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The E.S.R. Spectrum and Structure of Tetrapyridine Copper(II) Perchlorate

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Although tetrapyridine copper(II) perchlorate $(C_5H_5N)_4Cu(ClO_4)_2$, (1) has been known for many years [1], the compound has escaped study by electron spin resonance spectroscopy. This is surprising because the spectroscopic data reported to date have been ambiguous in that two alternative structures have been offered from different interpretations of similar data. Brown *et al.* [2] deduced from infrared measurements that (1) was essentially isostructural with the Mn(II), Co(II) and Ni(II) analogues. These compounds have octahedral site symmetry about the metal ion, the perchlorate groups being within the coordination sphere of the metal ion, bound in the axial positions. Later a study by Jones and Bull [3] included infrared and electronic absorption spectra. They deduced that while the perchlorate groups may have been close enough to copper to show i.r. frequencies similar to those found for the Mn(II), Co(II) and Ni(II) analogues, the electronic absorption spectrum was certainly indicative of a square planar environment about copper, with no indication of any covalent metal–perchlorate interaction.

In order to clarify the structural ambiguities implied by the previous studies, we performed e.s.r. experiments on (1) as a powder and in CH_2Cl_2/toluene solution.

The compound (1) was prepared according to the method of Brown *et al.* [2] and recorded the e.s.r. spectra of (1) as a powder at 293 K and in a frozen CH_2Cl_2/toluene glass at 77 K.

The powder spectrum of (1) at 293 K (Fig. 1) is typical of many square planar copper(II) complexes [4], having $g_{\parallel}$ = 2.245 and $g_{\perp}$ = 2.059 with $A_{\parallel}$(Cu) = 181.39G. In the square-planar case, $g_{\parallel} = g_z$ and $g_{\perp} = g_y = g_x$ whereas for an octahedral stereochemistry $g_y \neq g_x$ and the values might be similar to those for $[Cu(H_2O)_6]^{2+}$ where g_x = 2.09, g_y = 2.25 and g_z = 2.32 [4]. The solution spectrum at 77 K is well resolved, and with a detailed analysis, similar to that outlined by Symons *et al.* [5] yields much information. Values for $g_{\parallel}$ and $A_{\parallel}$(Cu) are obtained using standard second-order analysis of the parallel features. The true value of $A_{\perp}$(N) is obtained by the analysis of the hyperfine splitting on the parallel copper component indicated in Fig. 2. The often neglected values of $A_{\perp}$(Cu) and $A_{\parallel}$(N) can then be obtained from careful analysis of the perpendicular hyperfine components indicated where feature a = $(A_{\parallel} + A_{\perp})$N and b = $A_{\perp}$(Cu). Using these methods, $g_{\parallel}$ = 2.237, $g_{\perp}$ = 2.046, $A_{\parallel}$(Cu) = 189.34G, $A_{\perp}$(Cu) = 30.86, $A_{\perp}$(N) = 13.3G and $A_{\parallel}$N = 16.23G. The analysis of the spectrum can be tested to some degree by comparison of the observed and calculated magnetic moments. Using the standard formula

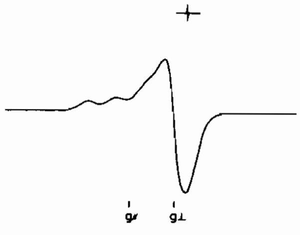

Fig. 1. E.S.R. powder spectrum of (1) at 293 K. Reference is DPPH.

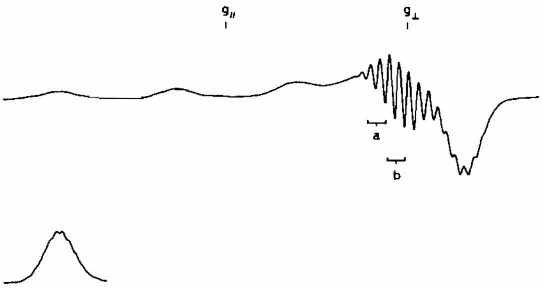

Fig. 2. E.S.R. Spectrum of (1) in toluene/CH_2Cl_2 glass at 77 K; the inset shows the first Cu(II) hyperfine line under greater resolution showing the $A_{\perp}$(N) components.

$$\mu_{B.M.} = \frac{1}{3}(g_{\parallel} + 2g_{\perp})\sqrt{s(s+1)}$$

and inserting the g-values found in this work, the calculated magnetic moment 1.84 B.M. compares favourably with the experimental value of 1.89 B.M. [3].

That the e.s.r. parameters for compound (1) are clearly characteristic of square-planar coordination by four nitrogen donor ligands about the copper(II) centre confirms that the structural conclusions proposed by Jones and Bull [3] are correct and that the perchlorate groups are not coordinated to Cu. This report is preliminary to an investigation by e.s.r. and electronic absorption spectroscopy of novel copper(II)–nitrogen donor systems in which the copper atom is in a square-planar or distorted square-planar environment and a more rigorous molecular orbital treatment of the results will be included in subsequent publications.

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