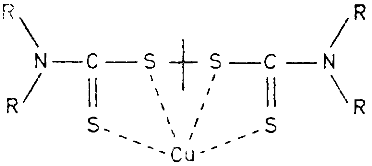
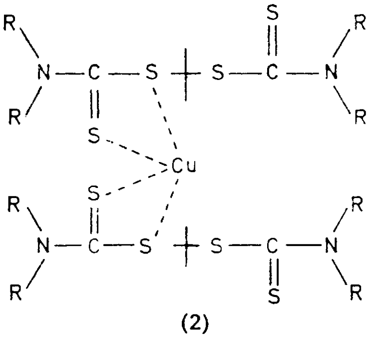
Electron Spin Resonance Studies of Copper-doped Dipiperidyl- and Tetramethyl-thiouram Disulphides

By **Ross A. Palmer** and **William C. Tennant,*** Chemistry Division, Department of Scientific and Industrial Research, Private Bag, Petone, New Zealand
Michael F. Dix and **Alan D. Rae**, Department of Physical Chemistry, The University of New South Wales, P.O. Box 1, Kensington 2033, Australia

Single-crystal e.s.r. studies are reported for copper-doped dipiperidylthiouram disulphide (Cu–dptd) and tetramethylthiouram disulphide (Cu–tmtd). Results for the former can be interpreted in terms of D_{2h} point symmetry about Cu^{2+}, being similar to copper-doped dithiocarbamates. Cu–tmtd on the other hand appears to be one of the rare cases of Cu^{2+} in predominantly tetrahedral co-ordination. Unusually small hyperfine interaction constants then arise from $3d^84p$ hybridisation which is allowed under tetrahedral symmetry.

THIOURAM DISULPHIDES and their related dithiocarbamates are of great interest chemically because of their importance as fungicides and vulcanising agents. From a structural point of view, the nature of the bonding and the metal-ion site occupancy has been a subject of speculation.[1] It is also of interest to consider the single-crystal e.s.r. interpretation in terms of crystal symmetry.[2] The work reported in this paper is a continuation of similar e.s.r. studies of copper-doped tetraethylthiouram disulphide (Cu–tetd) [1] and *X*-ray structural studies.[3]


(1)


(2)

Copper(II) thiouram disulphides are chemically interesting as they form complexes with sulphur as the co-ordinating atom. Two methods of complexing of Cu^{2+} in the thiouram matrix can be envisaged: first, the metal ion may be sited in the distorted tetrahedron formed by the sulphurs of a single thiouram molecule (1); or, secondly, the ion may cross-link two molecules of the thiouram (2). In either case the disulphide link of the thiouram is broken and the complex may be thought of as a dialkyldithiocarbamate diluted in the thiouram crystal. In case (2) the symmetry would be expected to be square planar,[1] and we would expect to

[1] R. M. Golding and W. C. Tennant, *Mol. Phys.*, 1972, **24**, 301.
[2] A. D. Rae, *J. Chem. Phys.*, 1969, **50**, 2672.
[3] M. F. Dix and A. D. Rae, *Cryst. Struct. Comm.*, 1973, **2**, 159.

be able to distinguish this from (1) by its e.s.r. spectrum and bonding parameters.

In this paper we report single-crystal e.s.r. studies of copper-doped tetramethylthiouram disulphide (Cu–tmtd) and dipiperidylthiouram disulphide (Cu–dptd). Powder studies were also carried out to confirm the interpretation of the single-crystal results. A necessary preliminary to this study was a knowledge of the detailed X-ray crystal structures and crystal morphology. The X-ray structures of dptd [3] and tmtd [4] are available, and the relations between the crystallographic parameters and crystal morphology have also been given elsewhere [5] (see Figure 1). The detailed single-crystal e.s.r. studies reported here were supplemented by crystal models to allow the site occupancy to be elucidated.

EXPERIMENTAL

The method of preparation of the thiouram disulphides has been given elsewhere.[1] Copper-doped crystals of the thiourams were crystallised from ethanol–chloroform solution.

E.s.r. spectra of Cu–tmtd and Cu–dptd crystals were obtained at 77 K on a Varian V4502 spectrometer with Fieldial II magnetic-field regulation operated in the X band. Fields were measured on the Fieldial and then calibrated by proton resonance. The klystron frequency was measured with a Hewlett–Packard frequency counter in conjunction with a Hewlett–Packard transfer oscillator.

Two different techniques were used to align and solve for the principal values and directions of the g and A tensors of the two crystals. Tetramethylthiouram disulphide crystallises in the space group $C2/c$, $Z = 4$, with the tmtd molecule on the two-fold rotation axis parallel to b. It was shown that the two-fold axis was also a principal direction of the g and A tensors. The remaining two directions were then found by searching the (010) plane of the crystal. Dipiperidylthiouram disulphide on the other hand crystallises in the space group $P2_12_12_1$. In a general direction one could expect to observe four species, and a principal g or A direction would not in general coincide with one of the crystal axes.[2] The crystal of Cu–dptd was rotated about each of the three crystallographic axes in turn by mounting it first with c vertical and subsequently on the well defined (110) and ($1\bar{1}0$) faces of the crystal on the end of a quartz rod carefully ground to the appropriate angles. The elements of the g^2 and A^2 tensors were constructed from the observed maxima and minima of the apparent g^2 and A^2 variation in each plane. The direction cosines and initial estimates of the principal values of the two tensors were obtained by numerical diagonalisation.

The e.s.r. results were fitted to the Hamiltonian (1). In

$$\mathscr{H} = \mu_B B \,.\, g \,.\, S + I \,.\, A \,.\, S + I \,.\, P \,.\, I \qquad (1)$$

both cases the final e.s.r. parameters were obtained by an iterative least-squares procedure utilising exact diagonalisations of the Hamiltonian matrix. With this program [6] the real and complex Hamiltonian matrices were diagonalised numerically and the values adjusted automatically to achieve the best fit between calculated and observed peak positions. For the Cu–tmtd crystal the refinement was carried out over the four ^{63}Cu lines in each of the three principal directions, 12 lines in all. For Cu–dptd, data were refined from six directions, the maxima and minima

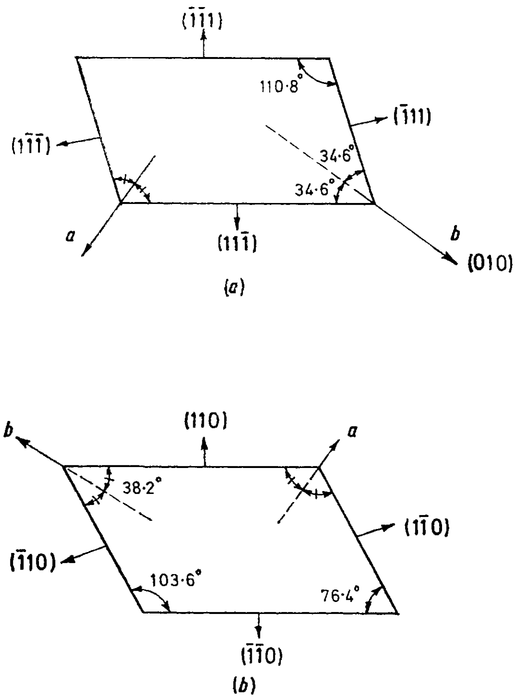


FIGURE 1 Relations between crystal-lattice parameters and crystal morphology: (a) tmtd; (b) dptd

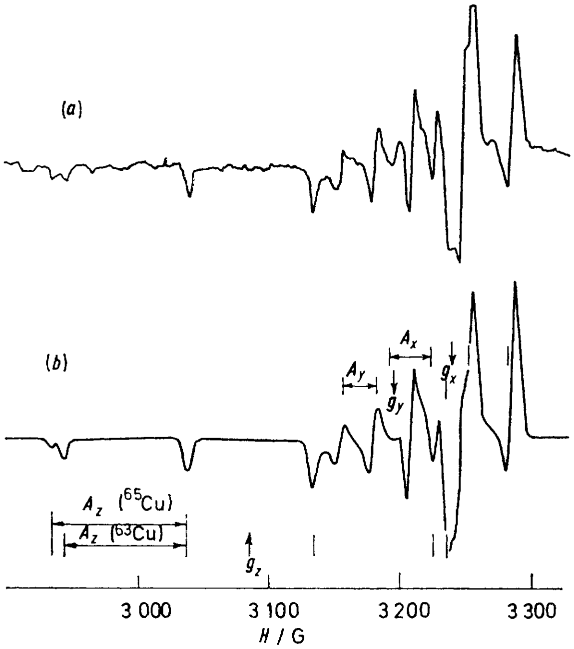


FIGURE 2 Observed and computer-simulated powder spectra for Cu–tmtd

---

[4] Kjartan Marøy, *Acta Chem. Scand.*, 1965, **19**, 1509.

[5] M. F. Dix, Ph.D. Thesis, The University of New South Wales, 1972.

[6] R. A. Palmer, W. A. Singers, and W. C. Tennant, N.Z. Dept. of Scientific and Ind. Research, 1976, Report No. C.D. 2226.

in each of the (100), (010), and (001) crystal planes, 24 lines in all.

Crystals of the two complexes were crushed and spectra of the powders obtained at 77 K. The powder spectra were analysed by computer simulation using a histogram technique,[7] the perturbation energies being taken to second order.

RESULTS

The single-crystal and powder results for Cu–tmtd are listed in Table 1(*b*). Figure 2 compares the experimental and computer-simulated powder spectra. The single-crystal study of Cu–tmtd showed that the principal direction with maximum g and A coincided with the crystal b axis. The other two principal directions were located in the (010) plane of the crystal, the g_x direction making an angle of 45° with c. The hyperfine tensor was found to have nearly axial symmetry but there was considerable anisotropy in the g tensor. Within the limits of experimental accuracy, the principal directions of the g and A tensors coincided. The errors in the principal values of the nuclear electric quadrupole tensor, P_x, P_y, and P_z, are uncertain but from our refinements the terms seem meaningful.

TABLE 1

(*a*) Initial estimates and directions for Cu–dptd (^{63}Cu isotope only, A values in 10^{-4} cm^{-1})

Parameter	Estimate	Direction cosines with respect to *a*,*b*,*c*		
g_x	2.0459	−0.419	−0.906	0.057
g_y	2.0546	−0.908	0.418	−0.029
g_z	2.1327	−0.003	0.065	0.998
A_x	24.8	−0.446	−0.883	0.147
A_y	33.1	−0.890	0.455	−0.034
A_z	136.4	0.097	0.116	0.988

(*b*) Refined values for Hamiltonian parameters (A and P values in 10^{-4} cm^{-1})

Cu–tmtd	g_x	g_y	g_z	A_x	A_y	A_z	P_x	P_y	P_z
(single crystal)	2.0209	2.0514	2.1253	30.0	26.3	91.9	1.1	−2.2	1.1
(powder)	2.021	2.052	2.126	26	25	93			
Cu–dptd									
(single crystal)	2.0496	2.0465	2.1277	29.8	30.7	140.4			

TABLE 2

Comparison of e.s.r. results of copper-doped thiourams with copper-doped dithiocarbamates

System	State	g			Hyperfine constants (10^{-4} cm^{-1})			Ref.
$[Cu(S_2CNEt_2)_2]$–$[Ni(S_2CNEt_2)_2]$	Single crystal	2.020	2.025	2.084	36	42	165	9
$[Cu(S_2CNEt_2)_2]$–$[Zn(S_2CNEt_2)_2]$	Single crystal	2.0236	2.0236	2.1085	23	23	150	[a]
$[Cu(S_2CNC_5H_{10})_2]$–$[Ni(S_2CNC_5H_{10})_2]$	Powder	2.037	2.037	2.101	48	48	171	[b]
$[Cu(S_2CNMe_2)_2]$–$[Ni(S_2CNMe_2)_2]$	Powder	2.036	2.036	2.098	47	47	171	[b]
$[Cu(S_2CNC_5C_{10})_2]$	$CHCl_3$, 77 K	2.039	2.039	2.100	45	45	167	[b]
$[Cu(S_2CNMe_2)_2]$	$CHCl_3$, 77 K	2.038	2.038	2.101	46	46	170	[b]
$[Cu(S_2CNC_5H_{10})_2]$	$CHCl_3$, 293 K	g_{iso} 2.065			A_{iso} 75			[b]
$[Cu(S_2CNMe_2)_2]$	$CHCl_3$, 293 K	g_{iso} 2.064			A_{iso} 75			[b]
Cu(1)–tetd [c]	Single crystal	2.0194	2.0194	2.0876	30.9	30.9	158.4	1
Cu(2)–tetd [c]	Single crystal	2.0166	2.0166	2.1030	23.0	23.0	141.4	1
Cu–dptd	Single crystal	2.0496	2.0465	2.1277	29.8	30.7	140.4	[b]
Cu–tmtd	Single crystal	2.0209	2.0514	2.1253	30.0	26.3	91.9	[b]
	Powder	2.021	2.052	2.126	26	25	93	

[a] T. R. Reddy and R. Srinivasan, *J. Chem. Phys.*, 1965, **43**, 1404. [b] This work. [c] Copper enters two sites in tetd.

The single-crystal spectrum of Cu–dptd contained two species in general directions collapsing to one when the magnetic flux density was parallel to the crystallographic a, b, or c axes. The crystal-structure analysis [3] of dptd indicated space group $P2_12_12_1$, $Z = 4$, with an inherent two-fold axis parallel to a and the longest direction of the molecule approximately parallel to b. The principal direction with maximum A coincided with the c axis within the limits of experimental accuracy, indicating why two rather than four species were observed in general directions. The principal values of g and A obtained from the six-point method used here [Table 1(*a*)] must be regarded as estimates only since only first-order estimates of the apparent g^2 and A^2 factors were used as input. In addition one should strictly use the tensor $g \,.\, A \,.\, A \,.\, g$ rather than $A \,.\, A$ to obtain the hyperfine values.[8] Improved values can be obtained by using second-order estimates of g^2 and A^2 but we preferred to use the complete diagonalisation least-squares method. The Hamiltonian parameters so obtained are listed in Table 1(*b*). In this case the quadrupole terms were zero.

Table 2 shows for comparison a summary of the data obtained for the two crystals under study together with the results for related dithiocarbamates obtained from various single-crystal, polycrystalline, and liquid solution e.s.r. studies.

DISCUSSION

From Table 1, the g and A tensors for Cu–dptd are very close to axial. Comparison of the Hamiltonian parameters (Table 2) shows a close similarity to copper piperidyldithiocarbamate and indeed to other copper dithiocarbamates and Cu–tetd for which square (D_{4h})

---

[7] W. C. Tennant, N.Z. Dept of Scientific and Ind. Research, 1974, Report, No. C.D. 2153.

[8] H. Zeldes and R. Livingston, *J. Chem. Phys.*, 1961, **35**, 563.

or possibly somewhat lower (D_{2h}) local symmetries about the copper atom have been shown to exist.[1,9,10] The ground-state wavefunction is then predominantly $^2B_1$ (or ^2A for D_{2h}) and various molecular-orbital[11,12] and extended-molecular-orbital[10] calculations could be expected to apply in the present case. For example, Keijzers and De Boer[10] calculated the traceless components of the hyperfine coupling constants [$A_{xx} = A_x - \frac{1}{3}\mathrm{tr}(A)$, *etc.*] for copper-doped nickel diethyldithiocarbamate to be $A_{xx} = 40.5 \times 10^{-4}$, $A_{yy} = 39.5 \times 10^{-4}$, and $A_{zz} = -80.0 \times 10^{-4}$ cm^{-1} assuming reasonable values for the empirical parameters involved and D_{2h} point symmetry for Cu^{2+}. From Table 1(*b*), the comparable values observed for Cu-dptd are $A_{xx} = 37.5 \times 10^{-4}$, $A_{yy} = 36.6 \times 10^{-4}$, and $A_{zz} = -73.4 \times 10^{-4}$ cm^{-1} respectively.

It remains to locate the impurity ion in the thiouram lattice. From Table 1 we see that one principal direction (*i.e.* the one with maximum g and A) coincides with the crystallographic c axis. The other principal (approximately axial) directions must therefore lie in a plane perpendicular to c and this must also be approximately a plane of four sulphur atoms to which the copper bonds. Furthermore all such copper sites must conform to the space-group symmetry of the crystal since, apart from site splitting, only one spectrum is observed in general directions. In similar e.s.r. studies of Cu–tetd a square-planar configuration was achieved by cross-linking of two thiouram molecules by doping Cu^{2+} in two non-equivalent positions.[1] However, construction of a crystal model showed that a similar situation cannot occur in the present instance and the only site available to the doping Cu^{2+} is within the four sulphur atoms of a single thiouram molecule. The most likely position of the impurity ion is then at fractional co-ordinates (0.38, 0.89, 0.5). The resulting calculated Cu–S bond lengths are then 2.36, 1.46, 1.35, and 2.33 Å. The two longer lengths are close to the average observed Cu–S bond lengths. The two short bonds link the copper to the two sulphur atoms of the disulphide link. These can be expected to be considerably lengthened by the breaking of the disulphide bond necessary to accommodate the Cu^{2+} ion. Subsequent to breaking of this bond the sulphur atoms must flatten into the (001) crystal plane to be consistent with the observed e.s.r. results.

The Cu–tmtd e.s.r. results do not lead to such a simple interpretation. In this case the A tensor has nearly axial symmetry about the b axis of the crystal but the g tensor is clearly rhombic [Table 1(*b*)] suggesting lower than D_{2h} local symmetry about the paramagnetic ion. The magnitudes of the principal g values are however similar to those observed for other Cu–S complexes, in particular those listed in Table 2. The rather large quadrupole terms obtained for Cu–tmtd are also indicative of a distorted site for Cu^{2+} and, since $P_x \neq P_y$, then again lower than D_{2h} symmetry is suggested.

The maximum A value is very low [Table 1(*b*)] being much lower than that for the related copper dimethyldithiocarbamate (Table 2) or any other reported copper dithiocarbamate (Table 2). Indeed, so far as we are aware, no smaller A_z value has been reported for any Cu–S complex. The low value may possibly arise from an increase in the covalent character of the Cu–S bonds, but the calculations of Keijzers and De Boer[10] (for D_{2h} symmetries) do not support this and any proposed increase in the covalency is not reflected in the g values which are very similar for the two complexes under study. The e.s.r. results suggest that the paramagnetic species is located on or near the crystallographic b axis. This would include the centre of the thiouram sulphur tetrahedron, and consideration of a crystal model again leads to the conclusion that this is the most likely site for the doping Cu^{2+} ion. However, whereas in Cu–dptd the impurity ion apparently results in a flattening of the sulphur tetrahedron, in the present instance the rhombic g tensor and the unusually low A_z value caused us to investigate the possibility that the predominantly tetrahedral configuration of the sulphur atoms is retained.

Molecular-orbital calculations for Cu–S systems have generally been restricted to high (D_{4h} or D_{2h}) symmetries since otherwise there are too many unknowns involved. The absence of a centre of inversion for systems of predominantly tetrahedral point symmetry introduces however an important fundamental difference from those with simple distortions of octahedral symmetry; this is the possibility of mixing $3d^84p$ and $3d^9$ wavefunctions. Bates *et al.*[13] have shown that for Cu^{2+} in a predominantly tetrahedral field the calculated hyperfine constants can be greatly reduced by assuming hybridisation of the $3d,4p$ wavefunctions; such hybridisation is strictly forbidden under octahedral symmetry. The equations derived by Bates *et al.*[13] admittedly contain a large number of unknowns but substitution of 'reasonable' values led to hyperfine interaction constants $\leqslant 20$ G * for a $4p$ admixture of *ca.* 30% for the organic complex Cu^{2+}($\alpha\alpha'$-bromo)dipyrromethene, for which tetrahedral symmetry was proposed.[13]

The present case is even more indeterminate since we have no values for the crystal-field splittings. However, if it can be assumed that the isotropic part of the hyperfine interaction constants arises dominantly from exchange polarisation of the core electrons *via* the Fermi-contact term (as found experimentally for Cu^{2+} in octahedral surroundings[14] and theoretically for the free Cu^{2+} ion[15]), then we may obtain some evidence from

---

* 1 G = 10^{-4} T.

[9] M. J. Weeks and J. P. Fackler, *Inorg. Chem.*, 1968, **7**, 2548.

[10] C. P. Keijzers and E. De Boer, *J. Chem. Phys.*, 1972, **57**, 1277.

[11] A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, 1958, **29**, 31.

[12] D. Kivelson and R. Neiman, *J. Chem. Phys.*, 1961, **35**, 149.

[13] C. A. Bates, W. S. Moore, K. J. Standley, and K. W. H. Stevens, *Proc. Phys. Soc.*, 1962, **79**, 73.

[14] A. Abragam, J. Horowitz, and M. H. L. Pryce, *Proc. Roy. Soc.*, 1955, **A230**, 169.

[15] J. H. Wood and G. W. Pratt, jun., *Phys. Rev.*, 1957, **107**, 995.

the changes in the isotropic and anisotropic parts of the A tensor in going from the essentially square-planar environment of Cu^{2+} in nickel diethyldithiocarbamate to the distorted environment of Cu–tmtd. From Table 2 the isotropic and anisotropic parts of the A tensor (in units of 10^{-4} cm^{-1}) are, for copper-doped nickel diethyldithiocarbamate, $A_{iso} = -90$, $A_{aniso} = 41$, 41, and -82, and for Cu-tmtd, $A_{iso} = -49.4$, $A_{aniso} = 19.4$, 23.1, and -42.5. The calculations of Freeman and Watson[16] show that the mixing of 4s and 3d orbitals would lead to a positive shift in the contact interaction. Such mixing may occur[9] when the symmetry is lower than D_{2h} and the suggested positive shift has indeed been observed[9] for Cu^{2+} in zinc diethyldithiocarbamate where a distorted trigonal-bipyramidal site has been proposed for Cu^{2+}. However, little change in the magnitude of the anisotropic part of the A tensor is expected from this mechanism, whereas for Cu–tmtd both the isotropic and anisotropic hyperfine constants are greatly different from those observed for copper-doped nickel diethyldithiocarbamate. Reduction of both the isotropic and anisotropic interactions would be expected[13] if mixing of 4p orbitals occurs, thus offering qualitative evidence in favour of tetrahedral symmetry. However, in the absence of absolute signs for the experimental hyperfine interaction constants, this assignment must remain rather speculative.

Hence, while it is not possible to definitely exclude other distorted environments, the present e.s.r. results are consistent with Cu^{2+} being situated in the distorted tetrahedron of the four sulphurs of a single thiouram molecule [fractional co-ordinates $(0,y,\frac{1}{4}), y =$ *ca.* 0.16] and we tentatively propose that the unusually low A_z value arises from the resulting admixture of $3d^84p$ and $3d^9$ wavefunctions of Cu^{2+}. The calculations of Bates *et al.*[13] indicate that the extent of mixing need only be small.

[6/899 *Received*, 10*th May*, 1976]

---

[16] A. J. Freeman and R. W. Watson, *Phys. Rev.*, 1961, **123**, 2027.