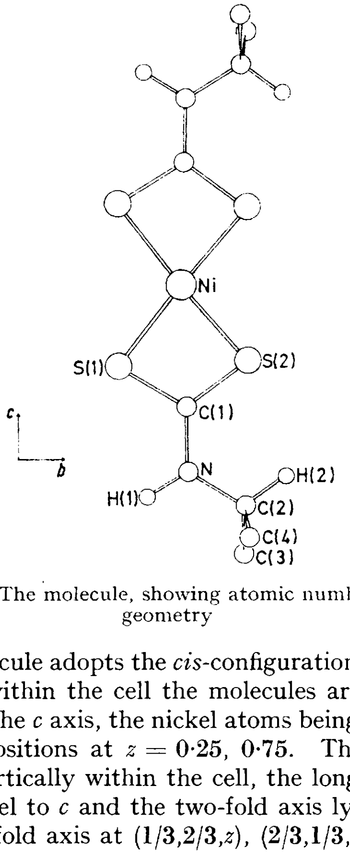

FIGURE 1 The molecule, showing atomic numbering and geometry

The point-symmetry of the NiS_4 molecular core in these derivatives is normally close to D_{2h}, although deviations of up to 0·02 Å in the agreement between

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‡ For details see Notice to Authors No. 7, in *J.C.S. Dalton*, 1973, Index issue (items less than 10 pp. are supplied as full-size copies).

[11] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[12] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

Ni–S(1,2) in previous structures have been attributed to hydrogen-bonding effects. Such a difference is, in fact, observed in the present structure [Ni–S(1,2) 2·222 and 2·202(4) Å], being significant at the 3σ level; the mean distance (2·212 Å) is typical of those derivatives with substituents which generate a weak crystal field. Within the NiS_2C ring, the NiS_2 and CS_2 angles [78·9(10) and 112·2(9)°] are in good agreement with those reported previously (Table **3**, ref. 7); the difference in the Ni–S–C angles, although significant, is not great [83·5, 85·4(5)°]. However, the C_2 site-symmetry does not constrain equality of the angles S(1)–Ni–S(1^{III}) and S(2)–Ni–S(2^{III}) and they show a very large difference [104·6(2), 97·9(2)°].

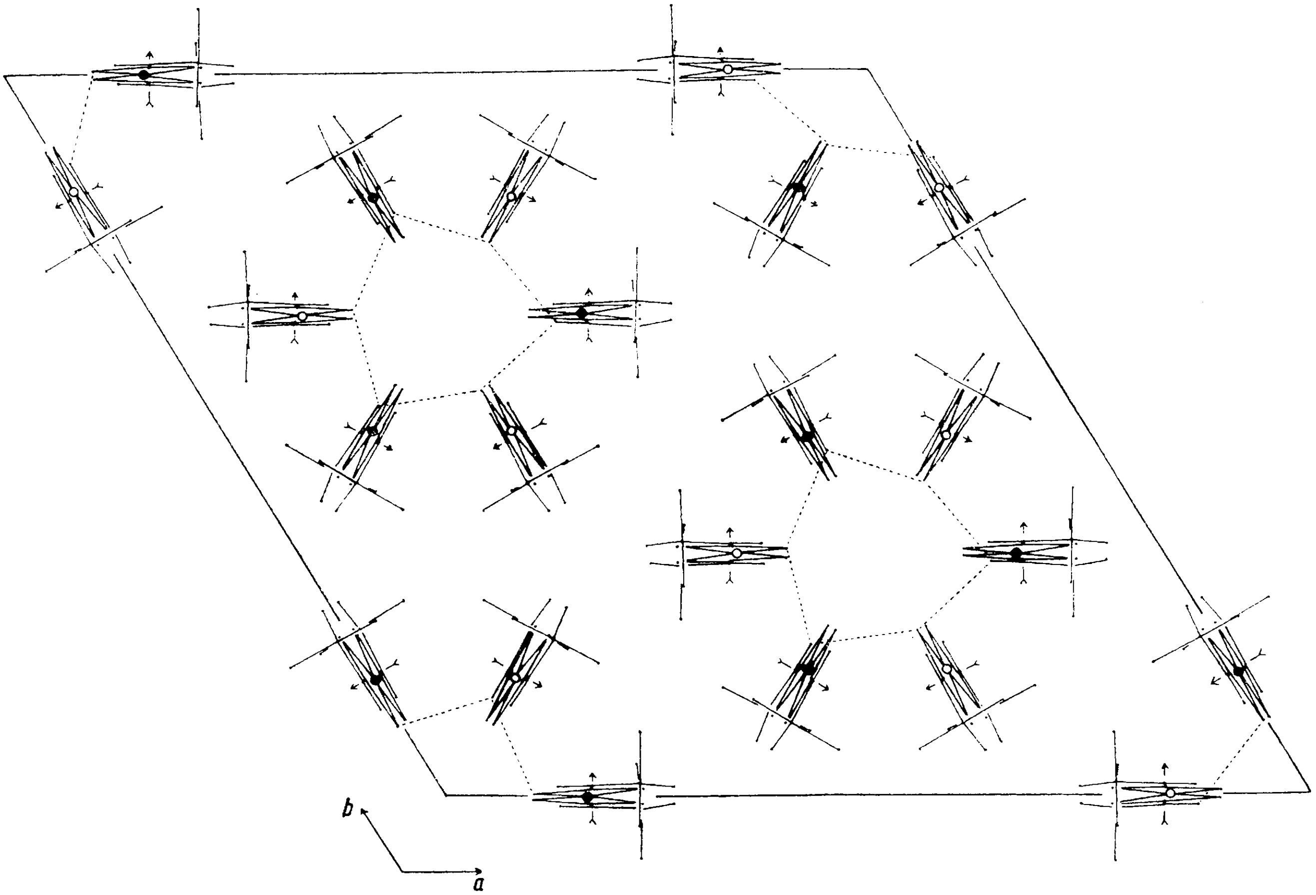

FIGURE 2 Unit-cell contents viewed down *c*. Those molecules shown with nickel atoms as closed circles have the nickel $z = 0·75$; those with nickel atoms shown as open circles have $z = 0·25$. Arrowheads indicate the upper end of each molecule. Dotted lines indicate only those contacts from the lower hydrogen atoms in the upper molecules to the upper sulphur in the lower molecules

The conjugated-carbon–nitrogen distance [1·38(2) Å] does not differ at the 3σ level from the usual value [*ca.* 1·32—1·34 Å];[13] N–C(2) and C(2)–C(3,4) are likewise as expected. The isopropyl substituent has a similar geometry to its counterpart in the di-isopropyl derivative,[8] C(3)–C(2)–C(4) being splayed to 112° while N–C(2)–C(3,4) are correspondingly reduced below the tetrahedral angle (106, 105°). The overall planarity of the S_2CNC system is good, as is usual; the NiS_4 molecular core is not constrained to be planar as is the case in derivatives with inversion centres, and the nickel atom deviates markedly from the ligand plane (0·12 Å).

[3/2203 *Received*, 26*th October*, 1973]

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[13] R. Eisenberg, *Progr. Inorg. Chem.*, 1970, **12**, 295.