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Spectral, magnetic and electrochemical properties of metal oxa- and oxathia-porphyrins †

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Metal derivatives (Cu^{II}, Ni^{II}) of monooxa-, dioxa- and oxathia-tetraphenylporphyrins and their one-electron oxidised and reduced species have been studied. Electronic spectra of the monooxa and oxathia derivatives exhibit split Soret bands and a complicated pattern of Q-bands revealing their lower symmetry. The spectra of one-electron reduced species show only marginal shifts while the one-electron oxidised product of copper monooxaporphyrins show broad, red-shifted bands. Cyclic voltammetric studies indicated one-electron metal-centered reduction at fairly low potentials forming copper(I) and nickel(I) porphyrins. The ring-oxidised product exhibits weak antiferromagnetic interaction between the unpaired electrons of copper and the porphyrin ring. The ESR spectra of the copper dioxa- and oxathia-porphyrins exhibit rhombic symmetry with unusually small metal hyperfine couplings. A comparison of A^{Cu} values and the $E_{\frac{1}{2}}$ values for metal reduction suggests that distortion towards tetrahedral symmetry and the presence of a soft donor atom like sulfur in porphyrins are required to generate spectral and electrochemical properties like those observed for the type I copper center in proteins.

Replacement of pyrrole N atoms in the porphyrin core by other heteroatoms such as S, Se, Te and O alters the core sizes and electronic structure.[1,2] Recent studies on these systems have resulted in the synthesis of diverse porphyrins such as tetrathiaporphyrin dication,[3] tetraoxaporphyrin dication,[4] tetraoxa[22]porphyrin[5] and tetraoxa[26]porphyrin dications ([22] and [26] refer to the number of π electrons),[6] dithia-, diselena-, monothia-, monoselena- and monotellura-porphyrins.[1,2] The tetrathia and tetraoxa derivatives cannot bind metal ions because of their dicationic nature while metal complexes of dithia and diselena derivatives have not been reported. However, monothiaporphyrin forms complexes with metal ions such as Fe^{II}, Cu^{II}, Ni^{II} and Rh^{II}, *etc.*;[7,8] only the nickel(II) complex of monoselenaporphyrin has been reported.[9] The crystal structure of nickel(II) thiaporphyrin revealed a distorted square pyramid around the metal with an axial chloride ligand, leading to five-co-ordination.[7,8] The unique feature of the structure is the co-ordinated thiophene ring which is bent out of the plane of the remainder of the ligand core and bound to the metal in a η^1 fashion. Further, it has been shown that the derivatives of Cu^{II} and Ni^{II} undergo one-electron metal-centered reduction[10] to form the corresponding complexes of Cu^I and Ni^I and the nickel(I) ion has a nearly planar geometry and surprisingly short Ni–N and Ni–S bonds.[11]

However, relatively few reports[2] exist on the synthesis of oxaporphyrins and mixed oxathiaporphyrins in which one or more pyrrole rings have been replaced by furan rings and/or thiophene rings. To the best of our knowledge there are only two recent reports on the metal (Ni^{II}) binding properties of oxaporphyrins by Latos-Grazynski and co-workers[12] and Gross *et al.*[13] Both monooxa- and dioxa-porphyrins form nickel(II) complexes, which can easily be reduced to the corresponding nickel(I) derivative and the crystal structures reveal a nearly in-plane co-ordination of the furan moiety as opposed to the side-on co-ordination observed for the thiophene and selenophene porphyrins.[7] We have been interested in the core modification of tetraarylporphyrins and our earlier studies on thiaporphyrins have revealed many interesting similarities and differences in optical, electrochemical and photochemical properties.[14] Further, our recent study[15] on free base oxa- and oxathia-porphyrins revealed that the oxaporphyrins behave more like the parent tetraphenylporphyrin in their spectroscopic properties while their electrochemical properties resemble those of thiaporphyrins.

In this paper we report the metal binding (Cu^{II} and Ni^{II}) properties of monooxa-, dioxa- and oxathia-porphyrins and their one-electron reduced and oxidised species. Specifically, electronic absorption spectra have been used to study ground-state properties while the redox chemistry has been monitored by cyclic voltammetry. The changes occurring in the electron delocalisation pathway and the metal–ligand bond strength upon binding of Cu^{II} have been studied by ESR spectroscopy. It has been shown that the first reduction is metal centered, corresponding to the formation of complexes of Cu^I and Ni^I, while the first oxidation of copper monoxaporphyrins is ring based with a weak antiferromagnetic coupling between the metal and the ring unpaired electrons.

Results

The metallation of oxaporphyrins can readily be done using literature methods.[12] The copper(II) and nickel(II) derivatives of monooxa and monothia derivatives are stable both in the solid and solution states, the dioxa derivative on a chromatographic column undergoing gradual demetallation while the oxathia derivative on standing for few hours in the solid decomposes to give the corresponding free base porphyrin. The electronic absorption spectra of various neutral, one-electron-reduced and -oxidised copper oxaporphyrins are shown in Fig. 1 and the data are in Table 1. In general, the optical bands are red shifted both in the Soret and Q-band region relative to the parent [M(tpp)] (M = Cu or Ni) and the magnitude of the shifts are smaller for oxaporphyrins compared to their thiaporphyrin counterpart.[14] The ε values are significantly reduced for the core-modified porphyrins relative to the parent [M(tpp)].[16]

The EPR spectra of the copper porphyrins described here were recorded in toluene–CH_2Cl_2 (1 : 1) at room and liquid nitrogen temperature. Fig. 2 compares room temperature spectra of $[CuL^S(Cl)]$ and $[CuL^O(Cl)]$. Only the former exhibited superhyperfine couplings from the co-ordinated nitrogens at room temperature. However, at low temperature, these couplings are observed for monooxaporphyrins while the

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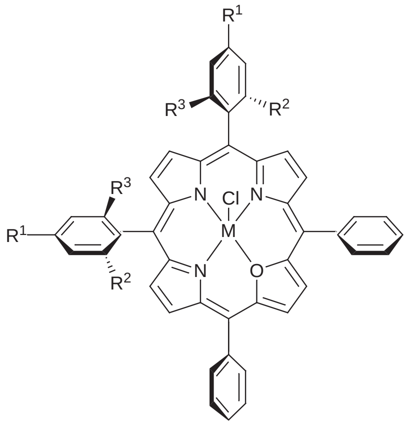
† *Non-SI units employed*: G = 10^{-4} T, $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

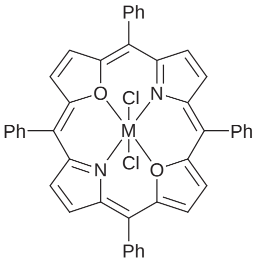
Table 1 Electronic spectral data of various copper and nickel porphyrins in CH_2Cl_2

	λ_{max}/nm (10^{-4} ε/M^{-1} cm^{-1})				
Porphyrin	Soret band		Q-bands		
$[CuL^S(Cl)]$	463 (8.5)	429 (9.2)	705 (5.4)	557 (12.2)	—
$[CuL^O(Cl)]$	430 (7.0)	416 (7.9)	625 (1.4)	572 (6.3)	534 (8.0)
$[CuL^{O,Me}(Cl)]$	434 (11.5)	421 (10.1)	634 (2.1)	575 (7.1)	538 (9.3)
$[CuL^{O,OMe}(Cl)]$	436 (5.5)	—	639 (1.9)	580 (4.5)	542 (5.9)
$[CuL^{O,Br}(Cl)]$	434 (10.6)	418 (7.0)	636 (3.0)	579 (8.2)	538 (10.9)
$[CuL^{2O}Cl_2]$	417 (7.6)	—	670 (3.0)	600 (2.6)	507 (8.1)
$[CuL^{OS}Cl_2]$	454 (12.4)	437 (12.5)	688 (12.6), 644 (13.2), 578 (11.9), 538 (14.4)		
$[NiL^S(Cl)]$	466 (8.0)	428 (17.6)	710 (6.9), 675 (7.0), 612 (8.8), 547 (11.6), 511 (22.7)		
$[NiL^O(Cl)]$	428 (8.6)	416 (8.4)	738 (1.6), 707 (1.7), 633 (2.8), 579 (8.6), 551 (7.6)		
$[NiL^{2O}Cl_2]$	417 (13.5)	—	688 (4.6), 665 (4.5), 604 (4.1), 504 (14.0)		



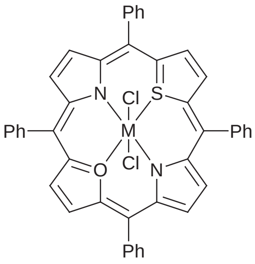
Monooxaporphyrin

R^1	R^2	R^3	$M = Cu^{2+}$	$M = Ni^{2+}$
H	H	H	$[CuL^O(Cl)]$	$[NiL^O(Cl)]$
Me	H	H	$[CuL^{O,Me}(Cl)]$	
OMe	H	H	$[CuL^{O,OMe}(Cl)]$	
Br	H	H	$[CuL^{O,Br}(Cl)]$	



Dioxaporphyrin

$M = Cu^{2+}$ $[CuL^{2O}Cl_2]$
$M = Ni^{2+}$ $[NiL^{2O}Cl_2]$



Oxathiaporphyrin

$M = Cu^{2+}$ $[CuL^{OS}Cl_2]$

Table 2 Spin Hamiltonian parameters evaluated from ESR spectra for various copper porphyrins

Porphyrin	$A_{\parallel}^{Cu}$	$A_{\perp}^{Cu}$	$A_{\perp}^{N}$	$g_{\parallel}$	$g_{\perp}$	α^2
[Cu(tpp)]	209	32.8	16.4	2.1870	2.032	0.8277
$[CuL^S(Cl)]$	159	28.4	14.2	2.2120	2.056	0.7218
$[CuL^O(Cl)]$	118	25.7	12.9	2.2493	2.036	0.6540
$[CuL^{O,Me}(Cl)]$	115	25.5	12.7	2.2506	2.042	0.6528
$[CuL^{O,OMe}(Cl)]$	114	27.2	13.6	2.2561	2.040	0.6535
$[L^{O,Br}(Cl)]$	110	n.r.	n.r.	2.2569	2.036	0.6390
	A_{xx}	A_{yy}	A_{zz}	g_{xx}	g_{yy}	g_{zz}
$[CuL^{2O}Cl_2]$	75	30	102	2.01	2.08	2.29
$[CuL^{OS}Cl_2]$	78	29	99	2.01	2.085	2.31

The A values are in 10^{-4} cm^{-1}. n.r. = Not resolved.

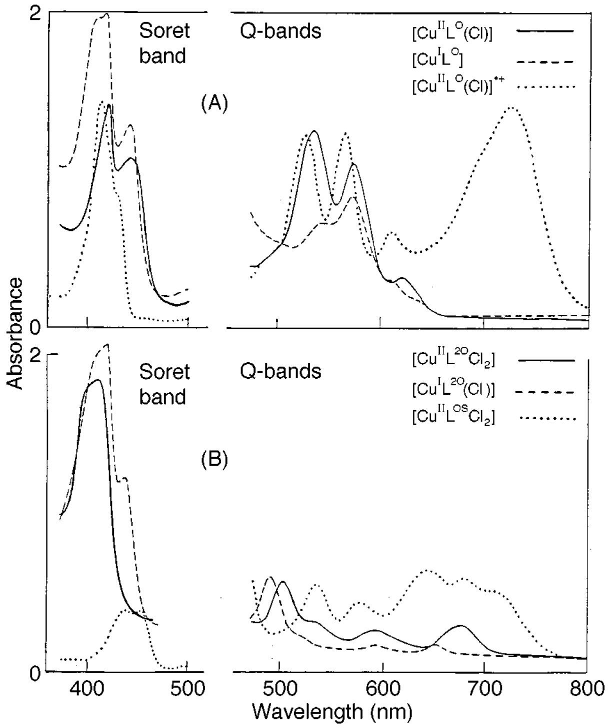


Fig. 1 Electronic absorption spectra of (A) copper monooxa derivatives and their one-electron-oxidised and -reduced species in CH_2Cl_2. The concentrations used were: Soret band, 2.6×10^{-6}; and Q-bands, 2.6×10^{-5} M. (B) Copper dioxa and oxathia derivatives and one-electron-reduced copper dioxaporphyrin in CH_2Cl_2; concentrations as in (A)

dioxa- and oxathia-porphyrins did not show any superhyperfine couplings in frozen solution or in the solid diluted in a diamagnetic matrix (free base dioxaporphyrin) even at low temperature (Fig. 3). The spin Hamiltonian parameters[17] evaluated from the observed spectra are listed in Table 2. In general, the EPR spectra reveal the presence of a distorted tetragonal copper site[17,18] in the monooxa derivative while the dioxa and oxathia derivatives show rhombic spectra. Replacement of a N-donor atom of a pyrrole ring by O or S results in a decrease in the A^{Cu} values with a concomitant increase in g values.[19] The nitrogen superhyperfine splittings observed for some derivatives show only a minor variation on going from [Cu(tpp)] to its oxa and thia derivatives, suggesting a predominantly isotropic interaction.[17,18]

Cyclic voltammetric studies in CH_2Cl_2 containing NBu_4ClO_4 as the supporting electrolyte show one-electron quasi-reversible (ΔE_p 90–140 mV) reduction at fairly low potentials except for $[NiL^O(Cl)]$ and $[CuL^{OS}Cl_2]$ which show irreversible reduction. Fig. 4 compares cyclic voltammograms of $[NiL^S(Cl)]$, $[CuL^S(Cl)]$ and $[CuL^O(Cl)]$. In all the cases the separation between the anodic and cathodic peaks was dependent on the

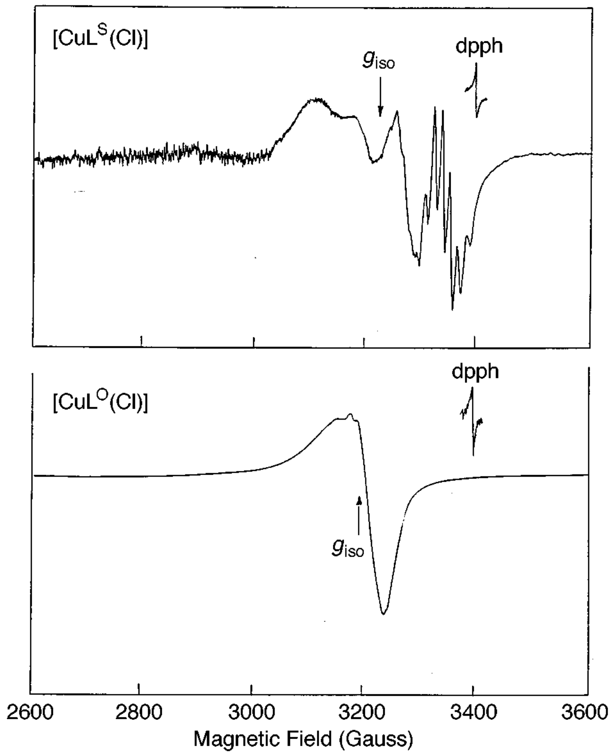


Fig. 2 Room temperature EPR spectra of copper monooxa (L^O) and monothia (L^S) complexes in toluene–CH_2Cl_2 (1 : 1). The concentrations used were ≈10^{-3} M; dpph = diphenylpicrylhydrazyl

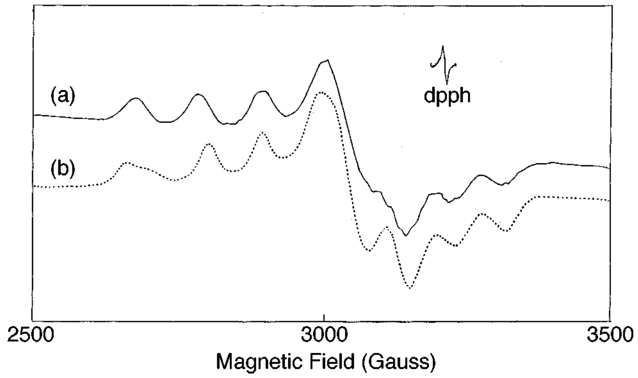


Fig. 3 (a) The EPR spectrum of copper dioxaporphyrin frozen in toluene–CH_2Cl_2 (1 : 1). The concentration used was ≈10^{-3} M. (b) Simulated spectrum; spin Hamiltonian parameters in Table 2

Table 3 Reduction potential for the M^{II}–M^{I} coupling for various copper and nickel porphyrins

Porphyrin	$E_{\frac{1}{2}}(M^{II}–M^{I})$/V	ΔE_p/mV
$[CuL^S(Cl)]$	−0.05	130
$[CuL^O(Cl)]$	−0.22	131
$[CuL^{O,Me}(Cl)]$	−0.24	145
$[CuL^{O,OMe}(Cl)]$	−0.25	118
$[CuL^{O,Br}(Cl)]$	−0.24	114
$[CuL^{2O}Cl_2]$	−0.37	105
$[CuL^{OS}Cl_2]$	−0.11	294
$[NiL^S(Cl)]$	−0.06	106
$[NiL^O(Cl)]$	−0.42	350
$[NiL^{2O}Cl_2]$	−0.36	97

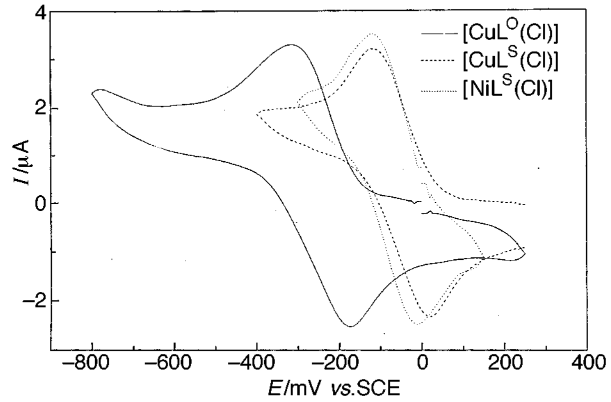


Fig. 4 Cyclic voltammograms of copper monooxa-, monothia- and nickel monothia-porphryins in CH_2Cl_2 recorded at 100 mV s^{-1} scan speed; 0.1 M NBu_4ClO_4 was used as the supporting electrolyte in CH_2Cl_2

scan rate and an illustration of this effect for $[CuL^{OS}Cl_2]$ along with cyclic voltammograms of the dioxa derivatives of Cu^{II} and Ni^{II} are shown in Fig. 5. The half wave potentials (Table 3) evaluated for this reduction in all the cases are outside the range accessible to porphyrin ring reduction in the same solvent. For example, the first ring reductions of the free oxa, dioxa and oxathia base derivatives fall in the range −0.90 to −1.20 V.[15] Based on earlier work on thiaporphyrins from this laboratory[14] and others[7] and the electronic spectra of the ring-reduced products,[20] this reduction is assigned to the metal-centered reduction corresponding to the formation of porphyrins of Cu^{I} and Ni^{I}. It is pertinent that Latos-Grazynski and co-workers[12] have recently isolated the nickel(I) complexes of oxa- and dioxa-porphyrins.

The chemical oxidation of copper(II) monooxa derivatives with a one-electron oxidant leads to the formation of ring-oxidised products and the absorption spectra exhibit the changes which would be expected upon ring oxidation[20] [Fig. 1(A)]. The oxidised species are EPR silent both in the solid and solution state at room temperature suggesting their diamagnetic nature. Repeated magnetic susceptibility measurements at room temperature show a small magnetic moment in the range 0.8–1.1 μ_B suggesting a weak antiferromagnetic interaction. This value may be contrasted with 2.40 μ_B measured for [Cu(tpp)] radical cation in CD_2Cl_2.[21] A recent study from this laboratory on a distorted copper(II) porphyrin cation radical also showed an antiferromagnetic interaction between the two unpaired electrons of the metal and ring both in the solid and solution state.[22] Chemical oxidation of $[CuL^{2O}Cl_2]$ and $[CuL^{OS}Cl_2]$ resulted in demetallation leading to free base dications as revealed by the absorption spectra.

Discussion

Electronic absorption spectra

The absorption spectra of the metal oxa and thia derivatives show characteristic Soret and Q-bands in the region 400–800 nm.[16] The monooxa, monothia and oxathia derivatives exhibit split Soret bands and a complicated pattern of Q-bands, unlike [M(tpp)] (M = Cu or Ni), revealing their lower symmetry. On the other hand, the spectra of metal dioxaporphyrins are not too much different from those of the corresponding free base derivatives.[15] The one-electron-reduced species show small blue shifts of absorption bands while the one-electron-oxidised $[CuL^O(Cl)]$ exhibits significant changes. This is not surprising considering the fact that the first ring reduction involves the metal center and on going from M^{II} to M^{I} the porphyrin ring does not undergo any major change in its π-electron conjugation. On the other hand, the oxidation of the porphyrin ring affects the porphyrin π-electron conjugation because of the removal of an electron from the π system[10,20] and is expected to show broad red-shifted Q-bands and the Soret band as observed. The ε values of the metal derivatives are about 50% smaller than those of the corresponding free base derivatives, suggesting a decreased π-electron conjugation upon metal

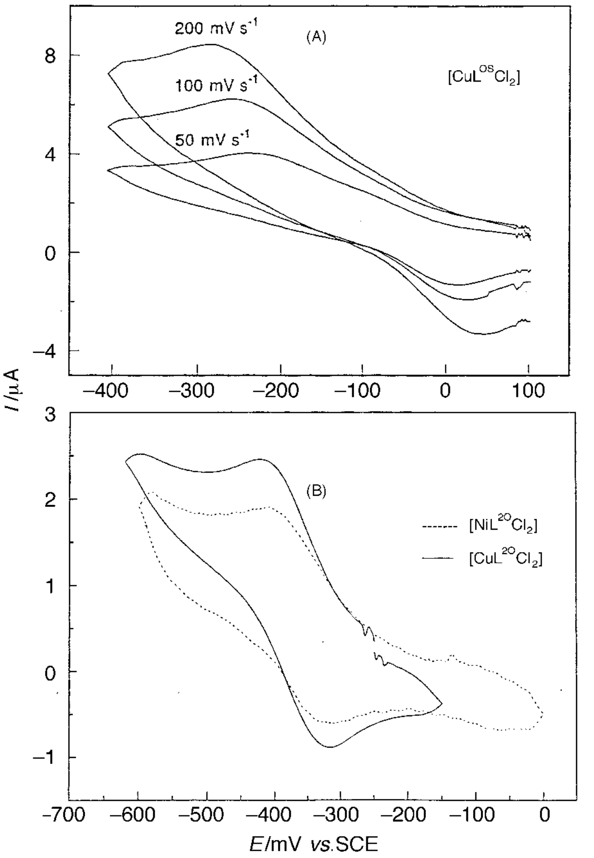


Fig. 5 Cyclic voltammograms of (A) the copper oxathiaporphyrin in CH_2Cl_2 at various scan speeds. (B) Comparison of cyclic voltammograms of copper and nickel dioxaporphyrins in CH_2Cl_2 at scan speed 200 mV s^{-1}

interaction. This probably is due to the distorted geometry of the porphyrin ring around the metal (see below).

ESR spectra

The spread of g values, $g_{\parallel}$ in particular, for CuX_4 systems with X = S, O and N is well documented.[19,23] Generally, the $g_{\parallel}$ values decrease and increase respectively for X = S and O donors relative to X = N. This has been interpreted in terms of the relative hard and soft nature of the donor atoms.[24] Thus, on going from CuN_4 to CuN_3S for a monothiaporphyrin the value is expected to decrease slightly if the core structure around the metal remains square planar in CuN_3S. However, the $g_{\parallel}$ value increases slightly ($\Delta g_{\parallel} = 0.025$) for CuN_3S suggesting a distortion from the regular planar geometry. The dioxa and the oxathia derivatives result in further distortion around the metal centre and the lower symmetry is reflected in the rhombic spectra observed for these complexes.

The decrease in the A values has been attributed to the direct mixing of 4s metal orbitals with the ground state of Cu^{II} caused by the symmetry lowering.[7] This is substantiated by recent work of Solomon and co-workers[25] on the reduced and oxidised site of blue copper proteins. They have ascribed the small EPR hyperfine splittings observed for the oxidised form of blue copper proteins to the extremely high covalency of the copper $3d_{x^2-y^2}$ HOMO which is highly anisotropic with 42% Cu and 36% S (cysteine) and <2% on each histidine nitrogen. It has been shown that only the mixing of the unoccupied 4s/4p orbitals and the half occupied copper $3d_{x^2-y^2}$ orbital with the filled ligand levels contributes to the strength of the individual Cu–L bonds. In the present study the changes occurring upon distortion can at least be evaluated for the Cu–N in-plane σ bond through the covalency factor α^2 which represents the bonding coefficient of the b_1 molecular orbital.[18] The stronger the in-plane σ bond between the Cu^{II} and N, the higher is the

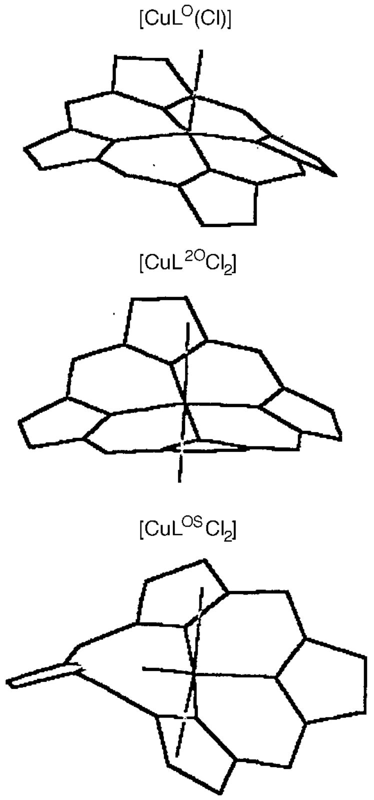


Fig. 6 Calculated optimised structures of [CuL^{O}(Cl)], [CuL^{2O}Cl$_2$] and [CuL^{OS}Cl$_2$]. The *meso* phenyl rings are omitted for clarity

energy of the b_1 molecular orbital because of its antibonding character. The gradual decrease in the value of α^2 observed on distortion (Table 2) suggests a lowering of the energy of the b_1 molecular orbital relative to that of [Cu(tpp)] and a weaker Cu–N σ bond in the distorted porphyrins. Strong support for such a conclusion comes from (a) the observed small decrease in $A_{\perp}^{N}$ values for copper(II) monooxaporphyrins relative to [Cu(tpp)] and (b) comparison of measured bond distances for Cu–N in [Cu(tpp)][26] [1.981(7) Å] and [CuL^{S}(HCO$_3$)][7] (1.993, 2.042 and 2.067 Å).

The energy-optimised structures calculated for the monooxa, dioxa and oxathia copper(II) derivatives shown in Fig. 6 further confirm the existence of distortion. However, it should be pointed out that the geometry-optimised structures give only a rough idea about the geometry around the metal centre and this should be taken as a qualitative explanation. A comparison of structures revealed maximum distortion for the oxathia derivative which is not surprising because of the different co-ordination modes of thiophene sulfur and furan oxygen. It is known from the crystal structures reported for nickel(II) complexes of thia- and oxa-porphyrins that the furan oxygen co-ordinates in a η^1 fashion without serious distortion while the thiophene sulfur is bent out of the plane of the porphyrin ring upon co-ordination.[11] However, the observed distortion for [CuL^{2O}Cl$_2$] is surprising in view of the reported structure of [NiL^{2O}Cl$_2$] which shows a pseudo-octahedral geometry in which the pyrrole and furan rings are coplanar. It is possible that Cu^{2+} being a Jahn–Teller ion can still be distorted and this is not expected for the corresponding nickel(II) derivative. The observation that the Soret band of [CuL^{2O}Cl$_2$] is broad compared to that of [NiL^{2O}Cl$_2$] probably suggests a lower symmetry in the copper(II) complexes. Only crystal structures can confirm this point.

Electrochemical studies

The electrochemical data of the complexes establish the presence of one-electron metal-centered reduction in each case and the reduction potentials are raised to more positive values by partial replacement of N-donors by S and/or O. However, the individual $E_{\frac{1}{2}}$ values vary depending on the metal and the number and nature of the donor atoms. For the copper porphyrins, $E_{\frac{1}{2}}$ varies as $[CuL^S(Cl)] > [CuL^O(Cl)] > [CuL^{2O}Cl_2]$ while for the nickel porphyrins $[NiL^S(Cl)] > [NiL^{2O}(Cl)] > [NiL^O(Cl)]$. In both cases the thiaporphyrins show more positive values compared to those of the oxaporphyrins. This establishes that the presence of a soft donor atom like S may be one of the factors responsible for the more positive values by stabilisation through its π-acceptor capability.[23,27] Comparison of Ni–S bond distances measured from the crystal structures of thiaporphyrins of Ni^{II} and Ni^I establishes this possibility (Ni^{II}–S 2.296 and Ni^I–S 2.143). If, on the other hand, the magnitude of distortion towards tetrahedral geometry is the only deciding factor for the more positive $E_{\frac{1}{2}}$ value, then $[CuL^{2O}Cl_2]$ and $[CuL^{OS}Cl_2]$ would be expected to show more positive $E_{\frac{1}{2}}$ values relative to the others. Since the measured $E_{\frac{1}{2}}$ values do not show this trend, clearly both the geometrical changes upon reduction and the nature of the donor atom in the porphyrin core are important in deciding the magnitude of $E_{\frac{1}{2}}$ for the M^{II}–M^I couple. This is further substantiated by the conclusions of Solomon and co-workers[25] in their electronic structure studies on the reduced and oxidised site of blue copper proteins. It has been pointed out that the two factors which are important for high reduction potentials are: (a) the weakening of the copper–thioether axial bond in the oxidised state and (b) the formation of a strong copper–thiolate equatorial π bond through the overlap of π orbitals on S with the $3d_{x^2-y^2}$ orbital on Cu. However, it should be mentioned that recent work on bis(pyrazole) complexes of Cu^{II} with only N and O donors also revealed high reduction potentials for the Cu^{II}–Cu^I couple and this has been explained on the basis of the availability of an appropriate ligand geometry for stabilisation of Cu^I.[28]

In general, the reversibility of the M^{II}–M^I couple depends on the structural change accompanying the reduction process.[29] If no hindrance is expected to the adoption of a tetrahedral stereochemistry upon reduction, then the redox couple exhibits Nernstian behaviour, while any structural change such as ligand loss or ligand substitution under the reaction conditions results in a quasi-reversible or irreversible couple. For example, the irreversible nature of $[Cu(Me_4cyclam)]^{2+}$ (Me_4cyclam = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) reduction is associated with ligand substitution in the reduced form, while the reversible nature of the $[Cu(dth)_2]^{2+}$–$[Cu(dth)_2]^+$ (dth = 2,5-dithiahexane) couple is assigned to the adoption of tetrahedral symmetry without hindrance.[19,23] The deviation from the electrochemical reversibility of porphyrin complexes of Cu and Ni observed in the present study suggests that the M^{II}–M^I reduction is accompanied by a relatively slow structural rearrangement because of the macrocyclic constraints. That the peak separation depends on the scan rate further justifies such a conclusion.

Magnetic studies

Earlier magnetic studies[21,30] on the $[Cu(tpp)]^{\bullet +}$ radical indicate that the radical cation is completely diamagnetic in the solid state and paramagnetic ($S = 1$) in solution. The diamagnetism in the solid was explained on the basis of the dimeric nature of the radical cation and the crystal[21] structure reveals the presence of a ruffled core which removes the orthogonality between the metal $d_{x^2-y^2}$ orbital and the porphyrin a_1 (π) orbital, facilitating d–π coupling. However, in solution, it was assumed that $[Cu(tpp)]^{\bullet +}$ is monomeric with a planar core where a strict orthogonality of magnetic orbitals prevents d–π coupling. The observed weak antiferromagnetic coupling for the copper monooxa radicals here again supports the presence of distorted cores at the metal both in solution and in the solid as revealed by EPR spectra.

Conclusion

It has been demonstrated that the core-modified oxa- and oxathia-porphyrins bind metal ions and their spectral and electrochemical properties parallel those observed for the thiaporphyrins. The metallation of oxathiaporphyrin establishes the co-ordination of pyrrole nitrogen, thiophene sulfur and furan oxygen in a single porphyrin unit. The unusually small A^{Cu} values observed for $[CuL^{2O}Cl_2]$ and $[CuL^{OS}Cl_2]$ represent the lowest values observed to date for any copper(II) porphyrin. Furthermore, this study has demonstrated that the maximum distortion towards tetrahedral symmetry does not necessarily shift the reduction potential for the M^{II}–M^I couple to more positive values at least for porphyrin systems, and the presence of a soft donor atom is necessary to generate the low A^{Cu} values and the more positive reduction potentials observed for blue copper proteins. Probably the copper(II) complex of a dithiaporphyrin could highlight this observation. Unfortunately, the dithiaporphyrin reported in which the two thiophene rings are opposite to each other does not form a copper(II) complex. Currently, we are exploring the synthesis of core-modified expanded porphyrins in which a CuN_2S_2 co-ordination geometry can be achieved.

Experimental

Syntheses of complexes

Free base oxa- and dioxa-porphyrins were prepared and characterised following the reported procedure[2c,12] and the oxathiaporphyrin was prepared and characterised as described in our earlier work.[15] All the chemicals used for the syntheses were reagent grade unless otherwise specified. Solvents for spectroscopic measurements were purified and dried according to the standard methods.

$[CuL^O(Cl)]$. A solution of $CuCl_2 \cdot 2H_2O$ (0.040 g, 1.173 mmol) in ethanol (5 cm^3) was added to a solution of 5,10,15,20-tetraphenyl-21-oxaporphyrin (0.030 g, 0.048 mmol) in dichloromethane (50 cm^3) and the mixture refluxed for 3 h with stirring. It was cooled and then the solvent was removed under reduced pressure. The solid was dissolved in dichloromethane and washed several times with water. The organic fraction was dried over anhydrous sodium sulfate and chromatographed on a basic alumina column using dichloromethane–methanol (95 : 5). The first fraction was identified as free base and the metallated porphyrin was eluted next with dichloromethane–methanol (90 : 1). The solid obtained after evaporation of solvent under reduced pressure was dried in vacuum which gave pure $[CuL^O(Cl)]$ (0.027 g, 79%). FAB mass spectrum: m/z 678 ($M - Cl$) (calc. 678.27) (Found: C, 74.4; H, 3.8; N, 5.5. $C_{44}H_{28}ClCuN_3O$ requires C, 74.04; H, 3.95; N, 5.88%). A similar procedure was followed for other copper(II) monooxaporphyrins.

$[CuL^{2O}Cl_2]$. A solution of $CuCl_2 \cdot 2H_2O$ (0.030 g, 0.879 mmol) in ethanol (5 cm^3) was added to a solution of 5,10,15,20-tetraphenyl-21,23-dioxaporphyrin (0.040 g, 0.065 mmol) in dichloromethane (50 cm^3) with stirring. The mixture was heated under reflux for 8 h. It was cooled and the solvent removed under reduced pressure. The solid was washed with water till the filtrate was colourless, then extracted with dichloromethane and the solution concentrated. An equal volume of hexane was added and kept for crystallisation. Attempted purification by column chromatography using alumina resulted in demetallation. The solid residue was separated by filtration which gave the pure product $[CuL^{2O}Cl_2]$ (0.022 g, 46.1%). FAB mass spectrum: m/z 680 ($M - 2Cl$) (calc. 680.26) (Found: C, 70.1; H, 3.5; N, 3.6. $C_{44}H_{28}Cl_2CuN_2O_2$ requires C, 70.35; H, 3.72; N, 3.75%).

$[CuL^{OS}Cl_2]$. This complex was prepared using the same procedure as above. When kept for a long time even in the solid state slow demetallation of copper to form the free base occurred. Attempts to record the FAB mass spectrum resulted in demetallation giving the free base. Combustion analysis also indicated demetallation. Only UV/VIS and ESR spectra were used to infer the formation of [CuL^{OS}Cl$_2$].

[CuL^{O}(Cl)]$^{\bullet+}$[SbCl$_6$]$^-$. The complex [CuL^{O}(Cl)] (0.010 g, 0.014 mmol) in dichloromethane (10 cm^3) was stirred for 10 min under argon and 1.1 equivalent of tris(*p*-bromophenyl)-ammonium hexachloroantimonate (0.012 g, 0.015 mmol) solution in dichloromethane (5 cm^3) was added and stirred for about 3 h. The progress of the reaction was monitored by checking the absorption spectra at different time intervals. After completion of the reaction the solution was filtered, solvent evaporated under reduced pressure and the product obtained recrystallised from dichloromethane–hexane (yield 0.010 g, 80%) (Found: C, 50.34; H, 2.51; N, 4.35. $C_{44}H_{28}Cl_7$-CuN_3OSb requires C, 50.42; H, 2.69; N, 4.01%).

The nickel(II) derivatives of the monooxa- and dioxa-porphyrins were prepared following the reported procedure.[12]

Measurements

The electronic spectra were recorded on a Shimadzu UV-160 spectrophotometer, proton NMR spectra on a Bruker 200 MHz spectrometer. Analyses (C, H, N) were done on a Heraeus Carlo Erba 1108 elemental analyser. The FAB mass spectra were recorded using a JEOL SX-120/DA6000 spectrometer with Ar as the FAB gas, ESR spectra on a Varian E-109 X-band spectrometer at room and liquid nitrogen temperature. Cyclic voltammetric and controlled potential coulometric studies were done on a EG/G Par model 273A polarographic analyser interfaced to a computer. A three-electrode system consisting of a platinum working electrode, a platinum-mesh counter electrode and a commercially available saturated calomel electrode (SCE) as the reference electrode were used. This reference electrode was separated from the bulk of solution by a fritted glass bridge filled with the solvent–supporting electrolyte mixture. Half-wave potentials were measured as the average of the cathodic and anodic peak potentials. Solid-state magnetic susceptibility measurements were done by the Faraday technique using a locally built magnetometer. The set-up consisted of an electromagnet with constant-gradient pole gaps (Polytronic Corporation, Bombay, India) and a Sartorius M25-D/S balance (Germany). The system was calibrated using Hg[Co(SCN)$_4$]. Susceptibilities were corrected for diamagnetic contribution. The energy-optimised structures were calculated using HYPERCHEM version 5.0 software[31] on a Pentium 120 MHZ personal computer. A MM$^+$ force field was employed with the use of the Polare-Ribere conjugated gradient with convergence limit at 0.001.

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