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X- and Q-Band ESR Studies of Binuclear Copper(II) Complexes with 3-Alkyl-2-pyridone Bridging Ligands

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Synopsis. The ESR spectra of polycrystalline samples of bis(*N*,*N*-dimethylformamide)tetrakis(3-ethyl-2-pyridonato)dicopper(II) and its 3-methyl-2-pyridone analogue have been measured at X-band (≈9.5 GHz) and Q-band (≈34 GHz) frequencies. The spectra are characteristic of S=1 species and the parameters (g_z 2.30, g_{xy} 2.05 and D≈0.29 cm^{-1}) are discussed in terms of the known binuclear structure.

Many binuclear copper(II) complexes are known in which two copper(II) ions are bridged by four carboxylato groups.[1,2] Analogous compounds in which nitrogen atoms are the donor atoms in the bridging unit are fewer in number,[3] and those in which the four bridges each contain one N and one O donor atom are even rarer[4] though they are well-established for other metal ions.[5]

Two complementary techniques have been customarily employed to study the electronic nature of such binuclear copper(II) compounds with the classic copper(II) acetate structure. Studies of the temperature dependence of the magnetic susceptibility generally show that the pair of copper(II) atoms are antiferromagnetically coupled, giving an $S=0$ ground state and $S=1$ level $|2J|$ above this. Application of the Bleaney and Bowers equation[6] permits evaluation of $|2J|$ and, for powder samples, an average g value. Measurement of the ESR spectra arising from those molecules within the thermally accessible $S=1$ state and application of the spin Hamiltonian (1) permit derivation of the zero-field splitting

$$\mathscr{H} = g\beta B.\hat{S} + D\hat{S}_z^2 + E(\hat{S}_x^2-\hat{S}_y^2) - 2D/3 \qquad (1)$$

parameters D and E and the g values g_x, g_y, g_z if $E\neq0$, or g_z and g_{xy} if $E=0$.

It has recently been shown by X-ray methods[4] that bis(*N*,*N*-dimethylformamide)tetrakis(3-ethyl-2-pyridonato)dicopper(II) has a structure of the copper(II) acetate type but with N,O donor atom bridges. This has afforded us the opportunity of comparing the ESR parameters for such a bridging unit with those of bridges containing only O or N atoms as donors.

Experimental

The complexes [Cu_2(3-ethyl-pyr)$_4$(dmf)$_2$] and its 3-methyl-2-pyridone analogue were prepared as described previously.[4] Their ESR spectra were obtained as polycrystalline samples at room temperature using Varian E12 X-band (≈9.5 GHz) and Bruker ER200 Q-band (≈34 GHz) spectrometers.

Results and Discussion

The X- and Q-band ESR spectra of [Cu_2(3-ethyl-pyr)$_4$(dmf)$_2$] are shown in Figs. 1 and 2 respectively.

Solution of the spin Hamiltonian (1) for the situation where $D<h\nu$ and $E=0$ yields four allowed ($\Delta m_s=1$) transitions at resonance field B_{z1}, B_{z2}, B_{xy1}, and B_{xy2} given by:[7]

$$B_{z1} = (g_e/g_z)|B_0-D'| \qquad B_{z2} = (g_e/g_z)(B_0+D')$$
$$B_{xy1}^2 = (g_e/g_{xy})^2B_0(B_0-D') \qquad B_{xy2}^2 = (g_e/g_{xy})^2B_0(B_0+D')$$

where $B_0=h\nu/g_e\beta$ and $D'=D/g_e\beta$. In addition the formally forbidden $\Delta m_s=2$ transition between the $|-1\rangle$ and $|+1\rangle$ levels, the so-called half-field transition, is often observed.

Assignments of the observed transitions in Figs. 1 and 2 are summarized in Table 1 for the parameters $g_{xy}=2.05$, $g_z=2.30$, and $D=0.287$ cm^{-1}. The values of B_{z2} and B_{xy2} are such that the transitions are virtually coincident at Q-band frequency (calculated values of 13,203 and 13,230 gauss respectively at 33.90 GHz). Consequently the low intensity B_{z2} band is hidden by the much stronger B_{xy2} band. Changing the microwave frequency to X-band enables a clear separation of these transitions to be made (Fig. 2). Conversely, the B_{z1}, B_{xy1}, and $\Delta m_s=2$ transitions could not have been unambiguously assigned from the X-band results alone because of appreciable band

Table 1. ESR Data for the Complexes[a)]

	[Cu(3-ethyl-pyr)$_2$(dmf)]$_2$		[Cu(3-methyl-pyr)$_2$(dmf)]$_2$	
At 33.90 GHz				
	Observed	Calcd[b)]	Observed	Calcd[c)]
$\Delta m_s=2$	5368	d)	5388	d)
B_{z1}	7875	7858	7859	7850
B_{xy1}	10163	10206	10187	10201
B_{z2}	e)	13203	e)	13212
B_{xy2}	13255	13230	13239	13234
At 9.503 GHz				
$\Delta m_s=2$	f)	d)	f)	d)
B_{z1}	≈300	279	≈250	270
B_{xy1}	≈1000	1019	≈1000	1003
B_{xy2}	4520	4572	4550	4575
B_{z2}	5580	5625	5580	5633

a) Resonance fields in gauss(=10^{-4} T). b) Calculated for $g_z=2.30$, $g_{xy}=2.05$, $D=0.287$ cm^{-1}. c) Calculated for $g_z=2.30$, $g_{xy}=2.05$, $D=0.288$ cm^{-1}. d) Not calculated. e) Hidden by stronger B_{xy2} band. f) Not resolved from nearby $\Delta m=1$ band.

Table 2. Comparison of D and $|2J|$ Values for Some Binuclear Copper(II) Complexes

Complex[a)]	Bridge donor atoms	Cu-Cu/Å	D/cm^{-1}	$2J$/cm^{-1}	Ref.
$Cu(CH_3CO_2)_2H_2O$	4O	2.615	0.34	286	1
$Cu(CH_3CO_2)_2\cdot$quin	4O	2.642	0.341	320	1
$Cu(CH_3CO_2)_2\cdot NCS^-$	4O	2.643	0.34	305	1,8
$Cu(HCO_2)_2\cdot NCS^-$	4O	2.716	0.44	485	1,8
Cu(3-Et-pyr)$_2\cdot$dmf	2O, 2N	2.550	0.287	395	4,b
Cu(ad)$_2\cdot 4H_2O$	4N	2.947	0.121	257	3
Cu(adH)$_2(ClO_4)_2\cdot 2H_2O$	4N	2.951	0.110	300	10, 11
Cu(adH)$_2Cl_2\cdot 3H_2O$	4N	3.066	0.127	270	12, 13

a) quin=quinoline; 3-Et-pyr=3-ethyl-2-pyridone anion; dmf=*N*,*N*-dimethylformamide; ad=adenine anion. b) This work.

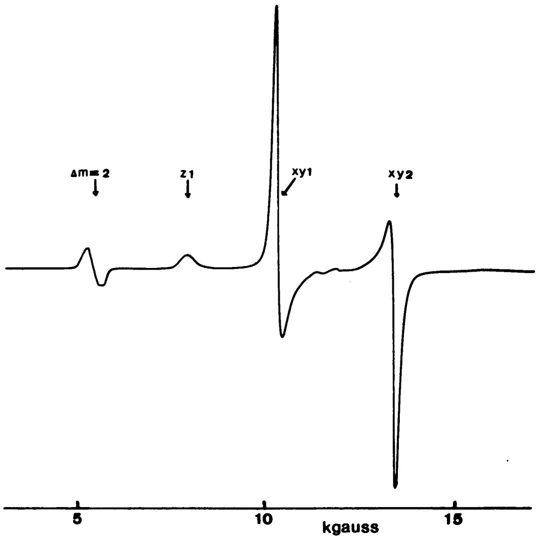

Fig. 1. Q-band ESR spectrum of [Cu$_2$(3-Et-pyr)$_4$-(dmf)$_2$](kgauss=10^{-1}T).

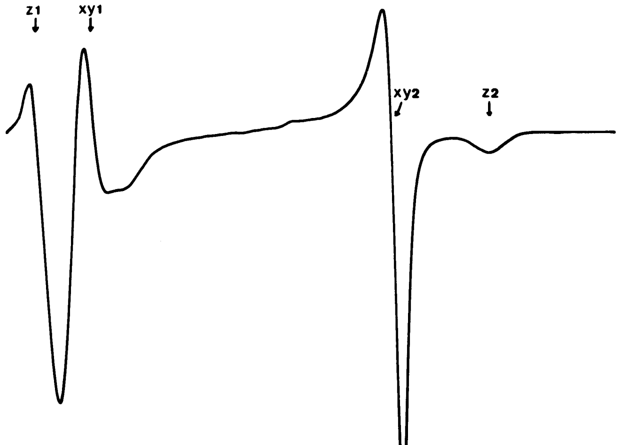

Fig. 2. X-band ESR spectrum of [Cu$_2$(3-Et-pyr)$_4$-(dmf)$_2$](kgauss=10^{-1}T).

overlap at that frequency. However these transitions are clearly resolved and readily assigned at Q-band frequency. The advantage of measuring such spectra at more than one microwave frequency is well demonstrated by these results.

The observation that $E=0$, or at least too small to be evident in any splitting of the B_{xy1} and B_{xy2} bands, is in good agreement with the results of the X-ray structural determination.[4)] The pairs of N and O donor atoms from the four pyridone bridges are arranged in cis-dispositions about each Cu atom and the angular and bond-length deviations from axial symmetry are small.

The ESR spectra of [Cu$_2$(3-methyl-pyr)$_4$(dmf)$_2$] are virtually identical to those disussed above, and the derived parameters and assignmens are listed in Table 1. This close similarity tallies well with the reported[4)] agreement of their magnetic properties. Moreover the average g value (2.15) derived from the temperature dependence of their magnetic susceptibilities[4)] is close to that (2.14) we obtain from the ESR spectra by using the expression: $g_{av}^2=(g_z^2+2g_{xy}^2)/3$.

The D values we observe ($\approx$0.29 cm^{-1}) are somewhat smaller than those (0.33—0.44 cm^{-1}) generally found for copper(II) carboxylate dimers[1,2,8)] but they are larger than the values (0.1—0.19 cm^{-1}) reported[3,9)] for analogous copper(II) dimers with nitrogen donor atoms in the bridges (see Table 2). It is interesting to note in this context that Brookes and Martin found $D\approx$0.27 cm^{-1} for Cu(CH$_3$CO$_2$)L$\cdot$X, where L represents the anion of 1,7-diazaindene and X=1,7-diazaindene or pyridine.[3)]

The observed D value, $D_{obs}=D_{dd}+D_{exch}$, where D_{dd} arises from dipole-dipole interaction, and D_{exch} from exchange. D_{dd}, which is expected to be negative, is approximately calculated[14)] from the equation based on a point dipole model, $R^3=0.65g_z^2/D_{dd}$, where R is the copper-copper distance. Use of the equation yields D_{dd}=0.207 cm^{-1}, and therefore D_{exch}=0.494 cm^{-1} for [Cu$_2$(3-ethyl-pyr)$_2$(dmf)$_2$](R=2.55 Å). Rough correlations between D_{exch} and $|2J|$, the energy separation between the singlet ground state and the triplet first-excited state, have sometimes been made,[2,14)] by means of the equation, $D_{exch}=-2J[(g_z\text{-}2)^2/4\text{-}(g_{xy}\text{-}2)^2]/8$. Use of this equation predicts a value of $|2J|$ of 198 cm^{-1}, whereas the experimental value[4)] is 395 cm^{-1}. The difference between the calculated and the experimental values may be due to the approximations assumed in deriving the equations, and also to the fact that the singlet-triplet splitting is not simply related to the strength of the exchange interaction, as pointed out elsewhere.[2,15,16]

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