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Studies on cobalt(II), nickel(II) and copper(II) derivatives of some new *meso*-aryl substituted octabromoporphyrins

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Abstract

A series of Co(II), Ni(II) and Cu(II) derivatives of a variety of porphyrins with tolyl (H₂TxTP) and naphthyl (H₂NxTP) moieties as *meso*-substituents are synthesised and characterised. H₂TxTP has the tolyl functions bonded to *meso*-carbons at the *o*-, *m*- or *p*-positions of the tolyl moieties while H₂NxTP has naphthyl groups bonded through their α - or β -positions. Their octabromo derivatives (MTxOBP and MNxOBP) were also synthesised by electrophilic substitution at the β -pyrrole positions. Optical spectra showed that the Q bands remain almost unaltered for both tolyl and naphthyl derivatives of the nonbrominated porphyrins while the B bands of their naphthyl derivatives are seen to be more red-shifted than their tolyl analogues. Even though a similar trend based on the *meso*-substituents is observed among all MTxOBP and MNxOBP derivatives, a substantial red-shift is seen for all the bromoderivatives compared to their nonbrominated species MTxTP and MNxTP. The energy difference $\Delta \bar{\nu}$ associated with this red-shift of the Soret band is seen to be in the range 1700–2050 cm⁻¹ for Co(II) and Ni(II) derivatives, the naphthyl derivatives always having higher values. Energy level reordering due to electron-withdrawing Br-substituents, distortion bringing about nonplanarity in the π -framework resulting in HOMO–LUMO level changes and the mesomeric effect due to *meso*-aryl moieties can be considered to be the reasons for the observed spectral changes. The EPR spectra of the Cu(II) derivatives of bromoporphyrins have lower A_{\parallel}^{Cu} hyperfine values compared to their nonbrominated analogues, indicating enhanced delocalisation of electron spin to the octabromoporphyrinato moiety. An enhanced Cu–N σ -covalency is seen in the Cu(II)–bromoporphyrins, as evident from their lower α^2 values.

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1. Introduction

Synthesis of varyingly substituted porphyrins and their metalloderivatives continues to be an active area of research owing to their wide applications as versatile catalysts, enzyme mimics, nonlinear optical materials and as candidates for photodynamic therapy [1–6].

The fact that there are twelve substitutional sites on the periphery and a highly tunable π framework which can act as an electron sink makes electronic and redox modulation of the porphyrin macrocycle an interesting and fruitful exercise leading to products of varying chemical, optical and photophysical properties [7–12]. We have been interested in developing electronically and structurally modified porphyrins, especially on solid polymer matrices, and have demonstrated their ability to carry out a few enzyme mimetic reactions efficiently [13–18]. Knowing the ability of Br substitution to bring

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about interesting electronic, redox and structural modification of aryl porphyrins, we have synthesised and studied some of the interesting properties of a series of octabromoporphyrins and also their Fe(III) and Mn(III) derivatives [19–21]. The studies on such perbrominated porphyrins are of great relevance in the context of growing interest on nonplanar porphyrins which are generated either by substitution of the β -pyrrole positions by bulky/electron withdrawing substituents or by incorporating bulky groups at the meso-positions. Realising the biological significance of such distorted porphyrins is one of the major concerns of experimental and theoretical chemists alike with regard to tracing the origin of their red-shifts [22-25]. In this work we report the synthesis and characterisation of Co(II), Ni(II) and Cu(II) derivatives of some meso-tolyl and mesonaphthyl porphyrins and also their octabromo derivatives and discuss salient features of their spectral properties.

2. Experimental

Pyrrole (Fluka) was distilled over KOH pellets, under reduced pressure before use. The α -naphthaldehyde and β -naphthaldehyde (E. Merck) were used as such. All the solvents employed in the present study were of spectral grade and were distilled before use. Liquid bromine procured from Ranbaxy and basic alumina obtained from Acmes were used as received. The metal salts (E. Merck) were also used without further purification. The UV-Vis spectral measurements were carried out with a Shimadzu 160A UV-Vis spectrophotometer. Elemental analyses were done using a Perkin-Elmer CHN analyzer. The EPR Spectra were measured on a Varian E-109 X-band spectrometer with the micropower set at 5 mW and with a modulation frequency of 100 K. The solution of copper(II) porphyrins was made in a toluene-methanol mixture with a concentration ca. 10^{-4} M. The 'g' marker employed was TCNE radical.

2.1. Preparation

2.1.1. Free-base porphyrins H_2TxTP , H_2NxTP , H_2TxOBP and H_2NxOBP

The free-bases of tetratolyl (H_2TxTP) and tetranaphthyl porphyrins (H_2NxTP) including those reported earlier [19] were synthesised by Adler's method involving the condensation between pyrrole and the respective aldehydes in propionic acid medium [26]. Their brominated free-bases, tolyl (H_2TxOBP) and naphthyl porphyrins (H_2NxOBP), were prepared by brominating the Cu(II) derivatives of the respective porphyrins H_2TxTP and H_2NxTP , based on the reported procedure [19,27]. The yields of the bromoderivatives were in the range 75–80%.

2.1.2. Cobalt(II), nickel(II) and copper(II) complexes of H_2TxTP and H_2NxTP

The metallation of the nonbrominated porphyrins H₂TxTP and H₂NxTP was carried out by a known procedure. The free-base tolylporphyrins H_2TxTP (0.5 g, 0.74 mmol) or free-base naphthylporphyrins H₂NxTP (0.5 g, 0.61 mmol) were dissolved in a suitable solvent mixture (CHCl₃:CH₃OH, 40 mL, 1:1, v/v). To this, the metal carrier CoCl₂ · 6H₂O (1.6 g, 7 mmol), Cu(CH₃- $COO_{2} \cdot 4H_{2}O$ (1.4 g, 7 mmol) or NiCl₂ · 6H₂O (1.7 g, 7 mmol) dissolved in glacial CH₃COOH (1.5 mL) was added for the synthesis of the respective metalloderivatives. NaOAc was employed as a base. On refluxing the reaction mixture on a water bath, the metallation gets initiated as evident from the UV-Vis spectral measurements. The metallation usually gets completed within 4 h for Co(II) derivatives, 6-8 h for Ni(II) derivatives and 2 h for Cu(II) derivatives. The reaction mixture was washed repeatedly with water to remove the unreacted metal salts and the metalloporphyrins formed were purified by column chromatography on basic alumina using CHCl₃ as eluent and were further purified by recrystallisation using hexane/CHCl3 mixture. Metallation was confirmed by UV-Vis spectroscopy. Yields were in the range of 80-85% for Co(II), 70-75% for Ni(II) and 85–90% for Cu(II) complexes.

2.1.3. Cobalt(II), nickel(II) and copper(II) complexes of H_2TxOBP and H_2NxOBP

The metallation of all the bromoporphyrins could be carried out at room temperature. To a solution of the metal carrier of CoCl₂ · 6H₂O (2 g, 8.75 mmol), Ni- $Cl_2 \cdot 6H_2O$ (2.12 g, 8.75 mmol) or $Cu(CH_3COO)_2 \cdot$ 4H₂O (1.75 g, 8.75 mmol) in CHCl₃:MeOH mixture (60 mL, 2:1, v/v) was added H_2TxOBP (0.60 g, 0.46 mmol) or H₂NxOBP (0.66 g, 0.46 mmol), 2 mL of glacial MeCO₂H and 1 g of powdered NaOAc. The reaction mixture was stirred either at room temperature or on a water bath for about 1–2 h. The completion of the metallation reaction was monitored by electronic spectroscopy. The mixture was then taken in a separating funnel, washed repeatedly with water after which the organic phase was separated and dried over anhydrous Na₂SO₄. The compound was purified by column chromatography (basic Al_2O_3 , CHCl₃ eluent) to obtain the metalloderivative and then by recrystallisation using hexane/CHCl₃ mixture (yield 95%).

3. Results and discussion

The free-base porphyrins, which are purified by careful column chromatography, are characterised by chemical analysis, electronic and ¹H NMR studies [19–21]. All the free-base porphyrins gave reasonably good ¹H NMR signals as reported by us earlier [19]. The effect due to various aryl groups at the *meso*-positions and also due to the Br substitution at the eight β -pyrrole positions on the optical absorption, fluorescence emission and redox potential of the free-base porphyrins has been reported by us recently [19,20].

As mentioned in the preparatory section all the metalloporphyrins were purified by column chromatography. The compounds were characterised by electronic and EPR studies. The various Co(II), Ni(II) and Cu(II) derivatives of both the nonbrominated and brominated porphyrins prepared are summarised in Table 1, wherein the substituents indicated in (1) are specified.



It is seen that among the nonbrominated porphyrins, the naphthyl derivatives undergo easier metallation than the tolyl derivatives. This could be attributed to the possible distortional change brought about on the porphyrin ring in H₂NxTP by the bulkier meso-naphthyl groups as compared to the tolyl porphyrins. The metallation of all the bromoporphyrins are also found to be very facile as it could be carried out at room temperature. It is known that all perbrominated porphyrins tend to exist in a highly distorted form because of the presence of bulky Br atoms at the eight β -pyrrole positions [27,28]. Since the mechanism of metallation involved has been proposed to be following a "sitting atop mechanism," such a distortion also can be expected to facilitate metallation processes. Further, the electron withdrawing effect due to the eight Br-atoms at the β -pyrrole positions can be expected to help substantially the deprotonation step of the -NH protons, augmenting the metallation. Compared to cobalt(II) and nickel(II) derivatives, the copper(II) metalloporphyrins are seen to be easily formed.

Table 1 The Co(II), Ni(II) and Cu(II) derivatives of porphyrins developed in the study

R	Х	М	Porphyrin	Analysis (%) ^a		
				С	Н	Ν
	Н	Со	CoNaTP	83.10(82.50)	4.19(4.12)	6.49(6.40)
$-\bigcirc$	Br	Co	CoNaOBP	47.20(47.90)	1.90(1.86)	3.40(3.70)
	Н	Ni	ΝίΝαΤΡ	82.76(82.60)	4.02(4.13)	6.32(6.42)
$\langle \bigcirc \rangle$	Br	Ni	NiNαOBP	48.20(47.90)	1.74(1.86)	3.60(3.72)
	Н	Cu	CuNaTP	82.18(82.14)	4.06(4.10)	6.36(6.38)
	Br	Cu	CuNαOBP	47.77(47.75)	1.82(1.85)	3.78(3.70)
	Н	Co	CoNβTP	82.62(82.50)	4.24(4.12)	6.50(6.40)
\backslash	Br	Co	CoNβOBP	47.45(47.90)	1.84(1.86)	3.68(3.70)
\bigcirc	Н	Ni	ΝίΝβΤΡ	82.71(82.60)	4.18(4.13)	6.38(6.42)
\cong	Br	Ni	ΝίΝβΟΒΡ	47.50(47.90)	1.99(1.86)	3.84(3.72)
\bigcirc	Н	Cu	CuNβTP	82.20(82.14)	4.11(4.10)	6.30(6.38)
	Br	Cu	CuNβOBP	47.92(47.75)	1.77(1.85)	3.74(3.70)
	Н	Co	CoToTP	79.32(79.20)	4.87(4.95)	7.63(7.70)
	Br	Co	CoToOBP	41.50(42.38)	2.12(2.06)	4.42(4.12)
	Н	Ni	NiToTP	79.10(79.22)	5.06(4.95)	7.76(7.70)
	Br	Ni	NiToOBP	42.48(42.39)	2.01(2.06)	4.24(4.12)
	Н	Cu	CuToTP	78.75(78.70)	4.86(4.91)	7.60(7.65)
	Br	Cu	CuToOBP	42.19(42.24)	2.10(2.05)	4.14(4.10)
	Н	Co	CoTmTP	79.14(79.20)	4.92(4.95)	7.80(7.70)
/	Br	Co	CoTmOBP	41.85(42.38)	2.18(2.06)	4.24(4.12)
$\neg \bigcirc$	Н	Ni	NiTmTP	79.26(79.22)	4.98(4.95)	7.74(7.70)
	Br	Ni	NiTmOBP	42.40(42.39)	2.03(2.06)	4.04(4.12)
	Н	Cu	CuTmTP	78.62(78.70)	4.96(4.91)	7.64(7.65)
	Br	Cu	CuTmOBP	42.31(42.24)	2.08(2.05)	4.13(4.10)
\rightarrow	Н	Со	CoTpTP	79.32(79.20)	4.87(4.95)	7.63(7.70)
	Br	Co	CoTpOBP	42.01(42.38)	2.36(2.06)	4.10(4.12)
	Н	Ni	NiTpTP	79.07(79.22)	5.05(4.95)	7.78(7.70)
	Br	Ni	NiTpOBP	42.33(42.39)	2.12(2.06)	4.26(4.12)
	Н	Cu	CuTpTP	78.79(78.70)	4.76(4.91)	7.69(7.65)
	Br	Cu	CuTpOBP	42.04(42.24)	2.17(2.05)	4.13(4.10)

^a Calculated values are given in parentheses.

3.1. Electronic spectra

The electronic spectra of the metal complexes were recorded in $CHCl_3$ at 298 K. The data are presented in Table 2. Some of the salient features associated with the electronic spectra are given below.

The Co(II), Ni(II) and Cu(II) porphyrins of the nonbrominated forms of the tetratolyl and tetranaphthyl porphyrins show characteristic absorption peaks of typical *meso*-aryl derivatives. We see that the B band of the naphthyl derivatives in all their metalloderivatives have absorptions at higher wavelength compared to their tolyl derivatives. However, we do not observe any perceptible difference in the absorption maxima for both B and Q bands among the various tolyl derivatives and also within the naphthyl species.

The cobalt(II) complexes of the brominated porphyrins manifest significant changes compared to their nonbrominated species. Both B and Q bands for the complexes are seen to be red-shifted compared to their nonbrominated derivatives. The red-shift $\Delta \bar{\nu}$ was calculated as the energy difference of the Soret band in wavenumbers between the complexes of brominated and nonbrominated porphyrins. The energy difference $\Delta \bar{\nu}$ for them is seen to be in the range $1915-2130 \text{ cm}^{-1}$, the naphthyl species having larger differences than the tolyl derivatives. As in the case of cobalt(II) derivatives, the nickel(II) species of all the brominated porphyrins also show red-shifted B and Q bands, which is evident from Table 2. The $\Delta \bar{v}$ for the B band for these complexes was found to be between 1770 and 1940 cm⁻¹ which is comparatively lower than that for their Co(II) derivatives.

In the case of Cu(II) bromoporphyrins, the expected red-shifts are also seen for both B and Q bands, but the significant feature, however, is the appearance of two overlapping peaks centered ca. 445 and 470 nm for the B band of the Cu(II) complexes of brominated porphyrins compared to their nonbrominated species. This phenomenon is not manifested by their analogous Ni(II) and Co(II) derivatives. In all the three metal derivatives, $\Delta \bar{v}$ is seen to be the lowest for the *ortho*-tolyl porphyrins and the highest for their naphthyl derivatives. The underlying factors involved in the above spectral features could be summarised as below.

The fact that the naphthyl porphyrins have a greater red-shifted Soret band as compared to the tolyl derivatives in all their Co(II), Cu(II) and Ni(II) complexes

Table 2

Electronic spectral data of Co(II), Ni(II) and Cu(II) derivatives of brominated and nonbrominated porphyrins in CHCl₃ at 298 K

Porphyrin	B band (nm) $(\varepsilon \times 10^{-4})^{a}$	Q band (nm) $(\varepsilon \times 10^{-4})^{a}$	$\Delta \bar{\nu} (\mathrm{cm}^{-1})^{\mathrm{b}}$
СоТоТР	409(19.95)	528(2.69)	
CoTmTP	412(21.38)	530(2.81)	
CoTpTP	412(20.89)	530(2.81)	
CoNaTP	414(20.42)	530(2.63)	
CoNβTP	416(20.89)	531(2.75)	
CuToTP	414(23.99)	537(2.39)	
CuTmTP	415(24.55)	538(2.51)	
CuTpTP	414(25.12)	540(2.51)	
CuNaTP	419(23.44)	541(2.39)	
CuNβTP	420(24.55)	542(2.34)	
NiToTP	415(16.22)	527(1.99)	
NiTmTP	416(16.98)	528(2.04)	
NiTpTP	417(17.38)	530(2.08)	
NiNaTP	419(16.60)	528(2.06)	
ΝίΝβΤΡ	420(16.98)	531(2.08)	
CoToOBP	445(16.60)	560(1.28)	1918
CoTmOBP	448(16.98)	562(1.35)	1950
CoTpOBP	450(17.38)	564(1.35)	2050
CoNaOBP	454(16.98)	565(1.31)	2128
CoNβOBP	454(16.98)	566(1.35)	2012
CuToOBP	446(13.18), 462(sh)	579(1.73) 624(sh)	1620, 2510
CuTmOBP	445(sh), 468(13.49)	581(1.77) 625(sh)	1725, 2729
CuTpOBP	448(sh), 469(13.80)	582(1.86) 628(sh)	1833, 2833
CuNaOBP	458(sh), 473(13.49)	583(1.82) 627(sh)	2032, 2725
CuNβOBP	467(13.50) (broad)	580(1.77) 627(sh)	2340
NiToOBP	448(24.55)	560(1.90)	1770
NiTmOBP	451(25.70)	561(1.95)	1920
NiTpOBP	451(26.30)	561(1.95)	1810
NiNαOBP	456(25.12)	563(1.99)	1940
ΝίΝβΟΒΡ	455(26.30)	563(1.95)	1800

^a Molar extinction coefficient ε in 10^{-4} /dm³ mol⁻¹ cm⁻¹.

^b $\Delta \bar{\nu} = \bar{\nu}_2 - \bar{\nu}_1$, where $\bar{\nu}_1$ is the energy of the B band for brominated porphyrin and $\bar{\nu}_2$ that for the corresponding nonbrominated porphyrin.

for both brominated and nonbrominated forms could be attributed to the higher mesomeric participation of the naphthyl moieties with the macrocyclic π -framework by adjusting the porphyrin-aryl dihedral angle. Because of a less extended π -system, the tolyl groups will have lesser conjugative participation with the porphyrin π -framework than their naphthyl analogues. The fact that all the metalloderivatives of o-tolyl porphyrins in their brominated and nonbrominated forms have their B and Q bands absorbing at lower wavelength could be attributed to the inability of the o-tolyl groups to tilt in order to reduce the dihedral angle for better conjugative interaction because of higher steric strain caused by -CH₃ groups at the ortho-position of the meso-tolyl moieties.

The pronounced red-shift observed for the Co(II), Ni(II) and Cu(II) derivatives of all the brominated porphyrins compared to their nonbrominated derivatives can be explained in terms of the electronic change caused by the electron-withdrawing Br-groups coupled with distortion of the porphyrin framework brought about by the bulky Br-atoms at the eight pyrrole β -positions [19,27,28]. The trend in the red-shift of B band observed for tolyl and naphthyl derivatives of the Br-substituted porphyrins is similar for their Co(II), Ni(II) and Cu(II) complexes and could be explained by considering the various factors which influence the energies of both the HOMO and LUMOs of the metalloporphyrins. It is evident that the eight Br substituents at the β -pyrrole positions would drain out electron density from the porphyrin - framework making the macrocycle more susceptible to reduction [19,27]. The concerted action by the electronegative Br atoms would also make the system resistant to oxidation. These would result in lowering of both LUMOs and the HOMO levels. One of the major factors for the red-shift of the porphyrins (in both B and Q) is essentially this electronic effect. Coupled with this electronic modulation there is also a significant effect due to a steric factor. The bulky Br-atoms at the eight pyrrole β-positions would bring about major structural distortion within the porphyrin framework to ease steric strain. Such a distortion would cause a significant pertur-

Table 3

	EPR spi	n-Hamiltonian	parameters of	copper(II)	derivatives of	of brominated	and n	onbrominated	porphyrins
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bation in conjugation, the effect of which would be signifalteration of π -energy levels including icant destabilisation of the HOMO and some lowering of the LUMOs. INDO level calculation has testified such a reordering in the energy levels of the frontier orbitals on distortion [29]. Because of the lowered symmetry the degenerate e_{σ}^{*} orbitals (LUMOs) can be expected to be split, lowering the energy of one component. A substantial reduction in the HOMO-LUMO gap is, therefore, expected because of such a geometry variation. The major red-shift observed on bromination can be attributed essentially to these factors.

It is known that while Co(II) and Ni(II) porphyrins show affinity to Lewis-bases and ligating solvents and coordinate them at the axial positions of the metal centre, while Cu(II) porphyrins exhibit no such tendency and remain unligated. We have verified this with Lewis-bases like pyridine and imidazole for all the MTxTP and MNxTP of nonbrominated porphyrins. We were, however, interested in knowing whether Cu(II) derivatives of bromoporphyrins would have any affinity towards Lewis-bases because of the strong electron accepting ability of the bromoporphyrinato framework (compared to the nonbrominated porphyrins). While Co(II) and Ni(II) derivatives of the bromoporphyrins were found to show enhanced affinity towards Lewisbases, their Cu(II) derivatives were still resistant to any adduct formation, as evident from practically no change seen in the electronic spectra even in an excess of base.

3.2. EPR spectra

The EPR spectra of all the Cu(II) porphyrins were measured at the X-band frequency to understand both the electronic and bonding features between the paramagnetic Cu(II) and the porphyrinato moiety. The spectra were recorded in a toluene-methanol mixture at liquid nitrogen temperature. While two hyperfine peaks of the parallel components of the anisotropic spectra are clearly discernible in the low field, the other two are seen overlapped in the perpendicular component. The spin

r K spin-manintoinan parameters of copper(n) derivatives of broininated and honoronininated porphythis								
Porphyrin	g_{\parallel}	g_{\perp}	$A_{\parallel}^{\mathrm{Cu}}\left(\mathrm{mT} ight)$	A_{\parallel}^{N} (mT)	A_{\perp}^{Cu} (mT)	A_{\perp}^{N} (mT)	α^2	
CuToTP	2.21	2.07	20.3	1.5	3.3	1.47	0.564	
CuTmTP	2.21	2.07	20.0	1.5	3.3	1.48	0.555	
CuTpTP	2.20	2.07	19.8	1.5	3.0	1.48	0.550	
CuNαTP	2.20	2.07	20.0	1.5	3.5	1.47	0.555	
CuNβTP	2.21	2.07	20.0	1.5	3.3	1.48	0.555	
CuToOBP	2.21	2.05	19.1	n.r ^a	3.1	1.50	0.532	
CuTmOBP	2.22	2.06	19.0	n.r ^a	3.0	1.51	0.528	
CuTpOBP	2.20	2.07	19.3	n.r ^a	3.0	1.52	0.535	
CuNαOBP	2.22	2.05	19.1	n.r ^a	3.1	1.51	0.535	
CuNβOBP	2.21	2.05	19.1	n.r ^a	3.1	1.51	0.532	

^a Not resolvable.

Hamiltonian parameters for the copper(II) compounds were extracted from the spectra by a known procedure [30], by considering the axial symmetry of the metalloporphyrins. The value of α^2 (σ -covalency factor) was also evaluated from the EPR parameters using the Kivelson and Neiman equation [31], $\alpha^2 = (A^{\parallel}/P +$ $(g_{\parallel} - 2.0023) + 3/7(g_{\perp} - 2.0023) + 0.04)$, where P is the spin-orbit coupling factor. It is known that metalloporphyrins are sensitive to the molecular environment around them. This has been well demonstrated by the difference in electronic spectra observed for these complexes. The EPR data also yield similar results, as exemplified by the variations in the spin Hamiltonian parameters for Cu(II) in different molecular environments. The various parameters evaluated for the Cu(II)-porphyrins are presented in Table 3.

The g_{\parallel} and g_{\perp} values, along with other parameters, are in conformity with a square planar geometry for all the brominated and nonbrominated copper(II) porphyrins studied [32,33]. The nature of the meso-aryl substituents is not seen to be affecting these parameters significantly. However, the hyperfine constants A_{\parallel}^{Cu} and A_{\perp}^{Cu} are found to be altered considerably in copper(II) bromoporphyrins compared to their nonbrominated porphyrins. All the brominated porphyrins have A_{\parallel}^{Cu} around 19 mT which is less than their nonbrominated porphyrins (A_{\parallel}^{Cu} ca. 20 mT). Similarly the A_{\perp}^{Cu} are found to be lowered from ca. 3.5 mT to ca. 3 mT on bromination. The lower Cu-hyperfine values seen for the copper(II) bromoporphyrins can be understood from the fact that the porphyrinato moiety, being depleted in electron density by the eight peripheral Br atoms, would withdraw electron density from the metal $d_{x^2-v^2}$ orbital thus delocalising the free electron significantly onto the ligand moiety compared to the Cu(II)-nonbrominated porphyrins. The higher Cu-hyperfine constants found for the metal derivatives of nonbrominated porphyrins implies more delocalisation of the unpaired Cu electron.

The α^2 value evaluated from the spin Hamiltonian parameters represents the bonding coefficient of the b_1 molecular orbital (which is a linear combination of metal $d_{x^2-y^2}$ and four in plane sp² hybridised orbitals of the porphyrinato moiety, one on each of the N atoms) and gives a qualitative idea about the measure of σ -covalency of the Cu–N bond. The stronger the in-plane σ -bond interaction between Cu²⁺ and N's, the higher is the energy of the b_1 molecular orbital because of its antibonding character. The α^2 values evaluated for all the Cu(II)-nonbrominated porphyrins are in the range 0.555–0.564, showing that the *meso*substituents have little influence on the nature of the M–N covalent bonding. However, in the case of the brominated species, the α^2 values are lowered to 0.528 indicating more σ -covalency between copper and nitrogen facilitated by the electron-withdrawing Br substituents, which are in direct interaction with the porphyrin π -system.

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