An Electron Spin Resonance Study of the Copper(II) Chelate of 2-(2′-Pyridylmethylenehydrazonomethyl)phenol and Related Compounds *

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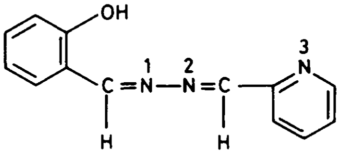
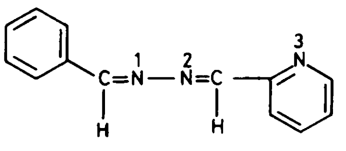
The e.s.r. spectrum due to the copper(II) chelate of 2-(2′-pyridylmethylenehydrazonomethyl)phenol (HL^1) shows that while the chelate is monomeric in *N,N*-dimethylformamide (dmf) solution at room temperature, dimerization occurs in frozen solution. The absence of dimerization in the copper(II) chelate of the aldazine derived from the reaction of pyridine-2-carbaldehyde with the hydrazone of benzaldehyde implicates the ionized hydroxy group in the dimerization process. Spin-Hamiltonian and structural parameters have been determined by computer simulation of the triplet-state e.s.r. spectrum due to the dimeric species. Monomeric forms of $Cu(L^1)_2$ occur in dmf solutions containing pyridine, imidazole, 2-methylpyridine, or 2,4,6-trimethylpyridine. Under these circumstances, the superhyperfine lines [from the bonding of copper(II) to four nitrogen atoms from the ligands], observed in the e.s.r. spectra due to the copper(II) chelate in frozen dmf solution containing the heterocyclic nitrogenous base become progressively more difficult to discern in the order pyridine < imidazole < 2-methylpyridine > 2,4,6-trimethylpyridine. Spin-Hamiltonian parameters and linewidth terms have been determined by computer simulation of the e.s.r. spectra due to monomeric forms of the copper(II) chelates where the loss of superhyperfine structure depends on the magnitude of the linewidth terms.

The compound formed by the water elimination reaction of pyridine-2-carbaldehyde with the hydrazone of salicylaldehyde is the aldazine 2-(2′-pyridylmethylenehydrazonomethyl)phenol (HL^1). The aldazine is a monobasic acid possessing a facultative ligand structure, for the co-ordination of metal ions, capable of forming chelates by several modes of attachment which include six-membered structures involving the donor set O,N(1) or the donor set O,N(2),N(3). To discern the possible modes of ligand co-ordination, the copper(II) chelate has been prepared and e.s.r. spectroscopy used, in favourable circumstances, to determine the atoms involved in the donor set. To provide information on the role played by the ionized hydroxy group in chelate formation it proved useful to prepare copper(II) chelates of the aldazine HL^2 derived from the reaction of pyridine-2-carbaldehyde with the hydrazone of benzaldehyde.



HL^1



HL^2

Results

The copper(II), nickel(II), and zinc(II) chelates of HL^1 have been isolated as their dihydrates. In addition, heterocyclic nitrogenous base forms of the copper(II) chelates have been prepared and the copper(II) chelate $Cu(HL^2)_2(NO_3)_2{\cdot}2H_2O$ synthesized. Magnetic susceptibility measurements on the copper(II) and nickel(II) chelates show $\mu_{eff.}$ values which are in the range expected for one electron per Cu^{II} centre and two electrons per Ni^{II} centre in a high-spin octahedral environment. In general terms chelate formation in solution is marked by an increase in the yellow colour due to the ligand while some further deepening of colour occurs as a result of addition of a heterocyclic nitrogenous base such as pyridine. A typical set of spectral results in the u.v.–visible region is shown by Figure 1.

The e.s.r. spectrum due to a *N,N*-dimethylformamide (dmf) solution (293 K) of the chelate $Cu(L^1)_2{\cdot}2H_2O$ is that expected from a monomeric copper(II) compound whose molecules are freely tumbling in the solution phase. A quite similar e.s.r. spectral result is obtained from solutions of the chelate in chloroform containing pyridine (10%, v/v). The e.s.r. spectrum due to a frozen (77 K) dmf solution of $Cu(L^1)_2{\cdot}2H_2O$ is similar to that reported for the cationic derivatives of phthalocyaninatocopper(II).[1] The well resolved component of the spectrum in the $g = 2$ region, showing evidence of superhyperfine interactions with ligand nitrogen atoms, is due to the monomeric form of the copper(II) chelate, while the broader features on the higher and lower magnetic positions are attributable to a dimeric form of the chelate which provides circumstances for the magnetic dipolar coupling between the copper(II) centres. These broader resonances are attributable to the $\Delta M_s = \pm 1$ transitions in the triplet state formed as a result of magnetic dipolar coupling.[2,3] Confirmation of this assignment was obtained from the observation at higher instrumental gain of an e.s.r. spectral component centred at $g = 4$ which arises from the spin-forbidden $\Delta M_s = \pm 2$ transitions within the triplet state. These spectra were computer simulated and results are given in Table 1.

The influence of the hydroxy group on the formation of dimeric species in frozen solution is illustrated by the e.s.r. spectrum due to $Cu(HL^2)_2(NO_3)_2{\cdot}2H_2O$ in frozen (77 K) dmf solution. The e.s.r. spectrum is due entirely to monomeric species where the superhyperfine lines on the $g_\perp$ and $g_\parallel$

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* *Non-S.I. unit employed:* mmHg = 101 325 Pa.

Table 1. Spin-Hamiltonian parameters for the dimeric form of $Cu(L^1)_2 \cdot 2H_2O$ in dmf

			Hyperfine constants ($\times 10^4$ cm^{-1})		Linewidths (mT)				Relative intensity $\Delta M_s = \pm 1 / \Delta M_s = \pm 2$	
	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$	$A_{\perp}$	$W_{\parallel}$	$W_{\perp}$	$\zeta/°$	r/Å	Expt.	Theory
$\Delta M_s = \pm 1$	2.1750 ± 0.005	2.0250 ± 0.005	220 ± 5	12.5 ± 1.0	3.00 ± 0.05	2.00 ± 0.05	18 ± 2	4.4 ± 0.1	55 ± 1	71 ± 12
$\Delta M_s = \pm 2$	2.1540 ± 0.005	2.0160 ± 0.005	220 ± 5	12.5 ± 1.0	3.00 ± 0.05	2.00 ± 0.05	18 ± 2	4.4 ± 0.2		

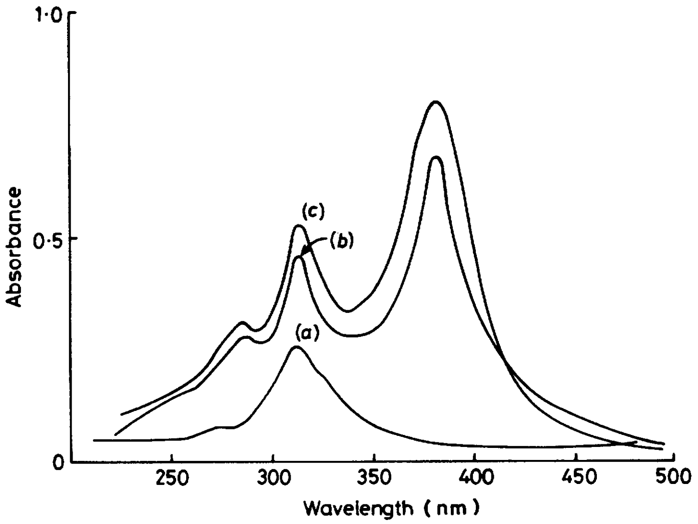

Figure 1. U.v.–visible absorption spectra, using 1-cm pathlength quartz cells, of a dmf solution of (*a*) HL^1 (2.0×10^{-4} mol dm^{-3}), (*b*) $Cu(L^1)_2 \cdot 2H_2O$ (2.0×10^{-4} mol dm^{-3}), and (*c*) $Cu(L^1)_2 \cdot 2(py)$ (2.0×10^{-4} mol dm^{-3})

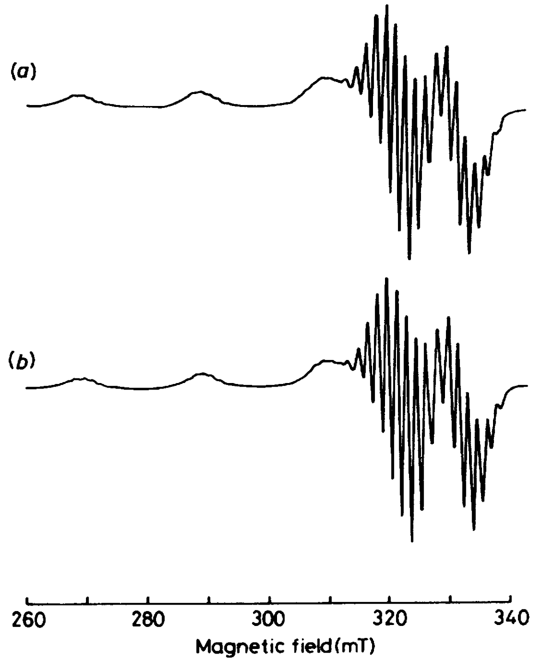

Figure 2. First-derivative e.s.r. spectrum of a frozen dmf solution at 77 K due to $Cu(L^1)_2 \cdot 2H_2O$ (3.0×10^{-3} mol dm^{-3}) containing pyridine (5%, v/v). Microwave frequency at 9.108 GHz. (*a*) Experimental spectrum. (*b*) Computer simulation using the spin-Hamiltonian parameters in Table 2(*a*) and linewidth terms of Table 2(*b*)

resonances provide evidence for the interaction of the unpaired electron of the copper(II) centre with four ^{14}N nuclei in the co-ordination sphere provided by the chelating ligands. The absence of the ionized hydroxy group in the ligand clearly removes the possibility of the formation of dimeric species in frozen dmf solution. In the bis(pyridine) and related nitrogenous base forms of the copper(II) chelates, axial interactions between the nitrogenous base and the central copper(II) ion will prevail and influence equatorial co-ordination by the chelating ligand. The disappearance of the triplet state type e.s.r. spectrum, due to the dimeric form of the chelate which occurs in frozen dmf solution, as a result of the addition of nitrogenous base, provides a means of monitoring the presence of axial interactions which occur on the addition of various bases.

The e.s.r. spectrum due to the bis(pyridine) solvate of $Cu(L^1)_2 \cdot 2H_2O$ in frozen (77 K) dmf solution containing pyridine (py) (5%, v/v) is shown by Figure 2. The spectrum is due to a monomeric form of the chelate which gives rise to clearly observed superhyperfine interactions in the e.s.r. spectrum as a result of interaction of the unpaired electron of the copper(II) centre with four nitrogen atoms from the ligand co-ordination sphere. The spectrum in Figure 2 is representative of a number of the results obtained in this work, the main difference arising in the degree of resolution of nitrogen hyperfine structure which is discussed later in terms of linewidths.

A small change to the total structure of the copper(II) chelate–axial base can be effected by using 2-methylpyridine (2Me-py) as the base. Figure 3 shows the e.s.r. spectrum obtained from $Cu(L^1)_2 \cdot 2H_2O$ in frozen (77 K) dmf containing 2-methylpyridine (5%, v/v) to be due to an axially ligated

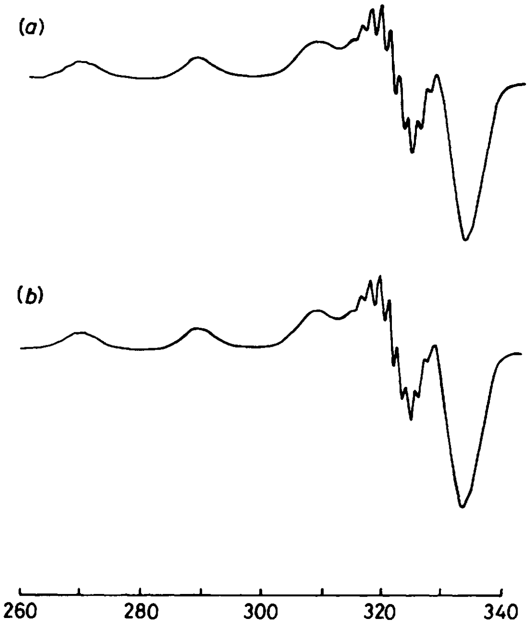

Figure 3. First-derivative e.s.r. spectrum of a frozen dmf solution at 77 K due to $Cu(L^1)_2{\cdot}2H_2O$ (3.0×10^{-3} mol dm^{-3}) containing 2-methylpyridine (5%, v/v). Microwave frequency 9.108 GHz. (*a*) Experimental spectrum. (*b*) Computer simulation using the spin-Hamiltonian parameters in Table 2(*a*) and linewidth terms of Table 2(*b*)

monomeric form, but one possessing superhyperfine lines which are barely discernible compared to those when pyridine is present in the axial positions. This reduction in resolution also occurs when $Cu(HL^2)_2(NO_3)_2{\cdot}2H_2O$ is used. Thus, in the presence of pyridine, the resolution of the superhyperfine lines due to the chelate alone is maintained. When 2-methylpyridine is added to $Cu(HL^2)_2(NO_3)_2{\cdot}2H_2O$ in dmf, an e.s.r. spectrum closely similar to that shown by Figure 3 is obtained, showing a marked reduction in the resolution of the superhyperfine lines. When 2,4,6-trimethylpyridine (2,4,6Me$_3$-py) is added (5%, v/v) to a dmf solution of $Cu(L^1)_2{\cdot}2H_2O$ superhyperfine lines are completely absent from the e.s.r. spectrum. Addition of imidazole to a dmf solution containing $Cu(L^1)_2{\cdot}2H_2O$ gives an e.s.r. spectrum whose appearance is intermediate between those depicted by Figures 2 and 3, showing some loss of resolution of the superhyperfine lines compared with those observed when pyridine was present.

The chemical effect of heterocyclic base addition to $Cu(L^1)_2{\cdot}2H_2O$ in dmf solution is to form monomeric species which may be identified at room temperature and in frozen solution by characteristic e.s.r. spectra. However, addition of the potentially bidentate heterocyclic base 1,10-phenanthroline to a dmf solution of $Cu(L^1)_2{\cdot}2H_2O$ leads to the disappearance of the e.s.r. spectrum observed formerly at room temperature, while in frozen (77 K) solution conditions the e.s.r. spectrum consists of a broad almost isotropic resonance in the $g = 2$ region flanked by equally broad resonances though of diminished intensity. These results are interpretable in terms of a linking together of chelate units by 1,10-phenanthroline to form dimeric and polymeric forms at room temperature where magnetic relaxation interactions between the copper(II) centres removes observable resonances, while in frozen solution the single broad resonance occurs as a result of multiple magnetic dipolar interactions.

Interpretation of E.S.R. Spectral Data.—(*a*) *The dimeric form of the chelate.* The 'triplet'-state e.s.r. spectrum arising from largely magnetic dipole–dipole coupled copper(II) centres in the dimeric form of the chelate which occurs in frozen solvent can be explained satisfactorily by a model of the magnetic axes which takes into account the symmetry of the copper(II) centres. The appropriate spin Hamiltonian may be written in this case by equation (1) where the nomenclature is identical to that used previously.[2]

$$\mathscr{H} = \sum_{i=1,2} \{\beta[g_{\|}B_zS_{iz} + g_{\perp}(B_xS_{ix} + B_yS_{iy})] + A_{\|}S_{iz}I_{iz} + A_{\perp}(S_{ix}I_{ix} + S_{iy}I_{iy})\} + \mathscr{H}(\text{dipolar}) - JS_1{\cdot}S_2 \quad (1)$$

It is taken that $|J| \leqslant$ *ca.* 30 cm^{-1} and that no 'pseudo-dipolar' contributions are needed. The best-fit magnetic parameters obtained for the triplet-state e.s.r. spectrum are summarized in Table 1 and were obtained using the computer program GNDIMER.[2]

The evaluation of the linewidth terms, $W_{\|}$ and $W_{\perp}$, for the computed $\Delta M_s = \pm 1$ and ± 2 lineshapes makes possible a comparison of the ratio of peak intensities in the $\Delta M_s = \pm 1$ and ± 2 regions of the experimental spectrum with the ratio derived from the final simulated lineshape. The results of these calculations are shown in Table 1. The results are in reasonable agreement and close to those found previously from the e.s.r. spectral data pertinent to the formation of dimeric phthalocyanine species.[1]

(*b*) *Spin-Hamiltonian parameters and linewidth terms associated with monomeric forms of the copper*(II) *chelates.* The magnetic parameters associated with the e.s.r. spectra due to the monomeric copper(II) chelates have been determined by computer simulation using an axially symmetric Hamiltonian,[4] appropriate to tetragonal symmetry, for $S = \frac{1}{2}$, I (copper nuclear spin) $= \frac{3}{2}$, and I^N (nuclear spin of nitrogen ligand) $= 1$:

$$\mathscr{H} = \beta[g_{\|}B_zS_z + g_{\perp}(B_xS_x + B_yS_y)] + A_{\|}S_zI_z + A_{\perp}(S_xI_x + S_yI_y) + \sum_{i=1}^{4} A_i^NS_i^NI_i^N \quad (2)$$

equation (2), where the parameters have their usual meanings. In order to retain overall axial symmetry, even in the presence of nitrogen ligand hyperfine structure, some simplification of the last term in equation (2) is made. It is assumed that $A_{\|}^N$ is the ligand hyperfine constant parallel to the molecular symmetry axis ($\|$ or z) and $A_{\perp}^N$ the value in the molecular plane. This is not necessarily correct but appears to be satisfactory since $A_{\|}^N \sim A_{\perp}^N$.

The values of the magnetic parameters obtained from the best-fit of the experimental spectrum are shown in Table 2 where g values are determined ± 0.001 throughout unless otherwise stated. It has been assumed that the complexes have axial symmetry. While it might be thought that measurements at *Q*-band (35 GHz), for example, would resolve g_x and g_y values this is not so, and in view of the linewidth data obtained at *X*-band, most unlikely.

Details concerning the method of computer simulation and the generation of linewidths now follow. Computer simulations

$$S(\nu_c,B) = C\sum_{i=1}^{2}\sum_{M_I}\sum_{M_N}\sum_{\theta=0}^{\pi/2} a(i)b(M_N)\overline{g_i^{\,2}}f(\nu_c - \nu_o[B],\sigma_v)\Delta\cos\theta \quad (3)$$

of the e.s.r. spectra due to monomeric copper(II) chelates have been carried out using equation (3),[4] where the parameters $a(i)$ are the fractional abundances of ^{63}Cu and ^{65}Cu, $b(M_N)$

Table 2. Spin-Hamiltonian parameters (*a*) and linewidth terms (*b*) for the monomeric forms of $Cu(L^1)_2{\cdot}2H_2O$ in dmf with different nitrogenous bases[a]

	(*a*)						(*b*)					
			Hyperfine constant[b] ($\times 10^{-4}$ cm^{-1})									
Base	$g_\perp$	$g_\parallel$	$^{Cu}A_\perp$	$^{Cu}A_\parallel$	$^{N}A_\perp$	$^{N}A_\parallel$	$\sigma_{R_\perp}$/MHz	$\sigma_{R_\parallel}$/MHz	$C_{1\perp}$	$C_{1\parallel}$	$C_{2\perp}$/MHz	$C_{2\parallel}$/MHz
Pyridine	2.053	2.212	16	203	16	14	13	13	0.0006	0.0007	2.2	2.0
Imidazole	2.053	2.212	15	196	15	14	12	13	0.0010	0.0012	3.0	3.1
2-Methylpyridine	2.048	2.216	15	195	15	15	12	13	0.0016	0.0020	3.4	3.5
2,4,6-Trimethylpyridine	2.044	2.225	15	183	16	15	13	13	0.0040	0.0045	4.0	5.3

[a] Error values: $g = \pm 0.001$, $^{Cu}A_\perp = \pm 1$, $^{Cu}A_\parallel = \pm 2$, $^{N}A_\perp$ and $^{N}A_\parallel = \pm 1$, $\sigma_{R_\perp}$ and $\sigma_{R_\parallel} = \pm 1$, $C_{1\perp}$ and $C_{1\parallel} = \pm 0.0001$, $C_{2\perp}$ and $C_{2\parallel} = \pm 0.5$. [b] To convert hyperfine values to MHz, multiply numbers in table by 3, *i.e.* 205×10^{-4} cm^{-1} $\equiv$ 615 MHz.

the intensities due to n equivalent ligands [*e.g.* $b(M_N) =$ 1:4:10:16:19:16:10:4:1 when $n = 4$], $\overline{g_i^2}$ the powder average expression for the effect of g anisotropy on intensity, and f the lineshape function, assumed to be Gaussian. Here also ν_c is the constant applied microwave frequency, $\nu_o[B]$ the frequency difference between the levels involved in a transition at a magnetic field B, and σ_v the linewidth (in frequency units). First-derivative computed spectra are obtained by numerical differentiation of $S(\nu_c, B)$ as a function of B. The resonance condition is given by equation (4), where it is assumed that

$$h\nu_o[B] = g\beta B + AM_I + A^N M_N + \text{(second-order corrections)} \quad (4)$$

metal and ligand hyperfine interactions can be treated independently (A and A^N are the hyperfine splittings for copper and the nitrogens along the magnetic field direction; M_I is the copper nuclear quantum number). This is an approximation whenever $A_\perp^{Cu}$ is about equal to A^N. Since all four nitrogens are assumed to be equivalent, no summation is required at the third term of equation (4).

To determine the resonance field positions,[4] B_r, we assume $\nu_o[B] = \nu_c$ and define $B_o = h\nu_c/g\beta$, thus giving equation (5).

$$B_r = B_o - \frac{A}{g\beta}M_I - \frac{A^N}{g\beta}M_N - \text{(second order corrections)} \quad (5)$$

This result is needed to establish the line centre for calculation of the contribution of a particular transition to equation (3).

By means of equation (3)[4,5] introduction of the g^{-1} factor of Aasa and Vanngard[6] is avoided to effect the frequency-to-field transformation when $f(\nu_c - \nu_o[B], \sigma_v)$ is replaced by $(h/g\beta)f_B(B - B_r, \sigma_B)$, but for which *a priori* assumptions must be made about f_B, *i.e.* it must be symmetric, a condition not always fulfilled in field-swept e.s.r.[5,7–9]

Determination of the linewidth, σ_v, used in the linewidth function is carried out as described by Froncisz and Hyde[10] to explain the M_I dependence of the widths of 'parallel' lines in copper(II) hyperfine structure and the dependence upon microwave frequency. Their argument was that such effects arise because of correlated random strains which manifest themselves indirectly in two parameters, $\sigma_{A_\parallel}$ and $\sigma_{g_\parallel}$, the half-widths of Gaussian distribution of $g_\parallel$ and $A_\parallel$ about their measured (mean) values. Froncisz and Hyde[10] determined $\sigma_{A_\parallel}$ and $\sigma_{g_\parallel}$ in terms of the bonding parameters (α, β, β_1, *etc.*) used in the Kivelson and Nieman[11] theory of tetragonally symmetric copper(II) for the case when copper(II) is bound to four planar oxygen-containing ligands. The bonding parameters are mixing coefficients used in the metal–ligand molecular orbitals. In the present analysis, attention is focused on the use of σ_{g_i} and σ_{A_i} ($i = \parallel$ or $\perp$) to expedite a meaningful and usable computer simulation.

To understand the basis of Hyde and Froncisz's argument[10] we consider the first-order expressions for $g_\parallel$ and $A_\parallel$ [equations (6a) and (6b)], where λ is the spin–orbit constant [-828 cm^{-1}

$$g_\parallel = 2 - 8\lambda\alpha^2\beta_1{}^2/\Delta_z \quad (6a)$$

$$A_\parallel = P\left[-\alpha^2\left(K + \frac{4}{7}\right) + \left(g_\parallel - 2\right) + \frac{3}{7}(g_\perp - 2) + \ldots\right] \quad (6b)$$

for copper(II)], Δ_z the energy splitting between $|x^2 - y^2\rangle$ and $|xy\rangle$, $P = 2g_n\beta\beta_n\langle r^{-3}\rangle_{3d}$, and K the core polarization parameter for *s*-electron contributions to hyperfine structure. Clearly $g_\parallel$ and $A_\parallel$ are linearly related and a correlation between the previously mentioned variances in $\sigma_{g_\parallel}$ and $\sigma_{A_\parallel}$ is expected.

While the corresponding expression for $A_\perp$ shows a linear dependence upon $g_\perp$, the fact that $(g_\perp - 2) \approx 0.05$ whereas $(g_\parallel - 2) \approx 0.2$ shows that the effect will not be as striking.

The first-order resonance condition, equation (4), in frequency units is given by equation (7).

$$\nu_o[B] = g\beta B + AM_I + A^N M_N \quad (7)$$

Neglecting any random strain effects in A^N, and assuming correlated σ_g and σ_A values, the strain-broadened width may be written, for the principal direction, and assuming perfect correlation, by equation (8) ($i = \parallel$ or $\perp$).

$$\sigma_{gA_i} = |\beta B\sigma_{g_i} + M_I\sigma_{A_i}| \quad (8)$$

Using equation (8) to calculate βB, equation (9) can be written. If $|A_i\sigma_{g_i}/g_i| \ll \sigma_{A_i}$ then equation (10) applies.

$$\sigma_{gA_i} = \left|\frac{\nu_o - A_iM_I}{g_i}\sigma_{g_i} + M_I\sigma_{A_i}\right| \quad (9)$$

$$\sigma_{gA_i} \approx \left|\nu_o\frac{\sigma_{g_i}}{g_i} + M_I\sigma_{A_i}\right| \quad (10)$$

Table 3. Spin-Hamiltonian parameters (*a*) and linewidth terms (*b*) for $Cu(HL^2)_2(NO_3)_2{\cdot}2H_2O$ in dmf with different nitrogenous bases[a]

	(*a*)						(*b*)					
			Hyperfine constant[a] ($\times 10^{-4}$ cm^{-1})									
Base	$g_\perp$	$g_\parallel$	$^{Cu}A_\perp$	$^{Cu}A_\parallel$	$^{N}A_\perp$	$^{N}A_\parallel$	$\sigma_{R_\perp}$/ MHz	$\sigma_{R_\parallel}$/ MHz	$C_{1\perp}$	$C_{1\parallel}$	$C_{2\perp}$/ MHz	$C_{2\parallel}$/ MHz
Pyridine	2.058	2.196	13	200	17	13	12	16	0.0007	0.0006	1.3	2.0
Imidazole	2.053	2.212	15	196	15	14	12	16	0.0010	0.0007	1.9	3.1
2-Methylpyridine	2.053	2.213	15	196	15	15	12	16	0.0019	0.0011	4.7	3.1
2,4,6-Trimethylpyridine	2.044	2.228	15	184	16	15	12	16	0.0050	0.0053	7.0	6.3
Dmf solution	2.053	2.212	15	203	16	15	12	16	0.0006	0.0012	3.5	6.9

[a] Error values: $g = \pm 0.001$, $^{Cu}A_\perp = \pm 1$, $^{Cu}A_\parallel = \pm 2$, $^{N}A_\perp$ and $^{N}A_\parallel = \pm 1$, $\sigma_{R_\perp}$ and $\sigma_{R_\parallel} = \pm 1$, $C_{1\parallel} = \pm 0.001$, $C_{2\perp}$ and $C_{2\parallel} = \pm 0.5$. [b] See footnote *b* of Table 2.

In the simulation program the parameters used are given by equations (11a) and (11b). Since the program calculated $|A|$

$$C_{1i} = \sigma_{g_i}/g_i \qquad (11a)$$

$$C_{2i} = -\sigma_{A_i} \qquad (11b)$$

values, the minus sign is used in equation (11b). The important point is that, at *X*-band, the low-field 'parallel' components in the e.s.r. spectra due to copper(II) are the narrowest. In neglecting the $A_i\sigma_{g_i}/g_i$ term in equation (9) we follow Froncisz and Hyde.[10]

A residual width, σ_R, must be allowed for to account for unresolved ligand hyperfine structure and spin–spin coupling. Assuming two principal values, $\sigma_{R_\parallel}$ and $\sigma_{R_\perp}$, and the convolution of two Gaussians of width σ_{R_i} and $\sigma_{gA_i}{}^2$, the resulting principal widths are given by equation (12).

$$\sigma_{v_i}{}^2 = \sigma_{R_i}{}^2 + \sigma_{gA_i}{}^2 \qquad (12)$$

In the present version of the program (MONQF)[4] the angular behaviour of the width is calculated using equation (13). This equation gives correct values of the width when $\theta = 0$ and 90° respectively but not necessarily at intermediate orientations.

$$\sigma^2 = \sigma_{v_\parallel}{}^2\cos^2\theta + \sigma_{v_\perp}{}^2\sin^2\theta \qquad (13)$$

To accomplish the computer simulation of the experimental e.s.r. spectrum, preliminary values of the spin-Hamiltonian parameters are obtained from the experimental data and refined by computer lineshape fitting. Initial estimates of the linewidth parameters σ_R, C_{1i}, and C_{2i} are determined from estimates of the experimental linewidths where, for Gaussian shape function, σ [equation (3)] refers to the half peak–peak width of the derivative. Solutions of a set of three simultaneous equations based on equations (10) and (11), where the experimental linewidth (σ_v) and the corresponding nuclear spin quantum number (*e.g.*, $M_I = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}$) and the microwave frequency are the constants used to determine trial values of σ_R, C_{1i}, and C_{2i}.

The numerical values of the spin-Hamiltonian parameters and the linewidth terms obtained from computer simulations of the experimental spectra due to the monomeric copper(II) chelates in the presence of various heterocyclic bases are shown in Tables 2 and 3. Successful computer simulations of the experimental e.s.r. spectra were obtained by employing four equivalent nitrogen atoms in the donor set. Computations of lineshapes using non-equivalent pairs of nitrogen atoms in the donor set, which might be thought to be appropriate considering the ligand structure, were quite unlike the experimental spectra.

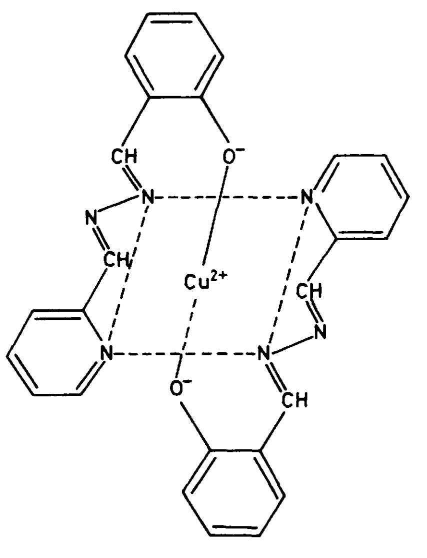

Figure 4. A diagrammatic representation of the monomeric form of the chelate $Cu(L^1)_2$

Discussion

The e.s.r. spectral evidence obtained from the chelate $Cu(HL^2)_2(NO_3)_2{\cdot}2H_2O$ points to the formation of monomeric species with an N_4 donor set. The related chelate $Cu(L^1)_2{\cdot}2H_2O$ exists in frozen dmf solution in a monomer–dimer equilibrium system. The monomeric form has an N_4 donor system represented by Figure 4. The formation of the dimeric species is determined by the presence of the ionized hydroxy group. A structure of the dimeric form of $Cu(L^1)_2$ which is compatible with the distance of 4.4 Å between the copper(II) centres and arrived at by the use of molecular models is shown by Figure 5. A notable feature of the spin-Hamiltonian parameters pertinent to the dimeric form of $Cu(L^1)_2$ is the somewhat high value of $^{Cu}A_\parallel$ (220×10^{-4} cm^{-1}), which is higher than any other value obtained here including that observed for $Cu(HL^2)_2(NO_3)_2{\cdot}2H_2O$ in dmf solution (203×10^{-4} cm^{-1}). Initially it was thought that this high value may result from a packing of the chelates in a largely planar form rather like that observed in dimeric forms of porphyrin and phthalocyanine copper(II) chelates where there is a diminished axial interaction. However,

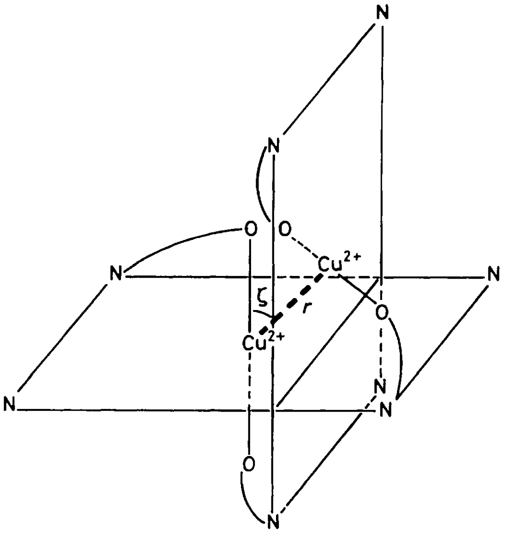

Figure 5. A diagrammatic representation of the dimeric form of the chelate $Cu(L^1)_2$; ζ is the angle between the symmetry axis of an individual copper(II) site and the Cu ··· Cu vector

Table 4. Elemental analyses and magnetic susceptibility data

Compound	Found (%)			Calc. (%)			
	C	H	N	C	H	N	$\mu_{eff.}$
HL^1	69.25	4.80	18.50	69.35	4.90	18.65	
$Cu(L^1)_2 \cdot 2H_2O$	56.55	4.30	15.45	57.00	4.40	15.35	1.98
$Ni(L^1)_2 \cdot 2H_2O$	57.40	4.40	15.60	57.50	4.55	15.45	3.32
$Zn(L^1)_2 \cdot 2H_2O$	56.55	4.25	15.35	56.80	4.35	15.30	
$Cu(L^1)_2 \cdot 2(py)$	64.75	4.35	17.00	64.50	4.50	16.70	1.82
$Cu(L^1)_2 \cdot 2(2Me\text{-}py)$	65.95	4.40	16.55	64.40	4.85	16.05	1.84
$Cu(L^1)_2 \cdot 2(2,4,6Me_3\text{-}py)$	67.05	5.65	14.65	66.90	5.55	14.85	1.89
$Cu(L^1)_2 \cdot 2(im)$	59.50	4.35	21.50	59.30	4.30	21.60	1.80
HL^2	72.80	5.50	21.40	73.10	5.65	21.30	
$Cu(HL^2)_2(NO_3)_2$	51.45	3.60	18.40	51.55	3.65	18.50	1.91
$Ni(HL^2)_2(NO_3)_2$	51.80	3.60	18.55	51.50	3.65	18.65	3.12
$Zn(HL^2)_2(NO_3)_2$	51.25	3.55	18.35	51.35	3.60	18.35	

in such a structure there is no obvious role for the ionized hydroxy group, and every reason to expect dimer formation to occur with $Cu(HL^2)$.

For the two series of compounds formed by the copper(II) chelates with heterocyclic nitrogenous bases, consistent trends occur in the numerical values of the spin-Hamiltonian parameters and linewidth terms. When L^1 is involved, axial ligation by the base involves replacement of the ionized hydroxy group. Taking pyridine as the starting point for comparison, the introduction of a methyl group at the 2-position of the axial base, which is a subtle choice of molecular structure, has a profound influence on the occurrence of e.s.r. spectral superhyperfine lines arising from in-plane bonding with the N_4 donor set. In general terms the in-plane bonding will be affected by the net transfer of electron density from axial positions involving electron donation and any back-bonding effects. The simplistic picture is that 2-methylpyridine increases the transfer of electron density to the copper(II) centre relieving the requirement for electron sharing from the in-plane donor set, an effect which will be more marked with increased methyl group substitution as in 2,4,6-trimethylpyridine, provided that steric effects do not become too influential. A measure of these changes is the value of $A_{\parallel}$ for both series of copper(II) chelates which falls appreciably as a result of changing axial base interactions. Diminishing values of $A_{\parallel}$ may arise from changing covalent contributions to the metal–ligand bonds, particularly increasing values of α [equation (6b)] assuming other parameters which determine $A_{\parallel}$ remain constant. This is also broadly consistent with a slight corresponding increase in $g_{\parallel}$ values [equation (6a)]. In the present circumstances where the donor sets in the equatorial and axial positions remain the same, changes in the e.s.r. spectra arise from increased availability of electron density from the axial positions. As shown in Tables 2(*a*) and 3(*a*) for the copper(II) aldazine chelates, falling values of $^{Cu}A_{\parallel}$ occur in the order pyridine > imidazole > 2-methylpyridine > 2,4,6-trimethylpyridine. However, much more noticeable changes take place in numerical values of the linewidth terms outlined in Tables 2(*b*) and 3(*b*), particularly those of the *g*-strain coefficients $C_{1\parallel}$ and $C_{1\perp}$. Greater experience in assessing the value that these terms may have in a wide variety of copper(II) compounds is required before their full significance may be realised, but the present variation in $C_{1\perp}$ and $C_{2\parallel}$ with different axial base may be a sensitive measure of the distortion of the symmetry of the equatorial donor set which occurs as a result of increased electron-density transfer from axial ligation. The bulkier the substituent groups the more likely small, but significant, distortions of the structure will occur and this contributes to increased linewidth dependence from $\sigma_{g_{\parallel}}$, $\sigma_{g_{\perp}}$, $\sigma_{A_{\parallel}}$, and $\sigma_{A_{\perp}}$ terms.

Experimental

The e.s.r. spectra, recorded as the first derivative of absorption, were obtained using a Varian E-12 spectrometer with an E-101 microwave bridge at *X*-band (*ca.* 9.15 Hz). Low temperatures of the sample were achieved by means of a Varian E-257 variable-temperature accessory (above *ca.* 100 K) or at liquid-nitrogen temperature using narrow-tail quartz dewars. Magnetic fields were calibrated against proton n.m.r. frequencies using a Hewlett Packard HP5254L frequency counter. Microwave frequencies were measured using a direct reading EIP 548A counter.

Computer simulations were carried out using an on-line VAX computer at the Monash Computer Centre coupled to a digital plotter.

U.v.–visible spectra were recorded on a Varian 635 spectrophotometer at room temperature using 1-cm glass and silica cuvettes. Measurements of magnetic susceptibility were made at room temperature by the Gouy method with a glass tube calibrated for diamagnetism. Microanalyses were carried out by the CSIRO Microanalytical Service, Melbourne.

Preparation of HL^1 *and Related Ligands.*—A dmf solution (50 cm^3) of pyridine-2-carbaldehyde (3.0 g) was added to a solution of salicylaldehyde hydrazone (2.70 g) in dmf (50 cm^3), and refluxed for 1 h. Most of the dmf was removed by heating at diminished pressure (10 mmHg) and ethanol (100 cm^3) added to precipitate the product which was washed further with portions (20 cm^3) of cold ethanol. Yield: 3.4 g, 77%.

The ligand HL^2 (yield: 2.9 g, 72%) was prepared by a similar procedure.

Preparation of Metal Chelates.—The copper(II) chelate of HL^1 was prepared by addition of a dmf (50 cm^3) solution of copper nitrate hexahydrate (2.95 g) to a dmf (50 cm^3) solution of HL^1 (4.5 g) and refluxed for 30 min. Most of the dmf was removed by distillation at diminished pressure (10 mmHg) and the chelate isolated after addition of water (100 cm^3). The product was washed with several portions (20 cm^3) of warm methanol and air dried. Yield: 3.9 g, 70%.

The nickel(II) and zinc(II) chelates of HL^1 were prepared in a similar manner, as were the copper(II), nickel(II), and zinc(II) chelates of HL^2.

The compounds formed by reaction of the copper(II) chelates with nitrogenous bases were isolated typically as follows. $Cu(L^1)_2 \cdot 2H_2O$ (0.5 g) was dissolved in the minimum amount of dmf and pyridine added (2 cm^3). Methanol was added to the solution to precipitate the product from which any remaining solvent was removed by pumping at diminished pressure (0.1 mmHg).

The elemental analyses of all the compounds obtained are summarized in Table 4.

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