

EPR, ENDOR, and DFT Studies on (β -Octahalo-*meso*-tetraarylporphyrin)copper Complexes: Characterization of the Metal($d_{x^2-y^2}$)–Porphyrin(a_{2u}) Orbital Interaction

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A series of planar (porphyrin)copper(II) complexes and their β -octahalogenated saddled derivatives have been studied by Electron Paramagnetic Resonance (EPR) spectroscopy, Electron Nuclear Double Resonance (ENDOR) spectroscopy, and Density Functional Theoretical (DFT) calculations. Both EPR/ENDOR spectroscopy and DFT calculations indicate a decrease in spin density on the central copper(II) ion and on the nitrogen atoms in the saddled compounds relative to the planar complexes. The EPR/ENDOR measurements show that the hyperfine coupling decreases by 12% on the nitrogen atoms and 9% on the copper ion, in going from planar (5,10,15,20-tetraphenylporphyrin)copper (Cu[TPP]) to saddled (2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrin)copper (Cu[Br₈TPP]). Accordingly, saddling results in a decrease in the spin density on the copper ion and on the nitrogen atoms. DFT calculations on Cu[Br₈TPP] yield spin populations of 42.4% on the copper ion, 9.9% on

each nitrogen atom and 4.9% on each *meso* carbon atom, relative to DFT spin populations of 62, 10.2 and 0.3% on the copper ion, each nitrogen and each *meso* carbon atom, respectively, for porphinecopper (Cu[P]). These calculations further indicate that the decrease in spin density on the copper ion in the saddled complexes results from a saddling-induced Cu($d_{x^2-y^2}$)–porphyrin(a_{2u}) orbital overlap whereby some of the Cu spin density is delocalized onto the porphyrin ring. The decrease in nitrogen spin population with saddling appears to be a more subtle effect caused by a superposition of two opposing factors. Saddling decreases the overlap between the nitrogen lone pairs and the Cu $d_{x^2-y^2}$ orbital on one hand and enhances the overlap between the copper $d_{x^2-y^2}$ orbital and the porphyrin a_{2u} HOMO on the other.

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Introduction

Nonplanar conformations of porphyrins and related cofactors occur as conserved features of several metalloproteins, and it has been proposed that this nonplanarity is actually of biological importance.^[1] Nonplanar deformations such as ruffling and saddling (Figure 1) exert a strong influence on the chemical properties of metalloporphyrins and related molecules; these properties include electrochemical half-wave potentials,^[2,3] electronic absorption^[4,5] and vibrational spectra,^[6–8] energetics of different spin states and electron density distributions as reflected in NMR and EPR spectra,^[9–17] DFT calculations,^[18] and reactivity toward axial ligands, etc.^[9,10,12,13,15,16,18] Many of these effects arise from specific metal(d)–porphyrin(π) orbital interactions that are symmetry-forbidden in planar metalloporphyrins, but which become allowed as a result of nonplanar deformations. For example, ruffling switches on the metal(d_{xy})–porphyrin(a_{2u}) orbital interaction, where the

d_{xy} orbital is a “ t_{2g} -type” d orbital (in the notation of the O_h point group). Electronic spin density distributions reflecting this orbital interaction have been extensively studied by NMR spectroscopy for ruffled iron(III) porphyrins.^[9–12,14,15] Saddling switches on the metal($d_{x^2-y^2}$)–porphyrin(a_{2u}) orbital interaction (as shown

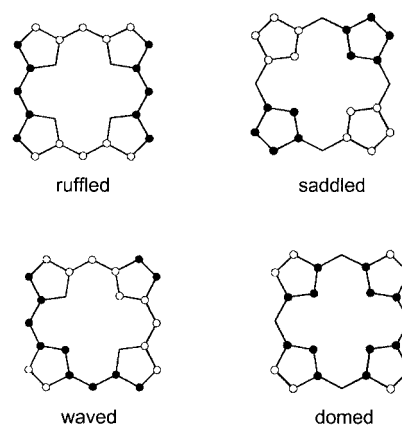


Figure 1. Nonplanar distortions of porphyrins; filled and open circles represent the displacement of the core atoms above and below the porphyrin mean plane

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in Figure 2),^[7,19] where the $d_{x^2-y^2}$ orbital is a “ e_g -type” d orbital (in the notation of the O_h point group). NMR studies on saddled iron(III) porphyrins have also thrown light on this orbital interaction.^[13,16] In this paper, we further^[7,19] explore the consequences of the metal- $(d_{x^2-y^2})$ -porphyrin(a_{2u}) orbital interaction by EPR and ENDOR spectroscopic studies and density functional theory (DFT) calculations on saddled Cu^{II} porphyrins. The results provide a clear picture of saddling-induced redistribution of unpaired electron density in (porphyrin) Cu^{II} compounds.

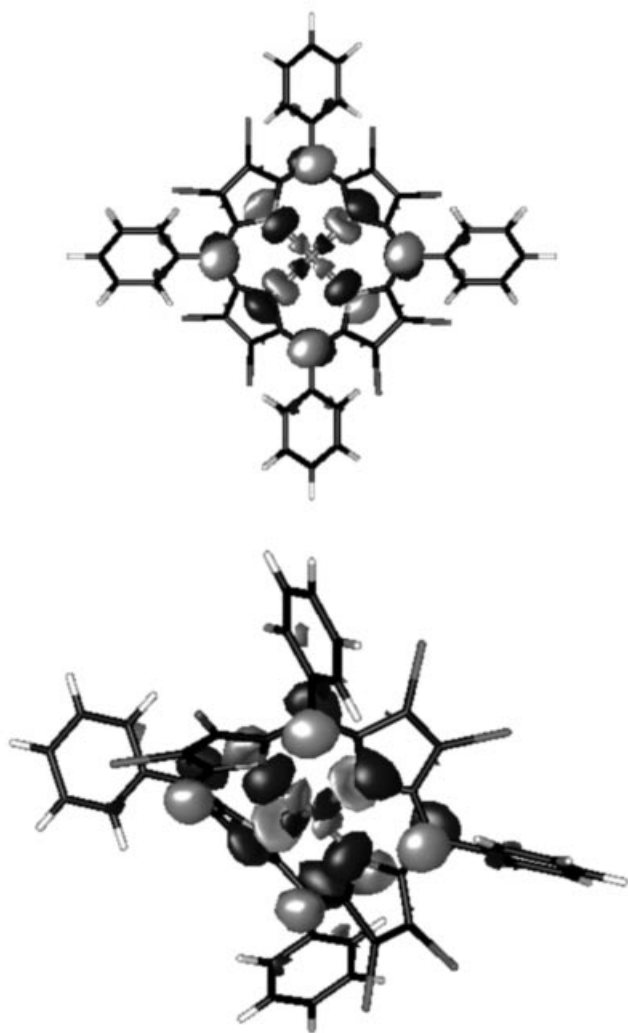


Figure 2. Two views of the singly occupied b_2 (a_{2u} -type) HOMO of $\text{Cu}[\text{Br}_8\text{TPP}]$ (D_{2d})

Investigations of single crystal $\text{Cu}[\text{TPP}]$ and $\text{Ag}[\text{TPP}]$ with ^{14}N , ^1H , and metal ENDOR spectroscopy by Brown and Hoffman have yielded the complete hyperfine coupling and ^{14}N quadrupolar tensors of the two complexes.^[20] Theoretical analyses of the spectra suggested metal spin populations of 0.62 for $\text{Cu}[\text{TPP}]$ and 0.38 for $\text{Ag}[\text{TPP}]$. DFT(PW91/TZP) calculations on Cu^{II} porphine yielded a Cu spin population of 50.7%.^[2] In this work, we present EPR and ^{14}N ENDOR measurements on the saddled Cu porphyrin derivatives $\text{Cu}[\text{Cl}_8\text{T}(p\text{-CF}_3\text{-P})\text{P}]$, $\text{Cu}[\text{Cl}_8\text{TPP}]$,

$\text{Cu}[\text{Br}_8\text{T}(p\text{-CF}_3\text{-P})\text{P}]$, and $\text{Cu}[\text{Br}_8\text{TPP}]$ (Figure 3), and DFT(PW91/TZP) calculations on $\text{Cu}[\text{Br}_8\text{TPP}]$, $\text{Cu}[\text{Br}_8\text{TPFPFPP}]$, $\text{Cu}[\text{Cl}_8\text{TPP}]$, and $\text{Cu}[\text{Cl}_8\text{TPFPFPP}]$ (Figure 4).

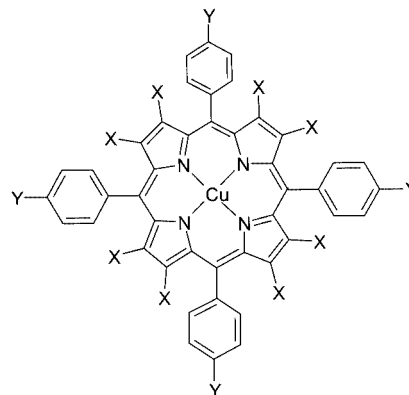


Figure 3. (Porphyrin)copper complexes studied by EPR and ENDOR spectroscopy: $\text{Cu}[\text{Cl}_8\text{T}(p\text{-CF}_3\text{-P})\text{P}]$ X = Cl, Y = CF_3 ; $\text{Cu}[\text{Cl}_8\text{TPP}]$ X = Cl, Y = H; $\text{Cu}[\text{Br}_8\text{T}(p\text{-CF}_3\text{-P})\text{P}]$ X = Br, Y = CF_3 ; $\text{Cu}[\text{Br}_8\text{TPP}]$ X = Br, Y = H

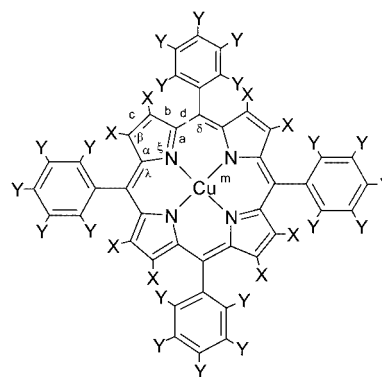


Figure 4. (Porphyrin)copper complexes studied by DFT calculations: $\text{Cu}[\text{Br}_8\text{TPP}]$ X = Br, Y = H; $\text{Cu}[\text{Br}_8\text{TPFPFPP}]$ X = Br, Y = F; $\text{Cu}[\text{Cl}_8\text{TPP}]$ X = Cl, Y = H; $\text{Cu}[\text{Cl}_8\text{TPFPFPP}]$ X = Cl, Y = F

Results

The EPR spectra of the (porphyrin) Cu complexes examined here are qualitatively similar to those of other tetragonal planar copper complexes. The $g_{\parallel}$ peaks partially overlap with the $g_{\perp}$ peaks. The $g_{\parallel}$, $g_{\perp}$ and $^{\text{Cu}}A_{\parallel}$ values were obtained by EPR simulations with WINEPR SimFornia (version 1.25, Bruker Analytische Messtechnik GmbH) and are listed in Table 1. In the EPR simulations, the nitrogen hyperfine tensors were taken from the ^{14}N ENDOR results. As can be seen from Table 1, the $g_{\parallel}$ (≈ 2.19) and $g_{\perp}$ (≈ 2.05) values of all the Cu porphyrin complexes examined are identical within experimental error. However, the absolute values of $^{\text{Cu}}A_{\parallel}$ differ significantly among the various compounds studied and decrease in the following order: $\text{Cu}[\text{T}(p\text{-CF}_3\text{-P})\text{P}] \approx \text{Cu}[\text{TPP}] > \text{Cu}[\text{Cl}_8\text{T}(p\text{-CF}_3\text{-P})\text{P}] \approx \text{Cu}[\text{Cl}_8\text{TPP}] > \text{Cu}[\text{Br}_8\text{T}(p\text{-CF}_3\text{-P})\text{P}] \approx \text{Cu}[\text{Br}_8\text{TPP}]$. These

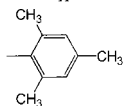
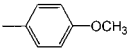
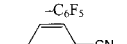
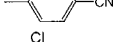
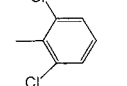
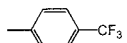
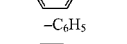
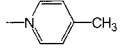
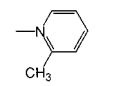
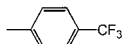
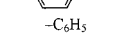
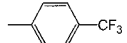
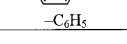
Table 1. $^{63,65}\text{Cu}$ and ^{14}N hyperfine couplings of (porphyrin)copper complexes^[a,b]

	Cu[T(<i>p</i> -CF ₃ -P)P]	Cu[TPP]	Cu[Cl ₈ T(<i>p</i> -CF ₃ -P)P]	Cu[Cl ₈ TPP]	Cu[Br ₈ T(<i>p</i> -CF ₃ -P)P]	Cu[Br ₈ TPP]
$^{\text{N}}A_1$ [MHz]	44.5(2)	44.1(2)	43.2(2)	42.5(2)	40.0(2)	38.7(2)
$^{\text{N}}A_2$ [MHz]	42.8(3)	42.8(3)	40.5(5)	40.0(5)	38.5(3)	37.6(3)
$^{\text{N}}A_3$ [MHz]	55.0(3)	54.2(3)	53.8(5)	53.0(5)	51.5(3)	50.0(3)
$^{\text{N}}A_{\text{iso}}$	47.4(2)	47.0(2)	45.8(3)	45.2(3)	43.3(2)	42.1(2)
$^{\text{Cu}}A_{\parallel}$ [MHz]	−618(4)	−615(4)	−591(8)	−591(8)	−588(4)	−585(4)
$g_{\perp}$	2.04(1)	2.04(1)	2.06(2)	2.06(2)	2.06(1)	2.06(1)
$g_{\parallel}$	2.17(1)	2.18(1)	2.18(2)	2.21(2)	2.17(1)	2.18(1)

^[a] $g_{\parallel} = 2.19 \pm 0.03$ and $g_{\perp} = 2.05 \pm 0.02$ for all complexes, within experimental error as obtained by X-band EPR spectroscopy at 77 K. ^{14}N ENDOR were taken at X-band and 4.2 K. ^[b] Simulations in all cases employed the quadrupole parameters found for Cu[TPP]: $P_1 = -0.3$, $P_2 = -0.6$, and $P_3 = 0.9$.^[20]

results are compared with those of other (porphyrin)copper complexes in Table 2.

Table 2. Spin-Hamiltonian parameters of (porphyrin)copper(II) complexes^[21]

Complex	Y ^[a]	X ^[a]	g	$g_{\perp}$	$^{\text{Cu}}A_{\parallel}$ ^[b]	ρ_{Cu} ^[c]	$^{\text{N}}A_{\text{iso}}$ ^[b]	Ref.
Cu[OEPP]	H	CH ₃ CH ₃	2.190	2.035	630	0.64	48	[21]
Cu[TMP]		H	2.185	2.031	624	0.64	48	[21]
Cu[TOMePP]		H	2.183	2.031	624	0.61	48	[21]
Cu[TF ₃ PP]		H	2.189	2.034	621	0.62	48	[21]
Cu[TCNPP]		H	2.180	2.034	618	0.60	48	[21]
Cu[TCl ₂ PP]		H	2.190	2.036	618	0.62	48	[21]
Cu[T(<i>p</i> -CF ₃ -P)P]		H	2.17	2.04	618	0.60	47.4	this work
Cu[TPP]		H	2.190	2.045	615	0.62	47.0	[20]
Cu[TMPyP(4)]		H	2.209	2.054	598	0.63	45.5	[26]
Cu[TMPyP(2)]		H	2.212	2.055	593	0.63	45.2	[26]
Cu[Cl ₈ T(<i>p</i> -CF ₃ -P)P]		Cl	2.18	2.06	591	0.58	45.8	this work
Cu[Cl ₈ TPP]		Cl	2.21	2.06	591	0.63	45.2	this work
Cu[Br ₈ T(<i>p</i> -CF ₃ -P)P]		Br	2.17	2.06	588	0.55	43.3	this work
Cu[Br ₈ TPP]		Br	2.18	2.06	585	0.57	42.1	this work

^[a] X and Y are functional groups marked in Figure 3. ^[b] Unit is in MHz. ^[c] Spin density on copper ion calculated with Equation (1).

Figure 5 displays the ^{14}N ENDOR spectra of Cu[TPP] and Cu[Br₈TPP] taken at $g_{\parallel}$ and $^{\text{Cu}}I_{-3/2}$, where only single-crystal-like spectra, derived from the molecules with their symmetry axis parallel to the static magnetic field, were collected for both samples. A significant hyperfine coupling shift (−5.4 MHz or −2.7 MHz peak-to-peak) between Cu[TPP] and Cu[Br₈TPP] was observed. Unlike the well-resolved double ENDOR spectra presented by Schweiger in his review on ENDOR studies of transition metal complexes,^[22] the ^{14}N ENDOR spectra of Cu[T(*p*-CF₃-P)P] at both parallel and perpendicular field positions are unre-

solved, as shown in Figure 6. The well-matched simulation results (obtained with GENSIM, a locally developed software) are also presented in Figure 6. The sharp simulated peaks reveal the positions of the hyperfine couplings ($A_n/2$, $n = 1, 2, 3$), nuclear Zeeman splitting ($2\nu_{\text{N}}$, since $A_n/2 > \nu_{\text{N}}$) and quadrupole splitting ($3P_n$, $n = 1, 2, 3$). The quadrupole splitting was taken from previous work on Cu[TPP] and are assumed to differ only slightly in other complexes. Numerous hyperfine coupling values were attempted in the simulation to best match the simulated and experimental spectra. The $^{\text{N}}A_{\perp}$ at $g_{\parallel}$ (or $^{\text{N}}A_1$) values, unlike the others, were measured directly from the spectra. Unlike the single-crystal-like spectra taken at the parallel field position, there are two components, $^{\text{N}}A_2$ (or $^{\text{N}}A_{\perp}$) and $^{\text{N}}A_3$ (or $^{\text{N}}A_{\parallel}$), at the perpendicular field position. These originate from the Cu–N vectors perpendicular and parallel to the magnetic field, respectively. The full ^{14}N ENDOR spectra

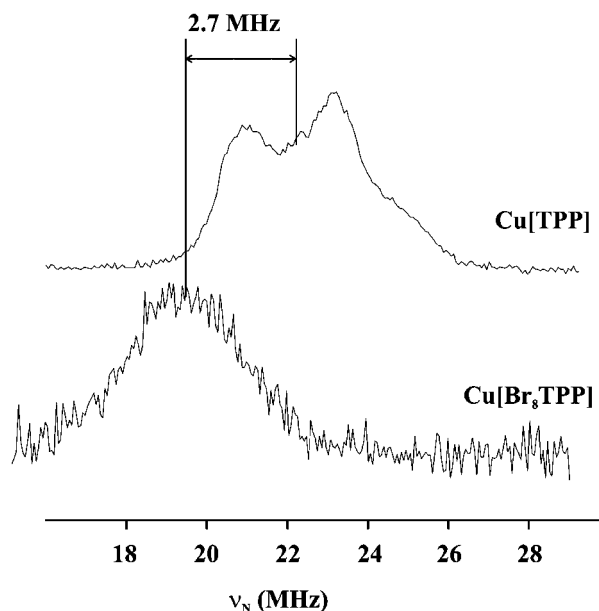


Figure 5. ^{14}N Davies ENDOR spectra of Cu[TPP] and Cu[Br₈TPP] at the parallel field position; the peak center ($A_1/2$) shift is marked between these two (porphyrin)copper complexes; experimental conditions: temperature, 4.2 K; microwave frequency, 9.715 GHz; magnetic field, 0.29 T; microwave pulse length, 32–16–32 ns; τ , 752 ns; RF pulse length, 20 ns; repetition rate, 20 ms; total points of each spectrum, 256; number of shots at each point, 300

of the various (porphyrin)copper complexes studied at parallel and perpendicular field positions, along with the simulated spectra, are shown in Figures 7 and 8, respectively. The arrows mark the hyperfine splitting peak positions in the spectra and the ^{14}N hyperfine couplings are listed in Table 1. The ^{14}N hyperfine couplings decrease in the same order as $^{\text{Cu}}A_{\parallel}$, namely $\text{Cu}[\text{T}(p\text{-CF}_3\text{-P})\text{P}] \approx \text{Cu}[\text{TPP}] > \text{Cu}[\text{Cl}_8\text{T}(p\text{-CF}_3\text{-P})\text{P}] \approx \text{Cu}[\text{Cl}_8\text{TPP}] > \text{Cu}[\text{Br}_8\text{T}(p\text{-CF}_3\text{-P})\text{P}] \approx \text{Cu}[\text{Br}_8\text{TPP}]$. This sequence is also depicted in the bar graph of Figure 9, which again shows that hyperfine couplings decrease on going from the β -unsubstituted to the β -octachloro and β -octabromo complexes.

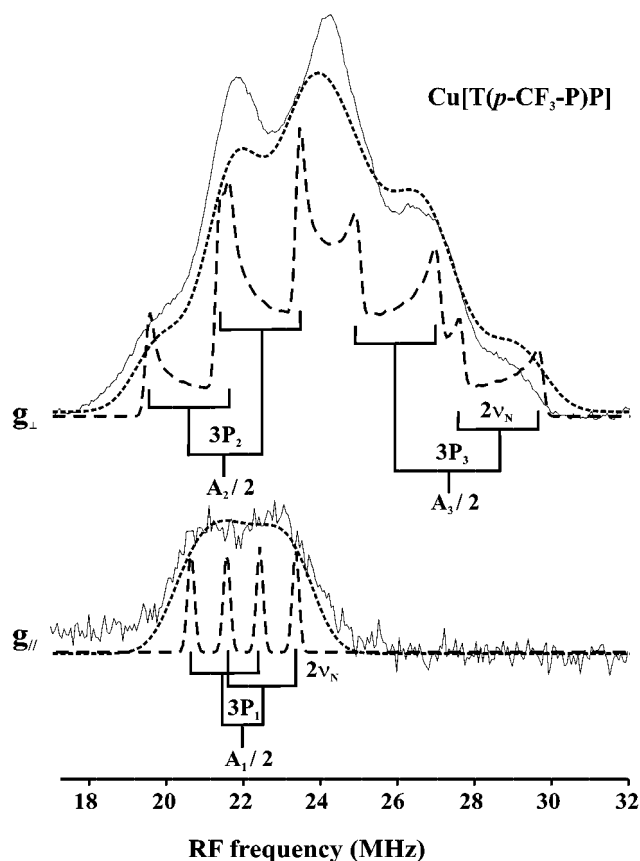


Figure 6. ^{14}N Davies ENDOR spectra of $\text{Cu}[\text{T}(p\text{-CF}_3\text{-P})\text{P}]$ at both parallel and perpendicular field positions; the solid lines are the experimental spectra, the dotted lines the simulated spectra, and the dashed lines the simulated lines with narrow line width to show the peak positions, which are marked in the graph; the experimental conditions are the same as in Figure 5

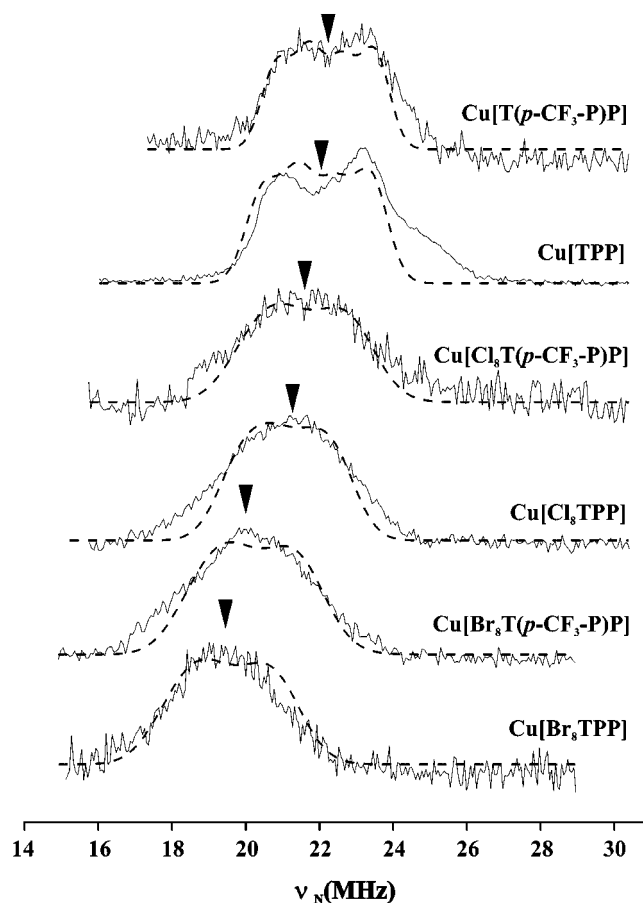


Figure 7. ^{14}N Davies ENDOR spectra of all the complexes at parallel field position; the arrows denote the centers of the hyperfine coupling peaks; the experimental conditions are the same as in Figure 5

Figure 10 shows the X-band (9 GHz, bottom) and K_a-band (35 GHz, top) proton and fluorine ENDOR spectra of $\text{Cu}[\text{Br}_8\text{T}(p\text{-CF}_3\text{-P})\text{P}]$. With the X-band, the ^{19}F splittings, arising from the trifluoromethyl group, overlap at the low-frequency shoulder of the proton hyperfine coupling profile. With the K_a-band, the hyperfine couplings from the two components are completely separated. Since there are no β -protons on the pyrrole rings in this compound, the proton signals are assigned to phenyl ring protons. This indicates that proton hyperfine couplings originally assigned to pyrrole hydrogen atoms^[20] are in fact associated with phenyl hydrogen atoms. Absent selective deuteration or chemical substitution, as done here, the distinction be-

Table 3. Selected optimized geometries [$\text{\AA}$, $^\circ$] and z -displacements [$\text{\AA}$]

Compound	Distances					Angles					z -displacements		
	a	b	c	d	m	α	β	ξ	δ	γ	z_α	z_β	z_{N}
$\text{Cu}^{\text{II}}[\text{Br}_8\text{TPP}]$	1.378	1.449	1.373	1.411	2.023	108.6	107.2	108.1	121.3	122.6	0.449	1.231	0.066
$\text{Cu}^{\text{II}}[\text{Br}_8\text{TPFP}]$	1.376	1.449	1.372	1.410	2.012	108.6	107.2	108.0	121.8	122.4	0.459	1.217	0.092
$\text{Cu}^{\text{II}}[\text{Cl}_8\text{TPP}]$	1.379	1.450	1.369	1.406	2.032	108.7	107.2	107.9	122.7	124.3	0.344	0.939	0.057
$\text{Cu}^{\text{II}}[\text{Cl}_8\text{TPFP}]$	1.378	1.450	1.368	1.405	2.027	108.7	107.2	107.8	123.3	124.3	0.334	0.868	0.084

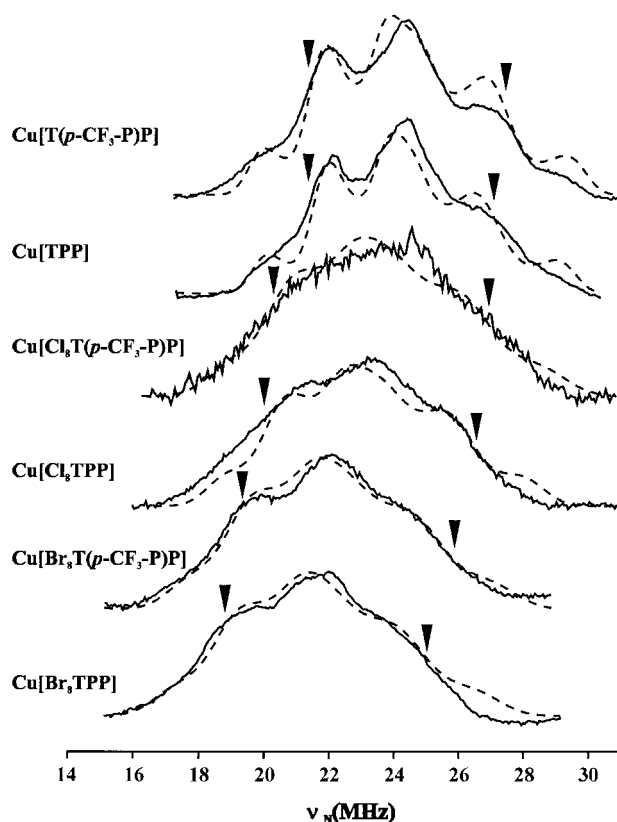


Figure 8. ^{14}N Davies ENDOR spectra of the whole complexes at the perpendicular field position; the arrows denote the centers of the hyperfine coupling peaks; the experimental conditions are the same as in Figure 5

tween these two types of proton at similar distances from Cu is very challenging.

Table 3, in conjunction with Figure 4, shows selected optimized geometry parameters for $\text{Cu}^{\text{II}}[\text{Br}_8\text{TPP}]$, $\text{Cu}^{\text{II}}[\text{Br}_8\text{TPFPP}]$, $\text{Cu}^{\text{II}}[\text{Cl}_8\text{TPP}]$, and $\text{Cu}^{\text{II}}[\text{Cl}_8\text{TPFPP}]$. As shown by the out-of-plane z -displacement of the β -carbon atoms (z_β), the β -octabrominated complexes are significantly more saddled than the corresponding β -octachlorinated analogues. However, analogous TPP and TPFPP derivatives are comparably saddled. The Cu–N bond lengths are approximately the same (2.01–2.03 Å) in all four molecules. Table 4 shows the calculated atomic spin populations for these four saddled porphyrins, and these data are discussed in the next section.

Table 4. Gross atomic spin populations

Compound	Metal	N_{porph}	C_α	C_β	C_{meso}
$\text{Cu}^{\text{II}}[\text{Cl}_8\text{TPP}]$	0.4465	0.1015	−0.0028	0.0039	0.0362
$\text{Cu}^{\text{II}}[\text{Br}_8\text{TPP}]$	0.4151	0.0983	−0.0105	0.0034	0.0531
$\text{Cu}^{\text{II}}[\text{Cl}_8\text{TPFPP}]$	0.4722	0.1025	−0.0029	0.0043	0.0212
$\text{Cu}^{\text{II}}[\text{Br}_8\text{TPFPP}]$	0.4388	0.0998	−0.0076	0.0040	0.0389

Discussion

Isotropic hyperfine coupling arises from the Fermi interaction and is proportional to the spin population on the observed nonmetal nucleus (nitrogen nuclei in this case) [Equation (1)],^{23]} where g_e is the electron g value, $g_{\parallel}$ the par-

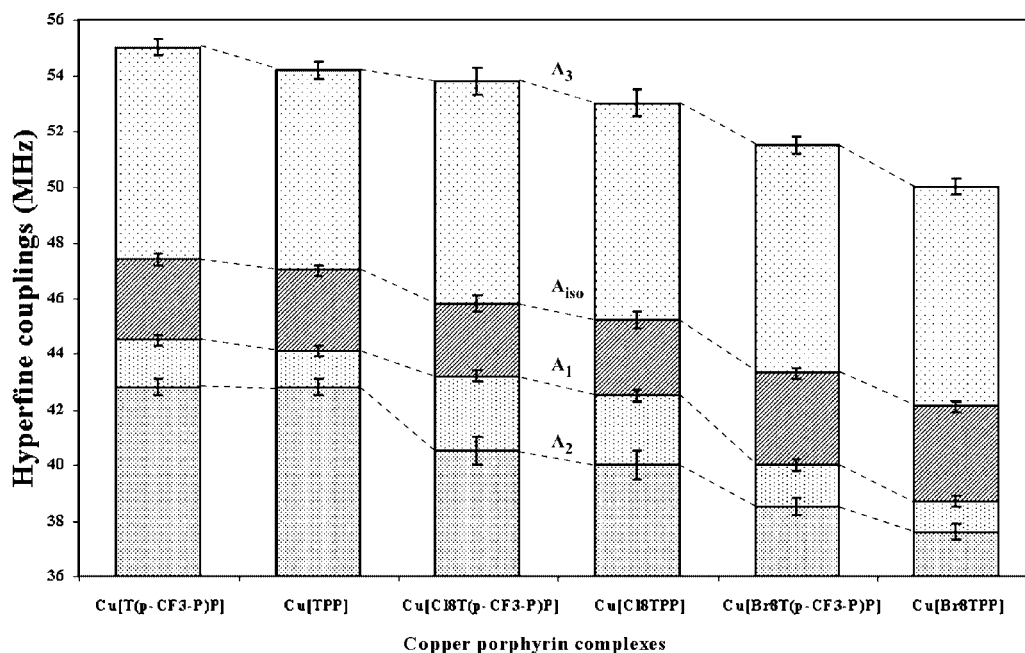


Figure 9. Bar graph of the hyperfine couplings of all (porphyrin)copper complexes

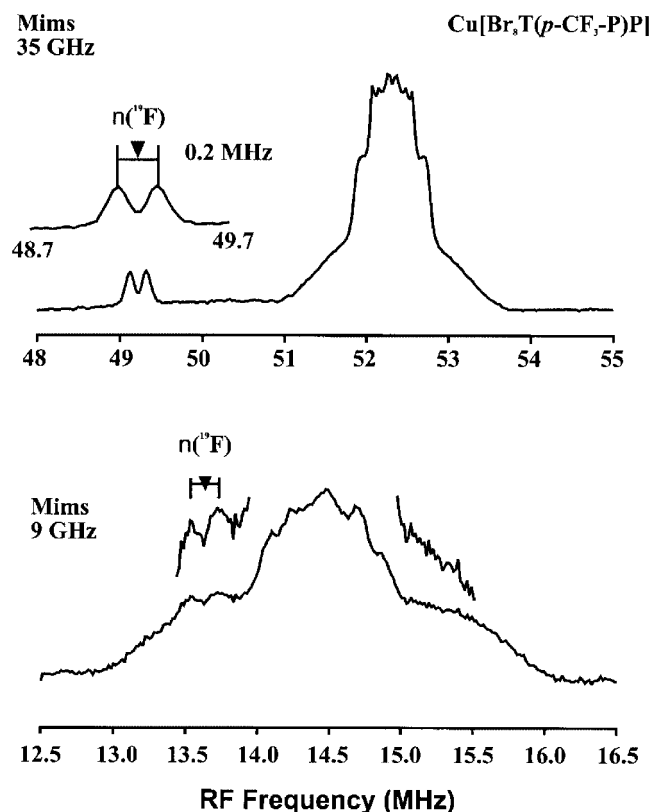


Figure 10. ^1H and ^{19}F Mims ENDOR spectra of $\text{Cu}[\text{Br}_8\text{T}(p\text{-CF}_3\text{-P})\text{P}]$ at 9 GHz and 35 GHz at the perpendicular field position; the arrows denote the center of the ^{19}F hyperfine coupling peaks; the experimental conditions at 9 GHz are: temperature, 4.2 K; microwave frequency, 9.720 GHz; magnetic field, 0.34 T; microwave pulse length, 16 ns; τ , 140 ns; RF pulse length, 10 ns; repetition rate, 30 ms; total points of each spectrum, 256; number of shots at each point, 300; the experimental conditions at 35 GHz are: temperature, 2 K; microwave frequency, 35.026 GHz; magnetic field, 1.234 T; microwave pulse length, 48 ns; τ , 300 ns; RF pulse length, 40 ns; repetition rate, 20 ms; total points of each spectrum, 256; number of shots at each point, 80

allel g value, $g_{\perp}$ the perpendicular g value, α_1^2 the odd electron populations on the copper ion, ignoring the interactions between copper $d_{x^2-y^2}$ and nitrogen 2s and 2p orbitals.

$$^{\text{Cu}}A_{\parallel} = ^{\text{Cu}}A_1 = P[-\kappa - 4/7\alpha_1^2 - 3/7(g_e - g_{\perp}) - (g_e - g_{\parallel})] \quad (1)$$

The parameter P is proportional to the radial expectation value of the square of the $d_{x^2-y^2}$ orbital amplitude of the metal, and κ is an empirical constant that describes the inner-shell polarization by the d-shell vacancy and quantifies the isotropic metal hyperfine coupling.^[24] By taking $P = 0.037$ and^[25] $\kappa = 0.406$ [adjusted value to obtain a spin density of 0.624^[20] on the copper ion in $\text{Cu}[\text{TPP}]$ with Equation (1)], we can empirically estimate the spin populations on all (porphyrin)copper complexes examined. Table 2 summarizes the EPR data for a wide range of (porphyrin)copper complexes, including the empirically estimated copper spin populations. The main conclusions based on Tables 1 and 2 are as follows.

As mentioned above, both the $^{\text{Cu}}A_{\parallel}$ and $^{14}\text{N}_{\text{iso}}$ hyperfine couplings decrease in the following order: $\text{Cu}[\text{T}(p\text{-CF}_3\text{-P})\text{P}] \approx \text{Cu}[\text{TPP}] > \text{Cu}[\text{Cl}_8\text{T}(p\text{-CF}_3\text{-P})\text{P}] \approx \text{Cu}[\text{Cl}_8\text{TPP}] > \text{Cu}[\text{Br}_8\text{T}(p\text{-CF}_3\text{-P})\text{P}] \approx \text{Cu}[\text{Br}_8\text{TPP}]$ (Table 1). In other words, Table 1 indicates that the $^{\text{Cu}}A_{\parallel}$ hyperfine couplings of the saddled complexes are generally considerably lower than those of their planar counterparts and are comparable only to those observed for highly electron-deficient *meso*-tetrakis(pyridiniumyl)porphyrin derivatives, $\text{Cu}[\text{TMPyP}]$ ^[26] (Table 2). This indicates that the spin populations on the Cu and N atoms decrease with increasing saddling of the macrocycle. The decrease in the Cu spin population is understandable as a simple consequence of the saddling-induced $\text{Cu}(d_{x^2-y^2})$ –porphyrin(a_{2u}) orbital overlap whereby some of the Cu spin density is delocalized onto the porphyrin ring. However, we believe that the decrease in nitrogen spin population with saddling reflects two opposing factors. On the one hand, saddling inhibits contact between the nitrogen lone-pairs and the Cu $d_{x^2-y^2}$ orbital. On the other hand, saddling encourages and enhances the overlap between the copper $d_{x^2-y^2}$ and the porphyrin a_{2u} HOMO. The combined result of these two factors is a certain decrease in spin population on the nitrogen atoms.

The decrease in spin density on going from the β -unsubstituted to the β -octahalogenated complexes, as measured by the $^{\text{Cu}}A_{\parallel}$ and $^{14}\text{N}_{\text{iso}}$ hyperfine couplings, is consistent with DFT calculations showing atomic spin populations for $\text{Cu}^{\text{II}}[\text{Br}_8\text{TPP}]$: Cu 42.4, N 9.9 and C_{meso} 4.9%. This can be compared with (porphine) Cu^{II} : Cu 50.7, N 10.8 and C_{meso} 0.2%. The DFT calculations indicate that the loss of spin density on the copper and nitrogen atoms in the saddled complexes is accompanied by an increase in the spin density on C_{meso} . This effect can potentially be explored by EPR and ENDOR analysis of $^{13}\text{C}_{\text{meso}}$ analogues of the relevant complexes, but such analyses have not yet been completed.

Conclusion

In summary, we have studied a number of (β -octahalo-*meso*-tetraarylporphyrins)copper(II) complexes by using EPR/ENDOR spectroscopy and DFT calculations to better understand the consequences of the saddling-induced metal($d_{x^2-y^2}$)–porphyrin(a_{2u}) orbital overlap on the electron distribution of (porphyrin)copper complexes. Both EPR/ENDOR spectroscopy and DFT calculations show that the spin populations on the central copper ion and on the nitrogen atoms are significantly decreased in these saddled complexes relative to their planar counterparts. The diminished spin density on the copper ion is directly attributable to the saddling-induced $\text{Cu}(d_{x^2-y^2})$ –porphyrin(a_{2u}) orbital overlap whereby Cu spin density is delocalized onto the porphyrin ring. The decrease in nitrogen spin population with saddling appears to be a more subtle effect caused by a superposition of two opposing factors. Saddling decreases the overlap between the nitrogen lone pairs and the Cu $d_{x^2-y^2}$ orbital on one hand and enhances the

overlap between the copper $d_{x^2-y^2}$ orbital and the porphyrin a_{2u} HOMO on the other.

Experimental Section

The β -octabrominated (porphyrin)copper complexes studied here have been described previously.^[3] The β -octachlorinated (porphyrin)copper complexes were prepared using a slightly modified version of the procedure described by Dolphin and co-workers^[27] for β -octachlorination of nickel porphyrins: [tetrakis(*para*-X-phenyl)porphyrin]Cu^{II} (X = H or CF₃) (0.3 mmol) and *N*-chlorosuccinimide (3.6 mmol, 12 equiv.) were dissolved in *o*-dichlorobenzene and heated to 140 °C. The reaction was monitored by UV/Vis spectroscopy and more *N*-chlorosuccinimide was added during the course of the reaction to ensure complete conversion into the β -octachlorinated product (the Soret absorbance changes from ca. 415 to ca. 436 nm). The total reaction time was approximately 24 h. The resulting crude product was purified by flash chromatography on silica gel with dichloromethane/*n*-hexane (2:1) as eluent and further purified on preparative (20 × 20 cm) TLC plates (silica, 0.5 mm thick) with dichloromethane/*n*-hexane (2:1) as eluent. EPR and ENDOR samples were prepared by dissolving the complexes in a mixed solvent consisting of 40% chloroform (99.9%, Aldrich) and 60% toluene (99.8+%, Aldrich) by volume. The samples were frozen in liquid nitrogen. Powder samples of the complexes were prepared by mixing each complex with NiTPP (which is EPR-silent) in a 1:100 ratio in toluene solution with subsequent evaporation of the toluene. In the case of the rather insoluble Cu[Cl₈T(*p*-CF₃-P)P] complex, a solid sample of this complex was diluted with Ni[Cl₈T(*p*-CF₃-P)P] to generate a powder sample suitable for EPR measurements. In general, the powder samples yielded spectra that were identical to the frozen solution spectra, except that the former exhibited slightly higher resolution. EPR spectra were obtained on a Varian E-4 EPR spectrometer at 77 K. Two home-built X-band and Q-band pulsed ENDOR spectrometers, which have been described elsewhere,^[28,29] were used to collect the ENDOR spectra at 4.2 K and 2 K, respectively. DFT calculations on selected saddled (porphyrin)copper complexes (Figure 4) were carried out using Slater-type valence triple- ζ with polarization basis sets, the VWN local functional, Perdew–Wang 1991 gradient corrections, a spin-unrestricted formalism, a fine mesh for numerical integration of matrix elements, full geometry optimizations, and the ADF program system.^[30,31]

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