

# Effect of peripheral substitution on spectral and catalytic properties of copper phthalocyanine complexes

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## Abstract

The effect of peripheral substitution on the spectral and catalytic properties of copper phthalocyanine complexes has been investigated. The complexes were characterized by elemental analysis, FT-IR, UV–VIS and electron paramagnetic resonance (EPR) techniques. The EPR spectra of solid samples were broad due to intermolecular spin–spin interactions while the frozen  $\text{H}_2\text{SO}_4$  solutions showed well resolved hyperfine and superhyperfine features due to copper and nitrogen nuclei, respectively. The unpaired electron occupies a  $3d_{x^2-y^2}$  orbital of copper(II). The ground state molecular orbital coefficients were estimated from the spin Hamiltonian parameters. The activity for epoxidation of styrene was more for complexes with electronegative substituents. The enhanced activity of substituted CuPc complexes has been correlated to the electronic and molecular structure parameters. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Copper phthalocyanine; Substituent effects; EPR; UV–VIS; Styrene epoxidation; Structure–activity correlation

## 1. Introduction

Metal phthalocyanine (MPc) complexes have been used as catalysts in polymerization of olefins [1] and in the oxidation of sulfide to thiosulfide compounds [2,3]. Ion et al. have reported the catalytic decomposition of hydrogen peroxide with crowned-ether phthalocyanines [4]. Dispersion of tetrasulfonate substituted CoPc on active carbon improved its catalytic activity in oil sweetening [5]. There are reports including those of ours on zeolite encapsulated MPc complexes [6–8]. Ab initio UHFS DV- $X\alpha$  calculations have revealed that the electronic structure of MPc complexes is sensitive to substituents on the Pc moiety and central metal ion [9]. By introducing

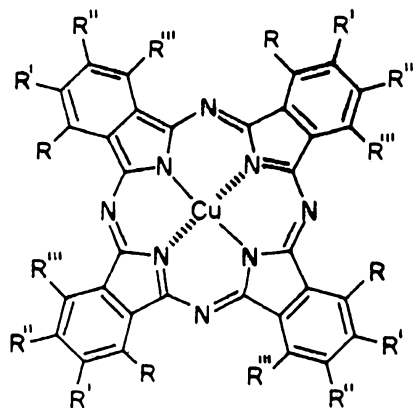
appropriate electron donating and withdrawing substituents in the macrocyclic Pc ring, one could, in principle, fine tune the electronic structure, suitably, to design a desired material or catalyst. The present study examines the effect of peripheral substitution on the spectral and catalytic oxidation properties of copper phthalocyanine (CuPc) complexes.

CuPc in solid state shows broad EPR signals due to intermolecular spin–spin interactions and thus, yields little information about the electronic structure and chemical bonding. These interactions, however, can be avoided by recording spectra in frozen solutions or by diluting the sample with diamagnetic ( $\text{H}_2\text{Pc}$  and  $\text{ZnPc}$ ) complexes. We report here, the studies on powder and frozen  $\text{H}_2\text{SO}_4$  solutions of several substituted CuPc complexes. The molecular structures of these are shown in Scheme 1. The effects of peripheral substitution on FT-IR, UV–VIS and EPR spectra of the complexes are investigated. The catalytic activities

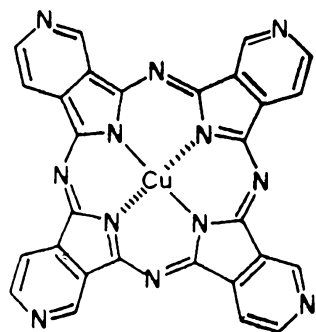
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Complex	R	R'	R''	R'''
CuPc	H	H	H	H
CuCl <sub>8</sub> Pc	Cl	H	Cl	H
CuCl <sub>16</sub> Pc	Cl	Cl	Cl	Cl
Cu(NO <sub>2</sub> ) <sub>4</sub> Pc		H	H	H
Cu(SO <sub>3</sub> Na) <sub>4</sub> Pc	SO <sub>3</sub> Na	H	H	H



CutetraazaPc

Scheme 1.

in styrene epoxidation with *tert*-butylhydroperoxide (TBHP) are also examined. The present study reveals that peripheral substitution has marked effects on both the spectral and catalytic properties of CuPc complexes.

## 2. Experimental

### 2.1. Materials

The complexes investigated are copper phthalocyanine (CuPc), copper 4,4',4'',4'''-tetraazaphthalocyanine (CutetraazaPc), copper phthalocyaninetetrasulfonic acid tetrasodium salt (Cu(SO<sub>3</sub>Na)<sub>4</sub>Pc), copper tetranitrophthalocyanine (Cu(NO<sub>2</sub>)<sub>4</sub>Pc), copper octachlorophthalocyanine (CuCl<sub>8</sub>Pc), and copper hexadecachlorophthalocyanine (CuCl<sub>16</sub>Pc). The complexes were procured from Aldrich, USA or Lona Industries Ltd., India.

### 2.2. Physical measurements

The purity of the complexes was checked by elemental analysis (Carlo Erba Elemental analyzer model EA 1108) (Table 1). The FT-IR spectra of the complexes were recorded as nujol mulls using a Perkin-Elmer 1500 spectrophotometer. UV–VIS spectra (200–900 nm) of the complexes were measured in concentrated H<sub>2</sub>SO<sub>4</sub> solutions by using a Shimadzu UV-2101 spectrometer. The spectra for the solid CuPc complexes were recorded in diffuse reflectance (DRUV–VIS) mode. EPR measurements were made using a Bruker EMX X-band spectrometer with 100 kHz field modulation. Measurements at 77 K were performed using a quartz finger Dewar. The spectra for frozen H<sub>2</sub>SO<sub>4</sub>

Table 1  
Chemical composition and spectral data of substituted CuPc complexes

Complex	Elemental analysis (%) <sup>a</sup>			FT-IR data (cm <sup>-1</sup> )				Electronic spectral data (H <sub>2</sub> SO <sub>4</sub> solution) (nm)			
	C	H	N	ν(C=N)	ν(C=C)	ν(C–N)	Skeletal	Soret	Q-bands	d–d bands	
CuPc	66.3 (66.7)	2.7 (2.8)	19.4 (19.4)	1589	1419	1090	1508, 1288	440	702, 792	639, 668	
CuCl <sub>16</sub> Pc	35 (34)	0 (0)	9.9 (9.9)	1556	1391	1096	1497, 1277	465	729, 770, 816, 861	584, 656	
CuCl <sub>8</sub> Pc	46.1 (45.1)	1.6 (0.9)	11.6 (13.1)	1568	1438	1088	1500, 1300	450	709, 746, 794, 838	569, 661	
Cu(NO <sub>2</sub> ) <sub>4</sub> Pc	49.7 (50.8)	1.4 (1.6)	21.8 (22.2)	1597		1090	1505, 1254	422	668, 705, 740, 764	613	
Cu(SO <sub>3</sub> Na) <sub>4</sub> Pc	–	–	–	1591	1420	1090	1503, 1286	440	703, 884	630, 668	

<sup>a</sup> Calculated values are given in parentheses.

solutions were recorded in the concentration range  $2 \times 10^{-2}$  to  $2 \times 10^{-4}$  M. Microwave frequency was calibrated with a frequency counter fixed in a ER 041 XG-D microwave bridge. The EPR spectra were simulated using the Bruker Simfonia software package.

### 2.3. Catalytic activity: styrene epoxidation

The catalytic activity studies were carried out, at 338 K, in a 50 ml double necked round bottom flask attached with a water cooled condenser. Styrene (4.8 mmol), acetonitrile (5 g) and TBHP solution (in decane, 4.8 mmol, Aldrich) and the catalyst (1 mg) were stirred using a magnetic stirrer. The products at the end of 24 h were analyzed by a gas chromatograph (HP 5880A, FID; 50 m  $\times$  0.2 mm capillary column).

## 3. Results and discussion

### 3.1. Spectral studies

#### 3.1.1. FT-IR

Substitution has a marked effect on the FT-IR spectra of CuPc complexes. Significant shifts in peak

positions and changes in the intensity were observed as a consequence of substitution. The FT-IR bands were, in general, broader for substituted complexes than for CuPc perhaps due to changes in molecular geometry and lowered symmetry of the Pc moiety in the former complexes. The FT-IR data for certain vibrational modes are listed in Table 1.

#### 3.1.2. DRUV-VIS

Fig. 1 reveals the effect of peripheral substitution on DRUV-VIS spectra of the solid complexes. The d-d bands of Cu(II) were masked by dominant ligand centered  $\pi$ - $\pi^*$  charge transfer bands (Q-bands). For planar  $D_{4h}$  symmetry two Q-bands (Q(0,0) and Q(1,0)) arising from the ligand centered transitions are seen. However, in the case of lower symmetry (than  $D_{4h}$ ) these bands split and show vibrational overtones viz. Q(0,1) and Q(1,1) as shoulders or resolved bands [10]. In addition to these, a broad Soret band was observed as a shoulder around 437 nm. Significant spectral changes were observed in the Q-band region. The DRUV-VIS spectra showed four Q-bands in all the complexes in the range 550–780 nm and revealed a lower molecular symmetry for the complexes in solid state. The bands were red shifted

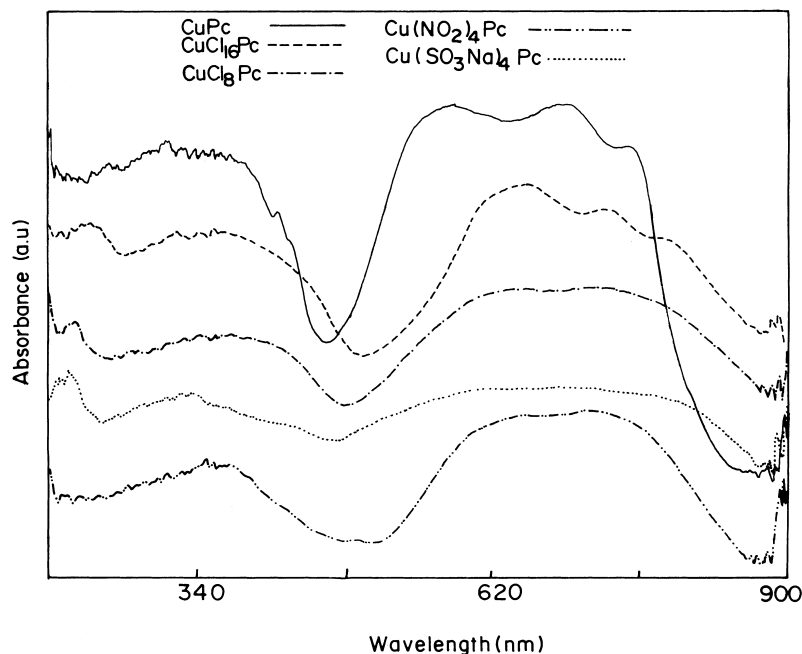


Fig. 1. DRUV-VIS spectra of substituted CuPc complexes.

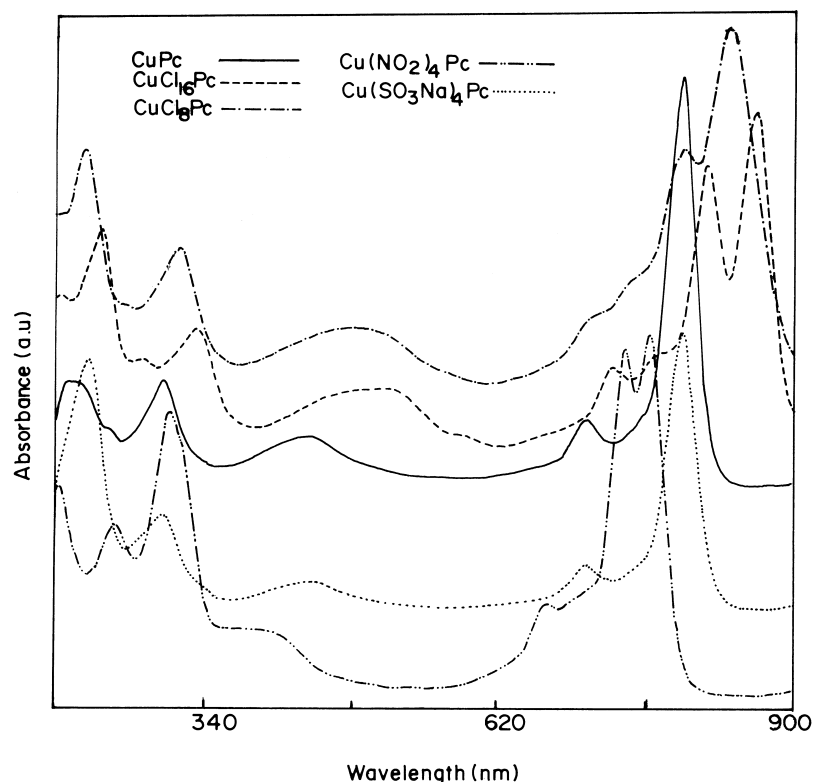


Fig. 2. UV–VIS spectra of substituted CuPc complexes in  $\text{H}_2\text{SO}_4$ .

and showed differences in the absorption coefficients (Fig. 1).  $\text{CuCl}_8\text{Pc}$ ,  $\text{Cu}(\text{NO}_2)_4\text{Pc}$  and  $\text{Cu}(\text{SO}_3\text{Na})_4\text{Pc}$  complexes exhibited diffused Q-bands while  $\text{CuPc}$  and  $\text{CuCl}_{16}\text{Pc}$  showed resolved bands.

UV–VIS spectra of the complexes in concentrated  $\text{H}_2\text{SO}_4$  are shown in Fig. 2. Unlike for the solid complexes, the bands for the solutions were sharp and narrow; the Q-bands and the Soret band were well resolved. In addition to the ligand centered (Soret and Q) bands, the spectra for solutions also showed two weak d–d bands in the range 620–690 nm, the positions of which were sensitive to the substituents and vary in the order of increasing energy as  $\text{CuCl}_{16}\text{Pc} < \text{CuCl}_8\text{Pc} < \text{CuPc} < \text{Cu}(\text{SO}_3\text{Na})_4\text{Pc} < \text{Cu}(\text{NO}_2)_4\text{Pc}$ .  $\text{CuPc}$  and  $\text{Cu}(\text{SO}_3\text{Na})_4\text{Pc}$  showed only two Q-bands attributable to  $D_{4h}$  molecular symmetry in solutions while the rest of the substituted complexes showed four Q-bands corresponding to lower molecular symmetry. The Q-band shifted to red side in solutions in the order  $\text{Cu}(\text{NO}_2)_4\text{Pc} < \text{CuPc} < \text{Cu}(\text{SO}_3\text{Na})_4\text{Pc} <$

$\text{CuCl}_8\text{Pc} < \text{CuCl}_{16}\text{Pc}$ . The macrocyclic Pc moiety adopts a variety of conformations including planar, saddled shaped and puckered [10]. A difference in the conformational geometry changes the spectral features. The electronic spectral data of the complexes in concentrated  $\text{H}_2\text{SO}_4$  are presented in Table 1.

### 3.1.3. EPR

The solid samples, in general, showed broad EPR spectra. Copper hyperfine features could not be resolved due to intermolecular dipolar and exchange interactions. However, marked differences were noticed in the nature of the spectra due to peripheral substitution. Except for CutetraazaPc, the rest of the complexes were characterized by an axial  $g$  tensor, with  $g_{\parallel} > g_{\perp}$ ; CutetraazaPc showed an isotropic signal. The  $g$  values obtained from the spectral simulations, considering the following axial spin Hamiltonian, are listed in Table 2.

Table 2  
EPR data for powder samples of substituted CuPc at 298 K

Complex	$g_{\parallel}$	$g_{\perp}$	$\Delta H_{\parallel}$ (G)	$\Delta H_{\perp}$ (G)
CutetraazaPc <sup>a</sup>	2.069		115	
Cu(NO <sub>2</sub> ) <sub>4</sub> Pc	2.123	2.045	65	50
Cu(SO <sub>3</sub> Na) <sub>4</sub> Pc	2.126	2.046	75	55
CuCl <sub>8</sub> Pc	2.132	2.046	80	55
CuPc	2.133	2.045	85	52
CuCl <sub>16</sub> Pc	2.142	2.045	85	50

<sup>a</sup> Isotropic  $g$  value; estimated error in  $g$  values is  $\pm 0.002$ .

$$\mathcal{H} = g_{\parallel}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) \quad (1)$$

Here  $\beta$  is Bohr magneton and the rest of the terms carry their usual meaning. The  $g$  values for solid samples (Table 2) do not represent the molecular values but are averaged due to intermolecular spin–spin interactions. It is apparent from Table 2 that peripheral substitution has a marked effect on the  $g$  and peak-to-peak line width ( $\Delta H$ ) parameters, especially in the parallel region. The  $g_{\parallel}$  value for the complexes decreases in the order CuCl<sub>16</sub>Pc > CuPc > CuCl<sub>8</sub>Pc > Cu(SO<sub>3</sub>Na)<sub>4</sub>Pc > Cu(NO<sub>2</sub>)<sub>4</sub>Pc.

The EPR spectra (Fig. 3) of frozen H<sub>2</sub>SO<sub>4</sub> concentrated CuPc (10<sup>−3</sup> M) showed resolved parallel hyperfine features due to copper. These features, especially the two in the low-field, were further split due to superhyperfine interaction with four equivalent nitrogen nuclei ( $I = 1$ ). Resolution of superhyperfine features was observed also in the perpendicular region. But, the hyperfine signals due to copper and the superhyperfine features due to nitrogen nuclei overlapped. The hyperfine features due to both the isotopes of copper

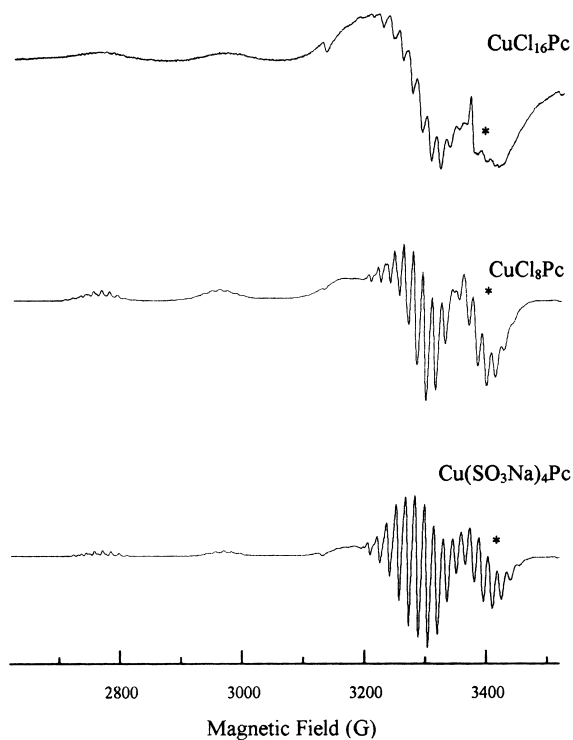


Fig. 3. EPR spectra (at 77 K) of frozen H<sub>2</sub>SO<sub>4</sub> solutions of substituted CuPc.

(<sup>63</sup>Cu and <sup>65</sup>Cu) were also resolved in the low-field region. The spectra of all the complexes, except the chloro-substituted complex, corresponded to an axial symmetry ( $g_x = g_y = g_{\perp}$  and  $A_x = A_y = A_{\perp}$ ) while that of the latter to a rhombic symmetry. The calculated spin Hamiltonian parameters are listed in Table 3.

Table 3  
EPR data for frozen H<sub>2</sub>SO<sub>4</sub> solutions of substituted CuPc at 77 K<sup>a</sup>

Complex	Species	$g_{\parallel}$ or $g_z$	$g_{\perp}$ or $g_x, g_y$	$-A_{\parallel}$ (Cu) (10 <sup>−4</sup> cm <sup>−1</sup> )	$-A_{\perp}$ (Cu) (10 <sup>−4</sup> cm <sup>−1</sup> )	$A_{\parallel}$ ( <sup>14</sup> N) (10 <sup>−4</sup> cm <sup>−1</sup> )	$A_{\perp}$ ( <sup>14</sup> N) (10 <sup>−4</sup> cm <sup>−1</sup> )
CutetraazaPc	I	2.19	2.060	203.5 (201.5)	19	13.9	15.2
	II	2.19	2.060	215	19	13.9	15.2
Cu(SO <sub>3</sub> Na) <sub>4</sub> Pc		2.19	2.060	204	18	13.9	15.2
CuPc	I	2.20	2.062	203.5 (200)	18.5 (18.5)	13.9	15.2
	II	2.20	2.062	215.5	18	13.9	15.2
CuCl <sub>16</sub> Pc		2.20	2.062	204	18	13	15.9
CuCl <sub>8</sub> Pc		2.20	2.052, 2.057	200 (196)	18	13	14.3 (14)

<sup>a</sup> Estimated error in  $g$  values is  $\pm 0.002$  and in  $A$  values is  $\pm 0.5$ .

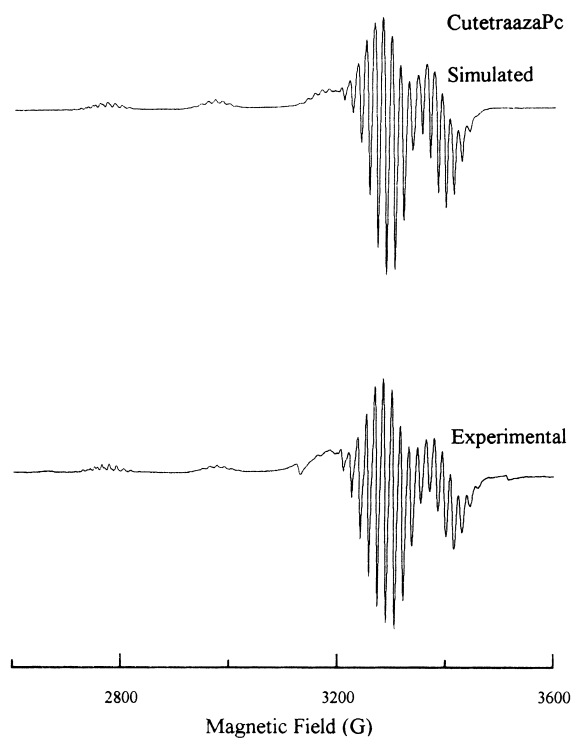


Fig. 4. Experimental and simulated EPR spectra (at 77 K) of CutetraazaPc in  $\text{H}_2\text{SO}_4$ .

Fig. 4 depicts a good agreement between the experimental and simulated EPR spectra of CutetraazaPc in concentrated  $\text{H}_2\text{SO}_4$ . Substituents showed marked effects on the  $g_{\parallel}$  values. These values (Table 3) vary in the order CutetraazaPc <  $\text{Cu}(\text{SO}_3\text{Na})_4\text{Pc}$  <  $\text{CuPc}$  <  $\text{CuCl}_8\text{Pc}$  <  $\text{CuCl}_{16}\text{Pc}$ . It is to be noted that the change in  $g_{\parallel}$  values is in line with the changes in the d–d band position in the UV–VIS spectra (Fig. 2; Table 1). Only marginal changes were observed in the  $A^{\text{Cu}}$  values. The superhyperfine coupling constants due to nitrogen ( $A^{\text{N}}$ ) are smaller for the  $\text{CuCl}_8\text{Pc}$  and  $\text{CuCl}_{16}\text{Pc}$  than for the rest of the complexes and indicate the delocalization of spin density onto the electron withdrawing chlorine atoms. The peripheral substituents on the phthalocyanine moiety are not passive but contribute to the ground state molecular orbital. The rhombic anisotropy for  $\text{CuCl}_8\text{Pc}$  indicates lower ( $\text{C}_{2v}$ ) symmetry around copper probably due to puckering of the Pc moiety. This observation agrees well with optical spectral results (vide supra).

Table 4  
MO coefficients and excitation energies of substituted CuPc complexes<sup>a</sup>

Complex	$\alpha^2$	$\alpha'^2$	$\beta^2$	$\delta^2$
$\text{Cu}(\text{SO}_3\text{Na})_4\text{Pc}$	0.83	0.25	0.56	0.70
$\text{CuPc}$	0.83	0.25	0.57	0.71
$\text{CuCl}_{16}\text{Pc}$	0.83	0.25	0.59	0.77
$\text{CuCl}_8\text{Pc}$	0.83	0.26	0.60	0.72

<sup>a</sup> Estimated error in  $\alpha^2$ ,  $\alpha'^2$ ,  $\beta^2$  and  $\delta^2$  is  $\pm 0.005$ .

### 3.2. Ground state wave function and chemical bonding

The approach developed by Maki and McGarvey [11] and later by Kivelson and Neiman [12] and Manoharan and Rogers [13] was employed to determine the ground state wave function and the chemical bonding of substituted CuPc complexes. Details of calculation of ground state MO coefficients were reported earlier [14]. The MO coefficients (Table 4) are smaller than unity and correspond to covalent nature of bonding between the metal and ligand orbitals. The in-plane  $\sigma$ -bonding parameter ( $\alpha$ ) is invariant. The peripheral substitution effects the in-plane and out-of-plane  $\pi$ -bonding parameters  $\beta^2$  and  $\delta^2$ , respectively. The value of  $\beta^2$  varies with substituents in order  $\text{Cu}(\text{SO}_3\text{Na})_4\text{Pc}$  <  $\text{CuPc}$  <  $\text{CuCl}_{16}\text{Pc}$  <  $\text{CuCl}_8\text{Pc}$  and  $\delta^2$  varies in order  $\text{Cu}(\text{SO}_3\text{Na})_4\text{Pc}$  <  $\text{CuPc}$  <  $\text{CuCl}_8\text{Pc}$  <  $\text{CuCl}_{16}\text{Pc}$  (Table 4). From the extended Huckel calculations, Zerner and Gouterman [15], estimated the energy separation between the  $e_g$  and  $b_{2g}$  orbitals of the order of  $1000\text{ cm}^{-1}$  for  $\text{CuPc}$ . The d–d band positions observed in the present investigation substantiate the theoretical studies.

The spectral studies revealed changes in molecular electronic structure and chemical bonding due to peripheral substitution. The manifestation of these effects on the catalytic activity of the substituted CuPc complexes in epoxidation of styrene is discussed in Section 3.3.

### 3.3. Catalytic activity

The catalytic activities of the different CuPc complexes in the epoxidation reaction of styrene in acetonitrile are presented in Table 5. The substituted CuPc complexes yielded styrene epoxide (EPO) and benzaldehyde (–CHO) as major products. On

Table 5  
Product distribution in epoxidation of styrene over substituted CuPc complexes<sup>a</sup>

Catalyst	Conversion (wt.%)	Product distribution				TON <sup>b</sup> (h <sup>-1</sup> )
		-CHO <sup>c</sup>	EPO <sup>d</sup>	-CH <sub>2</sub> CHO <sup>e</sup>	Others	
CuPc	8.8	84.5	9.6	1.6	4.3	10.2
CuCl <sub>8</sub> Pc	18.9	51.3	40.6	6.1	2.1	14.9
Cu(SO <sub>3</sub> Na) <sub>4</sub> Pc	26	37.5	51.1	10.2	1.7	17.6
CuCl <sub>16</sub> Pc	31.5	43.7	50.6	4.3	1.4	18.7

<sup>a</sup> Conditions: styrene (4.8 mmol); acetonitrile (5 g); TBHP (4.8 mmol); catalyst (0.001 g); temperature (333 K).

<sup>b</sup> Moles of styrene converted per mole of catalyst per hour.

<sup>c</sup> Benzaldehyde.

<sup>d</sup> Styrene epoxide.

<sup>e</sup> Phenylacetaldehyde.

the contrary, CuPc was selective for benzaldehyde. Phenylacetaldehyde (-CH<sub>2</sub>CHO) was observed as a minor product. The turnover number (TON) is more for complexes with electronegative substituents and varies in the order CuCl<sub>16</sub>Pc > Cu(SO<sub>3</sub>Na)<sub>4</sub>Pc > CuCl<sub>8</sub>Pc > CuPc.

An attempt is made to correlate the bonding parameters with the catalytic activity of the complexes in the homogeneous medium. The MO coefficients reveal that the metal–ligand bond is in general covalent. Although no one-to-one correspondence was observed, the results reveal more depletion of electron density at the metal site in the case of sulphonic acid substituted complexes than CuPc and chloro-substituted CuPc complexes. The depletion of electron density perhaps promotes the nucleophilic attack of the oxidant molecule e.g. *tert*-butylhydroperoxide at the metal centre forming the catalytically active intermediate metal-hydroperoxide. Further, the heterolytic cleavage of the metal-hydroperoxy complex is also facilitated. The ease of heterolytic cleavage of metal-hydroperoxy complexes has been related to epoxidation activity of transition metal complexes [16]. The ease of formation and heterolytic cleavage of hydroperoxy intermediates is more in complexes with electron withdrawing substituents and hence an increased catalytic activity is observed in these complexes.

#### 4. Conclusions

The effect of peripheral substitution on the UV–VIS and EPR spectra as well as the styrene epoxidation

activity of CuPc complexes was investigated. The present study demonstrates that the substituted complexes are more reactive in oxidation reactions than unsubstituted CuPc complex. A comparative spectroscopic and activity study points out that lower molecular symmetry and electron withdrawing substituents are responsible for the higher catalytic activity of the substituted CuPc complexes.

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