Crystal Structures of Bis-(*N*-methyl-*N*-phenyldithiocarbamato)-nickel-(II) and -copper(II)

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The crystal and molecular structures of the title compounds have been determined by single-crystal *X*-ray diffraction methods, using conventional Patterson and Fourier heavy-atom methods, followed by block-diagonal least-squares refinement to *R* 0·116 (Ni) and 0·125 (Cu) for 1106 and 1202 visually estimated independent observed reflections. The compounds are isomorphous and isostructural with monoclinic unit cells, space group $P2_1/a$, containing two discrete molecules: $[Ni(CS_2{\cdot}NMePh)_2]$: a = 19·30 ± 0·02, b = 6·592 ± 0·003, c = 7·658 ± 0·003 Å, β = 107·8 ± 0·1°; $[Cu(CS_2{\cdot}NMePh)_2]$: a = 19·40 ± 0·02, b = 6·612 ± 0·003, c = 7·701 ± 0·003 Å, β = 107·5 ± 0·1°.

The heavy atom in each structure occupies the special position (0,0,0), $(\frac{1}{2},\frac{1}{2},0)$ with symmetry $\bar{1}$ and is necessarily planar co-ordinated by four neighbouring sulphur atoms at approximately equal distances: Ni–S 2·208(3) and 2·198(3) Å, S(1)–Ni–S(2) 79·2(1)°; Cu–S 2·329(3) and 2·274(3) Å, S(1)–Cu–S(2), 77·7(1)°. The remainder of the S_2CNC_2 ligand fragment is planar and conjugated, with normal geometry. There is evidence for hydrogen–sulphur intermolecular interactions. The plane of the phenyl ring lies at 82° to that of the conjugated ligand fragment in both cases, apparently as a result of steric interaction with the methyl group, and as a consequence of this both compounds are monomeric although it is usual for bis-(*NN*-dialkyldithiocarbamato)copper(II) derivatives to be dimeric in the solid state.

We are studying a variety of bis-(*NN*-disubstituted-dithiocarbamato)nickel(II) complexes, $[Ni(CS_2{\cdot}NR_2)_2]$, in order to ascertain the influence of different substituents R on the geometry of this MS_2CN conjugated system.[1] We now report the structure determination of bis-(*N*-methyl-*N*-phenyldithiocarbamato)nickel(II), $[Ni(CS_2{\cdot}NMePh)_2]$; during the course of this investigation, it became apparent that the isomorphous and isostructural copper(II) analogue was also likely to be of interest and this structure determination is also reported.

EXPERIMENTAL AND RESULTS

The complexes were prepared from sodium *N*-methyl-*N*-phenyldithiocarbamate with nickel(II) and copper(II) sulphates, and were recrystallized from chloroform–ethanol. Crystals suitable for *X*-ray work were obtained as elongated plates by the slow evaporation of a chloroform–ethanol solution.

The crystals of both complexes were isomorphous. *X*-Ray data were collected on a crystal section *ca.* 0·10 × 0·08 × 0·05 mm (Ni) mounted alternately about *b* and *c* as spindle axes, and on a section of 0·13 × 0·13 × 0·07 mm (Cu) about the same axes. All intensity data was collected by the multiple-film pack equi-inclination Weissenberg method on a non-integrating Nonius Weissenberg camera. There was no evidence of deterioration in the crystals exposed to the atmosphere and the *X*-ray beam.

Unit-cell dimensions were obtained from zero-layer Weissenberg photographs about the *b* and *c* axes in both cases, calibrated with superimposed aluminium powder lines (a = 4·0494 Å),[2] and also from Guinier photographs on the powdered samples using copper $K_{\alpha1}$ radiation and thoria as calibrant. Nickel-filtered copper radiation was used throughout [$\lambda(K_{\alpha1})$ = 1·5406, $\lambda(K_{\alpha2})$ = 1·5444 Å].[3] Crystal densities were obtained by flotation in aqueous potassium iodide solution.

Crystal Data.—(i) *Bis-*N*-methyl-*N*-phenyldithiocarbamato)-nickel*(II). $C_{16}H_{16}N_2NiS_4$, M = 423, Monoclinic, a = 19·30 ± 0·02, b = 6·592 ± 0·003, c = 7·658 ± 0·003 Å, β = 107·8 ± 0·1°, U = 928 Å^3, D_m = 1·49 ± 0·02, Z = 2, D_c = 1·51 g cm^{-3}, $F(000)$ = 536. Space group $P2_1/a$ (C^5_{2h}, No. 14, ref. 4) from systematic absences: $[h0l]$, h =

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[1] P. W. G. Newman and A. H. White, following paper.

[2] B. W. Delf, *Brit. J. Appl. Phys.*, 1963, **14**, 345.

[3] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962, p. 59.

[4] Ref. 3, 2nd edn., vol. I, 1965, p. 99.

$2n + 1$, $[0k0]$, $k = 2n + 1$. Data collected for layers $h0$—$3l$, $hk0$—3; μ(Cu-K_α) = 57 cm^{-1}, transmission coefficient 0·59—0·80.

(ii) *Bis*-(N-*methyl*-N-*phenyldithiocarbamato*)*copper*(II). $C_{16}H_{16}CuN_2S_4$, $M = 428$, Monoclinic, $a = 19{\cdot}40 \pm 0{\cdot}02$, $b = 6{\cdot}612 \pm 0{\cdot}003$, $c = 7{\cdot}701 \pm 0{\cdot}003$ Å, $\beta = 107{\cdot}5 \pm 0{\cdot}1°$, $U = 942$ Å^3; $D_m = 1{\cdot}51 \pm 0{\cdot}02$, $Z = 2$, $D_c = 1{\cdot}52$, $F(000) = 538$. Space group $P2_1/a$ from systematic absences. Data collected for layers $h0$—$3l$, $hk0$—3; μ(Cu-K_α) = 57 cm^{-1}, transmission coefficient 0·50—0·70.

Intensities were estimated visually using an intensity strip calibrated with a Joyce Loebl Mark IIIB microdensitometer. For the nickel complex 1106 independent observed reflections were determined; for the copper derivative 1202. 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,[5] and after correction for Lorentz and polarization factors with a local program (SCAL 1), both sets of data were internally correlated and scaled,[6] all reflections being assigned unit weights.

Structure Determinations.—The densities and space group required, in both cases, occupancy of a special position of symmetry $\bar{1}$ by the metal atom. For the nickel derivative, an unmodified three-dimensional Patterson synthesis computed on all data verified this and enabled location of the sulphur atoms. The metal atoms were positioned at (0,0,0), ($\frac{1}{2}$,$\frac{1}{2}$,0) and the remainder of the atoms on general positions (x,y,z), $(\bar{x},\bar{y},\bar{z})$, $(\frac{1}{2} - x, \frac{1}{2} + y, \bar{z})$, $(\frac{1}{2} + x, \frac{1}{2} - y, z)$. Nickel and sulphur atoms were allocated arbitrary isotropic thermal parameters of 2·5 Å^2 yielding R 0·40. A three-dimensional Fourier synthesis computed on all data enabled the remaining atoms to be located, reducing R to 0·36, the remaining atoms being allocated arbitrary isotropic temperature factors of 3·0 Å^2. The structure was refined by block-diagonal least-squares methods (by use of local programs SFLS 1 and 2 by A.I.M.Rae), (3 × 3, 6 × 6), minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, a weighting scheme [7] of the form $w = (a + |F_o| + b|F_o|^2)^{-1}$ being introduced and a and b adjusted as refinement proceeded. Refinement converged to R 0·18, the weighted factor R' being 0·25 $[R' = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{\frac{1}{2}}]$. Nickel and sulphur atoms were then allowed to vibrate anisotropically according to 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 the final R of 0·116 and R' 0·160, the introduction of anisotropic thermal parameters being considered highly significant.[8] During the final cycle of least squares, all positional parameter shifts were $< 0{\cdot}1\,\sigma$ and all thermal parameter shifts $< 0{\cdot}2\sigma$; the heavy-atom parameter shifts were considerably better. Final weighting scheme constants were $a = 6{\cdot}03$, $b = 0{\cdot}042$. A difference-Fourier map computed at this stage was flat to better than 0·25 carbon atoms. There was no evidence for disorder in the structure.

The similarity of cell dimensions, space group, and intensity distribution suggested a close resemblance between this structure and that of the copper analogue. Accordingly, all positions from the final solution of the nickel structure were used to phase an initial electron density map, using arbitrary isotropic temperature factors of 2·5 Å^2 (copper and sulphur) and 3·0 Å^2 (remainder); R was then 0·36. The electron-density distribution revealed no serious discrepancies and a similar refinement procedure with a comparable weighting scheme to that for the nickel derivative was used. With isotropic thermal parameters for all atoms R and R' converged to 0·19 and 0·25; with the

TABLE 1

Final atomic and thermal parameters with least-squares estimated standard deviations in parentheses

(*a*) Nickel complex

Atom	x	y	z	B/Å^2
Ni(1)	0·0000	1·0000	0·0000	*
S(1)	0·01857(15)	1·2865(4)	0·1569(4)	*
S(2)	0·08074(18)	0·9013(5)	0·2563(4)	*
N(1)	0·1144(5)	1·2139(1)	0·4914(1)	3·9(2)
C(1)	0·0763(5)	1·142(2)	0·333(1)	3·6(2)
C(2)	0·1050(8)	1·426(2)	0·556(2)	5·7(3)
C(3)	0·1633(6)	1·080(2)	0·621(1)	4·0(2)
C(4)	0·1341(7)	0·956(2)	0·726(2)	5·1(2)
C(5)	0·1830(8)	0·826(3)	0·859(2)	6·3(3)
C(6)	0·2576(8)	0·833(2)	0·885(2)	6·3(3)
C(7)	0·2836(8)	0·963(2)	0·771(2)	5·6(3)
C(8)	0·2373(7)	1·096(2)	0·641(2)	5·0(2)
H(4)	0·0763(7)	0·960	0·705	
H(5)	0·1633	0·721	0·940	
H(6)	0·2942	0·741	0·989	
H(7)	0·3408	0·960	0·783	
H(8)	0·2574	1·203	0·561	

Atom	β_{11}	β_{22}	β_{33}
Ni(1)	0·00175(7)	0·0118(6)	0·0092(4)
S(1)	0·00318(7)	0·0214(6)	0·0222(5)
S(2)	0·00430(7)	0·0210(6)	0·0186(5)

Atom	β_{12}	β_{13}	β_{23}
Ni(1)	0·0008(3)	−0·0010(3)	0·0037(11)
S(1)	0·0013(4)	0·0004(3)	0·0095(13)
S(2)	0·0037(4)	−0·0032(4)	0·0008(12)

* Anisotropic thermal parameters of nickel and sulphur atoms.

(*b*) Copper complex

Atom	x	y	z	B/Å^2
Cu(1)	0·0000	1·0000	0·0000	†
S(1)	0·02061(17)	1·3005(5)	0·1654(4)	†
S(2)	0·08286(22)	0·9049(6)	0·2650(5)	†
N(1)	0·1139(5)	1·219(2)	0·492(1)	3·1(2)
C(1)	0·0769(7)	1·150(2)	0·332(2)	3·1(2)
C(2)	0·1056(6)	1·428(2)	0·556(2)	4·9(3)
C(3)	0·1623(9)	1·083(3)	0·620(2)	3·0(2)
C(4)	0·1338(8)	0·961(2)	0·726(2)	4·1(3)
C(5)	0·1808(9)	0·839(3)	0·862(2)	5·0(3)
C(6)	0·2534(9)	0·339(3)	0·881(2)	5·0(3)
C(7)	0·2818(8)	0·969(3)	0·779(2)	4·6(3)
C(8)	0·2363(7)	1·094(2)	0·641(2)	3·7(3)
H(4)	0·0757	0·961	0·702	
H(5)	0·1610	0·744	0·951	
H(6)	0·2885	0·736	0·978	
H(7)	0·3400	0·973	0·806	
H(8)	0·2572	1·193	0·556	

† Anisotropic thermal parameters of copper and sulphur atoms.

Atom	β_{11}	β_{22}	β_{33}
Cu(1)	0·00178(7)	0·0096(6)	0·0091(4)
S(1)	0·00249(9)	0·0136(7)	0·0179(6)
S(2)	0·00442(14)	0·0148(8)	0·0162(6)

Atom	β_{12}	β_{13}	β_{23}
Cu(1)	0·0010(4)	−0·0015(3)	0·0014(10)
S(1)	0·0015(4)	−0·0009(4)	0·0084(13)
S(2)	0·0059(6)	−0·0039(5)	−0·0004(14)

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

[6] W. C. Hamilton, J. S. Rollett, and R. A. Sparks, *Acta Cryst.*, 1965, **18**, 129.

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

[8] W. C. Hamilton, *Acta Cryst.*, 1965, **18**, 502.

copper and sulphur allowed to vibrate anisotropically, refinement converged to R 0·125 and R' 0·159. It was concluded that the introduction of thermal anisotropy was highly significant. Similar parameter shifts were obtained at convergence and the difference map was flat to better than 0·25 carbon atoms. Final weighting scheme constants were $a = 25{\cdot}0$, $b = 0{\cdot}01$.

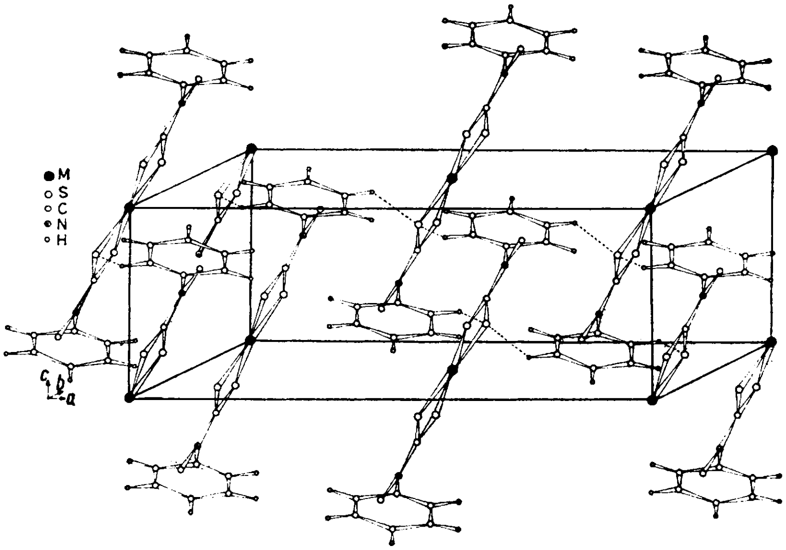

FIGURE 1 Unit cell contents for the two complexes

Scattering factors for both structures were taken from ref. 9 for the neutral atoms, nickel, copper and sulphur atoms being corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$) according to ref. 10. The final sets of observed and calculated structure factors are listed in Supplementary Publication No. 20449 (7 pp., 1 microfiche).† Final atomic positional and thermal parameters are listed in Tables 1(a) and (b), together with least-squares estimated standard deviations. The latter, derived from a block-diagonal refinement, are therefore likely to be underestimates. The unit-cell contents which are very similar for both structures are displayed in Figure 1; Figure 2 depicts the molecular geometry and atomic numbering system used for the asymmetric unit. Interatomic distances and angles [11] are given in Tables 2(a) and 2(b) together with estimated standard deviations. In both cases, the hydrogen-atom positions in the phenyl ring

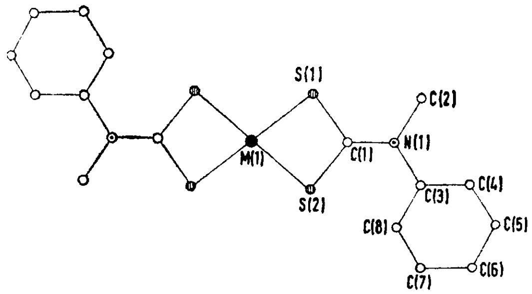

FIGURE 2 Molecular geometry and atom numbering in the complexes

TABLE 2

Molecular geometry

(a) Nickel complex

(i) Interatomic distances (Å) and angles (°) within the asymmetric unit

Ni(1)–S(1)	2·208(3)	S(1)–Ni(1)–S(2)	79·3(1)
Ni(1)–S(2)	2·198(3)	C(1)–S(1)–Ni(1)	85·0(4)
C(1)–S(1)	1·74(1)	C(1)–S(2)–Ni(1)	86·2(4)
C(1)–S(2)	1·70(1)	S(1)–C(1)–S(2)	109·3(6)
C(1)–N(1)	1·30(1)	N(1)–C(1)–S(1)	124·6(8)
N(1)–C(2)	1·51(2)	N(1)–C(1)–S(2)	125·8(8)
N(1)–C(3)	1·44(1)	C(2)–N(1)–C(1)	123·3(10)
C(3)–C(4)	1·38(2)	C(3)–N(1)–C(1)	119·0(9)
C(4)–C(5)	1·44(2)	C(2)–N(1)–C(3)	117·4(10)
C(5)–C(6)	1·39(2)	C(3)–C(4)–C(5)	117·9(12)
C(6)–C(7)	1·42(2)	C(4)–C(5)–C(6)	120·3(14)
C(7)–C(8)	1·42(2)	C(5)–C(6)–C(7)	118·6(14)
C(8)–C(3)	1·39(2)	C(6)–C(7)–C(8)	122·6(13)
		C(7)–C(8)–C(3)	115·7(12)
S(1) · · · S(2)	2·812(4)	C(8)–C(3)–C(4)	124·6(11)
C(2) · · · C(4)	3·34(2)	N(1)–C(3)–C(4)	117·7(10)
C(2) · · · C(8)	3·26(3)	N(1)–C(3)–C(8)	117·6(10)

(ii) Intermolecular interatomic distances (Å) < 4·0 Å *

Ni(1) · · · C($4^{\mathrm{II,III}}$)	3·81(1)	C(3) · · · C(8^{IV})	3·95(2)
S(1) · · · C(4^{III})	3·70(1)	C(4) · · · C(6^{VI})	3·96(2)
S(1) · · · C(5^{III})	3·93(2)	C(5) · · · C(6^{VI})	3·87(2)
S(1) · · · C(7^{IV})	3·87(2)	C(5) · · · C(6^{VIII})	3·79(2)
S(2) · · · C(7^{V})	3·95(2)	C(5) · · · C(7^{VIII})	3·62(2)
S(2) · · · C(8^{V})	3·91(1)	C(5) · · · C(8^{VIII})	3·97(2)
C(1) · · · C(7^{IV})	3·70(2)	C(6) · · · C($6^{\mathrm{VI,VIII}}$)	3·80(2)
C(2) · · · C(6^{IV})	3·99(2)	C(6) · · · C(7^{VI})	3·85(2)
C(3) · · · C(4^{VII})	3·71(2)	C(6) · · · C(8^{VIII})	3·93(2)
C(3) · · · C(5^{VII})	3·53(2)	C(7) · · · C(8^{V})	3·89(2)
C(3) · · · C(7^{IV})	3·77(2)	C(7) · · · N(1^{IV})	3·61(2)

* Roman numerals as superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z:

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

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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).

[9] Ref. 3, p. 210.

[10] Ref. 3, p. 213.

[11] M. E. Pippy and F. R. Ahmed, Div. Pure and Appl. Physics, N.R.C. Ottawa, Canada, Program No. NRC 12.

TABLE 2 (*Continued*)

(iii) Contacts (<3·5 Å) between phenyl hydrogen atoms and nickel and sulphur atoms.

[superscripts as defined in (ii)]

Ni(1) ··· H($4^{\text{II,III}}$)	3·06	S(2) ··· H(4)	3·48
S(1) ··· H(4^{III})	2·88	S(2) ··· H(4^{III})	3·26
S(1) ··· H(5^{III})	3·35	S(2) ··· H(5^{II})	3·49
S(1) ··· H(7^{IV})	2·85	S(2) ··· H(7^{IV})	3·33
		S(2) ··· H(8^{V})	3·28

(*b*) Copper complex

(i) Interatomic distances (Å) and angles (°) within the asymmetric unit

Cu(1)–S(1)	2·329(3)	S(1)–Cu(1)–S(2)	77·7(1)
Cu(1)–S(2)	2·274(4)	C(1)–S(1)–Cu(1)	83·2(5)
C(1)–S(1)	1·73(1)	C(1)–S(2)–Cu(1)	85·1(5)
C(1)–S(2)	1·72(1)	S(1)–C(1)–S(2)	113·9(7)
C(1)–N(1)	1·31(2)	N(1)–C(1)–S(1)	123·0(10)
N(1)–C(2)	1·49(2)	N(1)–C(1)–S(2)	123·0(10)
N(1)–C(3)	1·45(2)	C(2)–N(1)–C(1)	123·4(12)
C(3)–C(4)	1·38(2)	C(2)–N(1)–C(3)	117·6(13)
C(4)–C(5)	1·42(2)	C(3)–N(1)–C(1)	118·9(13)
C(5)–C(6)	1·37(2)	C(3)–C(4)–C(5)	119·2(16)
C(6)–C(7)	1·39(2)	C(4)–C(5)–C(6)	119·6(16)
C(7)–C(8)	1·42(2)	C(5)–C(6)–C(7)	120·5(15)
C(8)–C(3)	1·40(2)	C(6)–C(7)–C(8)	121·4(13)
		C(7)–C(8)–C(3)	116·3(12)
S(1) ··· S(2)	2·886(5)	C(8)–C(3)–C(4)	122·9(19)
C(2) ··· C(4)	3·33(2)	N(1)–C(3)–C(4)	118·3(15)
C(2) ··· C(8)	3·28(2)	N(1)–C(3)–C(8)	118·6(14)

(ii) Intermolecular interatomic distances <4·0 Å †

Cu(1) ··· C($4^{\text{II,III}}$)	3·81(2)	C(3) ··· C(8^{IV})	3·97(2)
S(1) ··· C(4^{III})	3·76(2)	C(5) ··· C(6^{VI})	3·87(2)
S(1) ··· C(5^{III})	3·96(2)	C(5) ··· C(6^{VIII})	3·87(2)
S(1) ··· C(7^{IV})	3·89(2)	C(5) ··· C(7^{VIII})	3·60(2)
S(2) ··· C(7^{V})	3·98(2)	C(6) ··· C($6^{\text{VI,VIII}}$)	3·80(2)
S(2) ··· C(8^{V})	3·94(1)	C(6) ··· C(7^{VI})	3·79(2)
C(1) ··· C(7^{IV})	3·76(2)	C(6) ··· C(8^{VIII})	3·97(2)
C(3) ··· C(4^{VII})	3·74(2)	C(7) ··· C(8^{V})	4·00(2)
C(3) ··· C(5^{VII})	3·60(2)	C(7) ··· N(1^{VI})	3·70(2)
C(3) ··· C(7^{IV})	3·86(2)		

† Roman numerals as superscripts refer to the following equivalent positions relative to the reference molecule at *x*, *y*, *z*:

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

(iii) Contacts (<3·5 Å) between phenyl hydrogen atoms and copper and sulphur atoms [Transformations are defined in (ii)]

Cu(1) ··· H($4^{\text{II,III}}$)	3·08	S(2) ··· H(4)	3·43
S(1) ··· H(4^{III})	2·94	S(2) ··· H(4^{III})	3·28
S(1) ··· H(5^{III})	3·38	S(2) ··· H(5^{II})	3·39
S(1) ··· H(7^{IV})	2·88	S(2) ··· H(7^{IV})	3·34
		S(2) ··· H(8^{V})	3·30

have been estimated assuming C–H 1·08 Å and H–C–C *ca.* 120°. Details of planes of best fit are tabulated, together with atomic deviations in Å in Tables 3(*a*) and 3(*b*).

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

DISCUSSION

Because the complexes are isomorphous and isostructural the only significant differences between them are in the immediate vicinity of the metal atom, *i.e.* the MS_4 molecular core.

Both crystals are composed of discrete monomeric units, and in each case the asymmetric unit is one half of the molecule, which is centrosymmetric, the metal atoms being located on the inversion centres at (0,0,0), ($\frac{1}{2}$,$\frac{1}{2}$,0). In both cases the metal atom is chelated by the two pairs of sulphur atoms from the two ligands; the MS_4 geometry is thus necessarily planar, the two pairs of metal–sulphur distances being approximately equal. The remainder of the molecule, except for the phenyl ring, is also tolerably planar (Table 3).

TABLE 3

Equations of best least-squares planes in the form $AX + BY + CZ = D$, where X, Y, and Z are orthogonal co-ordinates in Å, related to the crystallographic axes by $X = ax + cz\cos\beta$, $Y = by$, and $Z = cz\sin\beta$. Deviations (Å) of relevant atoms from the planes are given in square brackets

(*a*) Nickel complex

Plane (1):

Ni, S(1), S(2), N(1), C(1)—(3) $0{\cdot}8954X + 0{\cdot}2701Y - 0{\cdot}3539Z = 1{\cdot}813$

[Ni(1) −0·03, S(1) 0·06, S(2) −0·01, C(1) −0·02, N(1) 0·03, C(2) 0·06, C(3) 0·03, C(4) −1·19, C(5) −1·20, C(6) −0·02, C(7) 1·20, C(8) 1·24]

Plane (2):

C(3)—(8) $-0{\cdot}1028X + 0{\cdot}7191Y + 0{\cdot}6872Z = 8{\cdot}070$

[C(3) −0·01, C(4) 0·01, C(5) −0·01, C(6) 0·01, C(7) −0·02, C(8) 0·02, N(1) 0·04]

Plane (3):

S(1), S(2), C(1) N(1) $0{\cdot}9056X + 0{\cdot}2461Y - 0{\cdot}3453Z = 1{\cdot}675$

[Ni(1) −0·05, S(1) 0·01, S(2) 0·01, C(1) −0·03, N(1) 0·01, C(2) −0·10, C(3) 0·05, C(4) −1·14, C(5) −1·12, C(6) 0·08, C(7) 1·27, C(8) 1·27]

Plane (4):

Ni, S(1), S(2) $0{\cdot}8960X + 0{\cdot}2333Y - 0{\cdot}3778Z = 1{\cdot}538$

[C(1) −0·08, N(1) −0·08]

Standard deviation of distance of atom defining plane from plane: (1) 0·04, (2) 0·015, (3) 0·02 Å. Angles between planes: (1)—(2) 81·8, (3)—(4) 2·2°.

(*b*) Copper complex

Plane (1):

Cu, S(1), S(2) N(1), C(1)—(3) $0{\cdot}8971X + 0{\cdot}2638Y - 0{\cdot}3544Z = 1{\cdot}787$

[Cu(1) −0·04, S(1) 0·07, S(2) −0·01, C(1) 0·00, N(1) 0·02, C(2) −0·06, C(3) 0·02, C(4) −1·18, C(5) −1·21, C(6) −0·04, C(7) 1·16, C(8) 1·23]

Plane (2):

C(3)—(8) $-0{\cdot}1038X + 0{\cdot}7331Y + 0{\cdot}6721Z = 8{\cdot}146$

[C(3) −0·01, C(4) 0·00, C(5) 0·02, C(6) −0·03, C(7) 0·02, C(8) 0·00, N(1) 0·08]

Plane (3):

S(1), S(2), C(1), N(1) $0{\cdot}9074X + 0{\cdot}2431Y - 0{\cdot}3428Z = 1{\cdot}684$

[Cu(1) −0·08, S(1) 0·00, S(2) 0·00, C(1) −0·02, N(1) 0·00, C(2) −0·09, C(3) 0·05, C(4) −1·14, C(5) −1·13, C(6) 0·05, C(7) 1·24, C(8) 1·27]

Plane (4):

Cu, S(1), S(2) $0{\cdot}8951X + 0{\cdot}2271Y - 0{\cdot}3837Z = 1{\cdot}501$

[C(1) −0·06, N(1) −0·10]

Standard deviation of distances of atoms defining plane from plane: (1) 0·04, (2) 0·015, (3) 0·01 Å. Angles between planes: (1)—(2) 82·1, (3)—(4) 2·6°.

Within each ligand there appears to be a significant interaction between the methyl and phenyl substituents. The phenyl ring lies at an angle of 82° to the remainder of the ligand. A similar non-planar phenyl group has been reported in the structure of *N*-methylacetanilide,[12] in which the plane of the phenyl ring lies normal to the plane of the remainder of the molecule. In the present structures, lattice forces, and in particular, the intermolecular hydrogen–sulphur interactions are presumably responsible for constraining the phenyl ring at 82 rather than 90°. A consequence of this is that in both structures the phenyl group may be slightly tilted out of the ligand plane, the distortion of the axial carbon C(3) and C(6) being 0·05 and 0·08 Å (nickel) and 0·05 and 0·05 Å (copper). The methyl group C(2), is distorted out of the plane also by 0·10 (Cu), but on the opposite side of the ligand plane, so that it lies almost equidistant from C(4) and C(8) [3·34 and 3·26 Å (Ni), 3·33 and 3·28 (Cu)]. In both complexes, methyl carbon–nitrogen distances are longer [1·51 and 1·49(2) Å] than the usual alkyl carbon nitrogen distance of 1·47 Å; the phenyl carbon–nitrogen distances are shorter [1·44(1) and 1·45(2) Å]. These differences, although parallel, are not significant in terms of the standard deviations involved. The distances within the phenyl rings do not differ significantly from the typical value of 1·40 Å (Table 2).[13]

TABLE 4

Comparison of the intramolecular dimensions of bis-(*N*-methyl-*N*-phenyldithiocarbamato)-nickel(II) and -copper(II) 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·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·NHMe)$_2$] [b]	2·196, 2·203(3)	79·2(1)	1·70(1), 1·72(1)	1·30(1)	109·8(9)	1·47(2)
[Ni(CS_2·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·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_2·NMePh)$_2$] [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)
[Cu(CS_2·NMePh)$_2$] [e]	2·274, 2·329(3)	77·2(1)	1·72(1), 1·73(1)	1·31(2)	113·9(7)	1·45(2), 1·49(2)
[Cu(CS_2·NEt_2)$_2$] [f]	2·301, 3·339(2)	76·4(2)	1·71(1), 1·74(1)	1·33(1)	112·9(6)	1·46(1), 1·48(1)
	2·297, 2·317(2)	77·3(2)	1·71(1), 1·71(1)	1·35(1)	114·6(7)	1·47(1), 1·43(1)
[Cu(CS_2·NPr^n_2)$_2$] [g]	2·32, 2·32(1)	74·6(3)	1·67(4), 1·70(4)	1·33(5)	116(1)	1·47(5), 1·47(5)
	2·33, 2·33(1)	76·3(3)	1·68(4), 1·73(4)	1·33(5)	115(1)	1·46(5), 1·45(5)
[Cu(CS_2·N{CH_2}$_6$)] [h]	2·297(1)	77·8	1·72	1·33		1·48

[a] Ref. 17. [b] Ref. 16. [c] Ref. 14. [d] Ref. 15. [e] This work. [f] Ref. 18. [g] Ref. 19. [h] The brief report on this structure giving copper and sulphur positions only makes it clear that, like the present complex, this derivative is also monomeric in the solid state, presumably as a result of the constraint of nonplanarity imposed upon the geometry of the N(CH_2)$_6$ system by the aliphatic ring closure [Z. V. Zvonkova and V. I. Yakovenko, *Soviet Phys. Cryst*. 1968, **13**, 134].

The geometry within the S_2CN fragment of the ligand agrees well on the whole between the two compounds and with previous determinations. As in other molecules of this type the planarity of this grouping probably reflects the large degree of conjugation present. The dimensions of the MS_2CNC_2 fragment are tabulated for these and other dithiocarbamate derivatives of nickel(II) and copper(II) in Table 4. In the present structures the C(1)–N(1) bond may well be shorter than in dithiocarbamates studied hitherto. The C(1)–S(*i*) distances are erratic and will be dealt with subsequently.

The nickel–sulphur geometry in the nickel complex is normal and in good agreement with that of those nickel dithiocarbamate structures already determined. The $\bar{1}$ symmetry of the nickel site shows affinity with the structures of bis-(*NN*-diethyldithiocarbamato)nickel(II), [Ni(CS_2·NEt_2)$_2$],[14] bis-(*NN*-di-n-propyldithiocarbamato)-nickel(II), [Ni(CS_2·NPr^n_2)$_2$],[15] and bis-(*N*-methyldithiocarbamato)nickel(II), [Ni(CS_2·NHMe)$_2$],[16] rather than the unsubstituted parent, bis(dithiocarbamato)nickel(II), [Ni(CS_2·NH_2)$_2$],[17] in which the nickel atom is not centrosymmetric, neither is the NiS_4 fragment planar. Gasparri *et al.*[17] have shown that the molecular plane in the latter is irregular, deviations of up to 0·04 Å being found within the NiS_4 unit. These distortions are presumed to be caused by strong intermolecular hydrogen–sulphur interactions (and, in that case, a nickel–hydrogen interaction). Evidence for effects of this nature but of a lesser magnitude is reported for [Ni(CS_2·NH·Me)$_2$], in which both NiS_4 and S_2CN units are planar but inclined at an angle of 3°, the apparent cause again being intermolecular hydrogen-sulphur interaction.[16] In these two examples, such interactions are not surprising because the hydrogen involved is bonded directly to the nitrogen. There are similar distortions reported in [Ni(CS_2·NPr^n_2)$_2$],[15] the angle between the NiS_4 and S_2CN planes being 4°, and these also found in the present Ni structure, the angle being 2°. In both of these cases close contacts are found between at least one of the sulphur atoms and at least one of the aliphatic (or aromatic) protons. In the present Ni compound, S(1) is distorted from the molecular plane (but not the S_2CN plane) by *ca.* 0·06 Å by interaction with the adjacent phenyl ring. In view of these seemingly strong interactions involving contact distances appreciably less than the van der Waal's hydrogen–sulphur estimate of 3·05 Å [S(1)–H(7) 2·85 (Ni) and 2·88 Å (Cu)], it would not be unreasonable to expect changes in bond length associated with the sulphur atom involved. Although substantial non-equivalences of up to 0·04 Å are reported for the pair of

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carbon–sulphur distances in any given ligand in the range of compounds studied[14-17] and we suspect a rough correlation between the longer C(1)–S(*i*) bonds and the existence of hydrogen bonding interactions, it is not possible to obtain satisfactory agreement on this point. This may well be due once again to limited accuracy in the determinations made. Other intermolecular distances (apart from the hydrogen–sulphur contacts, Table 2) are not unusual; there are no close sulphur–sulphur or metal–sulphur contacts. Only in the parent compound [$Ni(CS_2{\cdot}NH_2)_2$], where the molecule itself is small, is such a distance of $<4{\cdot}0$ Å found (Ni · · · S 3·60 Å).

This hydrogen–sulphur intermolecular contact is also present in the copper derivative of the *N*-methyl-*N*-phenyldithiocarbamate ligand. These contacts probably play a large part in determining molecular packing. Nevertheless, in the reports on structure determinations of the analogous copper complexes, hydrogen–sulphur interactions do not appear to have been considered as significant as copper–sulphur intermolecular interactions; in the copper(II) dialkyldithiocarbamates, there is a dominant tendency to form dimers in the solid state, and to a much lesser extent in solution. In all derivatives studied in detail so far {bis-(*NN*-diethyldithiocarbamato)copper(II), [$Cu(CS_2{\cdot}NEt_2)_2$][18] and bis-(*NN*-di-n-propyldithiocarbamato)copper(II) [$Cu(CS_2{\cdot}NPr^n{}_2)_2$][19]}, there is an intermolecular copper–sulphur contact of $<2{\cdot}9$ Å. There is usually no isomorphism between the crystal of a nickel derivative of this series and its copper analogue; in the present investigation, the solution of the copper(II) structure was provoked by the apparent isomorphous and isostructural nature of the two compounds since the disposition of the molecule in the unit cell of the nickel(II) derivative made it apparent that, if the copper(II) derivative were isostructural, the closest copper–copper distance was *ca.* 6·6 Å, *i.e.* the *b* axis, since the *a* axis is very long, and it is the *ab* face which is centred. As expected, this was the case and this molecule provides a good example in the solid state of a monomeric bis-(*NN*-disubstituted-dithiocarbamato)copper(II) species. Dimerization usually occurs *via* a fifth co-ordination site of the copper atoms [Figure 3(a)] and it would appear that a requirement for such dimerization would be a substantially flat molecule, so that the molecular pair may approach in a parallel fashion to within the distance required for interaction (*ca.* 2·9 Å). In the present case, it appears that this interaction is pre-empted by the apparent necessity of the phenyl groups to lie almost normal to the plane of the remainder of the molecule by virtue of their interaction with the adjacent methyl substituent. The phenyl ring could thus project on either side by up to *ca.* 3·04 Å [*i.e.* (1·40 + 1·08 + 1·03) sin 60° sin 82°], the maximum projection of the molecule presumably normally being much less, and of the order of the van der Waal's radius of sulphur (1·85 Å). In the *trans*-configuration, superposition of the two molecules in a pair of the type depicted in Figure 3 must necessarily cause the phenyl group at one end of each molecule to foul the adjacent molecule. This, however, is not at all so in the case of a molecule with the *cis*-configuration. Since the energy of a free molecule of this latter type can be very little different from that of the *trans*-isomer, it would seem pertinent to ask why the substance crystallizes as the *trans*-form at all, since solution n.m.r. studies for related molecules[20] have led to the suggestion that a rotation about the C(1)–N(1) bond occurs which is slow on the n.m.r. time-scale but, presumably, fast according to that on which the crystals were grown. That the substance is monomeric and *trans* implies (i) that this suggestion is wrong, (ii) that the intermolecular interactions between copper and sulphur atoms leading to dimer formation are weaker than the results of previous structure determinations might suggest, and comparable with other lattice forces, (iii) that the energy of the *trans*-form is far below that of the *cis*-form, or (iv) in this case the *trans*-form is strongly favoured by the lattice energy.

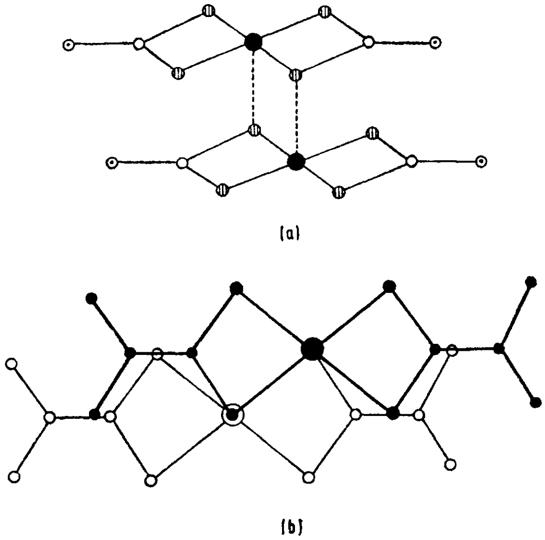

FIGURE 3 Disposition of the pair of $M(S_2CNC_2)_2$ entities in the dimeric bis-(*NN*-dialkyldithiocarbamato)copper(II) derivatives

The large disparity in the copper–sulphur distances in this structure is presumably due to the interaction between S(1) and the aromatic proton.

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