Crystal Structures of Bis(pyrrolidonecarbodithioato)-nickel(II) and -copper(II)

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The crystal structures of the title compounds have been established by single-crystal photographic X-ray diffraction methods. Crystals are triclinic, space group $P\bar{1}$, a = 7·477(4) [7·491(2)],† b = 7·971(3) [8·069(2)], c = 6·314(3) [6·379(2)] Å, α = 103·18(5) [104·83(2)], β = 93·47(6) [94·11(2)], γ = 75·45(5) [76·62(2)]°, Z = 1. The structures were solved by the heavy-atom method and refined by block-diagonal least squares to R 0·10 [0·10] for 857 [953] independent reflections. The structure consists of centrosymmetric molecules, the metal atom being planar co-ordinated by four sulphur atoms at 2·217(2) and 2·201(2) [2·342(2) and 2·345(2)] Å. Intraligand distances are normal. There is no evidence in the copper derivative for dimer formation by intermolecular metal–sulphur interaction.

As a further contribution in a series of studies [1-3] aimed at the delineation of structural changes resulting from substituent modification in the NN-dialkyldithiocarbamate ligand, $CS_2^{-}\cdot NR_2$, we report the crystal structure of bis(pyrrolidonecarbodithioato)nickel(II), $[Ni\{CS_2\cdot N\cdot[CH_2]_4\}_2]$ (this ligand had the weakest known crystal field of any of the substituted dithiocarbamates).[4-6] As it was evident from the isomorphous nature of the copper(II) analogue and the solution of the nickel structure, that the copper(II) derivative was monomeric rather than the pseudo-dimeric type often found,[7-8] its structure was also determined and is reported; throughout the paper values for the copper compound are given in square brackets following those for the nickel compound.

EXPERIMENTAL

The complexes were prepared from an aqueous solution of nickel(II) or copper(II) sulphate with the sodium salt of the ligand,[9] and recrystallized from chloroform; slow evaporation of dilute saturated chloroform solution yielded large well-formed crystals of both complexes.

In both cases, X-ray data were collected photographically on a single crystal of the complex, by methods described previously.[1-3] Unit-cell calibration was effected by the use of a Syntex $P\bar{1}$ diffractometer to centre and index 15 high-angle reflections in each case, the cell parameters being derived by a least-squares fit.

Crystal Data.—$C_{10}H_{16}N_2S_4Ni(Cu)$, M = 351 [356], Triclinic, space group $P\bar{1}$ (C_i^1, No. 2), a = 7·477(4) [7·491(2)], b = 7·971(3) [8·069(2)], c = 6·314(3) [6·379(2)] Å, α = 103·18(5) [104·83(2)], β = 93·47(6) [94·11(2)], γ = 75·45(5) [76·62(2)]°, U = 355·0(4) [362·7(2)] Å^3, D_m (flotation) = 1·65(2) [1·64(2)], Z = 1, D_c = 1·66 [1·63], $F(000)$ = 182 [183].

Data were collected for layers $h0$—$5l$, $hk0$—4, to give 857 [953] independent observed reflections by use of nickel-filtered Cu(K_α) radiation, λ = 1·5418 Å, μ(Cu-K_α) = 66 [72] cm^{-1}. The transmission coefficient range was 0·43—0·63 [0·38—0·47] and crystal size 0·12 × 0·15 × 0·15 [0·16 × 0·16 × 0·16] mm.

Data were processed and the structure solved and refined by our usual methods.[1-3] Relevant refinement parameters are:

	R		*R′* *	
All atoms isotropic	0·166	[0·180]	0·225	[0·226]
Metal only anisotropic	0·150	[0·172]	0·204	[0·204]
Metal, anisotropic	0·103	[0·109]	0·133	[0·134]

a		*b*	
1·57	[2·19]	0·020	[0·0111]

* $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w\,|F_o|^2)^{\frac{1}{2}}$, where $w = (a + |F_o| + b\,|F_o|^2)^{-1}$ (ref. 10).

Final difference maps showed no significant features, and at refinement termination all positional parameter shifts were $<0{\cdot}1\sigma$ and all thermal parameter shifts $<0{\cdot}2\sigma$. Scattering factors were for the neutral atoms,[11] those for

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† Throughout the paper values are quoted for the nickel complex with those for the copper complex in square brackets.

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

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

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

[10] D. W. Cruickshank, in 'Computing Methods in X-Ray Crystallography,' ed. J. S. Rollett, Pergamon Press, Oxford, 1965, p. 114.

[11] 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962, p. 210.

nickel, copper, and sulphur being corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$).[12] Final sets of $|F_o|$ and $|F_c|$ are listed in Supplementary Publication No. SUP 20690 (4 pp., 1 microfiche); ‡ in the case of the copper compound, certain reflections which appeared to be heavily affected by extinction were deleted from the data set and are marked E. Anisotropic thermal parameters are of the form: exp $[-(\beta_{11}h^2 + \beta_{12}hk + \beta_{13}hl + \beta_{22}k^2 + \beta_{23}kl + \beta_{33}l^2)]$. Block-diagonal ($3 \times 3$, 6×6) least-squares estimated standard deviations (probably underestimates), in the final digit are given in parentheses throughout the Tables of atomic parameters (Table 1) and interatomic distances and angles (Table 2).[13] Hydrogen atom positions were fixed according to the criteria H(i 1,2)–C(i) 1·08 Å and H(i 1,2)–C(i)–H(i 2,1)–C($i \pm 1$) 109·5°, where H(i 1,2) is attached to C(i). Least-squares planes (Table 3) are referred to an orthogonal frame (X,Y,Z) defined by:

$$[X,Y,Z] = \begin{bmatrix} a & b\,.\,\mathrm{Cos}\,\gamma & c\,.\,\mathrm{Cos}\,\beta \\ 0 & b\,.\,\mathrm{Sin}\,\gamma & c\,.\,(\mathrm{Cos}\,\alpha - \mathrm{Cos}\,\beta\,.\,\mathrm{Cos}\,\gamma)/\mathrm{Sin}\,\gamma \\ 0 & 0 & U/a\,.\,b\,.\,\mathrm{Sin}\,\gamma \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

Unit-cell contents are displayed in Figure 1; thermal ellipsoids are shown in Figure 2.

TABLE 1

Final atomic fractional cell positional and thermal parameters. (In this and subsequent Tables those parameters pertinent to the Cu derivative are given in square brackets after those of the Ni derivative.) Ni and Cu atoms lie on special positions at (0,0,0)

Atom	x	y	z	B/Å^2
S(1)	0·1693(3) [0·1776(4)]	0·9453(3) [0·9453(5)]	0·7044(3) [0·6965(3)]	*
S(2)	0·2622(3) [0·2769(4)]	0·8421(3) [0·8306(4)]	1·1042(3) [1·0915(5)]	*
N	0·510(1) [0·511(1)]	0·753(1) [0·753(1)]	0·782(1) [0·774(1)]	4·2(1) [3·9(1)]
C(1)	0·339(1) [0·341(1)]	0·836(1) [0·833(1)]	0·852(1) [0·842(1)]	4·2(1) [3·4(2)]
C(2)	0·579(1) [0·578(1)]	0·748(1) [0·756(2)]	0·562(1) [0·556(2)]	5·2(2) [5·6(3)]
C(3)	0·759(2) [0·752(2)]	0·612(1) [0·623(2)]	0·547(2) [0·536(2)]	6·7(2) [6·9(3)]
C(4)	0·827(2) [0·818(2)]	0·593(1) [0·593(2)]	0·767(2) [0·758(2)]	6·5(2) [6·1(3)]
C(5)	0·659(1) [0·653(2)]	0·662(1) [0·657(2)]	0·917(1) [0·901(2)]	5·4(2) [5·1(2)]
H(21) †	0·560 [0·603]	0·876 [0·883]	0·552 [0·557]	
H(22) †	0·485 [0·484]	0·708 [0·719]	0·435 [0·426]	
H(31) †	0·859 [0·853]	0·652 [0·669]	0·466 [0·467]	
H(32) †	0·740 [0·729]	0·486 [0·502]	0·454 [0·429]	
H(41) †	0·928 [0·921]	0·670 [0·666]	0·819 [0·824]	
H(42) †	0·890 [0·873]	0·455 [0·455]	0·765 [0·746]	
H(51) †	0·686 [0·681]	0·756 [0·744]	1·061 [1·052]	
H(52) †	0·619 [0·608]	0·555 [0·548]	0·964 [0·933]	

* Anisotropic thermal parameters ($\times 10^4$) (see text).

Atom	β_{11}	β_{12}	β_{13}	β_{22}	β_{23}	β_{33}
Ni	78(3) [142(3)]	−5(4) [−20(6)]	58(6) [70(7)]	102(3) [140(3)]	26(6) [97(7)]	143(5) [227(5)]
S(1)	174(4) [170(5)]	38(6) [95(10)]	77(7) [129(11)]	309(5) [317(7)]	205(8) [302(14)]	276(6) [310(8)]
S(2)	179(5) [188(5)]	35(6) [107(10)]	101(7) [142(11)]	294(5) [275(7)]	222(9) [278(13)]	293(6) [302(8)]

† Estimated (see text).

TABLE 2

Interatomic distances (Å) and angles (°)

(a) Within the asymmetric unit

Ni–S(1)	2·217(2)	[2·342(2)]
Ni–S(2)	2·201(2)	[2·345(2)]
S(1)–S(2)	2·825(3)	[2·850(4)]
C(1)–S(1)	1·707(8)	[1·735(8)]
C(1)–S(2)	1·713(8)	[1·720(7)]
C(1)–N	1·33(1)	[1·39(1)]
N–C(2)	1·50(1)	[1·51(1)]
N–C(5)	1·50(1)	[1·50(1)]
C(2)–C(3)	1·49(2)	[1·51(1)]
C(3)–C(4)	1·48(2)	(1·52[2)]
C(4)–C(5)	1·53(2)	[1·55(2)]
S(1)–Ni–S(2)	79·5(1)	[74·9(1)]
Ni–S(1)–C(1)	84·4(3)	[86·8(3)]
Ni–S(2)–C(1)	84·7(3)	[87·0(3)]
S(1)–C(1)–S(2)	111·4(5)	[111·2(4)]
S(1)–C(1)–N	125·2(6)	[126·6(6)]
S(2)–C(1)–N	123·4(6)	[122·2(6)]
C(1)–N–C(2)	123·8(7)	[122·9(8)]
C(1)–N–C(5)	124·2(7)	[126·4(9)]
C(2)–N–C(5)	112·0(7)	[110·7(8)]
N–C(2)–C(3)	102·6(8)	[103·2(7)]
C(2)–C(3)–C(4)	110·0(10)	[110·6(9)]
C(3)–C(4)–C(5)	106·5(9)	[104·0(10)]
C(4)–C(5)–N	104·1(8)	[107·2(10)]

(b) Intermolecular: hydrogen contacts <3·0 Å

Ni · · · H(41^{II})	2·79 [2·84]	S(2) · · · H(22^{IV})	2·83 [2·80]
S(1) · · · H(51^{III})	2·92 [3·03]	S(2) · · · H(52^{V})	3·00 [2·95]

Transformations of the asymmetric unit x, y, z:

II $x - 1, y, z$
III $1 - x, 2 - y, 2 - z$
IV $x, y, z + 1$
V $1 - x, 1 - y, 2 - z$

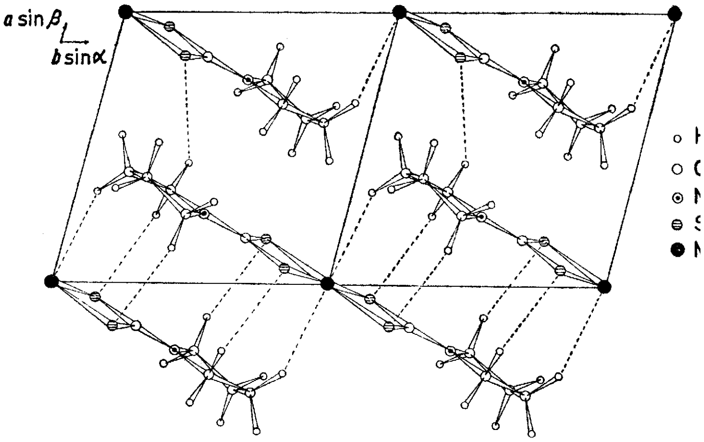

FIGURE 1 Unit cell contents

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‡ See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue. Items less than 10 pp. are supplied as full-size copies.

[12] Ref. 11, p. 213.

[13] M. E. Pippy and F. R. Ahmed, *Div. Pure and Appl. Phys.*, N.R.C. Ottawa, Canada, Program NRC 12.

Computing was carried out on a DEC PDP 10 at the University of Western Australia.

DISCUSSION

In both complexes, the asymmetric unit comprises one half of the molecule, the metal atom being situated on a centrosymmetric special position and necessarily planar co-ordinated by four sulphur atoms, as is usual in such nickel(II) derivatives. As in most of the bis(*NN*-dialkyldithiocarbamato)-nickel(II) and -copper(II) derivatives so far studied, the crystal packing is dominated by intermolecular proton contacts from the ligand substituent to the metal and sulphur atoms at distances less than the estimated van der Waals distance[14] (Figure 1, Table 2), and as a consequence both complexes may be regarded as monomers in the solid state. In the case of the copper derivative, this result, together with the recent structure determination of [Cu(CS_2·NMePh)$_2$],[2] and the brief report of the hexamethylene derivative,[15] [Cu{CS_2·N[CH_2]$_6$}$_2$], in which the molecules are also monomers, suggest that the earlier structure determinations of bis(*NN*-diethyl- and bis(di-n-propyl-dithiocarbamato)copper(II) [7,8] are misleading. In the latter, intermolecular copper–sulphur interaction led to distortion of the copper environment into a rectangular pyramid with the formation of ' dimers '; this was not the case in the nickel(II) analogues which remained monomeric.[16,17] The two more recent structures suggest that intermolecular copper–sulphur interactions in these complexes are comparable in energy to proton–sulphur and proton–metal interactions and should not be regarded as a necessary or general feature of the structural chemistry of these complexes.

Table 3

Least squares planes in the form $lX + mY + nZ = p$ with atomic deviations (Å) and standard deviations (σ Å) of the atoms defining the plane; the latter are italicized

	l	m	n	p	σ
Plane (i): S_2CN	0·5035 [0·4788]	0·7843 [0·7763]	0·3625 [0·4100]	7·981 [8·097]	0·00 [0·00]
	S(1) 0·00 [0·00], *S(2)* 0·00 [0·00], *C(1)* 0·00 [0·00]; *N* 0·00 [0·00], Ni 0·03 [0·06], C(2) 0·01 [0·03], C(3) −0·29 [−0·27], C(4) 0·05 [0·02], C(5) 0·05 [0·01]				
Plane (ii): NC_4	0·5499 [0·5302]	0·7872 [0·7728]	0·2790 [0·3488]	7·872 [8·094]	0·09 [0·09]
	N −0·05 [−0·04], *C(2)* 0·11 [0·10], *C(3)* −0·13 [−0·13], *C(4)* 0·10 [0·10], *C(5)* −0·03 [−0·03], *C(1)* 0·13 [−0·12], (S1) −0·10 [−0·13], S(2) −0·29 [−0·26], Ni −0·28 [−0·25]				

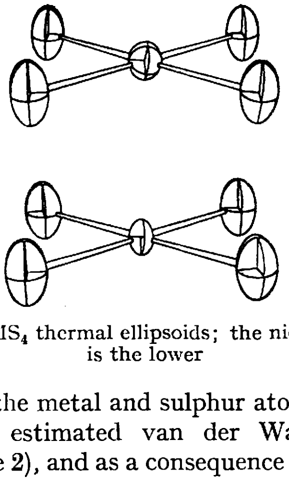

Figure 2 MS_4 thermal ellipsoids; the nickel complex is the lower

It was expected that the weak crystal-field strength of the present ligand might be reflected in the structural parameters of the two complexes, probably by way of unusually long metal–sulphur and carbon–nitrogen distances. The copper–sulphur distances [2·342 and 2·345(2) Å] are the largest hitherto observed in a dithiocarbamate complex and the nickel–sulphur distances [2·217 and 2·201(2) Å] are also unusually long and probably comparable with those in the parent complex [Ni(CS_2·NH_2)$_2$] [2·21 and 2·22 (1) Å]. In the case of the distance C(1)–N, 1·33(1) [1·39(1)] Å, that found in the copper derivative is certainly the longest yet reported; however, the lack of agreement with that for the nickel compound suggests that the discrepancy is random and its significance dubious (related distances and angles are tabulated in Table 4 of ref. 2). The associated MS_2 and CS_2 angles vary as expected, as does the S···S distance. The remainder of the S_2CN dimensions are normal and, as usual, the group is rigorously planar (Table 3). Although the C–N distances in the pyrrolidone ring are normal, the C(2)–N–C(5) angle (*ca.* 111°) is greatly reduced from the usual value of 117° found in complexes of this type with a pair of separated alkyl substituents. The strain within the ring is reflected in angles which are generally less than the tetrahedral angle, with the exception of those at C(3), C(2)–C(3)–C(4) 110·0 [110·6(9)°], which are a consequence of a distortion of this carbon from the ring plane by *ca.* 0·3 Å (Table 3).[18] [In retrospect it is apparent that a similar mechanism accounts for the nonplanarity of the pyrrolidine rings observed in the iron(III) analogue [Fe(CS_2·N[CH_2]$_4$)$_3$], in which atoms C(a4), C(b5), and C(c4) exhibit similar marked deviations from planarity.[6]]

The thermal ellipsoids of the sulphur atoms are markedly anisotropic (Table 1, Figure 2), and the agreement between the two derivatives for the analogous atoms is excellent, considering the use of the film data; this is also the case for the peripheral ligand atoms, and lends credibility to the pronounced differences in the

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[15] Z. V. Zvonkova and V. I. Yakovenko, *Soviet Phys.* (*Crystallography*), 1968, **13**, 134.

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[17] G. Peyronel and A. Pignedoli, *Acta Cryst.*, 1967, **23**, 698.

[18] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, ' Conformational Analysis,' Wiley–Interscience, New York, 1965, pp. 200—206 and references therein.

ellipsoids of the nickel and copper atoms, the former having a large anisotropy while the latter is almost spherical having a larger vibrational amplitude in the plane of the four sulphur atoms. This difference is presumably to be attributed to the longer metal–sulphur distance in the latter (a consequence of the additional *d* electrons), the bond presumably also being weaker and giving rise to lower MS_4 i.r. frequencies and facilitating thermal motion at room temperature. In these two derivatives the frequency of the predominantly MS_4 asymmetric stretch was measured and found at **384** [**330** cm^{-1}]; the latter band was considerably broader than the former (Nujol mull between CsI plates; Perkin-Elmer 521 instrument).

[3/150 *Received, 22nd January,* 1973]