Magnetic and Structural Studies on Copper(II) Dialkyldithiocarbamates

By **Peter D. W. Boyd** and **Samaresh Mitra**,† Research School of Chemistry, Australian National University, Canberra, 2600, Australian Capital Territory
Colin L. Raston, Graham L. Rowbottom, and **Allan H. White,*** Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, 6009, Western Australia

The magnetic susceptibilities of a series of copper(II) dialkyldithiocarbamates have been measured over the range 4—290 K, the alkyl groups being methyl, ethyl, isopropyl, and n-butyl. Contrary to a previous report of strong ferromagnetic interaction in the diethyl derivative, we find no evidence of any significant exchange interaction in this compound. The dimethyl and di-isopropyl analogues show weak antiferromagnetic interactions. Only the di-n-butyl derivative in the dialkyl series shows evidence of strong magnetic exchange interaction but of an antiferromagnetic nature; this effect is peculiar to the phase recrystallized from chloroform–light petroleum (α), the phase obtained from chloroform–ethanol (β) showing no such interaction. To seek the origin of the exchange interaction in the α derivative, its crystal structure has been determined by single-crystal *X*-ray diffraction methods at 295 K and refined by least squares to a residual 0.032 for 1 976 ' observed ' reflections. Crystals are triclinic, $P\bar{1}$, a = 15.29(1), b = 9.963(7), c = 9.243(7) Å, α = 67.94(7), β = 82.92(7), γ = 71.55(7)°, and Z = 2. The copper environment is the usual pseudo-square-planar array of four sulphur atoms from two bidentate ligands (⟨Cu–S⟩, 2.31 Å), but there is a long fifth interaction [Cu · · · S, 2.899(4) Å] through the inversion centre leading to pseudo-dimer formation. Although similar to the diethyl analogue in this respect, differences are observed in regard to (a) the bridging geometry in the ' dimer ' and (b) the proximity to the ' dimer ' sulphur ligands of sulphur atoms from neighbouring dimers at *ca.* 3.8 Å. The likely relative importance of these two features in determining the origin of the antiferromagnetic coupling is discussed. The structure of the β phase has also been determined, the final residual being 0.036 for 1 324 ' observed ' reflections. Crystals are monoclinic, $P2_1/n$, a = 14.593(5), b = 7.840(2), c = 10.822(5) Å, β = 101.55(3)°, and Z = 2. The molecules are located with the copper atoms on crystallographic centres of symmetry, and the only significant intermolecular interactions observed are S · · · H contacts. The CuS_4 entity is planar with ⟨Cu–S⟩ 2.30 Å.

THE magnetic,[1] spectroscopic,[2] and structural properties [3-6] of the bis(dialkyldithiocarbamato)copper(II) complexes, $[Cu(S_2CNR_2)_2]$, have been extensively studied in recent years. The complexes structurally are found either to have a ' dimeric ' structure in the solid state with the copper(II) ions bridged by two sulphur atoms, one from each dithiocarbamate ligand, as in the case of $[Cu(S_2CNEt_2)_2]$,[3] or discrete molecules of $[Cu(S_2CNR_2)_2]$ as in $[Cu(S_2CNMePh)_2]$,[4] $[Cu\{S_2CN(CH_2)_4\}_2]$,[5] or $[Cu(S_2CNMe_2)_2]$.[6]

Initial low-temperature magnetic susceptibility studies of the ' dimeric ' $[Cu(S_2CNEt_2)_2]$ complex (4.2—56 K) were interpreted by Villa and Hatfield[7] in terms of a ferromagnetic coupling between copper(II) ions, $2J$ = 24 cm^{-1}. A reinvestigation of the magnetic behaviour of $[Cu(S_2CNEt_2)_2]$ however showed that this complex behaves as a normal $S = \frac{1}{2}$ paramagnet in the temperature range 1—20 K with a Curie–Weiss constant of 0.25 K.[8] It appears then that in ' dimeric ' $[Cu(S_2CNEt_2)_2]$ there is only an extremely small exchange interaction between the copper(II) ions. This is a surprising result in view of the significant interactions found in sulphur bridged copper(II) complexes [9] and copper(II) complexes with extended polyatomic bridges.[10-12] The work of Hatfield and co-workers [10] and Hendrickson and co-workers [11-13] on a large variety of binuclear complexes has shown that even quite small structural changes in the dimers (even those simply induced by a change in counter ion) can lead to significant changes in the magnitude of exchange interactions.

Electron spin resonance studies of single crystals of mixtures of $[Cu(S_2CNEt_2)_2]$ and $[Zn(S_2CNEt_2)_2]$ down to 4 K have enabled detection of signals within the triplet state of copper(II) dimers.[14-16] The temperature dependence of the triplet-state spectrum has shown that this state lies below the singlet, indicating a ferromagnetic coupling between the copper(II) ions with $J \approx 8$ cm^{-1}. The structure of $[Zn(S_2CNEt_2)_2]$, whilst ' dimeric,' is considerably different from the copper(II) complex and it seems possible that the structure of the copper ' dimer ' doped in the mixed crystal may differ from that found in the pure complex.

In view of these reports we have reinvestigated the magnetic properties of $[Cu(S_2CNEt_2)_2]$ and some higher homologues to 4 K to ascertain the extent to which interactions may be observed in the dialkyl series. During this study evidence of significant antiferromagnetic interactions was found in $[Cu(S_2CNBu^n_2)_2]$ and detailed *X*-ray structures were determined to ascertain, if possible, the origin of this interaction in terms of the structure of the complex. The results of these magnetic and structural studies are presented in this paper.

EXPERIMENTAL

The dialkyldithiocarbamate complexes of copper(II), $[Cu(S_2CNR_2)_2]$, were prepared by addition of an aqueous solution of copper(II) chloride to an aqueous solution of the preformed sodium dithiocarbamate salt (1 : 2 mole ratio).[17] The resulting precipitate was filtered off, washed with water, and recrystallized from chloroform–light petroleum (b.p. 40—60 °C), or chloroform–ethanol mixtures.

In the case of the di-n-butyl derivative it was found that different magnetic properties were observed depending on the nature of the solvent system used. Crystals suitable for the *X*-ray study were obtained from the chloroform–light petroleum solutions (α phase) and from ethanol–chloroform (β phase) {Found for $[Cu(S_2CNBu_2)_2]$ (α phase): C, 46.1; H,

† *Present address*: Chemical Physics Group, Tata Institute of Fundamental Research, Colaba, Bombay, India; author to whom correspondence on the magnetism should be addressed.

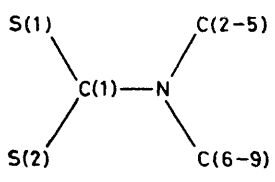
7.30; N, 5.70; S, 27.3. Calc. for $C_{18}H_{36}CuN_2S_4$: C, 45.8. H, 7.70; N, 5.95; S, 27.1%. Found for $[Cu(S_2CNBu_2)_2]$ (β phase): C, 46.0; H, 7.45; N, 5.70; S, 27.35%}. Magnetic susceptibilities were measured using a modified Oxford Instruments Faraday balance, previously described, in the temperature range 4.2—300 K at 1 T.[18] Several measurements were made on the $[Cu(S_2CNEt_2)_2]$ complex using different preparations and on a ground single crystal whose space group was verified to be that of the known dimeric $[Cu(S_2CNEt_2)_2]$ [3] by rotation and Weissenberg *X*-ray photography. To within experimental error all samples of $[Cu(S_2CNEt_2)_2]$ gave equivalent results.

Crystallography.—Crystal data. α phase. $C_{18}H_{36}CuN_2S_4$, *M* 427.3, Triclinic, space group $P\bar{1}$ (C_i^1, No. 2), $a = 15.29(1)$, $b = 9.963(7)$, $c = 9.243(7)$ Å, $\alpha = 67.94(7)$, $\beta = 82.92(7)$, $\gamma = 71.55(7)°$, $U = 1\,238(2)$ Å^3, $D_m = 1.26(1)$, $Z = 2$, $D_c = 1.26$ g cm^{-3}, $F(000) = 502$, monochromatic Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu = 11.8$ cm^{-1}.

β phase. $C_{18}H_{36}CuN_2S_4$, *M* 427.3, Monoclinic, space group $P2_1/n$ (variant of C_{2h}^5, No. 14), $a = 14.593(5)$, $b = 7.840(2)$, $c = 10.822(5)$ Å, $\beta = 101.55(3)°$, $U = 1\,213.1(8)$ Å^3, $D_m = 1.30(1)$, $Z = 2$, $D_c = 1.29$ g cm^{-3}, $F(000) = 502$, μ(Mo-K_α) = 12.9 cm^{-1}.

Structure Determination.—Data were recorded on Syntex $P\bar{1}$ and $P2_1$ four-circle diffractometers in the θ—2θ scan mode. A unique data set measured to $2\theta_{max.}$ 40° (α), 45° (β) yielded 2 326 and 1 596 independent reflections respectively; 1 976 and 1 324 (α,β) of these with $I > 2\sigma(I)$ were considered 'observed' and used in the structure solution and refinement after absorption correction. The structure was solved by the heavy-atom method and refined (for α) by (9 × 9) block-diagonal least squares but with hydrogen-atom positional parameters (where refined) included in the block of the parent carbon, and with the parameters of the CuS_4 molecular core refined jointly. The structure of the β form was refined similarly but with full-matrix least squares. The thermal parameters, U_H, were constrained at $\langle 1.25U_{ii}(C)\rangle$; all other atoms were assigned anisotropic thermal parameters. Hydrogen-atom co-ordinates (for α) were refined for the inner methylene groups, those for the peripheral hydrogen atoms being constrained at calculated tetrahedral positions. Positional parameters (for β) were refined for all hydrogen atoms. The final residuals were; *R* 0.032, *R'* 0.037, *S* 2.3 (for α); 0.036, 0.037, 1.15 (for β) with reflection weights: $[\sigma^2(F_o) + 0.000\,3(F_o)^2]^{-1}$. Neutral-atom scattering factors were taken from refs. 19—21 with those of non-hydrogen atoms corrected for anomalous dispersion (f', f''). All the calculations were carried out on a CYBER 73 computer using the '*X*-Ray '76' program system.[22] Table 1 lists the atomic co-ordinates and Table 2 the bond lengths and angles. Tables of structure factor amplitudes, thermal parameters, and hydrogen-atom parameters are deposited in Supplementary Publication No. SUP 22883 (20 pp.).*

Atom labelling within each ligand (designated a,b in α) is as shown below. Hydrogen atoms are labelled according to



the parent carbon, suffixed A,B, and C for distinguishing purposes.

The crystals (α only) undergo micaceous cleavage, the origin of which is evident from the cell diagram (Figure 3) and this factor rendered specimen selection difficult, and resulted in considerable 'streaking' in the data; in view of the latter, the final residual is surprisingly good, although the cell calibration is of limited precision.

RESULTS AND DISCUSSION

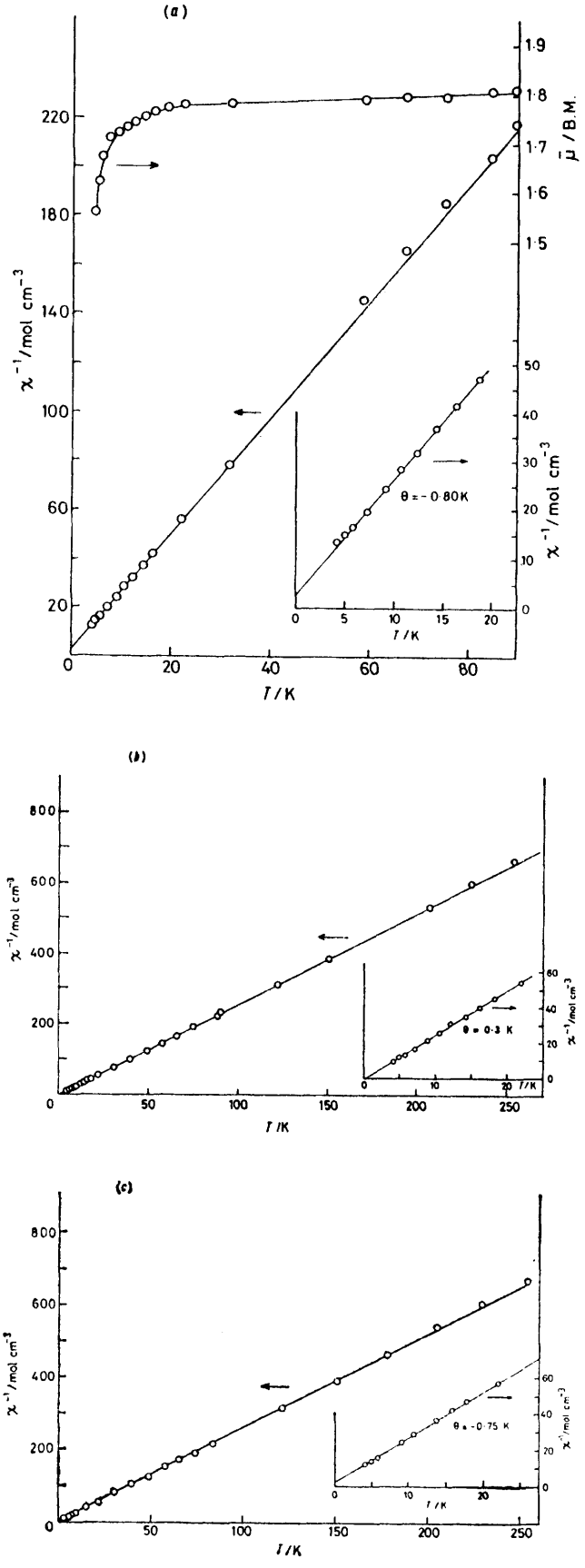
Magnetic Susceptibility Measurements.—The bulk magnetic susceptibilities of $[Cu(S_2CNR_2)_2]$ for several different alkyl groups (R = methyl, ethyl, isopropyl, or n-butyl) were measured in the temperature range 4.2—300 K. For R = methyl, ethyl, and isopropyl the susceptibilities obeyed the Curie–Weiss law, $\chi = C(T - \theta)^{-1}$, with small Curie–Weiss constants. Figure 1 shows plots of χ^{-1} against *T* for these complexes. The susceptibility of the $[Cu(S_2CNEt_2)_2]$ complex was measured several times using different polycrystalline preparations and

TABLE 1

Non-hydrogen atom fractional cell co-ordinates (× 10^4)

Atom	Ligand a *x*	*y*	*z*
(*a*) α phase			
Cu	8.0(4)	3 391.8(7)	1 923.6(7)
S(1)	−987(1)	2 417(1)	3 832(1)
S(2)	−105(1)	1 395(1)	1 337(1)
C(1)	−783(3)	1 061(5)	2 998(5)
N	−1 105(2)	−126(4)	3 595(4)
C(2)	−1 618(4)	−388(6)	5 073(6)
C(3)	−2 636(4)	405(7)	4 919(7)
C(4)	−3 126(4)	−67(8)	6 474(8)
C(5)	−4 116(5)	550(12)	6 413(10)
C(6)	−847(3)	−1 351(6)	2 954(7)
C(7)	−1 675(4)	−1 677(6)	2 545(7)
C(8)	−2 241(5)	−447(7)	1 214(7)
C(9)	−3 111(4)	−753(8)	984(8)
	Ligand b		
	x	*y*	*z*
S(1)	435(1)	4 854(1)	2 982(1)
S(2)	1 231(1)	4 029(1)	330(1)
C(1)	1 249(3)	4 999(5)	1 523(5)
N	1 839(2)	5 785(4)	1 311(4)
C(2)	1 789(4)	6 732(6)	2 235(7)
C(3)	2 666(4)	6 300(7)	3 099(7)
C(4)	2 893(4)	4 756(7)	4 347(6)
C(5)	3 851(6)	4 244(12)	4 969(9)
C(6)	2 513(4)	5 862(6)	20(6)
C(7)	3 361(4)	4 517(7)	371(7)
C(8)	3 965(4)	4 530(7)	−1 046(7)
C(9)	4 810(4)	3 153(9)	−726(10)
(*b*) β phase			
Cu	0	0	0
S(1)	510.4(7)	1 421(1)	1 882.9(9)
S(2)	1 031.1(8)	1 943(1)	−513.7(10)
C(1)	1 135(3)	2 626(5)	1 015(4)
N	1 656(2)	3 953(4)	1 481(3)
C(2)	1 712(3)	4 532(6)	2 782(4)
C(3)	1 012(4)	5 919(6)	2 920(5)
C(4)	981(4)	6 294(7)	4 275(5)
C(5)	317(6)	7 705(9)	4 423(7)
C(6)	2 192(3)	4 918(5)	690(5)
C(7)	1 640(4)	6 346(6)	−44(5)
C(8)	2 176(5)	7 190(7)	−981(5)
C(9)	2 176(7)	6 088(11)	−2 099(7)

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.



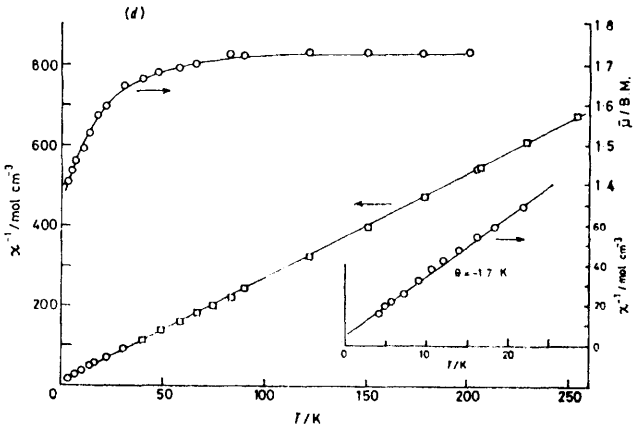


FIGURE 1 Plot of reciprocal molar magnetic susceptibility against temperature for (*a*) $[Cu(S_2CNMe_2)_2]$, (*b*) $[Cu(S_2CNEt_2)_2]$, (*c*) $[Cu(S_2CNPr^i_2)_2]$, (*d*) $[Cu(S_2CNBu^n_2)_2]$ (β phase). Full lines represent linear least-squares fits to data in the temperature range (1 B.M. = 9.274×10^{-24} A m²)

a ground single crystal. The temperature dependence of the susceptibility was identical in each case. Linear least-squares fits to the Curie–Weiss law in the temperature range 4—40 K gave $C = 0.375$ cm³ K, $\theta = 0.298$

TABLE 2

Molecular non-hydrogen geometry *

(*a*) Distances (Å)

Cu–S(1)	2.314(3), 2.310(2); 2.311(1)
Cu–S(2)	2.310(2), 2.333(3); 2.287(1)
S(1)–C(1)	1.725(6), 1.716(5); 1.716(4)
S(2)–C(1)	1.728(5), 1.724(6); 1.717(4)
S(1) · · · S(2)	2.881(3), 2.883(3); 2.874(2)
C(1)–N(1)	1.325(6), 1.325(7); 1.327(5)
N(1)–C(2)	1.465(6), 1.473(9); 1.467(6)
N(1)–C(6)	1.475(8), 1.474(6); 1.478(6)
C(2)–C(3)	1.503(7), 1.504(9); 1.520(7)
C(3)–C(4)	1.516(9), 1.499(8); 1.505(8)
C(4)–C(5)	1.442(10), 1.500(11); 1.500(10)
C(6)–C(7)	1.524(10), 1.503(7); 1.509(6)
C(7)–C(8)	1.492(8), 1.506(9); 1.548(9)
C(8)–C(9)	1.512(11), 1.519(9); 1.487(10)
Cu · · · S(2)^I	2.899(4)

(*b*) Angles (°)

S(1)–Cu–S(2)	77.10(6), 76.76(7); 77.37(5)
Cu–S(1)–C(1)	84.7(2), 85.1(2); 84.0(1)
Cu–S(2)–C(1)	84.8(2), 84.2(2); 84.8(1)
S(1)–C(1)–S(2)	113.1(3), 113.9(3); 113.7(2)
S(1)–C(1)–N	123.0(3), 123.8(4); 123.4(3)
S(2)–C(1)–N	123.9(4), 122.4(3); 122.9(3)
C(1)–N–C(2)	120.5(4), 121.9(4); 121.7(4)
C(1)–N–C(6)	122.0(4), 120.4(5); 120.8(3)
C(2)–N–C(6)	116.8(4), 117.4(5); 117.6(3)
N–C(2)–C(3)	114.8(4), 113.0(4); 114.0(4)
C(2)–C(3)–C(4)	111.2(4), 114.2(6); 112.8(4)
C(3)–C(4)–C(5)	115.0(6), 112.7(6); 113.2(5)
N–C(6)–C(7)	113.3(4), 114.0(4); 113.3(4)
C(6)–C(7)–C(8)	115.3(5), 112.3(4); 112.0(4)
C(7)–C(8)–C(9)	112.9(6), 113.0(5); 111.6(5)
Cu–S(2b) · · · Cu^I	92.05(8)
Cu^I · · · S(2b)–C(1b)	94.4(1)

Transformations of the asymmetric unit: I ($\bar{x}$, 1 − y, $\bar{z}$)

Other Cu angles: (α phase)

S(1a)–Cu–S(1b)	100.98(7)	S(1a)–Cu–S(2b)^I	102.93(8)
S(1a)–Cu–S(2b)	169.05(5)	S(1b)–Cu–S(2b)^I	102.06(8)
S(2a)–Cu–S(1b)	163.87(5)	S(2a)–Cu–S(2b)^I	94.00(7)
S(1b)–Cu–S(2b)	102.03(6)	S(2b)–Cu–S(2b)^I	87.95(8)

* The first two values in each entry are for ligands a,b of the α phase; the third is for the β phase.

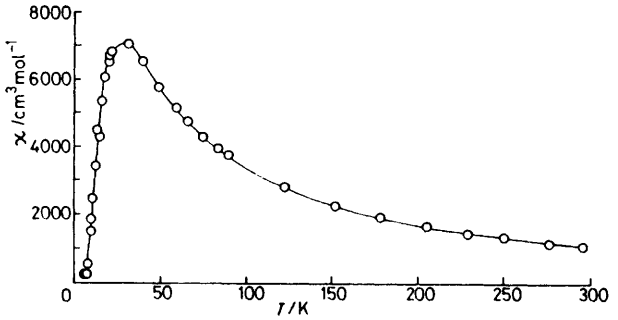


FIGURE 2 Plot of molar magnetic susceptibility against temperature for $[Cu(S_2CNBu^n_2)_2]$ (α phase). The full line represents the least-squares fit to the modified Bleaney–Bowers expression with parameters $g = 2.039$, $2J = -28.2$ cm^{-1}, $\theta = -2.4$ K

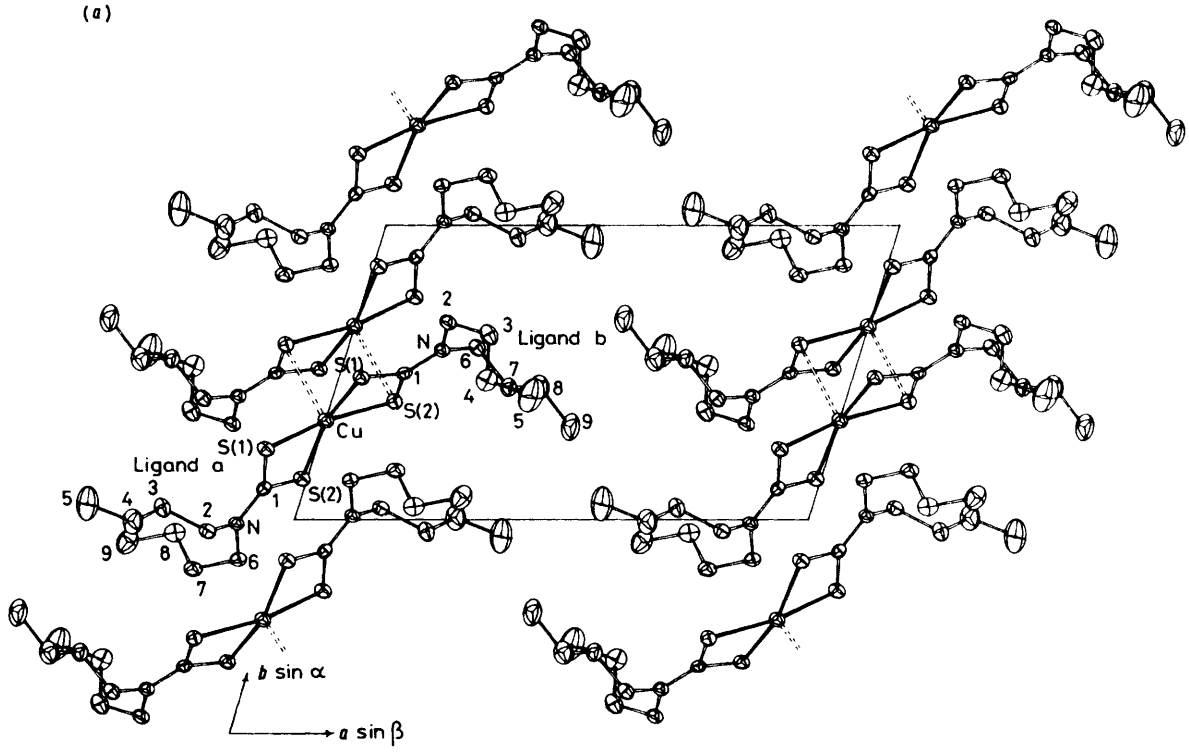
K compared to the values of Duyneveldt *et al.*,[8] $C = 0.397$ cm^3 K, $\theta = 0.25$ K. In contrast to $[Cu(S_2CNEt_2)_2]$, both $[Cu(S_2CNMe_2)_2]$ and $[Cu(S_2CNPr^i_2)_2]$ have negative Curie–Weiss constants, −0.80 and −0.75 K respectively, indicating a small antiferromagnetic coupling between the copper(II) ions.

For the n-butyl derivative measurements of the susceptibility for samples of the complex recrystallized from chloroform–light petroleum (α) and chloroform–ethanol (β) showed quite different temperature dependence. Figure 2 shows a plot of the susceptibility of the α phase against temperature. The susceptibility passes through a maximum at *ca.* 29 K and falls to a very small value at 6 K. The small rise in χ below 4.5 K is presumably due to the presence of a very small amount of a paramagnetic complex. This curve for the α phase is well explained by the modified Bleaney–Bowers equation for a pair of $S = \frac{1}{2}$ interacting ions[23] with $g = 2.039$, $\theta = -2.4$ K, and $2J = -28.2$ cm^{-1}. The β phase on

$$\chi = \frac{N\beta^2 g^2}{k(T-\theta)}\left[\frac{1}{3+\exp(-2J/kT)}\right]$$

the other hand obeys the Curie–Weiss law with $\theta = -1.70$ K (Figure 1).

The Crystal Structure of α- *and* β-$[Cu(S_2CNBu^n_2)_2]$.—The *NN*-disubstituted dithiocarbamates of copper(II), $[Cu(S_2CNRR')_2]$, which have so far been studied crystallographically may be distributed into two classes depending on the nature of the packing forces present. In one category, the dominant intermolecular forces arise from hydrogen-bonding interactions between substituent hydrogen atoms and the sulphur atoms; the examples known of this type are $[Cu(S_2CNMePh)_2]$ [4] and $[Cu\{S_2CN(CH_2)_4\}_2]$.[5] The other examples studied contain the molecules distributed in pseudo-dimeric pairs generated by close contacts between a fifth apical coordination site of the copper atom and a sulphur atom of an adjacent molecule; the ' dimer ' is usually (pseudo)-centrosymmetric so that a pair of parallel Cu · · · S interactions results (Figure 3). In neither case does a serious perturbation of the $Cu(S_2C)_2$ molecular core geometry result and it is clear that the S · · · H and S · · · Cu interactions (Table 3) observed must be of comparable energy. Since there is no obvious reason why similar pairs of Cu · · · S contacts should not occur on either side of the CuS_4 plane for any given molecule, it is possible to envisage that examples might be found containing pseudo-trimers, -oligomers, or -polymers, as well; an example of a quasi-polymeric system is provided in



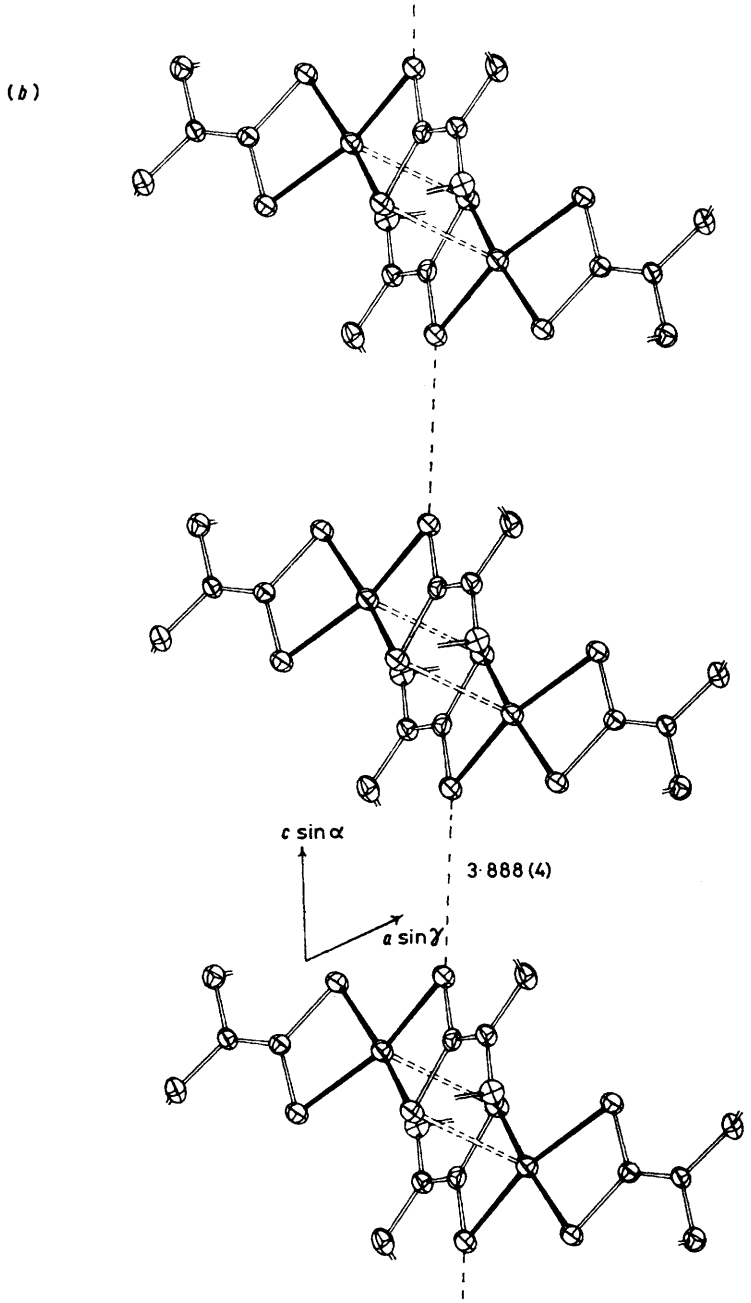


FIGURE 3 (*a*) Unit-cell contents of α-[$Cu(S_2CNBu^n_2)_2$] projected down *c*, showing non-hydrogen atom labelling and 20% thermal ellipsoids. Intradimer Cu · · · S interactions are shown with broken lines. (*b*) The same, projected down *b*; peripheral ligand carbon atoms have been omitted for clarity, and an array running along *c* is shown

the present series by the derivative [$Cu(S_2CNMe_2)_2$].[6] The nickel(II) analogues of the first series are generally isomorphous with their copper(II) counterparts; this is not true of the analogues of the second series.

In the present case it is clear that the α phase belongs to the second category. Within the unit cell, the asymmetric unit is comprised of one independent molecule, with the copper atoms situated close to crystallographic centres of symmetry, so that the copper atoms throughout the unit cell are distributed in pairs; the Cu · · · Cu distance is 3.785(4) Å. The copper atom is four-co-ordinated by the pair of chelating dithiocarbamate ligands, and the dominant contact within the ' dimer ' is Cu · · · S(b2) ($\bar{x}$, 1 − *y*, $\bar{z}$), 2.899(4) Å, together with its centrosymmetrically related image. Although the distortion of the copper/intraligand geometries as a result of the fifth contact is quite minor [*e.g.* Cu–S(b2) is 2.333(3) Å, *cf.* the mean of the others 2.31_1 Å], the interaction does have considerable effects, most noticeably in that the copper atom lies appreciably out of the S_2CNC_2 ligand planes (0.28, 0.08 Å respectively) and in that CuS_4 is itself not planar, deviations from the ' plane '

TABLE 3

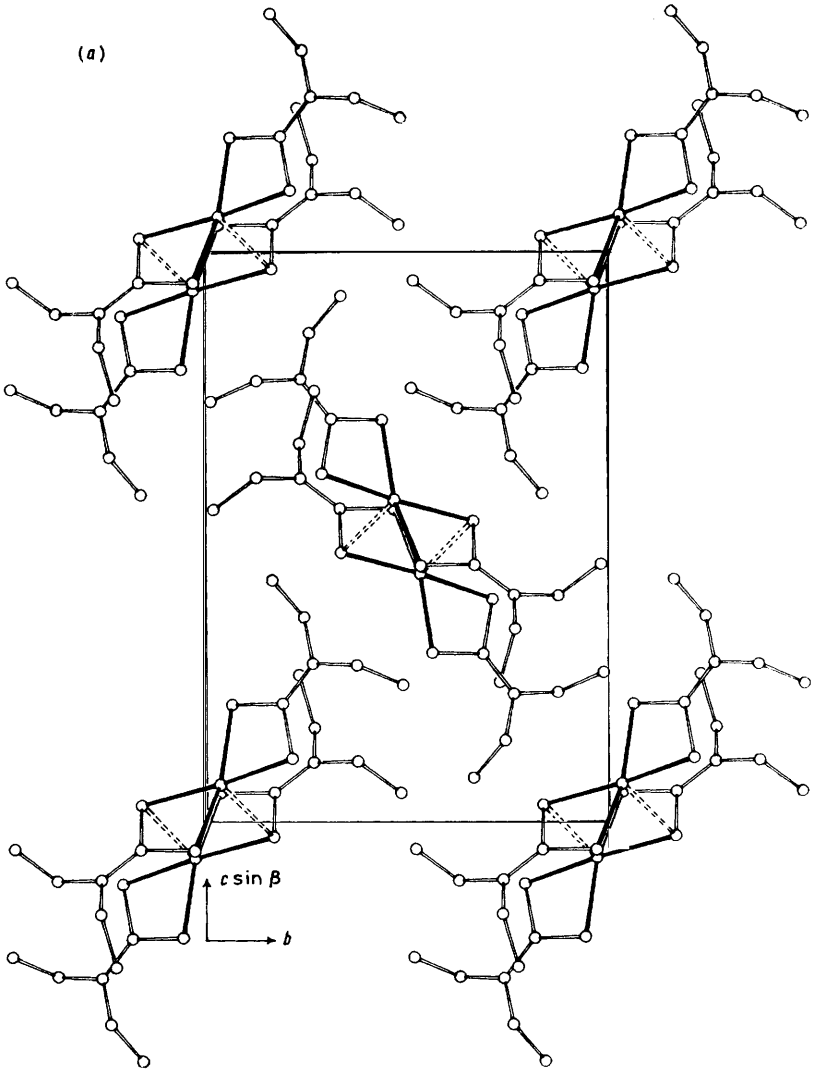
Non-bonded Cu, H · · · S interactions <3.0 Å

Atoms	Distance/Å
(*a*) α phase	
Cu · · · S(2b)[I]	2.899(4)
(*i*) Intramolecular S · · · H contacts	
S(1a) · · · H(2aB)	2.65(4)
S(2a) · · · H(6aA)	2.53(5)
S(1b) · · · H(2bB)	2.49(6)
S(2b) · · · H(6bA)	2.63(5)
S(2b) · · · H(7bB)	2.97(6)
(*ii*) Intermolecular S · · · H contacts	
S(1a) · · · H(6bA[I])	2.97(4)
(*b*) β phase	
(*i*) Intramolecular S · · · H contacts	
S(1) · · · H(2A)	2.61(4)
S(2) · · · H(6B)	2.66(4)
(*ii*) Intermolecular S · · · H contacts	
S(1) · · · H(6A[II])	2.99(4)

Transformations of the asymmetric unit: I ($\bar{x}$, 1 − y, $\bar{z}$); II ($\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$).

defined by the four sulphur atoms being S(1a), −0.05; S(1b), 0.05; S(2a), 0.05; S(2b), −0.05, with the copper atom deviation −0.27 Å on that side directed toward the approach of the centrosymmetrically related molecule. The close Cu · · · S contact produces no noticeable disparity in the S–C distances, and the remainder of the geometry of the conjugated ligand sections is as expected. In both α and β forms, the ' β ' carbon atoms of the substituent lie on the same side of the ligand plane (Table 4).

We now turn beyond the above intermolecular interactions, at distances less than the van der Waals sums, to seek some form of interaction which may assist in accounting for the unusual behaviour of the magnetism. It has been shown above that the present compound at low temperature is the only example studied exhibiting antiferromagnetism, among a variety of other bis(*NN*-dialkyldithiocarbamato)copper(II) derivatives including species such as the diethyl derivative which are also known to exhibit pseudo-dimeric molecular structures. It thus seems that the reason for this phenomenon might be sought by way of interactions of a long-range type, and thus far, none of any significance at distances less than the van der Waals sums have been noted. The present structure is shown in projection down the two



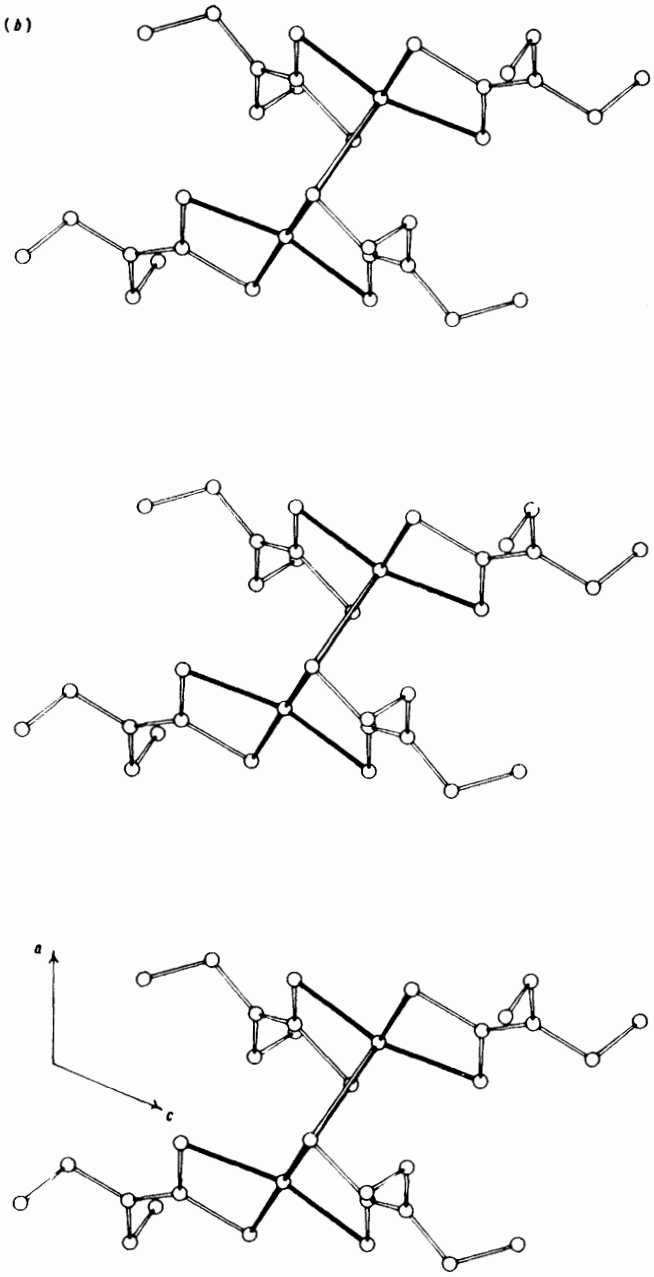


FIGURE 4 (*a*) A projection of the $[Cu(S_2CNEt_2)_2]$ structure down *a* showing the non-hydrogen cell contents. (*b*) A projection of the same down *b*, showing successive dimers up *a*; intermolecular interactions within the dimer are shown as solids because of overlap

shorter axes in Figure 3(*a*) and 3(*b*); both suggest that the nearest contacts of significance in the above context, *i.e.* those which permit interaction between the conjugated π systems of adjacent dimers, are to be found between adjacent dimeric members of the stacks along these axes. Expanding the search for contacts to a limit of 4.0 Å, we find that the only ones occurring between the CuS_2CN fragments are S · · · S interactions: S(1b) · · · S(1b) ($\bar{x}$, $1 - y$, $1 - z$), 3.888(4) Å. By contrast, projection of the structure of the diethyl analogue down the two short axes shows the probability of interaction to be in one direction only; even so, there are no contacts of the above type: the shortest is a sulphur–carbon interaction at 4.10 Å, with no others at less than 4.6 Å (Figure 4).

The structure of the β phase exhibits no tendency toward pseudo-dimer formation by Cu · · · S intermolecular interactions; the 'packing forces' of the lattice appear to comprise H · · · S contacts only (Figure 5). In fact, the array is so pure an example of the latter type, there being no Cu · · · S, S · · · S or S · · · C(1) intermolecular contact <5.0 Å, that it sheds no additional light on the magnetic characteristics of the $[Cu(S_2CNR_2)_2]$ system. The CuS_4 group is necessarily planar, because of the location of the molecule on a crystallographic inversion centre. The two Cu–S distances are

significantly different, the longer having a close intermolecular hydrogen-bonding interaction. As in the α phase, the ' β '-methylene carbon atoms of the ligand are disposed on the same side of the ligand plane (Table 4). The dihedral angle between the CuS_4 plane and the S_2CNC_2 least-squares plane of the ligand is 4.6°.

Exchange Interactions in the Copper(II) *Dialkyldithiocarbamates.*–The magnetic susceptibilities of the two known ' dimer ' $[Cu(S_2CNR_2)_2]$ complexes (R = ethyl or n-butyl) (α phase) behave quite differently at low temperatures. In the case of $[Cu(S_2CNEt_2)_2]$ the small positive Curie–Weiss constant suggests a *ferromagnetic* coupling of less than 1 K, whilst for the n-butyl complex (α phase) an *antiferromagnetic* interaction, $2J = -28.2$ cm^{-1}, is found.

The main factors that affect exchange interactions between paramagnetic species in bridged complexes such as these are the bridging geometry and the individual metal-ion stereochemistry as it affects the electronic structure of the metal ion and the relative orientations of the metal orbitals with respect to the bridging ligand orbitals. A detailed comparison of the $[Cu(S_2CNEt_2)_2]$ and α-$[Cu(S_2CNBu^n_2)_2]$ structures shows similar but not identical co-ordination geometry about the individual copper(II) ions and some changes in the bridging structure [R = Et, d(Cu–Cu) = 3.588 Å, Cu–S–Cu = 86.9°, d(Cu–S) in-plane = 2.33_9 Å, d(Cu–S) out-of-plane = 2.85_1 Å; R = Bu^n, d(Cu–Cu) = 3.78_5 Å, Cu–S–Cu = 92.1°, d(Cu–S) in-plane = 2.33_3 Å, d(Cu–S) out-of-plane = 2.89_9 Å], *i.e.* for the di-n-butyl complex the Cu–S–Cu angle increases by *ca.* 5° and the copper–sulphur out-of-plane distance increases compared to the diethyl complex.

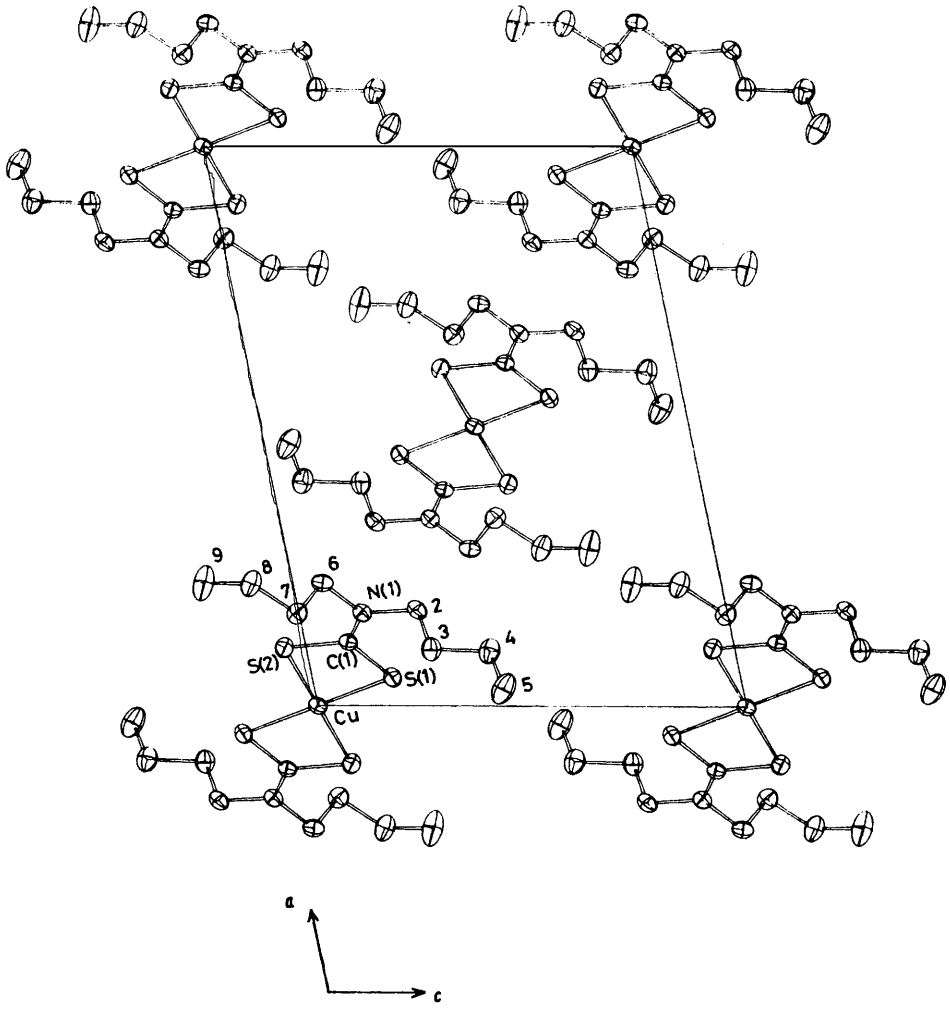


FIGURE 5 Unit cell contents of β-$[Cu(S_2CNBu^n_2)_2]$ projected down *b*, showing non-hydrogen atom labelling and 20% thermal ellipsoids for the non-hydrogen atoms

Two mechanisms which give rise to the antiferromagnetism in α-$[Cu(S_2CNBu^n_2)_2]$ are possible: (*i*) antiferromagnetic intramolecular pathways enhanced by changes in the bridge geometry and (*ii*) intermolecular pathways between dimeric units of the type Cu–S • • • S–Cu as suggested from the structure of α-$[Cu(S_2CNBu^n_2)_2]$.

There have been many cases in copper(II) dimer complexes where variations in the bond angle of the bridge as small as the 6° in this case have led to large changes in the magnitude (and even sign) of $2J$, the exchange interaction

TABLE 4

Least-squares planes through each ligand (defined by the S_2CNC_2 fragment) are given relative to the orthogonal right-hand Å frame (X,Y,Z) defined with X parallel to a, Z in the ac plane, in the form $pX + qY + rZ = s$

	α		β
	Ligand a	Ligand b	
10^4p	7 716	4 906	7 440
10^4q	−4 991	−7 959	−6 024
10^4r	3 945	3 548	2 893
s	0.381	−0.634	0.142
σ/Å	0.04	0.04	0.01
Atom deviations/Å			
S(1)	0.02	0.02	0.02
S(2)	0.01	−0.04	−0.01
C(1)	−0.02	0.01	0.00
N	−0.06	0.04	0.00
C(2)	0.02	−0.05	−0.02
C(3)	−1.30	1.12	−1.41
C(4)	−1.15	2.43	−1.43
C(5)	−2.39	3.60	−2.79
C(6)	0.04	0.02	0.02
C(7)	−1.10	1.36	−1.37
C(8)	−2.45	1.27	−1.32
C(9)	−3.56	2.62	−0.96
Cu	0.28	−0.08	−0.14
H(2A)	0.46	−0.89	0.37
H(2B)	0.66	−0.07	0.55
H(6A)	0.03	−0.70	0.53
H(6B)	0.95	−0.43	0.51

Angle between the two planes: 23.7° (α)

constant [*e.g.* for the $Cu(OH)_2Cu$ bridged system $2J$ varies from -510 cm^{-1} to 172 cm^{-1} for a Cu–O–Cu angle variation of 104 to 96° [9,24]] and it is possible that a similar effect is being observed in this case. Exchange pathways for such dimeric complexes as $[Cu(S_2CNR_2)_2]$ involve delocalization of the $d_{x^2-y^2}$ electron onto the sulphur atom and overlap with the orbitals of the second metal atom leading to a small antiferromagnetic or ferromagnetic coupling in the case of Cu–S–Cu = 90°; [25] *e.g.* one calculation suggests that there is extensive delocalization of the unpaired electron onto the sulphur donor, the principal components of the highest occupied molecular orbital being $0.73d_{x^2-y^2} + 0.38\ p_x - 0.37\ p_y$,[26] implying that it is the efficiency of the coupling from the sulphur to the second metal atom that is important and this will in turn depend quite sensitively on Cu–S–Cu angle. Support for this mechanism is also given from the data on the sulphur bridged antiferromagnetic $1H^+$-thiocarbonohydrazidium complex of copper(II) [d(Cu–S) out-of-plane = 3.31 Å, Cu–S–Cu = 88.4°], for which $2J = -24.8$ cm^{-1}.[9,27]

The second possible mechanism is suggested from a comparison of the environment around the 'dimeric' units in the ethyl and butyl complexes. That is, the coupling may arise *via* interaction between copper(II) ions from neighbouring dimers [Figure 3(*b*)] (the coupling between ions within each 'dimer' remaining small as in the ethyl case) through the sulphur–sulphur contacts of less than 4 Å. This leads to possible antiferromagnetic exchange pathways of the type $[(x^2 - y^2)Cu^1||pS^1||pS^2||(x^2 - y^2)Cu^2]$. The large contribution of sulphur p orbitals to the unpaired electron molecular orbital (see above) [26] suggests that if the sulphur–sulphur overlap is significant this could be an efficient pathway. Such interactions are known in other sulphur chelates of paramagnetic ions such as the dithioacetylacetone complexes of vanadium,[28] chromium,[29] and iron,[30] all of which fit the Curie–Weiss law with Curie–Weiss constants −20 to −30 K, and the $[Fe(S_2CNEt_2)_2X]$ complexes which show only a small ferromagnetic coupling of 0.12 K between iron(III) ions *via* Fe–S · · · S–Fe pathways where the S–S distance is less than found here for α-$[Cu(S_2CNBu^n_2)_2]$.[31]

Finally we comment on the differences in observed low-temperature magnetic properties between this work and previous reports.[7,8] In the last few years it has become evident that many co-ordination complexes can exist in a multiplicity of phases both solvated and unsolvated. This is particularly true of dithiocarbamate complexes as this and other work [32-34] has shown. Furthermore the existence of more than one phase of the complex can profoundly influence the behaviour of physical properties of the molecule in the crystal (as is found here in the case of low-temperature magnetic properties). It is then clear that it is almost mandatory for modern physical studies of such systems to not only have the prerequisite structural knowledge of the complex but to ensure that the phase studied physically is identical to the structure to be studied. In the case of $[Cu(S_2CNEt_2)_2]$ the early work reported was carried out on an analytically pure sample prepared by precipitation of a powder from aqueous solution followed by washing and drying.[7] Examination of an X-ray powder photograph of a sample prepared as previously reported [7] followed by comparison with a crystal sample ground up after establishing the cell to be identical to the previously determined structure [3] showed the two patterns to be the same. It is possible that some other factor not considered at the time may have produced the complex in some form or phase not yet discovered.

Conclusion.—The antiferromagnetic interaction in α-$[Cu(S_2CNBu^n_2)_2]$ between copper(II) ions arises either from a change in bridge geometry altering the efficiency of an antiferromagnetic superexchange pathway *or* from intermolecular coupling *via* pathways of the type Cu–S · · · S–Cu. It is not possible to distinguish completely between these two mechanisms from this study although the first is preferred by comparison with similar behaviour in the copper(II) complexes and the excellent description of the magnetic susceptibility by the Bleaney-Bowers equation. The large negative θ, −2.4 K, is then in accord with the smaller intramolecular antiferromagnetic coupling. A final separation of the two possible pathways awaits further combined magnetic and structural studies on the copper dithiocarbamate molecules that are 'dimeric'.*

* *Note added at proof:* The magnetic susceptibility of $[Cu(S_2CNEt_2)_2]$ has recently been reported as a function of temperature, frequency, and applied field, and the ferromagnetic intra-pair exchange interaction shown to be J *ca.* 0.9 K, with a corresponding antiferromagnetic interaction of $J' = 0.007$ K (J. A. van Santen, A. J. van Duyneveldt, and R. L. Carlin, *Inorg. Chem.*, 1980, **19**, 2152).

We thank Mr. P. Barlow and Mrs. J. Hope for technical assistance and the Australian Research Grants Committee for a grant in partial support of this work. We acknowledge in particular stimulating discussions with Dr. D. Mackey.

[0/266 *Received*, 14*th February*, 1980]

REFERENCES

[1] E. König and G. König, 'Numerical Data and Functional Relationships in Science and Technology,' Landolt–Bornstein, 1976, vol. 8, p. 847.
[2] J. Willemse, J. A. Cras, J. J. Steggerda, and C. P. Keijzers, *Structure and Bonding*, 1976, **28**, 83.
[3] M. Bonamico, G. Dessy, A. Mugnoli, A. Vaciago, and L. Zambonelli, *Acta Cryst.*, 1965, **19**, 886; B. H. O'Connor and E. N. Maslen, *ibid.*, 1966, **21**, 828.
[4] J. M. Martin, P. W. G. Newman, B. W. Robinson, and A. H. White, *J.C.S. Dalton*, 1972, 2233.
[5] P. W. G. Newman, C. L. Raston, and A. H. White, *J.C.S. Dalton*, 1973, 1332.
[6] F. W. B. Einstein and J. S. Field, *Acta Cryst.*, 1974, **B30**, 2928.
[7] J. Villa and W. E. Hatfield, *Inorg. Chem.*, 1971, **10**, 2038.
[8] A. J. Duyneveldt, J. A. Van Santen, and R. L. Carlin, *Chem. Phys. Letters*, 1976, **38**, 585.
[9] W. E. Hatfield, H. W. Richardson, and J. R. Wasson, *Inorg. Nuclear Chem. Letters*, 1977, **13**, 137.
[10] V. H. Crawford, H. W. Richardson, J. R. Wasson, D. J. Hodgson, and W. E. Hatfield, *Inorg. Chem.*, 1976, **15**, 2107.
[11] G. R. Hall, D. M. Duggan, and D. N. Hendrickson, *Inorg. Chem.*, 1975, **14**, 1956.
[12] T. R. Felthouse and D. N. Hendrickson, *Inorg. Chem.*, 1978, **17**, 444.
[13] D. M. Duggan and D. N. Hendrickson, *Inorg. Chem.*, 1974, **13**, 2929.
[14] R. K. Cowsik, G. Rangarajan, and S. Srinivasan, *Chem. Phys. Letters*, 1971, **8**, 136.
[15] R. K. Cowsik and R. Srinivasan, *Pramana*, 1973, **1**, 177.
[16] C. V. Manjunath, K. Santosh, and R. Srinivasan, *Pramana*, 1977, **9**, 283.
[17] A. R. Hendrickson, R. L. Martin, and N. M. Rohde, *Inorg. Chem.*, 1976, **15**, 2115.
[18] D. J. Mackey, S. V. Evans, and R. L. Martin, *J.C.S. Dalton*, 1976, 1515.
[19] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.
[20] D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.
[21] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.
[22] 'The *X*-Ray System, Version of March, 1976,' Technical Report TR–446, ed. J. M. Stewart, Computer Science Centre, University of Maryland, U.S.A.
[23] G. Kokoska and G. Gordon, *Transition Metal Chem.*, 1969, **5**, 181.
[24] D. J. Hodgson, *Progr. Inorg. Chem.*, 1975, **19**, 173.
[25] A. P. Ginsberg, *Inorg. Chim. Acta Rev.*, 1975, **5**, 45.
[26] C. P. Keijzers and E. de Boer, *Mol. Phys.*, 1975, **6**, 1743.
[27] A. M. M. Lanfredi, A. Tiripicchio, and M. T. Camellini, *J.C.S. Dalton*, 1975, 2168.
[28] P. D. W. Boyd, J. M. Hope, and R. L. Martin, unpublished work.
[29] G. A. Heath, R. L. Martin, and A. F. Masters, *Austral. J. Chem.*, 1972, **25**, 2547.
[30] G. A. Heath and R. L. Martin, *Austral. J. Chem.*, 1970, **23**, 1721.
[31] H. Wickman, *J. Chem. Phys.*, 1972, **56**, 976; G. E. Chapps, S. W. McCann, H. Wickman, and R. C. Sherwood, *ibid.*, 1974, **60**, 990.
[32] S. Mitra, C. L. Raston, and A. H. White, *Austral. J. Chem.*, 1976, **29**, 1899.
[33] P. C. Healy and E. Sinn, *Inorg. Chem.*, 1975, **14**, 109.
[34] E. J. Cukauskas, B. S. Deaver, and E. Sinn, *J.C.S. Chem. Comm.*, 1974, 698; *Inorg. Nuclear Chem. Letters*, 1977, **13**, 283.