Magnetic, catalytic, EPR and electrochemical studies on binuclear copper(II) complexes derived from 3,4-disubstituted phenol

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Abstract. New symmetrical compartmental binucleating ligands 2,6-*bis*[N-(2-{dimethylamino}ethyl)-N-methyl)aminomethyl]-3,4-dimethylphenol [HL^1] and 2,6-*bis*[N-(2-{diethylamino}ethyl)-N-ethyl)aminomethyl]-3,4-dimethylphenol [HL^2], and their copper(II) complexes [Cu$_2$L$^{1-2}$(X)]ClO$_4$, (X = NO$_2^-$, OAc$^-$ and OH$^-$) have been prepared. Spectral, catalytic, magnetic, EPR and electrochemical studies have been carried out. A catecholase activity study indicates that only HL^1 complexes have efficient catalytic activity due to a less sterically hindered methyl group and enhanced planarity (larger $-2J$ values) with respect to the oxidation of 3,5-di-*t*-butylcatechol to the corresponding quinone. Variable temperature magnetic susceptibility studies of the complexes show antiferromagnetic interaction between the copper atoms. X-band EPR signals could not be observed for polycrystalline samples both at room temperatures and liquid nitrogen, consistent with two antiferrromagnetically coupled copper centres in the solid state. EPR spectral studies in methanol solvent show well-defined four hyperfine signals at room temperature due to decomposition of the dimer into monomers. This however is not seen in frozen methanol glass, may be owing to restructuring of the monomers into dimers due to an increase in viscosity of the solvent. Electrochemical studies revealed chemically irreversible behaviour due to chemical or/and stereochemical changes subsequent to electron transfer.

Keywords. Dicopper(II) complexes; 3,4-disubstituted phenols; binucleating ligands.

1. Introduction

Magnetic interaction in binuclear complexes continues to be an area of research actively pursued in many laboratories. Over the past few years, emphasis has shifted from purely magnetic exchange coupling to magnetostructural correlations in exchange-coupled systems.[1,2] Since the spectral, electrochemical, EPR and magnetic features provide new insight into the structure of naturally occurring dicopper proteins such as hemocyanin, tyrosinase, catechol oxidase etc.[3–7] these dicopper complexes have great significance as new inorganic materials capable of showing peculiar magnetic and redox properties. Hence these model complexes have an application in magnetochemistry[8,9] and homogeneous catalysis.[10–13] The redox properties of binuclear complexes have received much

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attention in recent years, particularly to understand the redox function of copper proteins.[14,15] The catecholase activity of copper co-ordination compounds with different structural parameters has been investigated.[16] Nishida and co-workers[17] have found that square planar mononuclear copper(II) complexes exhibit only low catalytic activity while non–planar mononuclear copper(II) complexes show high activity. A steric match between substrate and complex is believed to be the determining factor: two metal centres have to be located in close proximity to facilitate binding of the two hydroxyl oxygen atoms of catechol prior to the electron transfer.[18] With this in view, using ligands HL[1] and HL[2] (scheme 1) a series of binuclear copper(II) complexes (scheme 2) have been prepared and characterized. The ligands have been prepared for synthesizing bimetallic copper complexes, mimicking the properties of naturally occurring metalloproteins. Results of the spectral, catalytic, magnetic exchange, EPR and electrochemical studies carried out on these complexes are presented in this work.

2. Experimental

2.1 *Physical measurements*

^{1}H and ^{13}C NMR spectra were recorded on a JEOL FX-400 FT–NMR spectrometer in $CDCl_3$ solution, using tetramethylsilane as the internal standard. The FAB mass spectra were recorded on a JEOL SX 102 1DA-6000 mass spectrometer/data system using argon/xenon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV and the spectra were recorded at room temperature. Electronic absorption spectra were obtained in acetonitrile solution with a Hitachi–320 UV-Vis double beam spectrometer using 1 cm quartz cells and solution concentrations of 10^{-3} mol dm^{-3}. IR spectra were recorded on a Perkin–Elmer IR 598 spectrophotometer using KBr disks. Elemental (C, H and N) analysis was performed with a Heraus Rapid analyzer. Copper was estimated by M. Avanta G.B.C., Australia atomic absorption spectrophotometer. Catalysis experiments were carried out on Ocean Optics, SD 1000 fibre optic spectrometer using methanol as a solvent.

Molar conductance (Λ_M) was measured by a control dynamics conductivity meter in acetonitrile solvent. Variable temperature magnetic susceptibility data of the powdered samples were measured in the range 80–300 K using a Princeton Applied Research Model 155 VSM in 5000 G magnetic field. Diamagnetic susceptibility corrections for ligand susceptibility were made using Pascal's constants[9]. Effective magnetic moments were calculated using the formula $m_{\text{ff}} = 2 \cdot 828 \, (c_M T)^{1/2}$, where c_M is the corrected molar susceptibility. The instrument was calibrated using metallic nickel. EPR spectra were recorded with a JEOL TES 100 ESR spectrometer. Low temperature measurements were made using a liquid nitrogen dewar. Cyclic voltammetric measurements were carried out at room temperature in acetonitrile under N_2 using an Auto Lab PGSTAT 12 controlled by general purpose electrochemical system software (GPES), running under MS-Windows 95. Purging dry nitrogen before measurements deoxygenated the solutions. A three-electrode cell configuration was used with a platinum disc as the working, a platinum rod as the counter electrode and a saturated LiCl–Ag/AgCl as the reference electrode. Tetrabutylammonium perchlorate was used as the supporting electrolyte (TBAP, 0·1 M).

2.2 *Materials*

All solvents and reagents were obtained from commercial source. Ethanol and methanol were distilled from magnesium oxide. Tetrabutylammonium perchlorate was prepared from tetrabutylammonium bromide (Aldrich) and 70% perchloric acid. This was recrystallized from ethanol and dried in vacuum. The compound $Cu(ClO_4)_2.6H_2O$ was prepared from its carbonates.

2.3 *Synthesis of compartmental ligands*

2.3a *2, 6-Bis[N-(2-{dimethylamino}ethyl)-N-methyl)aminomethyl]-3, 4-dimethylphenol [HL^1]^{18} (scheme 1):* 3,4-Dimethylphenol (0·025 mol) in ethanol (100 cm^3) was mixed with appropriate secondary amine (0·05 mol) (N,N,N′-trimethyl or N,N,N′-triethyl ethylenediamine) and stirred. Formaldehyde (7 cm^3) was added slowly with constant stirring. The solution was then heated to reflexed for 24 h. Formaldehyde (2·5 ml) was added at 8 h intervals. Ethanol was evaporated under vacuum and the resulting oil was washed with Na_2CO_3 and extracted with $CHCl_3$. The organic phase was dried with $MgSO_4$, filtered and its volume reduced, and a yellow oil obtained. Yield: 89%.

^{1}H NMR: CDCl$_3$, *d*$_{ppm}$ – 7·8 (*s*, 1H, ArH); 3·65, 3·5 (*s*, 4H, benzylic CH$_2$); 2·6–2·51 (*t*, 4H, NCH$_2$CH$_2$N); 2·5–2·4 (*t*, 4H, NCH$_2$CH$_2$N); 2·23 (*s*, 12H, N(CH$_3$)$_2$; 2·21, 2·22 (*s*, 6H, NCH$_3$); 2·16, 2·14 (*s*, 6H ArCH$_3$).

^{13}C NMR: CDCl$_3$, *d*$_{ppm}$ – 15·28 (*q*, CH$_3$); 19·80 (*q*, CH$_3$); 41·71 (*q*, NCH$_3$); 45·48 (*q*, N(CH$_3$)$_2$; 54·59, 56·73 (*t*, NCH$_2$CH$_2$N(CH$_3$)$_2$); 58·21 (*t*, benzylic CH$_2$); 120·13 (*s*, aryl); 121·72 (*s*, aryl); 126·02 (*s*, aryl); 129·88 (*s*, aryl); 134·96 (*s*, aryl); 154·57 (*s*, phenol – OH).

IR (KBr disc): ***n***$_{(aromatic\ C=C)}$: 1456 cm^{-1}; ***n***$_{N–CH}$: 1300 cm^{-1}; ***n***$_{C–H\ aliphatic}$: 2900–2800 cm^{-1}; ***n***$_{Phenol–OH}$: 3400–3500 cm^{-1}. *m/z*: 350.

2.3b *2, 6-Bis[N-(2-{diethylamino}ethyl)-N-ethyl)aminomethyl]-3, 4-dimethylphenol [HL^2]:* Similar work up and analyses gave the following results. Yield: 79%.

^{1}H NMR: CDCl$_3$, *d*$_{ppm}$: 6·83 (*s*, 1H, ArH); 3·8, 3·6 (*s*, 4H, benzylic CH$_2$); 2·6 (*t*, 8H, NCH$_2$CH$_2$N); 2·45 (*q*, 12H, NCH$_2$CH$_3$); 2·16, 2·15 (*s*, 6H, ArCH$_3$); 1·1–1·0 (*q*, 8H, NCH$_2$CH$_3$); 0·98–0·9 (*t*, 12H, NCH$_2$CH$_3$).

^{13}C NMR: CDCl$_3$, *d*$_{ppm}$ – 11·35 (N-Et); 11·55 (N-Et); 15·25 (*q*, CH$_3$); 19·83 (*q*, CH$_3$); 47·47 (N(Et)$_2$); 50·82, 50·56 (NCH$_2$CH$_2$NEt$_2$); 54·08 (*t*, benzylic CH$_2$); 120·86 (*s*, aryl); 121·67 (*s*, aryl); 126·02 (*s*, aryl); 129·50 (*d*, aryl); 134·54 (*s*, aryl); 154·69 (*s*, aryl-OH).

IR (KBr disc): ***n***$_{(aromatic\ C=C)}$ – 1456 cm^{-1}; ***n***$_{N–CH}$: 1378 cm^{-1}; ***n***$_{C–H\ aliphatic}$ – 2900–2700 cm^{-1}; ***n***$_{Phenol–OH}$: 3400–3600 cm^{-1}. *m/z*: 434.

2.4 *Synthesis of complexes*

The complexes were prepared using the procedure reported earlier[19–21].

Safety note: *Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be prepared in small quantities and handled with great caution.*

2.4a *Preparation of hydroxo bridged complexes:* (i) [Cu$_2$L^1(OH)](ClO$_4$)$_2$.CH$_3$OH (**1a**); (ii) [Cu$_2$L^2(OH)](ClO$_4$)$_2$.2H$_2$O.3CH$_3$OH (**1b**) (scheme 2) – To a solution of

Cu(ClO$_4$)$_2$.6H$_2$O (0·002 mol; 0·74 g) in methanol (50 cm^3) were added [HL^1] (0·001 mol; 0·44 g) and NaOH (0·003 mol, 0·12 g). The solution was stirred for 3 h at room temperature. The resulting green solution on slow evaporation gave a green powder substance, which was then recrystallized from hot methanol to give the complex. The analytical data for the complex (**1a**) are given in table 1. The complex (**1b**) was prepared by adopting the same procedure as (**1a**) using HL^2 instead of HL^1.

2.4b *Preparation of bis(acetato)bridged complexes:* (i) [Cu$_2$L^1 (OAc)$_2$]ClO$_4$.2H$_2$O. 4CH$_3$OH (**2a**); (ii) [Cu$_2$L^2(OAc)$_2$]ClO$_4$.2H$_2$O.4CH$_3$OH (**2b**) – An aqueous methanol solution (20 cm^3) of Cu(OAc)$_2$.H$_2$O (0·002 mol, 0·4 g) was mixed with a methanolic solution (50 cm^3) containing [HL^1] (0·001 mol, 0·44 g) followed by the addition of LiClO$_4$ (0·003 mol, 2 g). The final clear solution was left for slow evaporation. The green compound was recrystallized from hot methanol. The complex (**2b**) was prepared in the same way as (**2a**), using HL^2 instead of HL^1.

2.4c *Preparation of bis nitrito complexes:* (i) [Cu$_2$L^1(NO$_2$)$_2$]ClO$_4$.6CH$_3$OH (**3a**); (ii) [Cu$_2$L^2(NO$_2$)$_2$]ClO$_4$.H$_2$O.3CH$_3$OH (**3b**) – To a methanol solution containing ligand [HL^1] (0·001 mol, 0·44 g) and Cu(ClO$_4$)$_2$.6H$_2$O (0·002 mol, 0·74 g), a solution of NaNO$_2$ (0·003 mol, 0·207 g) dissolved in methanol (100 cm^3) was added. The resulting green solution was stirred for 3 h and kept for slow evaporation. The green powder obtained was recrystallized from hot methanol. Complex (**3b**) was prepared in the same way as (**3a**) using HL^2 instead of HL^1.

Methanol solutions of 3,5-DTBC (0·1 mmol dm^{-3}) and the copper(II) complexes (0·001 mmol dm^{-3}) in 25 cm^3 standard flasks were kept under ice cold conditions. Absorbance of a solution was monitored at intervals of 10 min immediately after exposing it to air.

3. Results and discussion

3.1 *Synthesis and characterization*

Binucleating ligands (HL^1 and HL^2) have been synthesized by the reaction of two moles of secondary amines, two moles of formaldehyde and one mole of 3,4-disubstituted phenols as per procedure.

Complexes (**1a**) and (**1b**) were prepared by using the methanolic solution of respective ligand and copper(II) perchlorate hexahydrate 1 : 2 molar ratio in the presence of sodium

Table 1. Analytical data for the copper(II) complexes.

| Complexes	Found (calc.) %			
	C	H	N	Cu
[Cu$_2$L^1(OH)](ClO$_4$)$_2$.CH$_3$OH (**1a**)	34·93 (34·96)	5·86 (5·88)	7·75 (7·75)	17·60 (17·62)
[Cu$_2$L^2(OH)](ClO$_4$)$_2$.2H$_2$O.3CH$_3$OH (**1b**)	38·28 (38·32)	7·20 (7·22)	6·15 (6·14)	13·96 (14·00)
[Cu$_2$L^1(OAc)$_2$]ClO$_4$.2H$_2$O.4CH$_3$OH (**2a**)	39·35 (39·39)	7·19 (7·20)	6·55 (6·58)	14·87 (14·86)
[Cu$_2$L^2(OAc)$_2$]ClO$_4$.2H$_2$O.4CH$_3$OH (**2b**)	39·18 (39·22)	7·39 (7·42)	6·52 (6·58)	14·80 (14·85)
[Cu$_2$L^1(NO$_2$)$_2$]ClO$_4$.6CH$_3$OH (**3a**)	36·56 (36·56)	6·61 (6·62)	9·84 (9·86)	14·88 (14·91)
[Cu$_2$L^2(NO$_2$)$_2$]ClO$_4$.H$_2$O.3CH$_3$OH (**3b**)	40·15 (40·14)	7·21 (7·28)	9·68 (9·72)	14·65 (14·68)
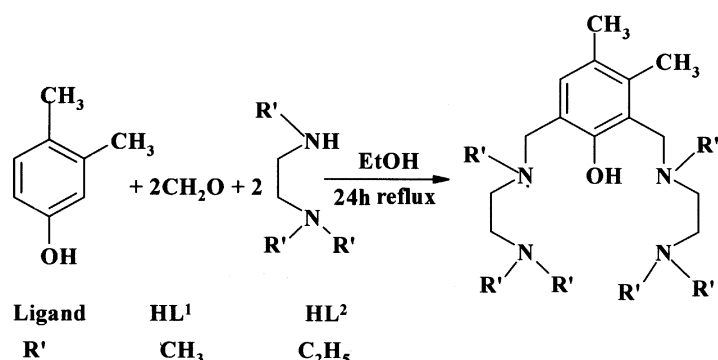
Scheme 1.

hydroxide. The bisacetato bridged complexes (**2a**) and (**2b**) were synthesized from the reaction of the ligands with copper(II) acetate monohydrate and lithium perchlorate.

Dinitrito compounds (**3a**) and (**3b**) were obtained using a $1:2$ molar ratio of the ligand and copper(II) perchlorate in the presence of sodium nitrite in aqueous methanol. The IR spectra of the complexes exhibit a symmetrical band at $1100\ cm^{-1}$ indicating the presence of uncoordinated perchlorate ion. All the complexes show a broad band around $3400\ cm^{-1}$ indicating the presence of coordinated or lattice water in the complex. The *bis*(acetato) bridged complexes[22] show strong bands at 1632 and $1458\ cm^{-1}$. IR bands due to the nitrite groups in nitrito complexes were observed at 1462 and $1249\ cm^{-1}$ which suggest a monodentate O-bonded mode for the nitrite groups[23]. All the complexes show bands at 480 and $280\ cm^{-1}$ indicating the presence of Cu–N and Cu–O groups respectively.[24]

Electronic spectra of the complexes were studied in acetonitrile, the data are given in table 2. The spectra of the complexes consist three bands. A low intensity band in the region 583–622 nm is indicative of square pyramidal geometry[25–29], and a shoulder in the region 356–382 nm is attributed to the phenolato to Cu(II) charge-transfer band[30]. The third band is assigned ligand band. Interestingly, in the electronic spectra of the complexes, the intensity of bands observed for OH bridged complexes at 365 nm $(300 = e/M^{-1}\ cm^{-1})$ and 368 nm $(970 = e/M^{-1}\ cm^{-1})$ are much lower than the corresponding bands in bisnitrito and bisacetato bridged complexes. Similar observations were made by Urbach *et al*,[31] Bertoncello *et al*[21] and Sornell *et al*[32] in related systems and were explained by suggesting that the pyramidal geometry around the phenolate oxygen atom in OH bridged complexes may give rise to poor ligand–metal orbital overlap. The intensities for the nitrito complexes are normal and are in line with those predicted for the trigonal planar geometry around oxygen. A red shift in the *d–d* band for the complexes (**1b**), (**2b**) and (**3b**) when compared to the complexes (**1a**), (**2a**) and (**3a**) indicates that the coordination geometry around the copper atom of the former complexes is more distorted than in the latter complexes.

The positive ion FAB mass spectra of two complexs $[Cu_2L^2(OH)](ClO_4)_2$. $2H_2O.3CH_3OH$ (**1b**), $m/z = 668$ and $[Cu_2L^1(OAc)_2]ClO_4.2H_2O.4CH_3OH$ (**2a**) $m/z = 758$ confirm the presence of dipositive binuclear core structure $[Cu_2L]^{n+}$.
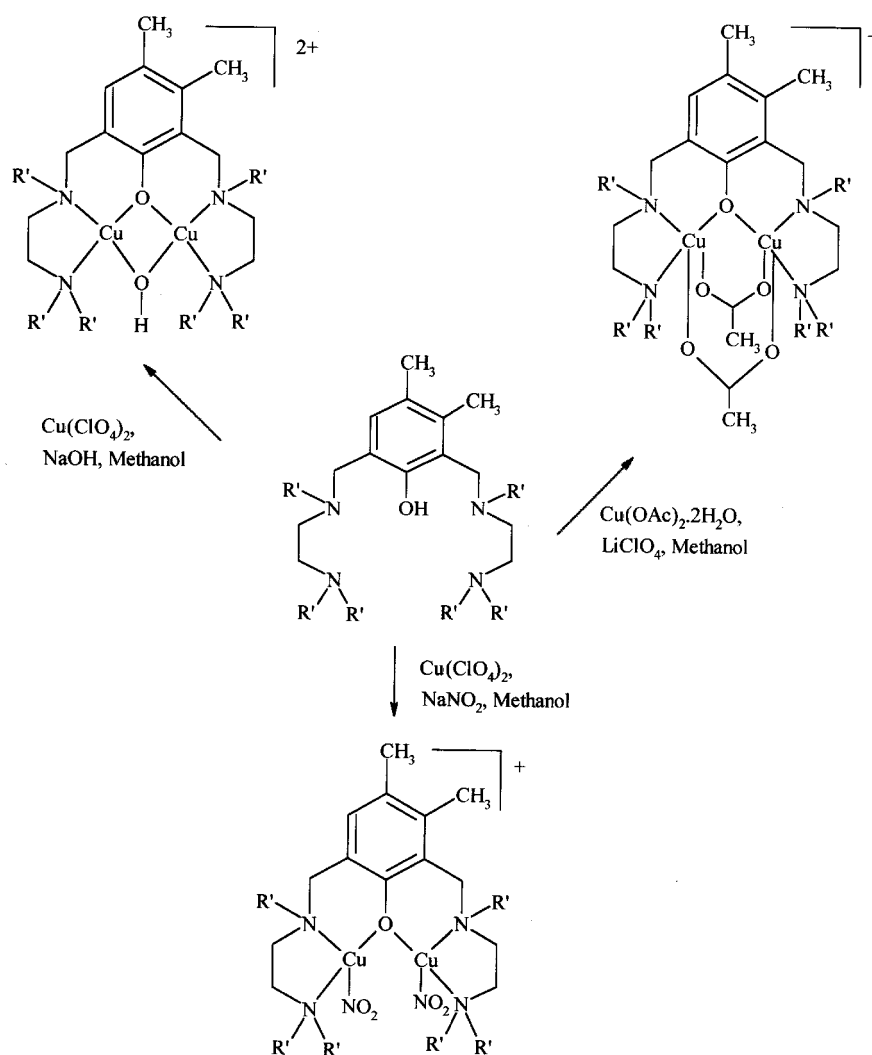
Scheme 2.

3.2 *Conductivity studies*

Molar conductances (Λ_M) of the complexes (table 3) have been studied using acetonitrile as solvent. We observed 1 : 1 electrolyte behaviour for acetate and nitrito complexes and 1 : 2 electrolyte behaviour for hydroxo-bridged complexes.

3.3 *Catecholase activity*

Catalytic studies were performed in methanol solution owing to the good solubility of the complexes as well as the substrate in methanol. The catecholase activity of binuclear

Table 2. Electronic, spectral[a] and magnetic[b] data for the copper(II) complexes.

Complexes	l_{max}/nm (e)*		m_{eff} (BM) at		
	d–d	CT	$-2J$ cm^{-1}	79 K	298 K
1a	611 (126)	365 (300), 277 (1350)	184	0·405	1·578
1b	622 (472)	368 (970), 279 (1551)	160	0·624	1·537
2a	589 (322)	360 (3830), 266 (12190)	216	0·683	1·456
2b	619 (283)	356 (3060), 267 (9450)	194	0·849	1·598
3a	583 (342)	368 (3060), 282 (9450)	266	0·488	1·537
3b	614 (222)	382 (2010), 288 (9090)	216	0·849	1·512

*l_{max} values are in nm, and e is M^{-1}cm^{-1}; [a] Electronic spectra were recorded in CH$_3$CN solvent; [b] $-2J$ values have been calculated using Bleaney–Bower's equation[31]; value of N_a was fixed at 60×10^{-6} cm^3 mol^{-1} for all magnetic simulations; parameters g and p are defined in text

Table 3. Electrochemical data for the complexes.

| Complexes	E_{pc}^1 (V)	E_{pc}^2 (V)	E_{pa} (V)	Molar (Λ_M)[a] conductance (ohm^{-1} cm^2 mol^{-1})	Types of electrolyte
1a	−0·92	−1·26	−0·79	261	1 : 2
1b	−0·24	−0·75	−0·87	240	1 : 2
2a	−0·43	−0·77	−0·25	132	1 : 1
2b	−0·20	−0·52	−0·20	130	1 : 1
3a	−0·45	−1·07	−0·50	140	1 : 1
3b	−0·23	−0·57	−0·25	140	1 : 1

Potential V vs Ag/AgCl; electrodes: Pt vs Ag/AgCl, scan rate 50 mV/s; supporting electrolyte: TBAP (1×10^{-1} M); concentration of the complex (1×10^{-3} M) in CH$_3$CN; [a] Expected ranges 120–160 in MeCN (1 : 1); 220–300 in MeCN (1 : 2)

copper(II) complexes has been studied with the help of electronic spectroscopy by monitoring the appearance of the absorption maximum of the substituted quinone product (l_{max} = 400 nm). In binuclear copper(II) complexes, larger magnetic exchange interaction was observed when the planarity of the metal centre increases.[33] Therefore, binuclear systems with larger magnetic interaction should exhibit greater catalytic activity. This has been found in the case of some binuclear complexes of 1,3,5-triketones.[34] The catecholase activity studies of a few of the present complexes reveal that only the complexes of HL[1] have significant catalytic activity with respect to the aerial oxidation of 3,5-DTBC (di-*t*-butylcatechol) to its corresponding quinones compared to complexes of HL[2]. The HL[2] complexes show little catalytic activity because the steric bulk of the ethyl group hinders the approach of the substituted catechol to the metal center for the formation of intermediates. We observe that the catalytic activity is also dependent on exogenous bridging groups. We investigated the catecholase activity of compounds (**1a**), (**2a**), and (**3a**) corresponding to the HL[1] and (**2b**) for HL[2] ligand framework (figures 1–3). The nitrito-bridged complex shows greater catalytic efficiency compared to other bridges. This assumes that the non-bridging coordination mode of nitrite with enchanced planarity favours the relaxed conformation. The acetate-bridged complexes show better catalytic activity compared to hydroxo group complexes, since it has a flexible polyatomic

bridging group, which favour the formation of intermediate to perform the facile electron transfer[35]. The poor catalytic efficiency of hydroxo-bridged complexes is due to strain in exogenous *m*-hydroxo bridge forcing rigidity in the ligand frame. Catechol binding by replacing the anion is facile in NO_2, less in OAc and difficult in OH bridge. The structural motif of a *m*-hydroxo and *m*-alkoxo bridged dicopper(II) complexes is significantly more stable than a bridging catechol coordination.[36] This makes it difficult to form intermediate complexes favorable to mediate the electron transfer. Based on the above results, we can conclude that the catalytic efficiency is the greatest for the complex with the highest exchange interaction ($2J$), which is in the order of $NO_2 > OAc > OH$.
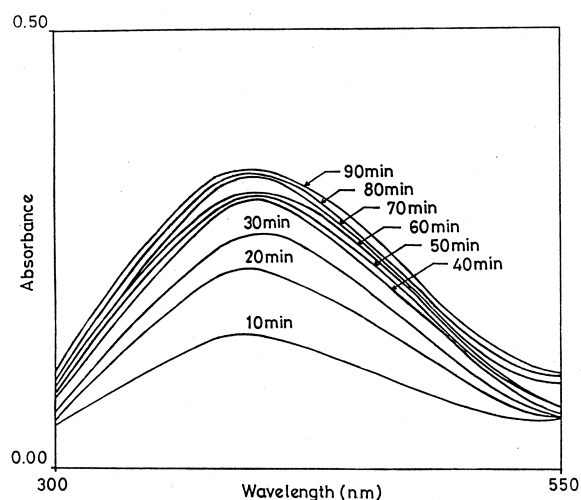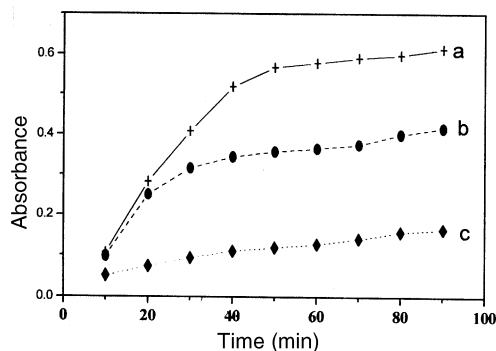

Figure 1.   Oxidation of 3,5-DTBC by a binuclear copper(II) complexes (**2a**).
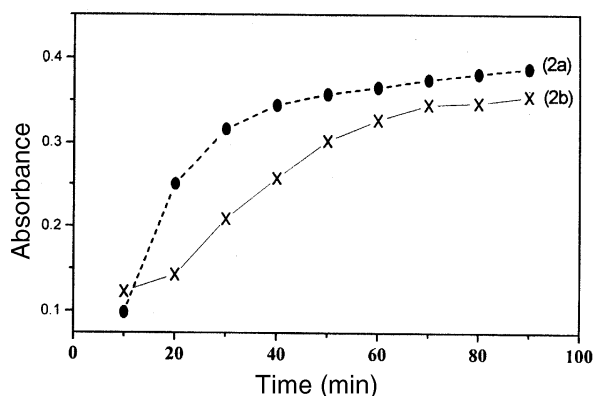
Figure 2.   Time-dependent formation of substituted quinones in presence of (**2a**) and (**2b**).

Figure 3. A comparison of time dependent oxidation of 3,5-DTBC by different complexes (a) $[Cu_2L^1(NO_2)_2]^{n+}$, (b) $[Cu_2L^1(OAc)_2]^{n+}$, (c) $[Cu_2L^1(OH)]^{n+}$.

3.4 *Magnetic properties*

Magnetic susceptibility values of powdered samples of the complex were measured in the temperature range 77–300 K using a vibrating sample magnetometer. Analysis was carried out using the modified Bleaney–Bowers equation,[37]

$$c_M = \{Ng^2b^2/kT\}[3 + \exp(-2J/kT)]^{-1}(1 - p) + (Ng_i^2b^2/4kT)P + N_a,$$

where c_M is the paramagnetic susceptibility per molecule after the correction for diamagnetism, p is the paramagnetic impurities, gi is the average g factor of the paramagnetic impurity, $-2J$ is the singlet–triplet energy separation and N_a is the temperature independent paramagnetism (TIP) assumed to be 60×10^{-6} cm^3 mol^{-1} for Cu(II) dimers.[38] The best fit to the experimental value for the complexes is summarized in table 2. The temperature dependence of the magnetic properties for the complex (**2a**) is given in figure 4. We observed that spin exchange coupling values $(-2J)$ are greater for (**1a**), (**2a**) and (**3a**) of HL^1 than for the complexes (**1b**), (**2b**) and (**3b**) of the ligand of HL^2 suggesting a weak antiferromagnetic interaction between the two Cu(II) centres. As explained in the optical and electrochemical properties of the complexes of the ligands (see below), the possible distortion in geometry and the bulky ethyl substituents in the donor nitrogen atom are probable reasons for the observed $-2J$ values of the complexes of HL^2 being lower than HL^1. Reports suggest that the factors i.e. reduction in electron density on the copper atoms[39] and the distorted structure[40–44] are less favorable for effective overlap resulting in small $-2J$ values for complexes of the ligand HL^2. The exogenous donor groups also influence the exchange interaction. A lower $-2J$ value was observed for acetato-bridged complexes when compared to the nitrito complexes. This indicates that in acetato complexes this is possibly due to the counter complementary nature of the overlap of the magnetic orbital involving monoatomic and three atom-bridging ligands.[45] The hydroxo-bridged complexes exhibit still weak antiferromagnetic interaction when compared to nitrito and acetato bridged complexes, due to p type overlap between the out-of-plane copper orbital and the non bonding pair on oxygen (p_x). This will be more significant than the s type overlap and hence gives rise to enhanced antiferromagnetism in the case of trigonal planar oxygen and reduced antiferromagnetism
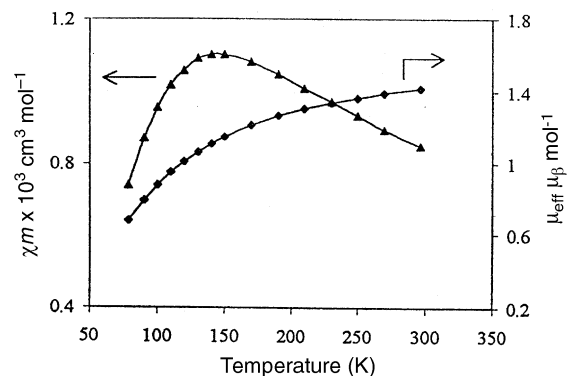
Figure 4. Experimental variation of the molar susceptibility (per Cu) and effective magnetic moment (m_{eff}) with temperature for $[Cu_2L^1(OAc)_2]ClO_4.2H_2O.4CH_3OH$ (**2a**).
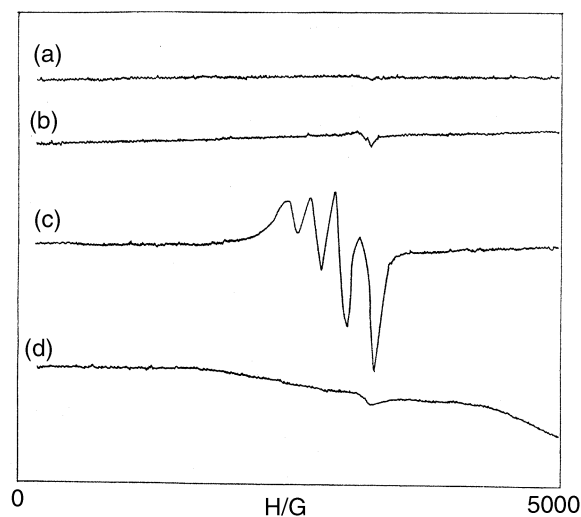
Figure 5. (a) X-band EPR spectrum of (**2b**) in polycrystalline sample at 298 K. (b) a frozen solid (**2b**) at 77 K. (c) EPR spectrum of (**2b**) in methanol solution at 298 K. (d) Spectrum of (**2b**) in frozen methanol (77 K). All the spectra were recorded with 1·6 mW microwave power, 1·26 mT field modulation amplitude, and 100 kHz-modulation frequency.

in pyramidal oxygen.[46] The above observations suggest that the magnitude of magnetic interaction is of the order $NO_2 > OAc > OH$.

3.5 *EPR studies*

No X-band EPR signal was observed for all polycrystalline samples both at room and liquid nitrogen temperatures, indicating the presence of strong antiferromagnetic

interaction in solid state. The solution EPR spectrum recorded in methanol shows well-defined four-hyperfine signals at room temperature (figure 5) ($g_{iso} = 2 \cdot 1$, $A_{iso} = 7 \cdot 4$ mT), which were not observed in frozen methanol (77 K).[47] As mentioned in one of our previous reports,[48] the appearance of a four-line pattern in solution at room temperature may be due to the decomposition of the dimer into monomers or due to slight loss of magnetic coupling between the two copper ions. At the same time, disappearance of the EPR spectrum at 77 K can be attributed to the recombination of the monomers into dimers due to an increase in the viscosity of the solvent.[48] $\Delta Ms = \pm 2$ half-field transitions were not observed in solid or in frozen solution.

3.6 *Electrochemistry*

Cyclic voltammetric studies of the complexes were performed in CH_3CN solution using TBAP as the supporting electrolyte in the potential range $0 \cdot 5$ to -2 V. The electrochemical data are summarized in table 3 and the cyclic voltammogram for complex (**3b**) is reproduced in figure 6. All the complexes show two reduction waves at different potentials in the forward scan. Coulometric experiments conducted at a potential 100 mV more negative than the second reduction wave indicate the consumption of two electrons per molecule. This indicates the electron transfer may occur as follows,

$$Cu(II) - Cu(II) \xrightarrow{\;+1e^-\;} Cu(II) \xrightarrow{\;+1e^-\;} Cu(I) \quad Cu(I).$$
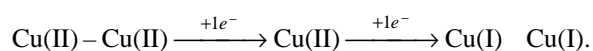
The peak current for the complexes varies with scan rates and the E_{pa}–E_{pc} values are greater than 200 mV (of the order of 320 mV), which indicates that the reduction
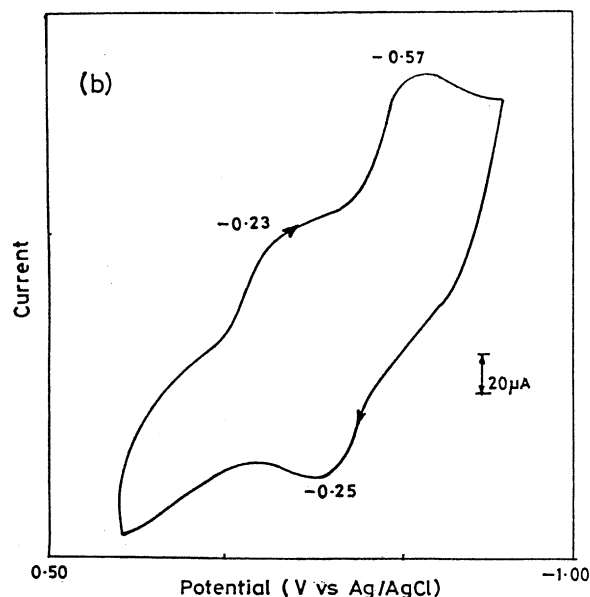
Figure 6. Cyclic voltammogram of $[Cu_2L^2(NO_2)_2]ClO_4 \cdot H_2O \cdot 3CH_3OH$ (**3b**) in CH_3CN at room temperature using TBAP as supporting electrolyte.

processes are irreversible in nature[49] and a chemical change occurs with the electron transfer. It may be due to the structural reorganization in coordination sphere. The electrochemical data show (table 3) that the first reduction potential of (**1b**), (**2b**) and (**3b**) are observed at relatively more positive potential than those of (**1a**), (**2a**) and (**3a**). Here both the ligands (HL^1 and HL^2) provide a similar N_4O donor set of atoms to the copper(II) ions. However, there is a structural difference in the arrangement of these atoms: the amine donor nitrogens of HL^2 contain bulky ethyl group, whereas HL^1 has a methyl substitution. Hence, the complexes of HL^2 are more flexible than HL^1 in metal coordination site, due to the bulky ethyl substitution. The deviation of the metal from its coordination plane should be larger for HL^2 complexes in order to destabilize the Cu(II) oxidation state. Thus, the electron density on the copper ions of the complexes (**1b**, **2b** and **3b**) is less and the copper coordination geometry may also be more distorted due to steric effect of the bulky ethyl group substituent. It has been suggested[50,51] that reduction in electron density on the copper ions and distortion in geometry influences facile conversion of Cu(II) $\rightarrow$ Cu(I) at less negative potential as observed in the complexes of the ligand HL^2 relative those of the ligand HL^1.

4. Conclusion

New symmetrical compartmental ligands capable of forming dimeric copper(II) complexes have been prepared and characterized. Observation of a single *d–d* band in the range 583–622 nm indicates that the complexes have square pyramidal geometry. Efficient catalytic activity is observed for complexes with less sterically hindered coordination site as well as for those with enhanced planar copper center. Variable temperature magnetic study of the complexes indicates the presence of strong anti-ferromagnetic interaction in solid state, which is dependent on the nature of the exo-genous group and the substituent in the donor nitrogen atoms ($NO_2 >$ OAc $>$ OH). Lack of an EPR signal in the solid state as well as frozen solution confirms strong antiferro-magnetic coupling between two metal centres. The solution EPR spectra at room tempera-ture exhibit four hyperfine signals, due to the decomposition of the dimers into monomers. Cyclic voltammetry studies indicate that the complexes undergo irreversible electron transfer due to chemical or/and stereochemical changes subsequent to electron transfer.

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