Crystal Structure of Bis(*NN*-di-isopropyldithiocarbamato)nickel(II)

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The crystal structure of the title compound has been established by single-crystal *X*-ray diffraction methods. Crystals are monoclinic, space group $P2_1/a$, $a = 15{\cdot}62 \pm 0{\cdot}03$, $b = 17{\cdot}83 \pm 0{\cdot}03$, $c = 8{\cdot}16 \pm 0{\cdot}01$ Å, $\beta = 110{\cdot}5(2)^\circ$, $Z = 4$. The structure was solved by Patterson and Fourier methods and refined by block-diagonal least-squares to R 0·11 for 1909 visually estimated reflections. The structure consists of two independent sets of planar molecules, the nickel atoms each being planar co-ordinated by four sulphur atoms at equal distances (mean Ni–S, 2·181 ± 0·005 Å) and significantly shorter than in previously reported nickel(II) dithiocarbamate structures (mean Ni–S > 2·20 Å), the trend in bond length paralleling crystal-field effects. The remainder of the ligand dimensions are normal [C–S, 1·70(1) Å, S–Ni–S, 79·2(5)°, C–N, 1·33(1) Å]. Steric interaction between the terminal i-propyl substituents leads to an interesting non-equivalence of these within each ligand.

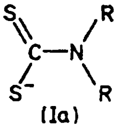
IN the tris-(*NN*-dialkyldithiocarbamato)cobalt(III) and -iron(III) derivatives, $[M(CS_2{\cdot}NR_2)_3]$, ligand substituent modifications effect appreciable changes in the field experienced by the metal atom in its D_3 environment of six sulphur atoms. In the cobalt(III) derivatives, the ^{59}Co n.m.r. chemical shift σ_{Co} (% relative to $K_3[Co(CN)_6]$) is a sensitive indicator of the change;[1] in the iron complexes the change is most sensitively observed *via* the relative sextet–doublet energy-level disposition as reflected in the magnetic moment, μ_{Fe}, at 300 K in chloroform solution.[2-4] By use of these parameters, it is possible to classify the ligands in terms of R as follows:

Class	$-NR_2$	σ_{Co}(%)	μ_{Fe}/B.M.
(i)	$-N(CH_2)_4$, $-NH_2$(Co only)	*ca.* 0·705—0·725	*ca.* 5·9
(ii)	$-N$(n-alkyl)$_2$, $-N(CH_2)_n(n \geqslant 5)$	*ca.* 0·664—0·670	*ca.* 4·1—4·5
(iii)	$-N(CHR_2)_2$, $-NPh_2$	*ca.* 0·626—0·632	*ca.* 2·2—2·6

Intermediate classes of behaviour may be obtained when a 'mixed' ligand, $CS_2^{-}{\cdot}NR^1R^2$, is used. This classification is less sensitively reflected in the electronic spectra of these complexes and their nickel analogues.[5]

To obtain an appreciation of the causes of this variety of behaviour in the cobalt(III) and the iron(III) series,[6,7] we have investigated structurally a series of nickel(II) complexes of these above ligand types, chosen because of the constant ground state, the good quality of the crystallographic data, the variety of related structures known, and their frequent structural simplicity.

In those nickel(II) complexes already studied the insensitivity of the electronic spectrum to substituent change is not reflected in other observables. Both C–N and Ni–S bonds change appreciably from class (i) to class (ii); in $[Ni(CS_2{\cdot}NH_2)_2]$ these bond lengths are 1·37(3), 1·38(3), and 2·207(7)—2·224(15),[8] whereas in class (ii) complexes they are 1·33(1), 1·33(1), and 2·197(2)—2·210(2).[9] Although doubt is cast on these by the high (full-matrix) standard deviations, they are paralleled by changes in the i.r. frequencies of these bonds. In $[Ni(CS_2{\cdot}NH_2)_2]$, ν(C–N) is *ca.* 1440 cm^{-1} and ν(Ni–S) *ca.* 378 cm^{-1}; for the dialkyl derivatives ν(C–N) is >1500 cm^{-1} and ν(Ni–S) *ca.* 383 cm^{-1}, (assignments are supported by normal co-ordinate analyses),[10-13] suggesting that, in terms of the canonical forms (I) and (II), form (II) is more pronounced in the latter.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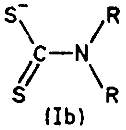
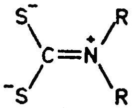

(Ib)


(II)

We have examined structurally a representative set of these complexes as follows: (i) $[Ni(CS_2{\cdot}N(CH_2)_4)_2]$,[13] $[Ni(CS_2{\cdot}NH_2)_2]$;[8] (i), (ii) $[Ni(CS_2{\cdot}NHMe)_2]$;[14] (ii) $[Ni(CS_2{\cdot}NEt_2)_2]$,[9] $[Ni(CS_2{\cdot}NPr^n_2)_2]$;[15] and (ii), (iii) $[Ni(CS_2{\cdot}NMePh)_2]$;[14] we now report the structure of the class (iii) complex $[Ni(CS_2{\cdot}NPr^i_2)_2]$.

EXPERIMENTAL AND RESULTS

$[Ni(CS_2{\cdot}NPr^i_2)_2]$ was prepared by the reaction of stoicheiometric quantities of the sodium salt of the ligand in aqueous solution with nickel sulphate, and recrystallized from chloroform–ethanol. Crystals suitable for *X*-ray work were obtained as blocks from the slow evaporation of chloroform–ethanol solution.

Non-integrated *X*-ray data was collected by the multiple-film equi-inclination Weissenberg method, on two crystals (both 0·12 × 0·10 × 0·15 mm) mounted with the spindle axis parallel to *b* and *c* respectively (the crystal axes being parallel to the crystal edges) for the layers *h*0—9*l*, *hk*0—4.

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Unit-cell calibration was effected by superimposing aluminium powder lines (a_{298K} = 4·0494 Å)[16] on zero-layer Weissenberg photographs. Nickel-filtered copper radiation was used throughout [λ(Cu-$K_{\bar{\alpha}}$) = 1·5418 Å].[17]

Crystal Data.—$C_{14}H_{28}N_2NiS_4$, M = 411, Monoclinic, a = 15·62 ± 0·03, b = 17·83 ± 0·03, c = 8·16 ± 0·02 Å, β = 110·5 ± 0·2°, U = 2127 Å^3, D_m = 1·28 ± 0·01 (flotation), Z = 4, D_c = 1·29. $F(000)$ = 872. Space group $P2_1/a$ (C_{2h}^5, No. 14).[18] μ(Cu-K_α) = 68 cm^{-1}, transmission coefficient 0·39—0·57.

The intensities of 1909 independent observed reflections were estimated visually by use of a calibrated intensity strip, only these non-zero reflections being used in the structure determination. The data was corrected for absorption by the ABSCOR routine,[19] for Lorentz and polarization factors, and scaled by internal correlation,[20] all reflections being assigned unit weights.

TABLE 1

Final atomic parameters of the asymmetric unit with estimated standard deviations in parentheses

(*a*) Fractional positional and isotropic thermal parameters

Atom	x	y	z	B/Å^2
Ni(1)	0·5000	0·5000	1·0000	
Ni(2)	0·5000	0·0000	1·0000	
S(1)	0·3527(2)	0·4857(2)	0·9313(4)	
S(2)	0·4570(2)	0·4959(2)	0·7154(4)	
S(3)	0·4317(2)	0·1047(2)	1·0190(6)	
S(4)	0·5956(2)	0·0823(2)	0·9655(5)	
N(1)	0·2727(7)	0·4773(5)	0·5795(13)	4·5(2)
N(2)	0·5351(8)	0·2220(7)	0·9884(15)	6·6(3)
C(1)	0·3486(7)	0·4849(6)	0·719(1)	3·6(2)
C(2)	0·5208(7)	0·1479(7)	0·992(2)	4·2(2)
C(3)	0·2703(8)	0·4790(7)	0·396(2)	4·7(2)
C(4)	0·1835(9)	0·4694(7)	0·607(2)	5·2(3)
C(5)	0·624(2)	0·249(1)	0·964(3)	10·4(6)
C(6)	0·468(1)	0·281(1)	0·995(2)	9·2(5)
C(7)	0·128(1)	0·541(1)	0·541(2)	7·7(4)
C(8)	0·135(1)	0·3971(9)	0·518(2)	7·3(4)
C(9)	0·301(1)	0·5536(9)	0·350(2)	7·1(4)
C(10)	0·321(1)	0·4120(9)	0·355(2)	7·0(3)
C(11)	0·458(1)	0·280(1)	1·170(3)	11·6(6)
C(12)	0·379(1)	0·273(1)	0·849(3)	10·3(5)
C(13)	0·599(2)	0·295(2)	0·800(4)	16·1(9)
C(14)	0·677(2)	0·297(2)	1·126(4)	15·8(9)

Postulated co-ordinates of the calculated secondary hydrogen atoms numbered according to the carbon atom to which they are attributed

H(3)	0·193	0·472	0·307
H(4)	0·194	0·462	0·759
H(5)	0·659	0·202	0·945
H(6)	0·501	0·339	0·973

(*b*) Anisotropic thermal parameters (× 10^4) of the form exp − ($\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl$)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{23}	β_{13}
Ni(1)	23(1)	25(1)	93(4)	−2(3)	6(4)	23(4)
Ni(2)	43(1)	16(1)	117(5)	3(2)	5(4)	47(4)
S(1)	45(1)	49(1)	168(5)	−5(2)	−4(5)	59(4)
S(2)	42(1)	68(1)	189(5)	−6(2)	5(5)	66(4)
S(3)	66(1)	33(1)	381(10)	−0(2)	7(5)	159(7)
S(4)	64(2)	39(1)	308(8)	1(2)	6(5)	126(6)

Structure Determination.—An unmodified three-dimensional Patterson function was computed from all data, all nickel and sulphur atoms being located; the carbon and nitrogen atoms were located in a subsequent three-dimensional Fourier synthesis. Positional and isotropic thermal parameters were refined by use of a block-diagonal (3 × 3, 6 × 6) least-squares routine (local versions of SFLS 1, A.I.M. Rae, and SFLS 2, B. J. Ong) and after four cycles the R was reduced to 0·23. A weighting scheme of the form $w = (a + |F_o| + b|F_o|^2)^{-1}$ was introduced[21] (a and b being recalculated at successive stages of refinement); refinement continued, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$, and converged to R 0·136, the value, R', $\{R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$ being 0·189. The nickel and sulphur atoms were allowed to vibrate anisotropically and refinement terminated at convergence (R 0·108, R' 0·146). Final weighting scheme parameters were a = 7·54 and b = 0·033. The introduction of anisotropic thermal parameters was justified on the basis of a ratio test.[22] A difference-Fourier map, computed after the final round of least squares, was flat to better than 0·2 of a carbon atom. There was no evidence for disorder in the structure. During the final cycle of least-squares refinement, parameter shifts in all atomic parameters were $<0{\cdot}1\sigma$ for the lighter atoms, those for the heavy atoms being considerably less. Scattering factors employed for neutral nickel, sulphur, carbon, and nitrogen atoms were taken from ref. 23, nickel and sulphur atoms being corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$).[24] The final set of observed and calculated structure factors is in Supplementary Publication No. SUP 20485

TABLE 2

Intramolecular bonding distances (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Distances

Molecule (1)		Molecule (2)	
Ni(1)–S(1)	2·183(3)	Ni(2)–S(3)	2·182(3)
Ni(1)–S(2)	2·179(3)	Ni(2)–S(4)	2·181(3)
S(1)–C(1)	1·711(11)	S(3)–C(2)	1·673(12)
S(2)–C(1)	1·714(12)	S(4)–C(2)	1·720(12)
C(1)–N(1)	1·329(15)	C(2)–N(2)	1·337(17)
N(1)–C(3)	1·48(2)	N(2)–C(5)	1·55(3)
N(1)–C(4)	1·49(2)	N(2)–C(6)	1·50(3)
C(4)–C(7)	1·53(2)	C(6)–C(11)	1·49(3)
C(4)–C(8)	1·54(2)	C(6)–C(12)	1·49(3)
C(3)–C(9)	1·50(2)	C(5)–C(13)	1·51(4)
C(3)–C(10)	1·53(2)	C(5)–C(14)	1·55(4)

(*b*) Angles

S(1)–Ni(1)–S(2)	79·6(1)	S(3)–Ni(2)–S(4)	78·9(1)
Ni(1)–S(1)–C(1)	85·6(4)	Ni(2)–S(3)–C(2)	86·3(4)
Ni(1)–S(2)–C(1)	85·6(4)	Ni(2)–S(4)–C(2)	85·3(4)
S(1)–C(1)–S(2)	109·2(6)	S(3)–C(2)–S(4)	109·5(7)
S(1)–C(1)–N(1)	124·9(9)	S(3)–C(2)–N(2)	127·6(10)
S(2)–C(1)–N(1)	125·9(9)	S(4)–C(2)–N(2)	122·8(9)
C(1)–N(1)–C(3)	124·0(10)	C(2)–N(2)–C(5)	118·2(13)
C(1)–N(1)–C(4)	118·7(10)	C(2)–N(6)–C(6)	124·3(13)
C(4)–N(1)–C(3)	117·3(10)	C(5)–N(2)–C(6)	117·4(14)
C(9)–C(3)–N(1)	111·8(11)	C(11)–C(6)–N(2)	109·8(16)
C(10)–C(3)–N(1)	111·7(11)	C(12)–C(6)–N(2)	112·0(16)
C(7)–C(4)–N(1)	108·6(11)	C(14)–C(5)–N(2)	107·3(18)
C(8)–C(4)–N(1)	109·9(11)	C(13)–C(5)–N(2)	108·6(19)
C(8)–C(4)–C(7)	113·6(12)	C(11)–C(6)–C(12)	112·8(18)
C(10)–C(3)–C(9)	113·7(12)	C(13)–C(5)–C(14)	110·3(22)

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(4 pp., 1 microfiche).* Final atomic fractional cell and thermal parameters are listed in Table 1. (Estimated standard deviations are derived from a block-diagonal refinement procedure and are therefore likely to be underestimates). Secondary hydrogen atom positions were estimated assuming C–H 1·08 Å, and $H-C-N = H-C-C' = H-C-C''$. Interatomic distances and angles were computed [25] and are given in Table 2.

Computation was carried out on the DEC PDP 10 machine at the University of Western Australia.

DISCUSSION

The crystals are composed of two distinct, independent sets of discrete molecules each being centrosymmetric about the nickel atoms which occupy $(0,0,0)$, $(\frac{1}{2},\frac{1}{2},0)$, and $(\frac{1}{2},0,0)$, $(0,\frac{1}{2},0)$ and lying closely coincident to the planes $y = 0,\frac{1}{2}$ and $z = 0,\frac{1}{2}$. (Least-squares planes through the $Ni(S_2CNC_2)_2$ fragments of each molecule were calculated in an orthogonal (Å) co-ordinate system $X = ax + cz \cos \beta$, $Y = by$, $Z = cz \sin \beta$:

Molecule (1): $-0{\cdot}1124X + 0{\cdot}9930Y - 0{\cdot}0374Z = 8{\cdot}007$

Molecule (2): $-0{\cdot}1255X + 0{\cdot}0095Y + 0{\cdot}9920Z = 8{\cdot}194$

In both cases, none of the thirteen atoms deviate significantly from the plane). The unit-cell contents are depicted in Figure 1. There is a significant difference in the accuracy of the determination of the parameters of the peripheral atoms of the two molecules, the second having substantially higher estimated standard deviations and thermal parameters and appearing to be less firmly constrained within the lattice. Molecular geometries and atomic designations are given in Figure 2.

TABLE 3

Comparison of the intramolecular dimensions of $[Ni(CS_2{\cdot}NPr^i{}_2)_2]$ with those of related structures

Compound	M–S/Å	S(1)–M–S(2) (°)	C(1)–S(*i*)/Å	C(1)–N/Å	S(1)–C(1)–S(2) (°)	N–C(2,3)
$[Ni(CS_2{\cdot}NH_2)_2]$ [a]	2·21, 2·22(1)	78·6(3)	1·68(2), 1·70(3)	1·37(3)	112(1)	
	2·21, 2·22(1)	78·4(2)	1·68(2), 1·70(3)	1·38(3)	112(1)	
$[Ni(CS_2{\cdot}NHMe)_2]$ [b]	2·196, 2·203(9)	79·2(1)	1·70(1), 1·72(1)	1·30(1)	109·8(9)	1·47(2)
$[Ni(CS_2{\cdot}NEt_2)_2]$ [c]	2·195, 2·207(2)	79·2(2)	1·70(1), 1·71(1)	1·33(1)	110·5(6)	1·48(1), 1·49(2)
$[Ni(CS_2{\cdot}NPr^n{}_2)_2]$ [d]	2·197, 2·209(2)	79·4(1)	1·69(1), 1·72(1)	1·33(1)	110·6(4)	1·46(1), 1·48(1)
$[Ni(CS_2NMePh)_2]$ [e]	2·198, 2·208(3)	79·3(1)	1·70(1), 1·74(1)	1·30(1)	109·3(6)	1·44(1), 1·51(2)
$[Ni(CS_2NPr^i{}_2)_2]$ [f]	2·183, 2·179(3)	79·6(1)	1·71, 1·71(1)	1·33(2)	109·2(6)	1·48, 1·49(2)
	2·182, 2·181(3)	78·9(1)	1·67, 1·72(1)	1·33(2)	109·5(7)	1·55, 1·50(3)

[a] Ref. 8. [b] Ref. 14. [c] Ref. 9. [d] Ref. 15. [e] Ref. 14. [f] This work.

Non-bonding Contacts.—The disposition of the i-propyl substituents is of interest. For both molecules, the symmetry approximates to C_{2h}; this is not strict, however, as the i-propyl groups do not have their mirror plane coincident with the molecular plane but are tilted slightly. This disposition seems a result of minimization of steric interaction between pairs of methyl substituents. As a result, the intramolecular S · · · H-(estimated) contacts are very short [S(1) · · · H(4), 2·42; S(4) · · · H(5), 2·38 Å], the estimated van der Waals' distance being 3·05 Å.[26] As in the other structures of the bis-(*NN*-dialkyldithiocarbamato)nickel(II) series, there are significant intermolecular S · · · H interactions [H(3) · · · S(4)$(\frac{1}{2} + x, \frac{1}{2} - y, z - 1)$, 2·83; H(4) · · · S(4)-$(\frac{1}{2} + x, \bar{y}, z)$, 2·77 Å]; the disparity in the C(2)–S(3,4) distances [1·67(1), 1·72(1)] may be a consequence of this. There is also a short intermolecular nickel–hydrogen contact [H(6) · · · Ni(1) 2·89 Å].

The Nickel Environment.—As in other complexes of this series, the nickel atom is co-ordinated by two dithiochelates, the NiS_4 core being necessarily planar with the four nickel–sulphur distances equal [2·179(3)—2·183(3) Å] and much shorter than in the complexes of the di-n-alkyl and parent-ligand complexes, differing from the latter by possibly as much as $0{\cdot}03_5$ Å (Table 3). Although some of the standard deviations are high, there is a close and strict correlation between the metal–sulphur distances and the ligand class and it is clear that a real contraction in bond length is observed.

The shorter bond length in the present complex may be accompanied by an increase in metal–ligand π-bonding. Eisenberg,[27] following Schrauzer,[28] regards the 1 : 1 dithiochelates as 'odd' ligands and attributes the greater length of the metal–sulphur bonds in such systems *vis-à-vis* those of the 1 : 2 dithiochelates as being indicative of a much greater π component in the latter complexes of the 'even' ligands. From the present results, it seems likely that π-bonding within the present series is not negligible, and the greater metal–sulphur distances in this series as compared to the 1 : 2 dithiochelate complexes may be as much a consequence of the smaller S–Ni–S angle imposed by the ligand (79° *cf.* 90°) as it is of orbital symmetry.

The behaviour of the complexes tris-(*O*-ethyl dithiocarbonato)-iron(III) and -cobalt(III), $[M(CS_2{\cdot}OR)_3]$, suggests a similarity between this and the class (iii) ligands.[1,3] In the nickel(II) derivative, the nickel–sulphur distance is appreciably longer [2·23(1) Å] than that of the present complex.[29] This also occurs with the cobalt(III) derivatives. In $[Co(CS_2{\cdot}OEt)_3]$, the cobalt–sulphur distances

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp are sent as full size copies).

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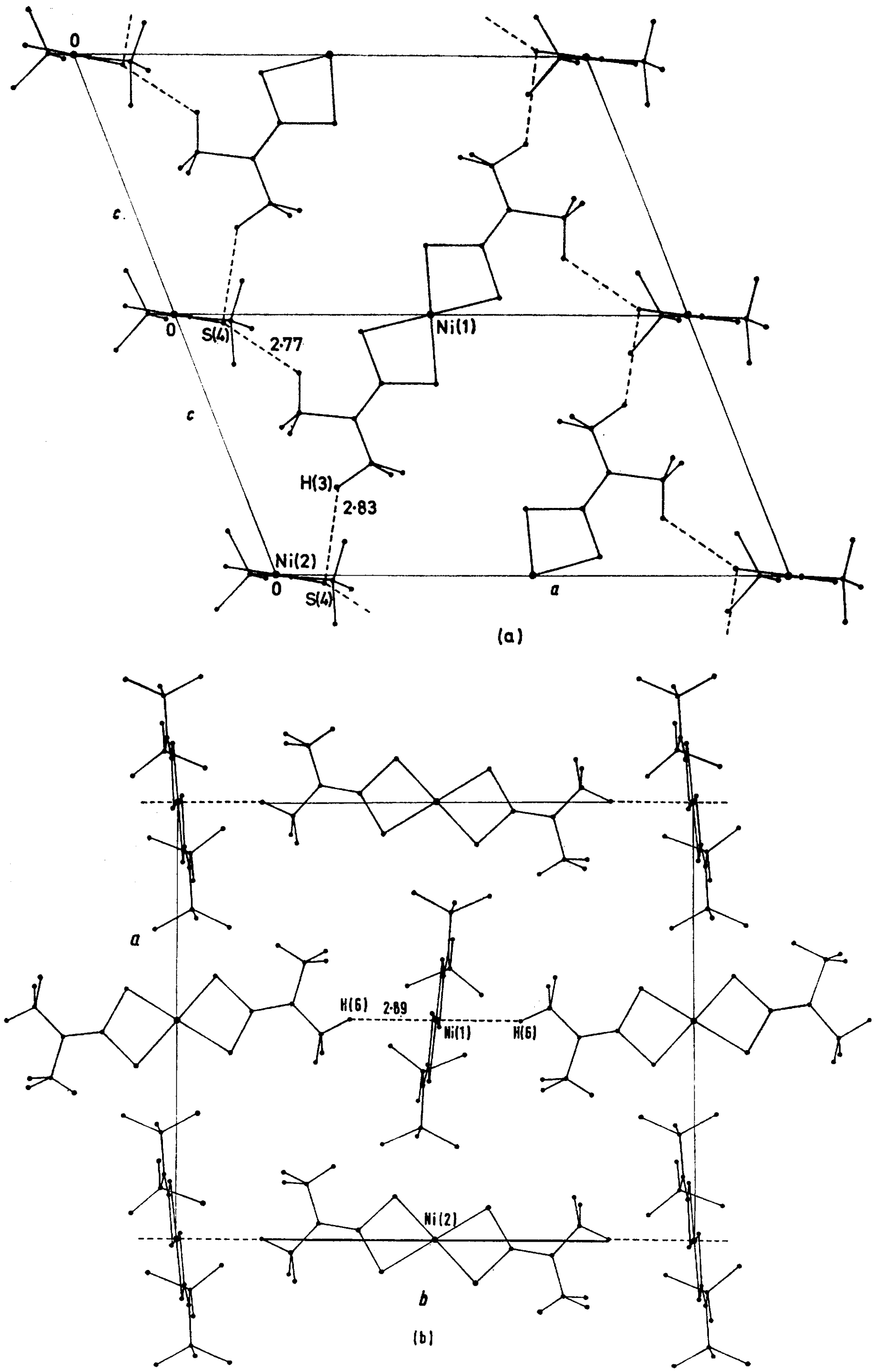

FIGURE 1 Unit-cell contents viewed down (a) the *b* axis showing CH hydrogen–nickel contacts, and (b) the normal to the *ab* face, showing CH hydrogen–sulphur intermolecular contacts

are 2·276(4) and 2·277(4); [30] in [$Co(CS_2{\cdot}NEt_2)_3$], they are 2·258(3)—2·268(3) Å,[31,32] suggesting that the parallel is superficial and that there may be significant differences in the crystal-field parameters of the two ligand types.

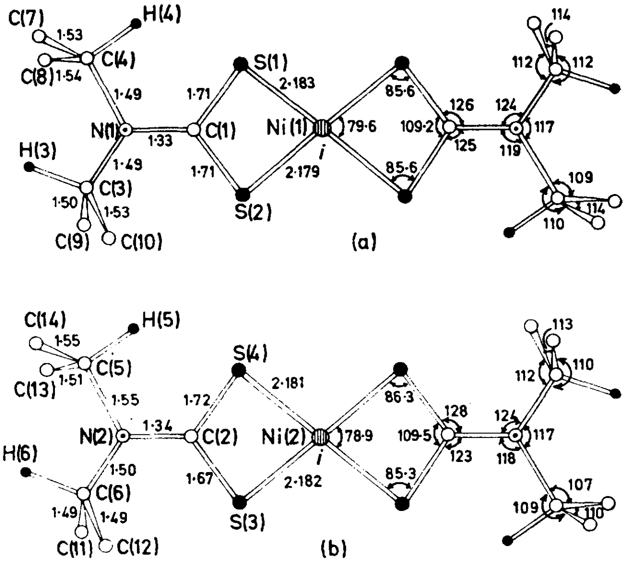

FIGURE 2 The molecular geometries of (a) molecule (1) and (b) molecule (2) showing the atomic numbering system used and the dimensions and the disposition of the isopropyl groups

The Ligand.—The ligand geometry within the conjugated system and its immediate appendages, S_2CNC_2, is not significantly different from the other substituted dithiocarbamates of nickel(II) (Table 3), and there is little or no significant or consistent trend throughout the series which could suggest an explanation of the substituent effects and their origins. In the present complex the nitrogen atom angles are distorted by the asymmetry of the i-propyl substituents; the usual median C–N–C angle of 117° is preserved but the C–N–C angles are *ca.* 124° on that side of the ligand where the terminal methyl groups are directed toward the sulphur and 118° on the other side where the hydrogen is associated with the sulphur (Figure 2). Within the isopropyl groups, similar distortions occur as a result of methyl–methyl and methyl–sulphur strain: the C–C–C angle is consistently larger than the tetrahedral angle [molecule (1) 114(1), 114(1)°; molecule (2), 110(1), 113(1)°] and in the substituents with the methyl groups directed toward the sulphur, the C–C–N angles are uniformly larger [112(1), 114(1); 112(2), 113(2)°] than in the other [107(2), 109(2); 109(1), 110(1)°].

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