ESR Spectra of New Dicopper(II) Complexes of Novel Binucleating Ligands

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Magnetic studies can probe structural relationships which may reflect intra- as well as inter-molecular electronic characteristics. In particular, epr spectra in non-dilute coordination complexes can be strongly influenced by exchange interactions. Some relationships between g values, linewidths and other parameters are correspondingly affected [1–3].

Bimetallic coordination complexes containing two copper ions in close proximity are currently under extensive study. These may serve as model systems for biological reactions involving molecular O_2 [4], such as oxygen transport [5] and oxygen activation [6, 7]. Amongst others, we are studying copper complexes of new binucleating ligands -xyl(py) (py = 2-pyridyl) in
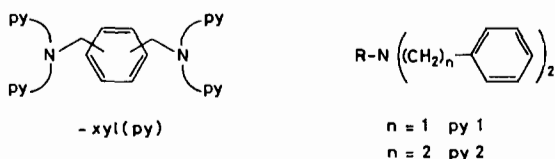
which two tridentate ligand donor groups are separated by an *ortho*-, *meta*-, or *para*- xylene bridge.

We have recently reported a novel biomimetic reaction of Cu(I) and *m*-xyl(py2), in which 'fixation' of oxygen occurs to give a binuclear, doubly-bridged (phenolate and hydroxo ligands) Cu(II) dimer, (*A*) [8]. We have also previously published an X-ray structure determination of $Cu_2Cl_4(p\text{-xyl(py2)})$ [9] containing two pentacoordinate CuN_3Cl_2 moieties 11.7 Å apart. A number of other halide derivatives have been synthesized, including $Cu_2[m\text{-xyl(py2)}]\text{-}Br_4(B)$, $Cu_2[p\text{-xyl(py2)}]Br_4(C)$, $Cu_2[m\text{-xyl(py1)}]\text{-}Cl_2(PF_6)_2(D)$ and $Cu_2[p\text{-xyl(py1)}]Cl_4(E)$. Since effective Cu···Cu distances would be expected to vary considerably in all of these compounds, magnetic interactions are expected to be interesting. We are undertaking single crystal esr studies and we now report preliminary poly-crystalline results.

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The ligands are synthesized by reaction of py1 or py2 with the appropriate xylyl compound as previously reported [8]. The halide complexes are formed by reaction of CuX_2 ($X = Cl^-$, Br^-) with the binucleating ligand in methanol. The precipitates formed are recrystallized from dimethylformamide–Et_2O. Compound *D* gave a blue solution in methanol, and the complex is isolated as a PF_6^- salt by addition of $NaPF_6$.

The esr spectra can be classified according to the three different stereochemical environments: (1) *meta*, (2) *para* and (3) dimer *A*.

In the first category (*meta*) there is some evidence for exchange interactions but it is weak in both the Br and Cl complex. A broad, almost structureless line was seen in both cases with $g_{isotropic} = 2.12$ for the Br complex *B* and $g_1 = 2.08$, $g_{11} = 2.16$ for the Cl complex *D*. Using the isotropic Van Vleck formula for estimating dipolar linewidths where d is the density and m is the

$$H_d = 4.2 \times 10^4 [S(S + 1)]^{1/2} \frac{d}{m}$$

molecular weight and using the experimental linewidth, a rough estimate of the exchange field may be made from the equation $\Delta H = K\, H_d^2/H_e$ where K is a constant of the order of magnitude of unity. The calculated value of H_e is about 2000 gauss, which suggests an effective exchange coupling of approximately 0.4 K.

In the para cases the linewidths are smaller by a factor of about 10 and the corresponding exchange field should be about 4 K. It is expected that there would be contributions from both inter- and intramolecular interactions in this case.

Of some significance is the occurrence of $g_{11} < g_\perp$ for the Br case *C* (see Fig. 1). Although the detailed shape may be associated with antiferro-distortive interactions [2], the lowest g value, 2.025 merits special consideration. In their authoritative review [1] Bertini, *et al.* suggest that a g value in a copper complex of less than 2.05 deserves close attention. This could reflect an unusual coordination geometry such as trigonal bipyramidal [10, 11]. The 3 g values in the chloride complex *E* are nearly normal (2.05, 2.13 and 2.18). It is of course possible that the spin orbit interaction of the halide produces the lower g value on the Br than Cl complex. This seems a less likely explanation since spin orbit interactions would normally lead to a broadening of the lines of the Br^- complex compared to the Cl^- complex due to antisymmetrical exchange effects [3], and this is not observed.

The strongest exchange is in the bridged dimer *A*. The temperature dependence of the ratio of the doubly integrated intensity of a portion of the dimer
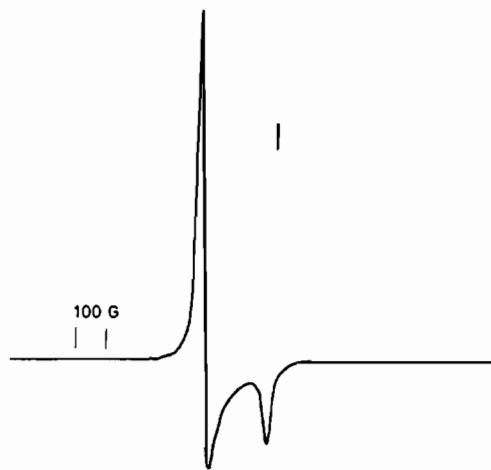
Fig. 1. Polycrystalline epr spectra of the bromide complex C, showing $g_\parallel < g_\perp$. The marker shows the position of DPPH.

signal with that of an ordinary $S = 1/2$ species indicates that the J value is about 600 K [12]. Furthermore, the zero field splitting is about 0.2 cm^{-1} but the uncertainty in this parameter is large since the principal axes of the zero field splitting tensor and the g values are not usually expected to be coincident in a planar bridged Cu(II) dimeric unit [13].

Acknowledgements

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