Magnetic Exchange in Copper(II)tetraphenylporphyrin

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Summary We report the first direct evidence for exchange interaction between neighbouring copper centres in the title compound, using e.s.r. spectroscopy to detect the low field $\Delta M_S = 2$ transition.

The e.s.r. spectrum of copper(II) tetraphenylporphyrin (CuTPP) was first observed by Ingram in 1956.[1] The powder e.s.r. spectrum recorded at 77 K exhibited hyperfine interaction from the copper nucleus ($I = 3/2$) and showed $g_{\parallel} = 2{\cdot}17$, $g_{\perp} = 2{\cdot}05$ and $A_{\parallel} = 250\ \text{cm}^{-1} \times 10^{-4}$. Since the e.s.r. spectrum was first reported, there have been many studies on CuTPP, with and without isotopic labelling by ^{63}Cu, in condensed phases[2,3] and in dilute solutions.[4] The e.s.r. behaviour of CuTPP continues to attract much interest, the most recent contribution being a double resonance (ENDOR) study to determine the spin Hamiltonian parameters to a high degree of accuracy.[5]

None of the previous studies have dealt with the possibility of exchange interaction between neighbouring copper nuclei. Unlike CuPc (Pc = phthalocyanin) which was found to exhibit considerable dipolar and anisotropic exchange,[6] it has been assumed that there is negligible or no exchange in CuTPP on the basis of there being an increased copper–copper internuclear distance in the crystal over that in CuPc. In CuPc, the Cu–Cu distance between neighbouring copper atoms is 4·72 Å,[6] whereas in CuTPP structural determinations have shown that the phenyl rings are orthogonal to the plane of the porphyrin, with the result that the Cu–Cu distance is 8·3 Å.[7] The resolution of hyperfine splitting in the powder e.s.r. spectrum of CuTPP is produced by the decrease in dipolar interaction due to the increase in the Cu–Cu distance,[3] while in CuPc no copper hyperfine splitting is observed owing to a combination of dipolar broadening and exchange narrowing effects.[6] It was noted by Assour[3] that very slight dipolar broadening of the hyperfine lines in the e.s.r. spectrum of CuTPP powder was indicated; however, no experimental or theoretical elaboration was offered or has since been discussed. We report here the first direct observation of the $\Delta M_S = 2$ transition in the e.s.r. spectrum of CuTPP.

We obtained two samples of CuTPP. One sample was commercially available (Strem Chemicals); the other was synthesized according to the literature[8] from copper acetate and free TPPH$_2$. Both samples were purified by column chromatography and were recrystallized from benzene solutions by the slow addition of methanol. Thus two samples of exceptionally high purity were obtained from independent sources. *X*-Band e.s.r. measurements were carried out at 295 K and 77 K.

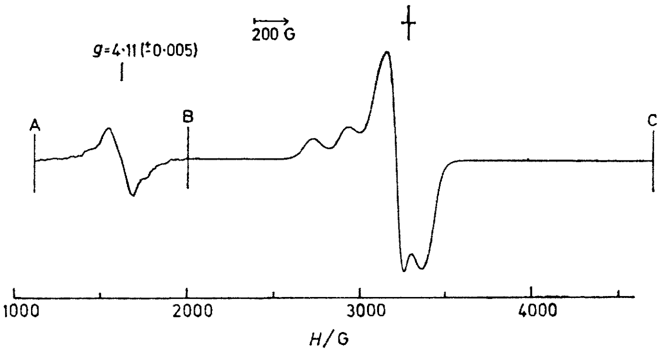

FIGURE. The e.s.r. spectrum of CuTPP at 77 K: A → B recorded at 2 × 10^5 gain, 2·0 G modulation width; B → C recorded at 1·25 × 10^3 gain, 0·2 G modulation width. The standard is diphenylpicrylhydrazyl, $g = 2{\cdot}0037$.

The e.s.r. spectra obtained from both samples were identical in all aspects. The e.s.r. spectrum is shown in the Figure, recorded at 77 K. The intensity of the low-field line decreased dramatically at ambient temperatures. The g-value of the low-field line is comparable with that for $\Delta M_S = 2$ lines in other[9] weakly exchange-coupled copper ions. All possibilities of the line being an artefact of the system [*i.e.* cavity or Dewar signals, or iron(III) impurities in the samples] have been carefully considered and examined experimentally, and may be completely discounted.

Although complete evaluation of the spin Hamiltonian describing the system is precluded in this short communication, we may make several qualitative deductions and observations upon the nature of the exchange interaction and the magnitude of the exchange integral J.

The Hamiltonian for a pair of interacting Cu^{2+} ions labelled 1 and 2 has the form[9] in equation (1), where $\mathscr{H}_1$ and

$$\mathscr{H} = \mathscr{H}_1 + \mathscr{H}_2 + \mathscr{H}_{\text{ex}} + \mathscr{H}_{\text{d}} \qquad (1)$$

$\mathscr{H}_2$ correspond to the spin Hamiltonians of the non-interacting ions and $\mathscr{H}_{\mathrm{ex}}$ and $\mathscr{H}_{\mathrm{d}}$ are the exchange and dipolar terms respectively When the magnitude of J is less than 50 cm^{-1} the exchange and dipolar terms may be treated together[9] In the simplest case $\mathscr{H}_{\mathrm{ex}} = - J\, S_1\, S_2$ where S_1 and S_2 are the effective spins Since no exchange interaction has been indicated in magnetic susceptibility measurements[10] at temperatures between ambient and 4 K, the magnitude of J must be less than 0 5 cm^{-1} The observation of both g-components in the e s r spectrum of CuTPP indicates that the interaction is very weak For CuPc J has been estimated[6] to be 9 8 × 10^{-3} cm^{-1} The presence of hyperfine interaction in the CuTPP spectrum indicates that J must be considerably less than that for CuPc and that the interaction is purely dipolar in origin In addition, it is reasonable to assume that the interaction is only between a copper centre and its two nearest neighbours The second nearest neighbours are each more than 16 Å away from any particular copper atom, and dipolar interactions become insignificant at distances greater than 12 Å

In conclusion, we have demonstrated that exchange interaction between copper atoms in CuTPP is not only possible, but observable directly, using e s r spectroscopy to detect the $\Delta M_S = 2$ transition This result demonstrates that exchange interaction should not be neglected *a priori* To date, no spin Hamiltonian describing CuTPP has considered or included an exchange term A detailed study of exchange in copper porphyrins, including a full variable temperature study to 4 K, and a more rigorous discussion of the spin Hamiltonian describing these systems will be reported elsewhere

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