Magnetic Susceptibility and Electron Paramagnetic Resonance Studies on Bis(2,2′-bipyridyl)thioureacopper(II) Perchlorate

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Single-crystal, polycrystalline, and frozen solution e.p.r. spectra of bis(2,2′-bipyridyl)thioureacopper(II) perchlorate are reported. The low temperature (1·6—67·7 K) magnetic susceptibility of a polycrystalline sample of the complex is also reported. The intermolecular exchange interaction was found to be extremely small (*ca.* $-0{\cdot}02$ cm^{-1}) which allowed the observation of magnetically non-equivalent sites. The molecular parameters determined ($g_z = 2{\cdot}020 \pm 0{\cdot}005$, $g_x = 2{\cdot}168 \pm 0{\cdot}005$, and $g_y = 2{\cdot}141 \pm 0{\cdot}005$ and $k \simeq 0{\cdot}64$) indicate a predominantly $d_{3z^2-r^2}$ ground state but with significant mixing of excited states and with substantial delocalization of the unpaired spin density.

THE formation of copper(II) complexes with thiourea has been reported by Montenero and Pelizzi.[1] The stabilization of the 2+ oxidation state in the presence of the sulphur donor was accomplished with either 1,10-phenanthroline or 2,2′-bipyridyl ligands which have

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[1] A. Montenero and C. Pelizzi, *Inorg. Chim. Acta*, 1972, **6**, 644.

strong π-bonding properties. An increasing amount of research is being carried out on systems of this type due to the probable biological importance of the Cu–S linkage.[2] The *X*-ray crystal structure of the title compound was recently reported by Ferrari *et al.*[3] The complex, which has distorted trigonal bipyramidal co-ordination around the copper(II), is monomeric and contains a relatively short Cu–S bond. In addition, the monomeric species are highly isolated in the solid state and this allows the observation of magnetically non-equivalent sites in the e.p.r. spectrum of the neat material; a situation that is unusual for monomeric copper(II) complexes.[4,5] The single-crystal, polycrystalline, and solution e.p.r. spectra of $[Cu(bipy)_2(tu)][ClO_4]_2$ are reported herein. The low-temperature magnetic susceptibility of a polycrystalline sample is also reported. The results of our measurements are discussed in terms of the crystal structure and ground-state properties.

EXPERIMENTAL

Preparation and Identification.—Deep green, needle-like, single crystals were collected from an aqueous solution containing bis(2,2′-bipyridyl)copper(II) perchlorate[6] and thiourea[1] [Found: C, 38·5; H, 3·05; N, 12·85. Calc. for $Cu(C_{10}H_8N_2)_2SC(NH_2)_2(ClO_4)_2$: C, 38·7; H, 3·1; N, 12·9%]. The crystal axes were determined from rotation and Weissenberg photographs using Cu-K_α (λ = 1·5418 Å) radiation. The cell parameters matched those of Ferrari *et al.*[3] exactly. The zero-level Weissenberg photograph also showed the systematic absences[7] appropriate for the reported space group, $P2_12_12_1$.

Bulk Magnetic Susceptibility Measurements.—The magnetic susceptibility of a polycrystalline sample of the complex was measured using a Foner-type vibrating-sample magnetometer as previously described.[8] The magnetometer was calibrated with the manganese Tutton salt, $(NH_4)_2Mn(SO_4)_2,6H_2O$,[9] and checked with a pure nickel sphere.[10]

E.p.r. Measurements.—A single crystal with dimensions 5 × 1 × 0·5 mm was mounted on a flat face (the normal to which makes an angle of 12° with the *a* axis) on a quartz rod (with goniometer). E.p.r. spectra were recorded every 10—15° around three mutually perpendicular rotation axes.

The e.p.r. spectra were taken on a Varian E-3 and a JEOL ME 3X spectrometer. A Magnion G-502 Precision Gaussmeter, a Hewlett–Packard 5245L frequency counter, and a DPPH sample were used to calibrate the magnetic field and klystron frequencies.

RESULTS

Bulk Magnetic Susceptibility.—The temperature variation of the magnetic susceptibility nearly obeys a Curie Law ($\chi_m = C/T$) over the entire temperature range; however, a somewhat better least-squares fit can be obtained by including a Weiss constant [$\chi_m = C/(T - \theta)$]. The best least-squares Curie–Weiss fit to the experimental data yields the constants $C = 0{\cdot}420$ c.g.s.u./K and $\theta = -0{\cdot}020$ K. The Weiss constant obtained from our fit is substantially different from the high-temperature extrapolation previously reported.[1]

Single-crystal E.p.r.—The single-crystal e.p.r. spectra of the complex revealed two magnetically non-equivalent sites (*vide post*) for crystal orientations where the magnetic field, ***H***, was not along a crystal axis. The two resonances merged into a single more intense line when the field became collinear with a crystal axis; it is required that all sites be magnetically equivalent for such orientations in orthorhombic symmetry.[11] Since the two absorptions are never separated sufficiently for complete resolution of both absorptions, the accuracy of the determination of the magnetic parameters is somewhat limited.

The variation of g^2 [$= (h\nu/\beta H)^2$] with angle, ψ, in the *ab*-plane is shown in Figure 1. When $\psi = 0°$, *H* is along the *a*-axis and when $\psi = \pm 90°$, *H* is along the *b*-axis. The solid curve in Figure 1 was calculated by

$$g^2 = g_1^2 \sin^2\theta \cos^2\phi + g_2^2 \sin^2\theta \sin^2\phi + g_3^3 \cos^2\theta \quad (1)$$

where $\phi = 0°$ and $\theta = \psi \pm \alpha$. α, the angle between the principal crystal *g*-values (g_i, i = 1, 2, 3) and the crystal axes, was found to be ±66°, *i.e.*, g_3 of site 1 makes an angle of 66° with the *a*-axis while g_3 of site 2 makes angle of −66° with the *a*-axis. The principal crystal *g*-values obtained from equation (1) are $g_1 = 2{\cdot}022 \pm 0{\cdot}005$ and $g_3 = 2{\cdot}172 \pm 0{\cdot}005$.

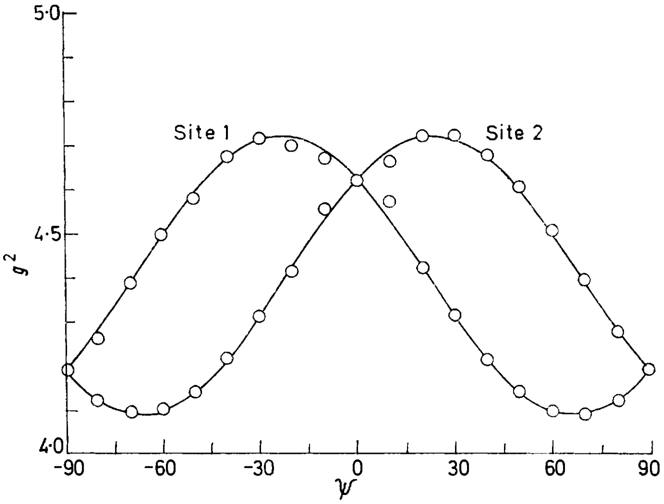

FIGURE 1 The angular variation of the e.p.r. spectra of the complex in the crystallographic *ab*-plane. ψ = 0 has ***H*** along the *a*-axis and ψ = ±90 has ***H*** along the *b*-axis. The solid curves are the best fits to equation (1)

An experimental value for g_2 was not obtainable since there was no suitable crystal face for rotation through the *ac*- or *bc*-planes.

Principal Values and Orientation of the Molecular g*-Tensor.*—Owing to small exchange interactions, it is almost always

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[2] J. Peisach, P. Aisen, and W. Blumberg, eds., 'The Biochemistry of Copper,' Academic Press, New York, 1966.

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[4] E. König, Landolt-Börnstein, New Series, Group II, Vol. 2, Springer, Berlin, 1966.

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[7] 'International Tables for *X*-Ray Crystallography,' Vol. 1, Kynoch Press, Birmingham, 1952.

[8] D. B. Losee and W. E. Hatfield, *Phys. Rev.*, 1974, **B10**, 212.

[9] F. R. McKim and W. P. Wolf, *J. Sci. Instr.*, 1957, **34**, 64.

[10] G. Aubert, *J. Appl. Phys.*, 1968, **39**, 504.

[11] K. Lonsdale and K. S. Kirshnan, *Proc. Roy. Soc.*, 1936, **A156**, 597.

the case that the single-crystal e.p.r. spectra at X-band frequencies of monomeric copper(II) complexes reveals only one resonance per orientation even though there are magnetically non-equivalent sites in the unit cell.[4,5] Since the exchange interactions cause the signals of non-equivalent sites to coalesce into one signal, it is supposed [12] that the g-values calculated from such a resonance are the arithmetical mean of the g-values of the 'exchanging' sites. This is clearly not the case in the present system since two different sites are observed. It is assumed therefore that the resonances correspond to the 'true' g-values of the molecular unit and not an exchange averaged g-value.

Since the molecular symmetry of the complex is sufficiently low such that the directions of the principal molecular axes cannot be inferred from the symmetry properties of the molecule, the orientation and values of the principal components were determined by the method of Geusic and Brown.[13] The principal co-ordinates obtained are described in Table 1.

Polycrystalline and Frozen Solution Spectra.—The e.p.r. spectrum of the polycrystalline sample appears to be a two-g-value spectrum. By assigning the transition fields according to Hathaway,[5] the g-values are calculated to be $g_{\parallel} = 2{\cdot}022$ and $g_{\perp} = 2{\cdot}165$, which is typical of trigonal bipyramidal geometry.

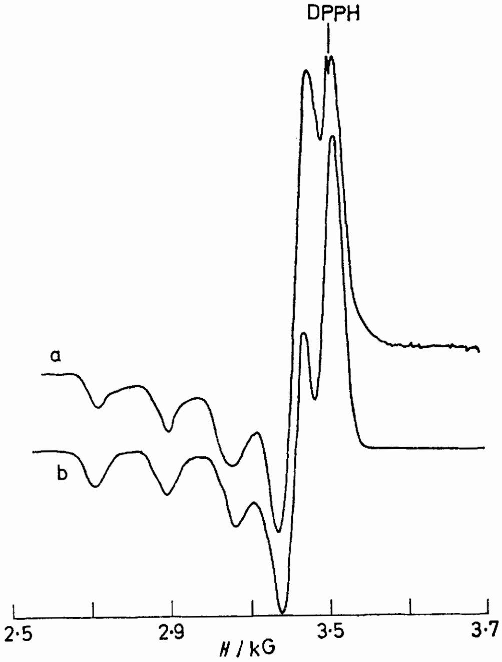

FIGURE 2 (a) The frozen nitromethane solution spectrum of the complex. (b) The computer simulation of the spectrum. The values $g_z = 2{\cdot}228 \pm 0{\cdot}003$, $g_x = 2{\cdot}055 \pm 0{\cdot}005$, $g_y = 2{\cdot}070 \pm 0{\cdot}01$, $A_z = 180 \pm 4 \times 10^{-4}$ cm^{-1}, and $A_x \simeq A_y < 10 \times 10^{-4}$ cm^{-1} were extracted from the simulation

The spectrum of the frozen nitromethane solution ($\sim10^{-3}$M) of the complex, which is typical of square pyramidal geometry, is shown in Figure 2a. Figure 2b is the computer simulation of the spectrum according to the Hamiltonian:

$$\mathcal{H} = \beta \boldsymbol{S}\cdot\boldsymbol{g}\cdot\boldsymbol{H} + \boldsymbol{S}\cdot\boldsymbol{A}\cdot\boldsymbol{I} \qquad (2)$$

The simulation assumes the g- and A-tensors to have coincident axes and accounts for all orientations of the principal co-ordinate system with respect to $\boldsymbol{H}$. The parameters extracted from the simulation are: $g_z = 2{\cdot}228 \pm 0{\cdot}003$, $g_x = 2{\cdot}055 \pm 0{\cdot}005$, $g_y = 2{\cdot}070 \pm 0{\cdot}01$, $A_z = 180 \pm 4 \times 10^{-4}$ cm^{-1}, and $A_x \simeq A_y < 10 \times 10^{-4}$ cm^{-1}.

DISCUSSION

The complex [Cu(bipy)$_2$(tu)][ClO$_4$]$_2$ crystallizes [3] in the non-centrosymmetric space group $P2_12_12_1$ with four formula units per cell. The co-ordination around each copper atom is best described as a distorted trigonal bipyramid composed of the nitrogen atoms from the bipyridyl groups and the sulphur atom of the thiourea group (see Figure 3). The closest approach of the copper(II) ions in the monomeric species is *ca.* 6·2 Å.

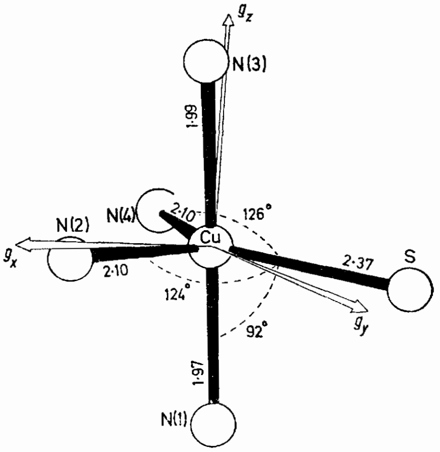

FIGURE 3 The orientation of the g-tensor components with respect to the molecule. Structural information was obtained from reference 3

Using the Curie constant extracted from the susceptibility data, an average value of g was calculated [$g^2 = 3kC/N\beta^2S(S+1)$] to be 2·12 which is in good agreement with the e.p.r. data. The effective magnetic moment ($\mu_{\text{eff}} = 2{\cdot}83\sqrt{\chi_m T}$) was found to be constant over the entire temperature range studied with a value of 1·82 ± 0·03 B.M. Even at the lowest temperature measured (1·6 K) no effects of intermolecular exchange were indicated by μ_{eff}.

TABLE 1

Principal molecular g-values and angles describing their orientation *

$g(z) = 2{\cdot}020$	$g(z)$–Cu–N(3)	6°
	$g(z)$–Cu–N(4)	102°
	$g(z)$–Cu–S	69°
$g(x) = 2{\cdot}168$	$g(x)$–Cu–N(3)	89°
	$g(x)$–Cu–N(4)	121°
	$g(x)$–Cu–S	113°
$g(y) = 2{\cdot}141$	$g(y)$–Cu–N(2)	97°
	$g(y)$–Cu–N(3)	109°
	$g(y)$–Cu–S	13°

* Values obtained from the matrix diagonalization (see text).

Some idea of the magnitude of the exchange interaction can be gained from molecular field theory.[14] Using the relation $J = 3k\theta/2ZS(S+1)$ yields a J-value

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[12] H. Abe and K. Ôno, *J. Phys. Soc.* (*Japan*), 1956, **11**, 947.

[13] J. E. Geusic and L. C. Brown, *Phys. Rev.*, 1958, **112**, 64.

[14] J. S. Smart, 'Effective Field Theories of Magnetism,' W. B. Saunders Co., Philadelphia, 1966.

of $-0{\cdot}02$ cm^{-1} for $Z = 2$. This extremely small value for J is consistent with the fact that non-equivalent sites are observed in the X-band e.p.r. spectrum.

Although potentially there exists four magnetically non-equivalent sites for some arbitrary orientation of $\boldsymbol{H}$, the number of sites is reduced to two so long as $\boldsymbol{H}$ is applied in an ij-plane ($i,j = a,b,c$). Moreover, the molecules are fortuitously arranged such that two of the sites cannot be distinguished due to the linewidth (not exchange narrowed) of the signal.

The orientation of the principal molecular g-values with respect to the molecule are shown in Figure 3. Although the lack of symmetry precludes any restrictions on the g-tensor orientation, the principal values tend to describe the idealized geometry of the complex, *i.e.* g_z is in the N(1)–Cu–N(3) plane and approximately bisects the deviation from 180°, *etc.* It should be noted that the xz-plane is parallel to the crystal ab-plane, within experimental error; this is also evident from a comparison of the crystal and molecular g-values. The fact that g_1 is 0·004 larger than g_x suggests that the principal molecular g-values are in slight error. This deviation most likely results from a combination of angle measurement error and transition-field assignment ambiguities with the latter being the dominant factor. The deviation is well within our assigned experimental error. Also, the molecular co-ordinate system obtained is orthogonal ($\pm 1°$).

In an effort to determine the nature of the bonding in the molecule, the method of Swalen and his co-workers [15] was used to analyse the g-values. These workers write the wave functions for the ground state Kramers doublet as

$$\psi = a\phi_1\alpha + b\phi_3\alpha + ic\phi_2\alpha - id\phi_4\beta - e\phi_5\beta$$
$$\psi^* = i(a\phi_1\beta + b\phi_3\beta - ic\phi_2\beta - id\phi_4\alpha + e\phi_5\alpha)$$

where $\phi_1 \simeq d_{3z^2-r^2}$, $\phi_2 \simeq d_{xy}$, $\phi_3 \simeq d_{x^2-y^2}$, $\phi_4 \simeq d_{yz}$, and $\phi_5 \simeq d_{xz}$. By assuming that $e = d$, the bonding coefficients may be evaluated in the usual way [15,16] from the expressions

$$g_z = 2 - 4d^2 - 4e^2 + 8bc + 4de$$
$$g_x = 2 - 4c^2 - 4e^2 + 4\sqrt{3}ad - 4ce + 4bd$$
$$g_y = 2 - 4c^2 - 4d^2 + 4\sqrt{3}ae - 4be + 4ce$$

The values calculated for [Cu(bipy)$_2$(tu)][ClO$_4$]$_2$ along with those for other reported trigonal bipyramidal complexes are listed in Table 2.

TABLE 2

Principal g-values and bonding parameters of trigonal bipyramidal complexes

Complex	g_x	g_y	g_z	a	b	c	d	e
[Cu(bipy)$_2$(tu)][ClO$_4$]$_2$	2·167	2·141	2·020	0·9867	0·1586	0·0174	0·0230	0·0230
Ag[Cu(NH$_3$)$_2$(SCN)$_3$]	2·207	2·207	2·004	0·9981	0·0313	0·0314	0·0311	0·0311
[Cu(bipy)$_2$I]I	2·169	2·169	2·033	0·9947	0·0661	0·0671	0·0276	0·0276

It is apparent from the wave-function coefficients that the ground state of all three complexes is predominantly d_{z^2}. The thiourea complex, however, has a much greater admixture of $d_{x^2-y^2}$ character in the ground state than either of the other two systems. The complex Ag[Cu(NH$_3$)$_2$(SCN)$_3$] which contains [17] a true D_{3h} CuN$_5$ species, has an almost entirely d_{z^2} ground state with only a minimal admixture of excited states. The other complex [Cu(bipy)$_2$I]I, which has the CuN$_4$I group in a somewhat distorted trigonal bipyramidal arrangement,[18] has more admixture of excited states as would be expected. The major difference in the two distorted complexes (CuN$_4$S deviating most from trigonal bipyramidal) is the admixture of the d_{xy} orbital; the thiourea complex has markedly less d_{xy} character. This implies that the orbital capable of accepting a ' reducing ' electron is not oriented appropriately to bond with the sulphur donor, hence the stabilization of the 2+ oxidation state is rationalized.

Additional bonding information can be obtained by determination of the orbital reduction parameter k. A value of $k = 0{\cdot}64$ is obtained from the susceptibility data by applying the expression [19] $\mu_{\text{eff}} = \mu_{\text{spin only}}$-$(1—2k^2\lambda/\Delta_2)$. This value is in remarkable agreement with the value obtained from the e.p.r. data ($k = 0{\cdot}63$) calculated according to [19] $g_\perp = 2(1—3k^2\lambda/\Delta_2)$, where $g_\perp$ was taken as the mean of g_x and g_y. The free-ion value for $\lambda = -828$ cm^{-1} and the reported value [1] of $\Delta_2 = 13\,000$ cm^{-1} was used in each case. The determined value of k is consistent with a substantial amount of π-bonding as predicted.

An attempt to gain further information concerning the delocalization of the unpaired spin density was made by taking frozen-solution spectra so that the hyperfine structure could be analysed. The data extracted from the frozen-solution spectrum may not be meaningfully compared to the solid-state data since the spectrum clearly shows that the trigonal bipyramidal arrangement is destroyed in solution. This fact tends to support the belief that trigonal bipyramidal co-ordination is produced by solid-state packing effects.

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