Crystal Structure of Bis(*N*-methyldithiocarbamato)nickel(II)

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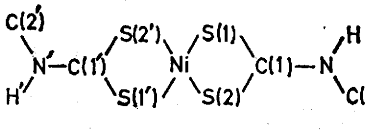
The crystal and molecular structure of the title compound has been determined by single-crystal *X*-ray diffraction methods, by conventional Patterson and Fourier heavy-atom techniques followed by block-diagonal least squares refinement to *R* 0·12 for 671 independent visually estimated observed reflections. Crystals are monoclinic space group $P2_1/a$, $a = 12{\cdot}20 \pm 0{\cdot}03$, $b = 9{\cdot}37 \pm 0{\cdot}03$, $c = 4{\cdot}20 \pm 0{\cdot}02$ Å, $\beta = 93{\cdot}4 \pm 0{\cdot}2°$, and $Z = 2$. The nickel atom occupies the special position with symmetry $\bar{1}$ and is planar co-ordinated by four sulphur atoms [Ni–S 2·203(9) and 2·196(9) Å; S(1)–Ni–S(2) 79·2(2)°]. The remainder of the ligand exhibits conjugation throughout the planar NiS_2CNC system, the dimensions being as expected: C–S 1·70(1) and 1·72(1) Å, S–C–S 109·8(7); C–N 1·30(1), N–C 1·47(2) Å.

STUDIES on complexes of the type $[M(CS_2{\cdot}NR_2)_2]$ have shown that for $M = Fe^{III}$ (ref. 1) or Co^{III} (ref. 2) and R = alkyl, modification of the ligand substituent can exert far-reaching effects on the crystal field experienced by the central metal atom. As the nickel(II) system is crystallographically more tractable than either of the former and likely to lead to a more accurate definition of the ligand system, we are examining a number of representative and appropriate derivatives in this series in an attempt to delineate the effects of change of ligand substituent on the ligand geometry and electron distribution.[3a]

We describe here the crystal structure determination of the complex (I) bis(*N*-methyldithiocarbamato)nickel(II), $[Ni(CS_2{\cdot}NHMe)_2]$.



(I)

(I) Showing the arbitrary numbering system used

EXPERIMENTAL AND RESULTS

The complex used in this study was prepared by the usual double-decomposition reaction between aqueous solutions of a nickel(II) salt and the sodium salt of the ligand,[3b] and was recrystallized from chloroform. Crystals suitable for *X*-ray work were obtained as needles from ether–heptane (Found: C, 18·00; H, 2·95; N, 10·35; Ni, 21·7; S, 47·3. Calc. for $C_4H_8N_2NiS_4$: C, 17·75; H, 3·0; N, 10·35; Ni, 21·6; S, 47·4%).

Preliminary photographs and unit-cell data were obtained by the multiple-film equi-inclination Weissenberg method on a non-integrating Nonius Weissenberg camera about the *b* and *c* axes as spindle axes on two identical needle sections 0·15 × 0·15 × 0·12 mm. (The needle axis of the crystal is *c* and the section diagonals *a* and *b*.) There was no evidence for deterioration in the crystal exposed to the atmosphere and the *X*-ray beam, from the quality of the reflections obtained or later agreement analyses.

Unit-cell dimensions were obtained from zero-layer Weissenberg photographs about *b* and *c*, calibrated with aluminium powder ($a = 4{\cdot}0494$ Å)[4] taken with nickel-filtered copper radiation [$\lambda(K_{\alpha1}) = 1{\cdot}5444$, $\lambda(K_{\alpha2}) = 1{\cdot}5406$ Å].[5]

Crystal Data.—$C_4H_8N_2NiS_4$, $M = 271$, Monoclinic, $a = 12{\cdot}20 \pm 0{\cdot}03$, $b = 9{\cdot}37 \pm 0{\cdot}03$, $c = 4{\cdot}20 \pm 0{\cdot}02$ Å, $\beta = 93{\cdot}4 \pm 0{\cdot}2°$, $U = 480$ Å^3, D_m (by flotation) $= 1{\cdot}88 \pm 0{\cdot}02$, $Z = 2$, $D_c = 1{\cdot}89$, $F(000) = 166$. Space group $P2_1/a$ (C^5_{2h}, No. 14, Ref. 6) from systematic absences, $\{h0l\}$, $h = 2n + 1$, $\{0k0\}$, $k = 2n + 1$. Cu-$K_{\alpha1,2}$ radiation, $\mu(\text{Cu-}K_{\alpha1,2}) = 100$ cm^{-1}.

The intensities of 671 independent observed reflections collected from the layers $h0$—$5l$ and $hk0$—2 were estimated visually by use of an intensity strip calibrated on a Joyce-Loebl Mark IIIB microdensitometer. Only these non-zero reflections were used in the subsequent structure determination. All intensities were corrected for absorption by use of a local variant of the program ABSCOR,[7] the range of

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[5] 'International Tables for *X*-ray Crystallography,' vol. III, Kynoch, Birmingham, 1962, p. 59.

[6] Ref. 5, vol. I, 1965, p. 383.

[7] N. W. Alcock, in 'Crystallographic Computing,' Munksgaard, Copenhagen, 1971, p. 271.

transmission coefficients being 0·27—0·46. After correction for Lorentz and polarization factors with a local program (' SCAL1 ') the data were internally correlated and scaled using a program based on the algorithm of Hamilton, Rollett, and Sparks,[8] all reflections being assigned unit weights to give an arbitrarily scaled set of $|F_o|$.

Structure Determination.—The density and space group require occupancy of a special position of symmetry $\bar{1}$ by the nickel atom. This was confirmed by an unmodified three-dimensional Patterson synthesis computed on all data, from which the sulphur atoms were located. The nickel atoms were positioned at (0, 0, 0) and ($\frac{1}{2}$, $\frac{1}{2}$, 0), and the remainder of the atoms located on general positions (x, y, z), $(\bar{x}, \bar{y}, \bar{z})$, $(\frac{1}{2} - x, \frac{1}{2} + y, \bar{z})$, and $(\frac{1}{2} + x, \frac{1}{2} - y, z)$. Nickel and sulphur atoms were allocated arbitrary isotropic thermal parameters of 2·5 Å yielding a discrepancy factor of R 0·30. A three-dimensional Fourier synthesis enabled the remaining atoms to be located, whereupon R was reduced to 0·24, the remaining atoms being allocated arbitrary isotropic thermal parameters of 3·0 Å^2. A weighting scheme of the form $w = (a + |F_o| + b|F_o|^2)^{-1}$ was introduced,[9] a and b being adjusted as refinement proceeded. The structure was refined using block-diagonal (3 × 3, 6 × 6) least-squares techniques, minimizing the function $\Sigma w(|F_o| - |F_c|)^2$. Refinement converged to R 0·158; the weighted value R' being 0·270 $[R' = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{\frac{1}{2}}]$. The nickel and sulphur atoms were then allowed to vibrate anisotropically the expression for the temperature factor being in the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$, whereupon refinement converged to a final R of 0·120 and R' 0·164; the introduction of anisotropic thermal parameters were considered significant at $>99\%$.[10] During the final cycle no parameter shift was $>0{\cdot}25\sigma$. Final weighting scheme constants were $a = 1{\cdot}77$, $b = 0{\cdot}141$. A difference map computed at this stage showed no peaks $>0{\cdot}5$ eÅ^{-3}. There was no evidence for disorder in the structure. Scattering factors were taken from ref. 11 for the neutral atoms, nickel and sulphur atoms being corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$) according to ref. 12. Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 20383 (3 pp., 1 microfiche).*

Final atomic positional and thermal parameters are given in Table 1; estimated standard deviations are derived from a block-diagonal least-squares refinement procedure and are therefore likely to be underestimates [Program: SFLS1,2, A.I.M. Rae (local)]. Interatomic distances and angles were computed using the BONDSCAN programme of Pippy and Ahmed[13] and are given in Table 2. Computing was carried out on the DEC PDP10 machine at the University of Western Australia.

TABLE 1

(*a*) Final atomic fractional co-ordinates and isotropic thermal parameters, with estimated standard deviations in parentheses

Atom	x	y	z	B/Å^2
Ni	0·0000	0·0000	1·0000	
S(1)	0·0891(3)	0·2036(3)	0·9717(8)	
S(2)	0·1459(3)	−0·0688(3)	0·7588(8)	
C(1)	0·1876(9)	0·1065(14)	0·799(3)	3·7(2)
C(2)	0·3616(12)	0·0710(17)	0·549(3)	5·2(3)
N	0·2795(9)	0·1561(12)	0·707(2)	4·3(2)
[H *	0·2987	0·2645	0·747]	

* Estimated position.

(*b*) Anisotropic thermal parameters (× 10^4) of nickel and sulphur atoms

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	42(2)	42(3)	332(17)	−11(4)	57(8)	−54(12)
S(1)	77(2)	91(3)	805(23)	−13(4)	109(10)	−73(15)
S(2)	75(2)	92(3)	707(19)	−6(4)	136(10)	−84(14)

TABLE 2

(*a*) Final bond lengths (Å) and angles (°) with the asymmetric unit with estimated standard deviations in parentheses

(i) Distances		(ii) Angles	
Ni–S(1)	2·203(9)	S(1)–Ni–S(2)	79·2(1)
Ni–S(2)	2·196(9)	Ni–S(1)–C(1)	85·6(4)
S(1)–C(1)	1·70(1)	Ni–S(2)–C(1)	85·3(4)
S(2)–C(1)	1·72(1)	S(1)–C(1)–S(2)	109·8(7)
C(1)–N	1·30(2)	S(1)–C(1)–N	125·4(9)
N–C(2)	1·47(2)	S(2)–C(1)–N	124·7(9)
[N–H	1·05] *	C(1)–N–C(2)	124·4(11)
		[C(2)–N–H	117·0] *

(*b*) Non-bonding distances (<4·0 Å) within the asymmetric unit

Ni–C(1)	2·68(1)	S(1)–C(2)	4·05(2)
Ni–N	3·97(1)	S(2)–N(1)	2·68(1)
S(1)–S(2)	2·81(1)	S(2)–C(2)	3·11(2)
S(1)–N	2·67(1)	C(1)–C(2)	2·45(2)
[S(1)–H	2·84] *		

* Estimated.

(*c*) Intermolecular contacts (<4·0 Å)

Ni–S(2^{II})	3·62(1)	S(2)–C(2^{VII})	3·62(2)
S(1)–C(1^{III})	3·72(1)	S(2)–N$^{\text{VII}}$	3·40(1)
S(1)–N$^{\text{III}}$	3·78(1)	S(2)–N$^{\text{VII}}$	3·50(1)
S(1)–S(2^{IV})	3·39(1)	C(1)–C(2^{III})	3·71(2)
S(1)–S(2^{V})	3·98(1)	C(1)–N$^{\text{III}}$	3·94(2)
S(1)–C(2^{VI})	3·84(1)	C(2)–N$^{\text{II}}$	3·71(2)
[H–S(2^{V})	2·75]	[H–S(2^{IV})	2·66]

Roman numerals as superscripts refer to the following transformations with respect to the asymmetric unit at x, y, z:

I x, y, z
II $x, y, z - 1$
III $x, y, z + 1$
IV $x, y, 1 - z$
V $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$
VI $x - \frac{1}{2}, \frac{1}{2} - y, z$
VII $\frac{1}{2} - x, y - \frac{1}{2}, \bar{z}$
VIII $\frac{1}{2} - x, y - \frac{1}{2}, 1 - z$
IX $\frac{1}{2} - x, \frac{1}{2} + y, 2 - z$

DISCUSSION

The crystals are composed of discrete centrosymmetric molecules, being similar in this respect to other derivatives in this series $[\mathrm{Ni(CS_2{\cdot}NR_2)_2}]$ *viz.* (II; R = H),[14] (III; N = Et),[15] and (IV; R = Pr^n).[16,17] The Figure shows the arrangement of the unit cell contents.

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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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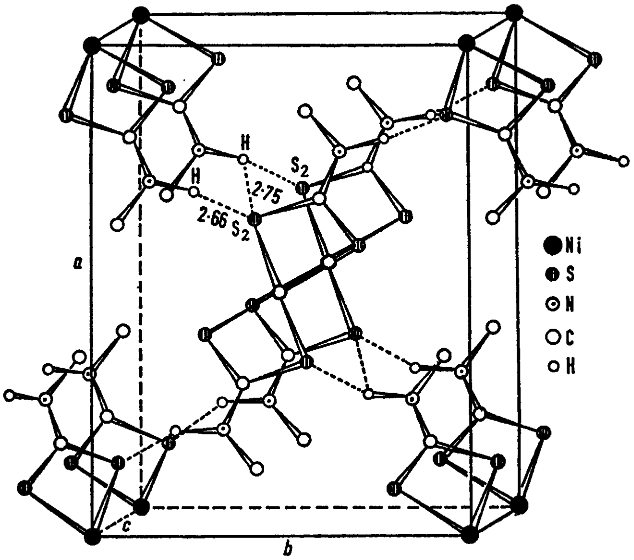


The unit cell viewed normal to the *ab* face

The nickel–sulphur geometry in this complex is normal and in good agreement with that of the complexes (II)—(IV) (see Table 3). The nickel atom has four sulphur atoms co-ordinated to it [as is also the case with (II)—(IV)], and necessarily coplanar with it because of the $\bar{1}$ symmetry of the nickel site. In this respect the molecule shows more affinity with the structures of (III) and (IV) than with that of the unsubstituted parent complex (II) in which distortions of the NiS_4 system from planarity occur; these are presumed to be the effects of hydrogen-bonding. In fact only in complex (II) does the nickel atom not occupy a centre of symmetry. Appreciable distortions from planarity are also found in the present molecule [plane (*c*), Table 4]; the molecule consists of a series of distinct intersecting planes [(*a*) and (*b*), Table 4] through the NiS_4 and S(1), S(2), C(1), N entities, the angle between these planes being 3·1°. The hydrogen atom position was estimated at (0·2987, 0·2645, 0·747), with N–H 1·05 Å, C(2)–N–H 117°, and the H atom slightly out of the S_2CN plane by 0·03 Å and on the same side of the plane as C(2) (which is found to deviate by 0·04 Å). With the hydrogen atom at this position (or, for that matter, at a variety of possible positions with N–H 1·05 Å and C(2)–N–H-angle 117°), very short intermolecular distances were found to the S(2) atom, the hydrogen appearing to bridge a pair of these in adjacent parallel molecules (Figure) at distances of 2·66 and 2·75 Å; the intramolecular distance to S(1) is 2·84 Å. It would therefore seem that hydrogen bonding effects are instrumental in this compound in determining both the molecular packing and out-of-plane distortions, although perhaps less than in (II). In (II), using the hydrogen positions estimated by Gasparri *et al.*[14] we have calculated the co-ordination about each hydrogen atom and tabulated these distances, together with those of the present compound in Table 5 (the van

TABLE 3

Comparison of mean dimensions of compounds $[Ni(CS_2{\cdot}NR_2)_2]$

Compound	Ni–S	S–Ni–S	C(1)–S
(II) [a]	2·21 Å	78·6°	1·69 Å
(I) [b]	2·20	79·2	1·71
(III) [c]	2·20	79·1	1·71
(IV) [d]	2·20	79·1	1·71
Compound	**C(1)–N**	**C(2)–N**	**S(1)–C(1)–S(2)**
(II) [a]	1·38 Å		111°
(I) [b]	1·30	1·47 Å	111
(III) [c]	1·33	1·48	110
(IV) [d]	1·33	1·47	110

[a] Ref. 14. [b] Present work. [c] Ref. 15. [d] Ref. 16.

TABLE 4

Equations * of best least-squares planes in the form $lX + mY + nZ = P$; deviations (Å) of atoms from the planes are given in square brackets

	l	*m*	*n*	*p*
Plane (*a*):				
Ni, S(1), S(2)	0·4222	−0·1869	0·8870	3·616
[C(1) 0·05, N 0·11, C(2) 0·11]				
Plane (*b*):				
S(1), S(2), C(1), N(1)	0·3799	−0·2046	0·9021	3·609
[Ni 0·08, S(1) 0·00, S(2) 0·00, C(1) 0·00, N 0·00, C(2) −0·04]				
Plane (*c*):				
Ni, S(1) S(2), C(1), N, C(2)	0·3973	−0·1980	0·8961	3·634
[Ni 0·03, S(1) −0·02, S(2) −0·02, C(1) 0·00, N 0·02, C(2) 0·00]				

Plane (*b*): σ For deviation of atoms defining plane: 0·00 Å. Angle between planes (*a*) and (*b*): 3·1°.

Plane (*c*): σ For atoms defining plane: 0·02Å.

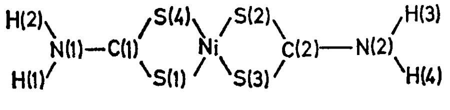
* Equations are referred to the orthogonal (Å) co-ordinates X, Y, Z related to cell co-ordinates x, y, z by the transformation $X = ax + cz \cos\beta$, $Y = by$, $Z = cz \sin\beta$.

TABLE 5

Intra- and inter-molecular S · · · H and associated S · · · N distances (Å) in (I) and (II) *

(*a*) Compound (I)			
(i) Intramolecular			
H · · · S(1)	2·84		
(ii) Intermolecular			
H · · · S(2)	2·66	N · · · S(2)	3·40
	2·75		3·50
(*b*) Compound (II)			
(i) Intramolecular (<3·0 Å)			
H(1) · · · S(1)	2·89	H(3) · · · S(2)	2·90
H(2) · · · S(4)	2·88	H(4) · · · S(3)	2·88
(ii) Intermolecular			
H(1) · · · S(2)	2·96	N(1) · · · S(2)	3·54
H(1) · · · S(3)	2·99	N(1) · · · S(3)	3·38
H(1) · · · S(4)	2·85	N(1) · · · S(4)	3·66
H(2) · · · S(3)	2·41	N(1) · · · S(3)	3·38
H(3) · · · S(2)	2·47	N(2) · · · S(2)	3·39
H(4) · · · S(4)	2·47	N(2) · · · S(4)	3·42
[H(4) · · · Ni	2·86]	[N(2) · · ·Ni	3·49]

* The atom numbering in (II) is that of Gasparri *et al.*[14]



(II)

der Waal's S · · · H distance is estimated at 3·05 Å and all distances less than this are tabulated). Also tabulated are the associated N · · · S distances (to be compared with an estimated van der Waal's N · · · S distance of 3·35, and those tabulated by Hossain for systems in which N–H · · · S interactions are presumed to occur which range between 3·24 and 3·50 Å).[18]

Such effects are also known in the related organic esters of the monosubstituted dithiocarbamic acids, $NHR^1\cdot CS_2R^2$, in which a high degree of molecular association has been shown to occur in benzene solutions by means of molecular-weight determinations;[19,20] it seems that these experimental results provide further testimony to the strength of N–H · · · S interactions in compounds of this type.

Within the ligand the carbon–sulphur, carbon–nitrogen, and terminal carbon–nitrogen distances and the angles between them are in good agreement with those previously reported in the square planar nickel(II) complexes of this 1 : 1 dithiochelate system (Table 5). There are no obvious or significant differences between the geometry of this and the previously reported complexes and it would seem that any attempt to draw a correlation between the intraligand geometry and crystal-field behaviour must await more extreme examples of the latter, and, perhaps, greater accuracy of structure determination.

Intermolecular contacts (<4·0 Å) given in Table 2 show that, as in (II)—(IV) there are no close metal–metal or metal–sulphur contacts, the nearest being 3·63 Å [Ni · · · S(2)]. This is in contrast to the copper analogues which, although isomorphous, display a tendency for dimer formation by the occupancy of a fifth copper co-ordination site by a sulphur atom from an adjacent molecule,[17] the corresponding copper–sulphur distance being of the order of 2·85 Å.

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[1/2330 *Received, 6th December*, 1971]

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