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EPR of Powder Copper Phthalocyaninate Substituted with Eight Tetraazamacrocycles and its Nonanuclear Ni^{2+}, Co^{2+}, Zn^{2+} and Cu^{2+} Complexes†

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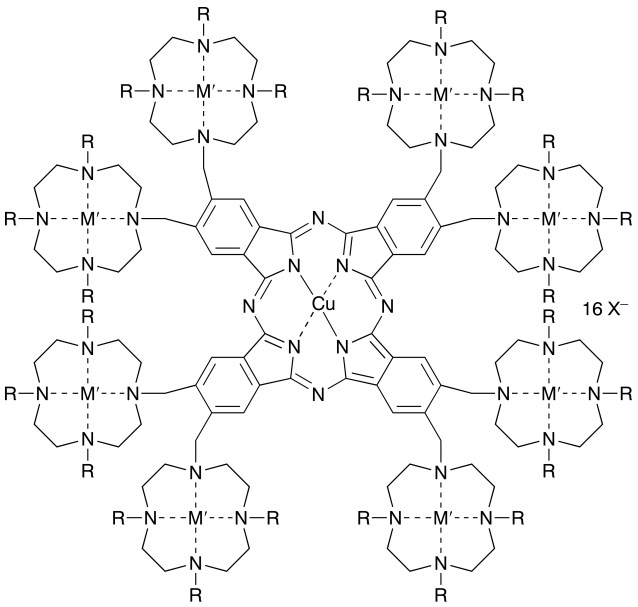
Variations of the electron paramagnetic resonance parameters of the copper phthalocyaninates due to the paramagnetic and diamagnetic metal ions substituted into the outer cells of eight 12-membered tetraazamacrocycles are found to be very slight and this slight difference is attributed to the electronegativity of the substituted metal.

Electron paramagnetic resonance (EPR) spectra of the copper phthalocyanine (CuPc) have been studied previously.[1–3] However, so far, Cu^{2+} phthalocyaninate substituted with eight 12-membered tetraazamacrocycles and its nonanuclear Ni^{2+}, Co^{2+}, Zn^{2+} and Cu^{2+} complexes have not been studied. It is the purpose of this study to investigate the EPR parameters of these complexes. The cells and the synthesis of the complexes shown in Fig. 1 are given in an earlier study.[4]

The energy level picture of the CuPc[5] is shown in Fig. 2. According to this orbital picture, the unpaired electron of the Cu^{2+} ion of CuPc is in the antibonding $d^*_{x^2-y^2}$ orbital. If α is the coefficient of $d^*_{x^2-y^2}$ in the antibonding orbital and λ is the spin–orbit coupling constant for a $3d$ electron, the $A_\parallel$ and $A_\perp$ components of the hyperfine structure constant are



M′	R	X
–	H	–
Ni^{II}	H	Cl
Cu^{II}	H	Cl
Co^{II}	H	Cl
Zn^{II}	H	Cl

Fig. 1 Nonanuclear M^{2+} complexes of copper phthalocyaninate substituted with eight tetraazamacrocycles

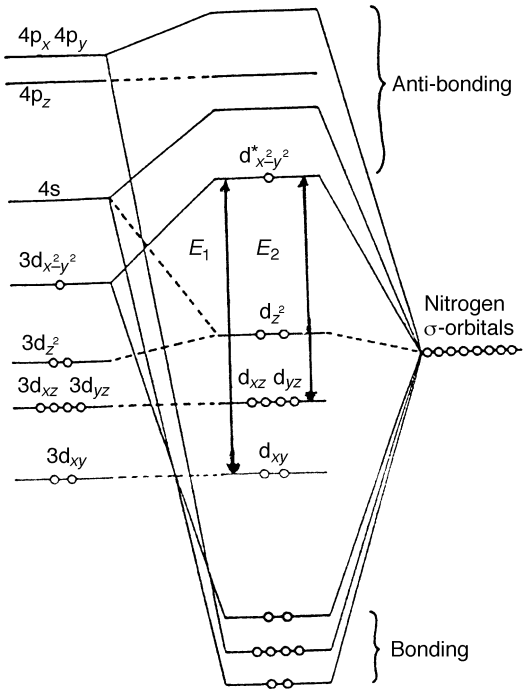


Fig. 2 Bonding picture of CuPc

given as:[5]

$$A_\parallel = P\left[\frac{4}{7}\alpha^2 - (g_\parallel - 2) - \frac{3}{7}(g_\perp - 2) + K\right]$$
$$A_\perp = P\left[\frac{2}{7}\alpha^2 + \frac{11}{14}(g_\perp - 2) - K\right] \quad (1)$$

where K is the Fermi contact parameter describing the s-electron effect on the Cu nucleus and $P = 2\beta g_N \beta_N \langle r^{-3}\rangle$ is the dipolar hyperfine coupling parameter of the unpaired electron ($P = 0.036\,cm^{-1}$). In this study, assuming both $A_\parallel$ and $A_\perp$ are negative and assuming $P = 0.036\,cm^{-1}$ [5,6] and the experimental $g_\parallel$, $g_\perp$ values, we obtained the K and α^2 values from eqn. (1).

Figure 3 shows the EPR spectrum of CuPc with eight 12-membered tetraazamacrocycles that are devoid of metal ions; the spectra in the presence of various paramagnetic and diamagnetic ions in the centres of the outer cells (Fig. 1) are similar to this. The upper spectrum is a simulation of the lower one. The spectra are axially symmetric and exhibit the nine superhyperfine structure lines from the four nearest N nuclei with an approximate intensity distribution of 1:4:10:16::19:16:10:4:1. The superhyperfine coupling constant of N is approximately 16 G. The $CuPcCu_8$ sample gives only one EPR line, $g = 2.146$, without hyperfine and

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Table 1 The experimental EPR parameters of powder copper phthalocyaninate substituted with eight tetraazamacrocycles and its nonanuclear Zn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} complexes ($\Delta g = 0.002$, $\Delta a = 0.4$ G)

Acronym	M′	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}/G$	$A_{\perp}/G$	g	a_G
CuPc(ϕ)	ϕ	2.154	2.052	212.0	17.0	2.086	82.0
$CuPcZn_8$	Zn	2.152	2.053	209.3	16.8	2.086	81.0
$CuPcCo_8$	Co	2.148	2.052	209.3	16.0	2.084	80.4
$CuPcNi_8$	Ni	2.148	2.052	209.3	16.0	2.084	80.4
$CuPcCu_8$	Cu	–	–	–	–	2.146	–

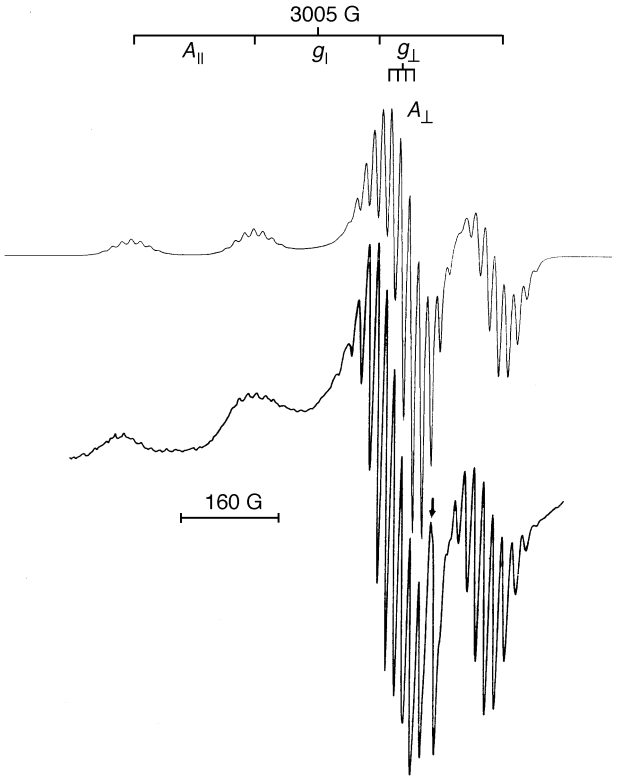

Fig. 3 EPR spectrum of CuPc with empty outer cells at room temperature; the upper spectrum is a simulation of the lower using the Bruker Win-EPR program

superhyperfine lines and has a width of ~200 G. The linewidth does not change very much with decreasing temperature (down to 113 K) and should be the result of the dipolar and exchange interactions between the copper ions.

Neimann and Kivelson[7] have shown that even in the presence of only diamagnetic metal ions the *Pc* complexes exhibit a strong characteristic EPR line, which they attributed to a free radical. We have also observed this line for all of our samples and it is indicated with an arrow in Fig. 3. The g value of this line is $g \cong 2.0037$ and is in complete agreement with that of the literature.[7]

The EPR parameters were obtained by simulating the spectra with the Bruker Win-EPR program. The results for the various copper phthalocyaninates are given in Table 1. As seen from Table 1, the hyperfine coupling (a) values

Table 2 The calculated EPR parameters of powder copper phthalocyaninate substituted with eight tetraazamacrocycles and its nonanuclear Zn^{2+}, Co^{2+} and Ni^{2+} complexes

Complex	K	α^2
CuPc(ϕ)	0.314	0.797
$CuPcZn_8$	0.311	0.785
$CuPcCo_8$	0.308	0.781
$CuPcNi_8$	0.308	0.781

decrease slightly as the substituted ion is varied, in the order ϕ, Zn, Co and Ni. This order is the same as the electronegativity order Cu (1.9) > Co ≅ Ni (1.8) > |n (1.6) > ϕ. The numbers in parentheses are the electronegativities of the elements.[8] Therefore, it may be stated that the ions in the outer cells of the CuPcs in this study attract the central unpaired electron according to their electronegativity. Within the limits of the experimental errors, the values of g in Table 1 do not appear to vary. The calculated results of K and α^2 values given in Table 2 seem to support the above conclusion since they decrease as the electronegativity increases, indicating an increase in the covalent character of the unpaired electron.

Experimental

The spectra were recorded at room temperature with a Varian E-109C model EPR spectrometer using 100 kHz modulation. The modulation amplitude was 0.6 G and the microwave power was around 2 mW. The low temperature measurements were made using a Varian temperature controller. The g factors were determined by comparison with a diphenylpicrylhydrazyl sample of $g = 2.0036$.

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References

1 E. M. Roberts and W. S. Koski, *J. Am. Chem. Soc.*, 1961, **83**, 1865.
2 M. Abkowitz, I. Chen and J. H. Sharp, *J. Chem. Phys.*, 1967, **48**, 4561.
3 S. E. Harrison and J. M. Assour, *J. Chem. Phys.*, 1964, **40**, 365.
4 E. Ağar, B. Batı, E. Erdem and M. Özdemir, *J. Chem. Res. (S)*, 1995, **16**.
5 T. F. Gibson, D. J. E. Ingram and D. Scholand, *Discuss. Faraday Soc.*, 1958, **26**, 72.
6 J. M. Assour, *J. Chem. Phys.*, 1965, **43**, 2477.
7 R. Neimann and D. Kivelson, *J. Chem. Phys.*, 1961, **35**, 162.
8 L. Pauling, 1960, *The Nature of the Chemical Bond*, Cornell University Press.