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Synthesis, spectral characterization, electrochemistry and catalytic activities of Cu(II) complexes of bifunctional tridentate Schiff bases containing O–N–O donors

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Paramagnetic copper(II) complexes of the type [Cu(PPh$_3$)(L)] (where L = bifunctional tridentate Schiff bases) were synthesized from the reaction of anthranillic acid with salicylaldehyde (H$_2$L^1), 2-hydroxy-1-naphthaldehyde (H$_2$L^2), *o*-hydroxyacetophenone (H$_2$L^3) and *o*-vanillin (H$_2$L^4) with monomeric metal precursor [CuCl$_2$(PPh$_3$)$_2$]. The obtained complexes were characterized by elemental analysis, magnetic susceptility and spectroscopic methods (FT-IR, UV–vis and EPR and cyclic voltammetry). EPR and redox potential studies have been carried out to elucidate the electronic structure, nature of metal–ligand bonding and electrochemical features. EPR spectra exhibit a four line pattern with nitrogen super-hyperfine couplings originating from imine nitrogen atom. These planar complexes possess a significant amount of tetrahedral distortion leading to a pseudo-square planar geometry, as is evidenced from EPR properties. Cyclic voltammograms of all the complexes display quasireversible oxidations, Cu(III)–Cu(II), in the range 0.31–0.45 V and reduction peaks, Cu(II)–Cu(I),in the range −0.29 to −0.36 V, involving a large geometrical change and irreversible. The observed redox potentials vary with respect to the size of the chelate ring of the Schiff base ligands. Further, the catalytic activity of all the complexes has been found to be high towards the oxidation of alcohols into aldehydes and ketones in the presence of *N*-methylmorpholine-*N*-oxide as co-oxidant. The formation of high valent Cu^{IV}=O oxo species as a catalytic intermediate is proposed for the catalytic process.

Keywords: paramagnetic copper(II) complexes; O–N–O donors; redox potentials; catalytic activity

Introduction

The preparation of Schiff base containing > C=O, > C=N, > C=N groups with potential ligating ability has drawn a lot of attention in recent years because of their use as chelating agents, analytical reagents, metal indicators in complexometric titrations and colorimetric reagents, in addition to biochemical research. The behaviour of the > C=N bond is strongly dependent on the structure of the amine moiety, which in turn controls the efficiency of the conjugation and may incorporate structural elements able to modulate the steric crowding around the coordination.[1] This class of ligands is flexible in terms of both size and charge.[2] Schiff base complexes of transition metals[3] having O and N donor atoms have shown an exponential increase as inorganic catalysts for various organic transformations. Transition metal phosphine complexes also find application in classical catalytic processes such as hydrogenation, isomerization, decarbonylation, reductive elimination, oxidative addition and in making C–C bonds.[4] Unquestionably, transition metal-based catalytic systems have established themselves as the most employed 'work horses' in modern oxidation chemistry for preparatory purposes.[5] Among these, catalytic oxidation of alcohols to carbonyl compounds is a pivotal reaction due to their utility in fine chemical and pharmaceutical industries.[6] No reports are available on the oxidation of alcohols into their carbonyl compounds catalysed by copper(II) Schiff base complexes in the presence of *N*-methylmorpholine-*N*-oxide (NMO) as co-oxidant. In copper (II) complexes the metal ions have either a four or six coordination geometry and there only a few exceptions to this. The 3d^9 configuration of Cu(II) is of particular interest because it represents a simple one magnetic hole system.[7]

In view of the rich photophysical and catalytic properties of organometallic copper(II) complexes, the introduction of Schiff bases with an O–N–O donor set to Cu(II) complexes containing triphenylphosphine has been carried out. As on extension of our preliminary communication[8] and to provide further insight into the catalytic and electronic behaviours, an extensive series containing Schiff bases has been synthesized and characterized. Further, the redox and electron paramagnetic resonance studies are also reported along with the catalytic activity of copper(II) complexes towards oxidation of primary alcohols. The tridentate Schiff bases were derived from

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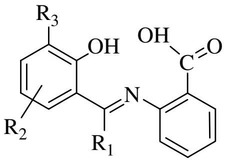
condensation of anthranilic acid and salicylaldehyde/2-hydroxy-1-naphthaldehyde/o-hydroxyacetophenone/*o*-vanillin (Scheme 1).

Experimental

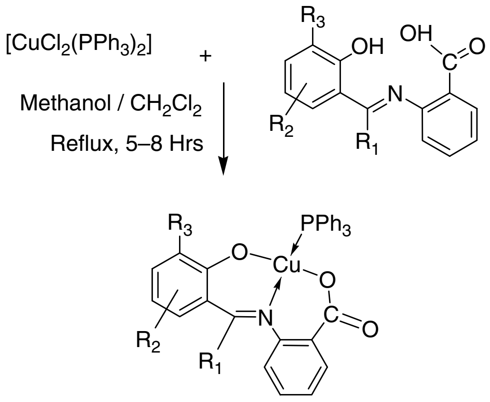
Materials and physical measurements

The Schiff bases were prepared by following the reported procedure.[8,9] All the reagents used were chemically pure and of analytical reagent grade. Solvents were purified and dried according to standard procedures. $CuCl_2.2H_2O$ was purchased from Loba Chemie Pvt Ltd, Bombay, India and was used without further purification. $[CuCl_2(PPh_3)_2]$ was prepared by the methods available in literature.[10] Microanalyses were performed at Sophisticated Test and Instrumentation Centre (STIC), Cochin University, Kerala, India. Infrared spectra were recorded using KBr pellets in the 4000–400 cm^{-1} region in a Shimadzu FT-IR 8000 spectrophotometer/Nicolet Avatar Model. Electronic spectra of the complexes were recorded in methanol solution with a Systronics-2202 double beam UV-spectrophotometer at 800–200 nm. Room temperature and frozen EPR spectra of powdered samples and solution samples were recorded on an E-112 Varian model instrument in X-band frequencies. Magnetic moments were measured on an EG&G PARC vibrating sample magnetometer. Cyclic voltammetric measurements were carried out on a Bio Analytical System (BAS) CV-50 electrochemical analyser using CH_2Cl_2 as solvent. Melting points were recorded with a Raaga apparatus and are uncorrected.



R_1	R_2	R_3	Abbreviation
H	H	H	H_2L^1
H	C_4H_4	H	H_2L^2
CH_3	H	H	H_2L^3
H	H	OCH_3	H_2L^4

Scheme 1. Structure of Schiff base ligands.



Scheme 2. Formation of new Cu(II) Schiff base complexes.

Synthesis of new Cu(II) Schiff base complexes containing triphenylphosphine

To a solution of $[CuCl_2(PPh_3)_2]$ (0.131g; 0.2 mmol) in ethanol the appropriate Schiff base ligand (0.2 mmol) in dichloromethane was added and heated under refluxed for 5–8 h. The resulting solution was concentrated to 5 cm^3 and cooled. The product was separated by the addition of small quantity of petroleum ether (60–80 °C; 5 cm^3) whereupon the complex separated out. The solid was filtered off, washed and recrystallized from chloroform–petroleum ether mixture and dried *in vacuo*. The purity of the complexes was checked by TLC (yield: 67–72%).

Catalytic oxidation

Catalytic oxidation of alcohols to corresponding aldehydes and ketones by copper(II) Schiff base complexes containing triphenylphosphine as co-ligand was studied in the presence of NMO as co-oxidant. A typical reaction using the complex $[Cu(PPh_3(L)]$ as a catalyst and alcohols as substrates at a 1 : 100 molar ratio is described as follows. A solution of copper(II) Schiff base complex (0.01 mmol) in 20 cm^3 CH_2Cl_2 was added to the solution of substrate (1 mmol) and NMO (3 mmol). The solution mixture was stirred at room temperature for 3 h and the solvent was then evaporated from the mother liquor by heating under reduced pressure. The residue was then extracted with petroleum ether (60–80 °C; 20 cm^3) and was then quantified as 2,4-dinitrophenylhydrazone derivative. The oxidation products are known and are commercially available.

Results and Discussions

Stable copper (II) complexes of the general formula $[Cu(PPh_3)(L)]$ (where L = dianion tridentate Schiff bases) have prepared by reacting $[CuCl_2(PPh_3)_2]$ with the respective tridentate Schiff bases in a 1 : 1 molar ratio in CH_2Cl_2–ethanol mixture as shown in Scheme 2. All the complexes are soluble in most common organic solvents. Their purity was checked by thin-layer chromatography on silica gel.

The analytical data for the new complexes agree well with the proposed molecular formula (Table 1). In all of the above reactions, Schiff bases behave as binegative tridentate ligands.

IR spectra

The IR spectra of the ligands were compared with those of the copper complexes in order to confirm the binding mode of the Schiff base ligands to the copper ion in the complexes (Table 1). In all the complexes, the $\nu_{(>C=N)}$ band is shifted to lower frequency, 1590–1610 cm^{-1}, indicating coordination of the Schiff bases through the azomethine nitrogen atom.[8,11,12] On complexation, the band due to phenolic C–O stretching has been shifted to a higher frequency range, 1310 cm^{-1}, showing that the other coordination site is through the phenolic oxygen atom. This has been further supported by the disappearance of the broad band around 3000 cm^{-1} due to O–H in the complexes.[13,14] The coordination of the azomethine nitrogen and phenolic oxygen are further supported by the appearance of two bands at 510–540 and 400–460 cm^{-1} due to ν_{M-O}[13]

Table 1. Physico-chemical, IR and analytical data of H_2L^1–H_2L^4 and new copper (II) Schiff base complexes

Sample no.	Complexes	Colour	Molecular weight	Melting point (°C)	Yield (%)	IR data $\nu_{(C=N)}$ (cm^{-1})	$\nu_{(Ph-C-O)}$ (cm^{-1})	$\nu_{asy(COO^-)}$ (cm^{-1})	$\nu_{sym(COO^{-1})}$ (cm^{-1})	$\nu_{(OH)}$ (cm^{-1})	$\nu_{(PPh3)}$ (cm^{-1})	Elemental analysis calculated (found) (%) C	H	N
1.	H_2L^1 $C_{14}H_{11}NO_3$	Orange	241.24	194	62	1605	1285	–	–	3240	–	69.90 (69.05)	4.60 (4.11)	5.81 (5.96)
2.	H_2L^2 $C_{18}H_{13}NO_3$	Yellow	291.30	231	68	1619	1291	–	–	3255	–	74.22 (75.00)	4.50 (4.91)	4.81 (5.13)
3.	H_2L^3 $C_{15}H_{13}NO_3$	Yellow	255.27	145	58	1612	1301	–	–	3260	–	70.58 (71.02)	5.13 (4.90)	5.49 (5.18)
4.	H_2L^4 $C_{15}H_{13}NO_4$	Red	271.27	229	64	1615	1298	–	–	3225	–	66.41 (66.09)	4.83 (4.78)	5.16 (5.20)
5.	[Cu $(PPh_3)(L^1)$] $C_{33}H_{27}CuNO_3P$	Yellow	580.09	220	74	1581	1330	1643	1430	–	‘1432	68.02 (67.95)	4.28 (4.11)	2.47 (2.38)
6.	[Cu $(PPh_3)(L^2)$] $C_{37}H_{29}CuNO_3P$	Yellow	630.15	226	68	1592	1327	1614	1409	–	1434	70.29 (69.86)	4.26 (4.09)	2.27 (2.01)
7.	[Cu $(PPh_3)(L^3)$] $C_{34}H_{29}CuNO_3P$	Blue	594.12	>250	61	1582	1365	1658	1431	–	1435	68.45 (67.79)	4.52 (4.06)	2.41 (2.13)
8.	[Cu $(PPh_3)(L^4)$] $C_{34}H_{29}CuNO_4P$	Dark red	610.12	>250	65	1583	1328	1646	1412	–	1436	66.93 (66.25)	4.79 (4.31)	2.30 (2.04)

Table 2. Electronic and EPR spectral data for [Cu(PPh$_3$)(L)] Schiff base complexes

		EPR parameter																	
Complexes	UV–vis (nm)	g_0	$g_{\|\|}$	$g_\perp$	G	$^{Cu}A_0{}^a$	$^{Cu}A_{\|\|}{}^a$	$^{Cu}A_\perp{}^a$	$^{N}A_0{}^a$	$K_{\|\|}$	$K_\perp$	$f(\alpha)$	α^2	α'^2	β^2	β'^2	γ^2	γ'^2	μ_{eff} BM
[Cu(PPh$_3$)(L^1)]	350, 380, 578	2.110	2.143	2.052	2.80	76.30	178	29.1	16.0	0.61	0.44	125	0.65	0.82	0.56	0.78	1.22	1.11	1.83
[Cu(PPh$_3$)(L^2)]	359, 420, 581	2.113	2.135	2.055	2.57	74.10	176	28.4	14.7	0.59	0.45	126	0.63	0.81	0.55	0.78	1.19	1.10	1.90
[Cu(PPh$_3$)(L^3)]	362, 395, 590	2.110	2.148	2.062	2.42	75.40	174	27.6	15.7	0.61	0.48	128	0.67	0.83	0.55	0.78	1.37	1.19	1.77
[Cu(PPh$_3$)(L^4)]	365, 405, 587	2.108	2.145	2.049	3.04	74.21	178	26.9	15.3	0.60	0.42	125	0.66	0.81	0.55	0.78	1.06	1.03	1.88

[a] A × 10^{-4} in cm^{-1}.
$G = (g_{||} - 2.0023)/(g_\perp - 2.0023)$.

Table 3. Cyclic voltammetric data[a] for new copper (II) Schiff base complexes

	Cu(II)–Cu(III)				Cu(II)–Cu(I)			
Complex	E_{pa} (V)	E_{pc} (V)	E_f (V)	ΔE_p (mV)	E_{pa} (V)	E_{pc} (V)	E_f (V)	ΔE_p (mV)
[Cu(PPh$_3$)(L^1)]	0.230	0.350	0.290	120	−0.160	−0.225	0.193	65
[Cu(PPh$_3$)(L^2)]	0.250	0.375	0.313	125	−0.200	−0.350	−0.275	150
[Cu(PPh$_3$)(L^3)]	0.460	0.350	0.405	110	−0.180	−0.400	−0.290	220
[Cu(PPh$_3$)(L^4)]	0.470	0.365	0.416	105	−0.190	−0.410	−0.300	220

[a] Working electrode, glassy carbon electrode; reference electrode, Ag–AgCl electrode; supporting electrolyte, [NBu$_4$]ClO$_4$ (0.01 M); concentration of the complex, 0.001m; scan rate, 100 mV s^{-1}; $E_f = 0.5(E_{pa} + E_{pc})$, $\Delta E_p = E_{pa} - E_{pc}$, where E_{pa} and E_{pc} are anodic and cathodic potentials.

and ν_{M-N},[15] respectively. For the anthranilic acid moiety, the bands observed in the 1614–1660 and 1409–1430 cm^{-1} regions arise from asymmetric [$\nu_{asy(COO^-)}$] and symmetric [$\nu_{sym(COO^-)}$] stretching of the carboxylate group. The difference between the asymmetric and symmetric stretching frequencies of the coordinated carboxyl group lies in the 205–248 cm^{-1} range, indicating that the third coordination site is a carboxyl group with the free carbonyl group.[16] The characteristic bands due to triphenylphosphine were observed in the expected regions.

Magnetic moment and UV–vis spectra

The magnetic moment of all the copper(II) Schiff base complexes at room temperature lie in the range of 1.77–1.90 B.M., indicating the presence of one unpaired electron. This also indicates that these complexes are monomeric in nature.

The ground state of copper (II) is $d_{x^2-y^2}$, three spin-allowed transitions are expected,[17,18] viz., $^2B_{1g} \rightarrow {}^2A_{2g}(d_{x^2-y^2} \rightarrow d_{z^2})$, $^2B_{1g} \rightarrow {}^2B_{2g}(d_{x^2-y^2} \rightarrow d_{xy})$ and $^2B_{1g} \rightarrow {}^2E_g(d_{x^2-y^2} \rightarrow d_{xz,yz})$. It is rather difficult to resolve these bands because they are very close in energy and individual transition cannot be distinguished. These bands are utilized for evaluating the covalency parameters from ESR studies.

The electronic spectra of the mononuclear copper(II) Schiff base complexes exhibit three main transitions. The moderately intense peak observed are due to an intra-ligand charge transfer transitions.[19] A shoulder in the range 365–350 nm is due to phenolato to Cu(II) complex [$p_\pi \rightarrow$ Cu(II) d_π LMCT transition], and shows a λ_{max} of 578–590 nm due to a d–d transition (Table 2), which is characteristic of a square planar geometry.[20]

ESR spectra

The ESR parameters observed for polycrystalline state (300 K) and in DMSO (77 K) are presented in Table 3. The spectra of all the complexes showed three lines with three different '*g*' values, indicating magnetic anisotropy in these system. The spectra of four coordinate complexes in frozen DMSO resolved four copper hyperfine lines, characteristics of monomeric copper(II) complexes. The values of $g_{||}$ and $g \perp$ were in the ranges 2.135–2.148 and 2.049–2.062. The fact that the $g_{||}$ values are less than 2.3 is an indication of significant covalent bonding in these complexes.[21] The empirical ratio $g_{||} : A_{||}$ from 170 to 250 cm suggests a distorted tetragonal symmetry (square planar structure) around the Cu(II) ion.

The EPR parameters $g_{||}$, $g \perp$, g_o, $A_{||(Cu)}$ and $A_{\perp(Cu)}$ and the energies of d–d transition were used to evaluate the bonding parameters α^2, β^2 and γ^2, which may be regarded as measures of the covalency of the in-plane σ bonds, in-plane π bonds and out of plane π bonds, respectively. The following simplified expressions were used to calculate the bonding parameters.[22]

$$K_{||}{}^2 = (g_{||} - 2.0023)\Delta_{||}/8\lambda_0$$
$$K_\perp{}^2 = (g_\perp - 2.0023)\Delta_\perp/2\lambda_0$$

where $K_{||} = \alpha^2\beta^2$ and $K_\perp = \alpha^2\gamma^2$, $K_{||}$ and $K_\perp$ are orbital reduction factors and λ_o represents the one electron spin orbit coupling constant which equals −828 cm^{-1}. Hathway,[23] has pointed out that for the pure σ-bonding $K_{||} \approx K_\perp \approx 0.77$, for in-plane π-bonding $K_{||} < K_\perp$, while for out-of-plane π-bonding $K_\perp < K_{||}$. In all the complexes it is observed that $K_\perp < K_{||}$, which indicates the presence of out-of-plane π-bonding.

For these complexes, the *G*-values are <4, suggesting the monomeric nature of copper(II) centres and consistent with a $d_{x^2-y^2}$ ground state having a small exchange coupling.[24] The value of the in-plane σ bonding parameter (α^2) was estimated from the expression[25]

$$\alpha^2 = -A_{||}/0.036 + (g_{||} - 2.0023) + (3/7)(g_\perp - 2.0023) + 0.04$$

The α^2 values (0.63–0.67) account for the fraction of the unpaired electron density located on the copper(II) ion. These values are comparable to that obtained for copper complexes

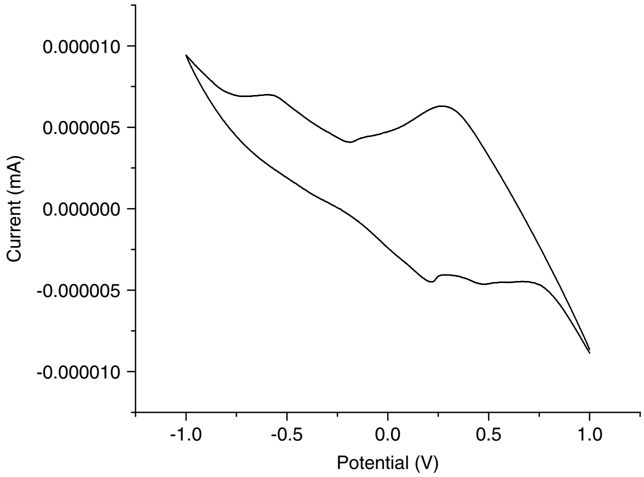


Figure 1. Cyclic voltammogram of $[Cu(PPh_3)(L^3)]$ complex.

Table 4. Catalytic oxidation of alcohols by Cu(II) Schiff base complexes in the presence of *N*-methylmorpholine-*N*-oxide as precursor

Complex	Substrate	Product	Yield (%)	Turnover number[a]
$[Cu\ (PPh_3)(L^1)]$	Cinnamyl alcohol	Cinnamaldehyde	57.56	58.08
	Benzyl alcohol	Benzaldehyde	55.73	57.79
	Cyclohexanol	Cyclohexanone	46.91	46.90
$[Cu\ (PPh_3)(L^2)]$	Cinnamyl alcohol	Cinnamaldehyde	60.23	60.18
	Benzyl alcohol	Benzaldehyde	57.34	59.46
	Cyclohexanol	Cyclohexanone	49.25	49.25
$[Cu\ (PPh_3)(L^3)]$	Cinnamyl alcohol	Cinnamaldehyde	53.27	54.11
	Benzyl alcohol	Benzaldehyde	52.06	53.98
	Cyclohexanol	Cyclohexanone	43.52	43.52
$[Cu\ (PPh_3)(L^4)]$	Cinnamyl alcohol	Cinnamaldehyde	58.21	59.03
	Benzyl alcohol	Benzaldehyde	56.55	58.64
	Cyclohexanol	Cyclohexanone	47.29	47.29

[a] Moles of product per mole of catalyst.

of Schiff bases,[24,26–29] indicating the presence of appreciable covalency in the σ-bond. The observed EPR parameters reflect the degree of tetrahedral distortion in square planar copper(II) complexes.[30]

Electrochemistry

Complexes were electrochemically examined at a glassy carbon working electrode in CH_2Cl_2 solution using cyclic voltammetry. A representative voltammograms has been depicted in Fig. 1 and the potential data are given in Table 3. The complexes display Cu(I)–Cu(II) and Cu(II)–Cu(III); the oxidation process Cu(II)–Cu(III) can be observed while scanning between 0 and +2.0 V. The redox potentials of the complexes were characterized by well–defined waves in the range 0.313–0.688 mV (oxidation) and −0.275 to −0.600 mV (reduction). Since the ligands used in this work are not reversibly reduced or oxidized in the applied potential range, the redox processes are assigned to the metal centres only. In the scan between 0 and −2.0 V, the reduction process is directly associated with reoxidation peak at 0.5 V in the reverse scan, suggesting one-electron redox change originating from the chemically reversible $[Cu(PPh_3)(L)] \rightarrow [Cu(PPh_3)(L)]^-$ but an electrochemically quasi-reversible Cu(II)–Cu(I) redox couple.[31]

Analysis of the cyclic voltammetric response of Fig. 1 for these complexes indicates that the ratio of i_{pa}/i_{pc} is approximately equal to unity and the peak-to-peak separation (ΔE_p) is in the range 65–220 mV. It is expected that the Cu(II)–Cu(I) couple experiences some structural reorganization barrier in view of the likely rearrangement from square planar Cu(II) to pseudo-tetrahedral Cu(I). It therefore originates from the chemical equilibrium between square-planar and tetrahedral (or pseudo-tetrahedral) geometries with concomitant departure from pure electrochemical reversibility for the Cu(II)–Cu(I) couple as measured by mean ΔE_p values of 65 mV at 0.01 V s^{-1} for the present series of complexes. The often interrelated factors which raise the $E_{1/2}$ value of the Cu(II)–Cu(I) couple may be considered to be:

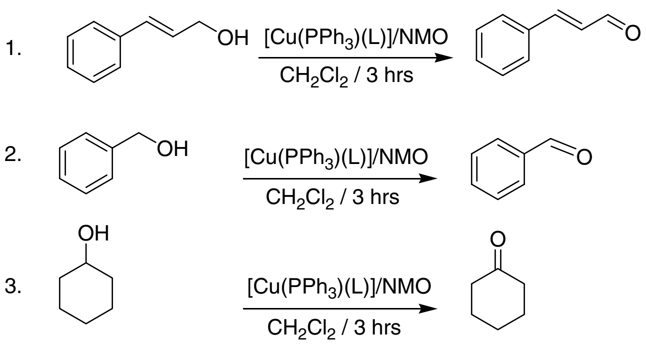
(1) those which stabilize Cu(II) species by reducing its crystal field stabilization energy (CFSE) either by decreasing the ligand σ-donor ability or by constraining the geometry of the copper centre favoring Cu(I); and

(2) the presence of π-acceptor ligands which favours the formation of Cu(I) species.[32] It has been shown that the softer ligands tend to favor more positive $E_{1/2}$ values while hard acids give rise to more negative values.[33]

The cyclic voltammetric behavior of $[Cu(PPh_3)(L)]$ between +1.0 and 0 V exhibits cathodic response in the range 230–470 mV with its counterpart in the range 350–375 mV. This feature corresponds to a quasi-reversible Cu(III)–Cu(II) redox process as indicated by ΔE_p values as non-equivalent current intensities of cathodic and anodic peaks ($\%i_{pc}/i_{pa}$). The redox process associated with oxidation of Cu(II) to Cu(III) for all the complexes may originate from the presence of phenolate oxygen centre and redox active carboxylate moiety. Moreover, the oxidation step results in the formation of a low-spin d^8 Cu(III) state with a preference for a square-planar geometry.[34] It is quite likely that this process does not proceed via a change in the geometry of the complex in CH_2Cl_2 solution. The cyclic voltammetric spectral data given in Table 3 indicates that the Cu(III) state can be stabilized at relatively lower oxidation potential.

Catalytic oxidation

The oxidation of benzyl alcohol, cinnamyl alcohol and cyclohexanol was carried out with the new copper(II) Schiff base complexes containing in the presence of *N*-methylmorpholine-*N*-oxide as co-oxidant and CH_2Cl_2 as solvent and the by-product water was removed using molecular sieves. The results are summarized in Table 4. Benzaldehyde was formed from benzyl alcohol. Cinnamyl alcohol and cyclohexanol were converted into cinnamaldehyde and cyclohexanone, respectively. The products formed were quantified as their 2,4-dinitrophenylhydrazone derivatives. There was no detectable oxidation of alcohol in the presence of *N*-methylmorpholine-*N*-oxide alone. All the complexes were found to catalyze the oxidation of alcohols to aldehydes/ketone, but the yields and the turnover number were found to vary with different catalysts. This was further supported by changes that occur on addition of NMO to a CH_2Cl_2 solution of the Cu(II) Schiff base complexes containing triphenylphosphine. The oxidation of cinnamyl alcohol to cinnamaldehyde took place with retention of the carbon–carbon double bond.



Scheme 3. Catalytic oxidation of alcohols by Cu(II) complexes.

$[Cu(PPh_3)(L)]$ was found to be an effective catalyst for the oxidation of various alcohols with NMO as the co-oxidant. It has been found that the substitution of groups on the Schiff base affects the catalytic activity of the complexes.[35] These complexes were used as catalysts in the oxidation of alcohols to aldehydes or ketones using NMO as the co-oxidant. The relatively higher product yield obtained for the oxidation of cinnamyl alcohol as compared with benzyl alcohol is due to the presence of the unsaturation in cinnamyl alcohol. The relatively higher product yield obtained for the oxidation of cinnamyl alcohol than for benzyl alcohol is due to the fact that the α-CH moiety of cinnamyl alcohol is more acidic.[36–38] The proposed catalytic oxidation of alcohols to their corresponding aldehydes and ketones by $[Cu(PPh_3)(L)]$ complexes is shown in Scheme 3.

References

[1] K. B. Gudasi, M. S. Patil, R. S. Vadavi, R. V. Shenoy, S. A. Patil, *Trans. Met. Chem.*, **2006**, *31*, 580.
[2] W. J. Evans, Cy. H. Ziller, *Polyhedron*, **2002**, *21*, 1683.
[3] M. Amirnasr, A. H. Mahmoud Khani, A. Gorji, S. Dehghnpour, H. R. Bijanzadeh, *Polyhedron*, **2002**, *21*, 2733.
[4] S. Yamada, *Coord. Chem. Rev.*, **1999**, *190*, 537.
[5] J. Y. Kim, M. J. Jun, W. J. Lee, *J. Orgonomet. Chem.*, **2003**, *665*, 87.
[6] S. Priyarega, R. Prabhakaran, K. R. Aranganayagam, R. Karvembu, K. Natarajan, *Appl. Organometal. Chem.*, **2007**, *21*, 788.
[7] R. Kripal, S. Misra, *J. Phys. Chem. Solids*, **2004**, *65*, 939.
[8] C. Jayabalakrishnan, R. Karvembu, R. Natarajan, *Trans. Met. Chem.*, **2002**, *27*, 790.
[9] G. Asgedom, A. Sreedhara, J. Kivikoshi, C. P. Rao, *Polyhedron*, **1997**, *16*, 643.
[10] J. Venanzi, *J. Chem. Soc.*, **1958**, 719.
[11] S. A. Ali, A. A. Soliman, M. M. Aboaly, R. M. Ramadan, *J. Coord. Chem.*, **2002**, *55*, 1161.
[12] P. Viswanathamurthi, N. Dharmaraj, K. Natarajan, *Synth. React. Inorg. Met.-Org. Chem.*, **2000**, *30*, 1273.
[13] R. C. Maurya, P. Patel, S. Rajput, *Synth. React. Inorg. Met.-Org. Chem.*, **2003**, *23*, 817.
[14] P. Viswanathamurthi, K. Natarajan, *Trans. Met. Chem.*, **1999**, *24*, 638.
[15] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*. Wiley-Interscience: New York. **1971**.
[16] S. D. Rabinson, M. F. Uttley, *J. Chem. Soc. Dalton Trans.*, **1973**, 1912.
[17] J. Manonmani, M. Kandaswamy, V. Narayanan, R. Thirumurugan, S. Shanmuga Sundara Raj, G. Shnamugam, M. N. Ponnusamy, H. K. Fun, *Polyhedron*, **2001**, *20*, 3039.
[18] V. T. Kasumov, F. Koksal, Y. Zeren, *Spectrochimica Acta Part A*, **2006**, *63*, 330.
[19] B. Harikumar, M. R. P. Kurup, T. N. Jayaprakash, *Trans. Met. Chem.*, **1997**, *22*, 507.
[20] P. Bindu, M. R. P. Kurup, *Trans. Met. Chem.*, **1997**, *22*, 578.
[21] P. Bindu, M. R. P. Kurup, T. R. Sathyakeerty, *Polyhedron*, **1999**, *18*, 321.
[22] B. N. Figgis, *Introduction to Ligand Fields*. Interscience: New York, **1966**, 295; b) D. X. West, *J. Inorg. Nucl. Chem.* **1984**, *43*, 3169.
[23] B. J. Hathway, G. Wilkinson, R. D. Gillard, J. A. McCleverty, (Eds). *Comprehensive Coordination Chemistry II*, Vol. 5. Pergamon: Oxford, **1987**; b) B. J. Hathway, *Struct. Bond.*, **1973**, *14*, 60.
[24] M. Joseph, V. Suni, M. R. P. Kurup, M. Nethaji, A. Kishore, S. G. Bhat, *Polyhedron*, **2004**, *23*, 2069.
[25] D. Kivelson, R. Neiman, *J. Chem. Soc. Dalton Trans.*, **1961**, *35*, 149; b) A. H. Maki, B. R. McGarvey, *J. Chem. Phys.*, **1958**, *29*, 35.
[26] R. P. John, A. Sreekanth, V. Rajakannan, T. A. Ajith, M. R. P. Kurup, *Polyhedron*, **2004**, *23*, 2549.
[27] A. Sreekanth, M. R. P. Kurup, *Polyhedron*, **2003**, *22*, 3321.
[28] R. P. John, A. Sreekanth, M. R. P. Kurup, A. Usman, A. R. Ibrahim, H. K. Fun, *Spectrochim. Acta Part A*, **2003**, *59*, 1349.
[29] C. G. Pierpont, *Coord. Chem. Rev.*, **2001**, *219–221*, 415.
[30] C. G. Pierpont, *Coord. Chem. Rev.*, **2001**, *216–217*, 99.
[31] A. M. Bond, R. L. Martin, *Coord. Chem. Rev.*, **1984**, *54*, 23.
[32] E. V. R. Askimova, A. Y. Nazarenko, L. Chen, P. W. Krieger, A. M. Herrera, V. V. Tarasov, P. D. Rabinson. *Inorg. Chim. Acta*, **2001**, *324*, 1.
[33] G. S. Patterson, R. H. Holm, *J. Bioinorg. Chem.*, **1975**, *4*, 1257.
[34] X. H. Bu, X. Ch. Cao, D. L. An, R. H. Zhang, C. Thomas, E. Kimura, *J. Chem. Soc., Dalton Trans.*, **1998**, 433.
[35] P. K. Bhattacharya, *Proc. Ind. Acad. Sci. (Chem. Sci.)*, **1990**, *102*, 247.
[36] K. M. Ibrahim, S. I. Mostafa, N. Nawar, Z. A. Younis, *Ind. J. Chem.*, **2004**, *43A*, 2294.
[37] R. Karvembu, C. Jayabalakrishanan, K. Natarajan, *Trans. Met. Chem.*, **2002**, *27*, 574.
[38] R. Karvembu, S. Hemalatha, R. Prabhakaran, K. Natarajan, *Inorg. Chem. Commun.*, **2003**, *6*, 486.