Copper(II) Complexes of Novel Tripodal Ligands containing Phenolate and Benzimidazole/Pyridine Pendants: Synthesis, Structure, Spectra and Electrochemical Behaviour†

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Mononuclear copper(II) complexes of tri- and tetra-dentate tripodal ligands containing phenolic hydroxyl and benzimidazole or pyridine groups have been isolated. They are of the type $[CuL(X)]\cdot nH_2O$, $[CuL(H_2O)]X\cdot nH_2O$ or $[CuL]\cdot nH_2O$ where X = Cl^-, ClO_4^-, N_3^- or NCS^- and n = 0–4. The electronic spectra of all the complexes exhibit a broad absorption band around 14 000 cm^{-1} and the polycrystalline as well as the frozen-solution EPR spectra are axial, indicating square-based geometries. The crystal structure of [CuL(Cl)] [HL = (2-hydroxy-5-nitrobenzyl)bis(2-pyridylmethyl)amine] revealed a square-pyramidal geometry around Cu^{II}. The mononuclear complex crystallises in the triclinic space group $P\bar{1}$ with $a = 6.938(1)$, $b = 11.782(6)$, $c = 12.678(3)$ Å and $\alpha = 114.56(3)$, $\beta = 92.70(2)$, $\gamma = 95.36(2)°$. The co-ordination plane is comprised of one tertiary amine and two pyridine nitrogens and a chloride ion. The phenolate ion unusually occupies the axial site, possibly due to the electron-withdrawing *p*-nitro group. The enhanced π delocalisation involving the *p*-nitrophenolate donor elevates the $E_{\frac{1}{2}}$ values. The spectral and electrochemical results suggest the order of donor strength as nitrophenolate < pyridine < benzimidazole in the tridentate and nitrophenolate < benzimidazole < pyridine in the tetradentate ligand complexes.

The enzyme galactose oxidase is unusual among metalloenzymes in appearing to catalyse the oxidation of several primary alcohols to aldehydes, involving two-electron redox chemistry at a mononuclear metal-ion active site.[1] A very recent report on the crystal structure[2] of this enzyme reveals Cu^{II} in a square-pyramidal environment. Amino acid Tyr-272, His-496, His-581 and an acetate ion form an almost perfect square with respective distances from copper of 1.94, 2.11, 2.15 and 2.27 ± 0.15 Å; the axial ligand Tyr-495 is 2.69 Å from copper. To establish the structure and spectroscopic effects of phenolate donors in this enzyme, we initiated a study of monomeric copper(II) complexes containing phenolate and imidazole donors.

In this paper are discussed the results from a detailed structural, spectroscopic and electrochemical study of mononuclear copper(II) complexes of linear tri- and tetra-dentate tripodal ligands containing one or two phenolic hydroxyl and benzimidazole (bzim) or pyridine (py) pendant groups. By varying the donor groups (py, bzim and phenolic hydroxyl) and the number of methylene groups between the ligating termini the structural and redox properties of the copper(II) ions can be controlled. While the *para*-substituted phenolic moiety resembles the amino acid tyrosine,[3] py nitrogens model the histidine imidazole (Him) in the enzyme active site. The incorporation of bzim, in addition to mimicking the imidazole donor function would result in distortions in co-ordination geometries owing to its steric bulk. Further, the tripodal nature of the present ligands may impose unusual geometries on Cu^{II}. The crystal structure of one of the complexes with an unusual axial co-ordination of phenolate oxygen to Cu^{II} has been reported[4] as a preliminary communication.

Experimental

Materials.—2-Aminomethylbenzimidazole dihydrochloride,[5] 2-(2-aminoethyl)benzimidazole dihydrochloride,[5] 2-chloromethyl-4-nitrophenol[6] and bis(2-pyridylmethyl)amine[7] were synthesised by published procedures. All reagents and solvents were used as received from G. F. Smith [$Cu(ClO_4)_2\cdot 6H_2O$, tetrahexylammonium perchlorate, tetrabutylammonium perchlorate], BDH, India ($CuCl_2\cdot 2H_2O$), Aldrich (2-chloromethylbenzimidazole, *o*-phenylenediamine, β-alanine, glycine), Fluka (2-chloromethylpyridine hydrochloride), Sisco, India (sodium tetrafluoroborate, tetraethylammonium bromide), and Loba Chemie, India (ammonium thiocyanate). The supporting electrolytes $N(C_6H_{13})_4ClO_4$ and $NBu^n{}_4ClO_4$ were recrystallised twice from aqueous ethanol and tetraethylammonium tetrafluoroborate thrice from ethyl acetate–water (3:1). The following solvents were distilled before use in the electrochemical studies: dimethylformamide (dmf), from P_4O_{10} under reduced pressure after neutralising the phosphoric acid generated using crystalline NaOH; methanol, from $Mg(OMe)_2$.

Synthesis of Ligands and Copper(II) *Complexes.*—$[CuL^1(Cl)(H_2O)]\cdot 3H_2O$. Bis(benzimidazol-2-ylmethyl)(2-hydroxy-5-nitrobenzyl)amine (HL^1) was obtained as described below and used for complexation. A tetrahydrofuran (thf) solution (40 cm^3) of 2-aminomethylbenzimidazole dihydrochloride (1.10 g, 5 mmol) was added dropwise to a solution of 2-chloromethylnitrophenol (0.94 g, 5 mmol) in methanol (30 cm^3) and then NEt_3 (1.53 g, 15 mmol) was added. The mixture was heated under reflux for 2 h. Charcoal was then added, the solution filtered and the filtrate rotaevaporated to obtain a syrup. The latter was dissolved in methanol (25 cm^3) and NEt_3 (0.51 g, 5 mmol) was added followed by $CuCl_2\cdot 2H_2O$ (0.85 g, 5 mmol) in methanol (5 cm^3). The green precipitate formed immediately was filtered off, washed with methanol and dried under vacuum over P_4O_{10}.

$[CuL^1(H_2O)]ClO_4\cdot 3H_2O$. This complex was prepared as above using $Cu(ClO_4)_2\cdot 6H_2O$ (1.85 g, 5 mmol) in methanol (5.5 cm^3) instead of $CuCl_2\cdot 2H_2O$.

$[CuL^2(H_2O)]ClO_4\cdot 2H_2O$. Bis(benzimidazol-2-yl[2-ethyl])(2-hydroxy-5-nitrobenzyl)amine (HL^2) was prepared following

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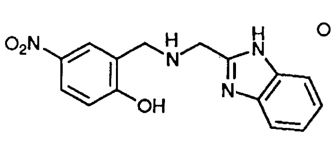
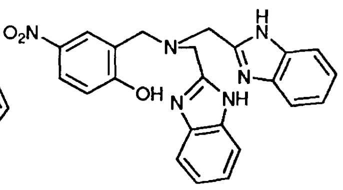
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.



HL^1



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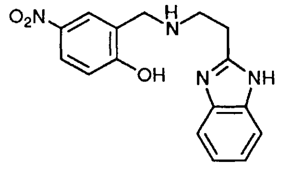

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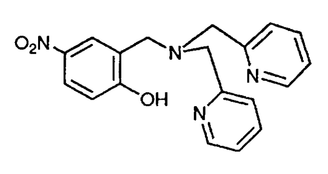

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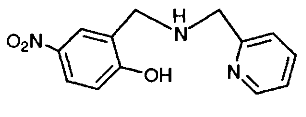

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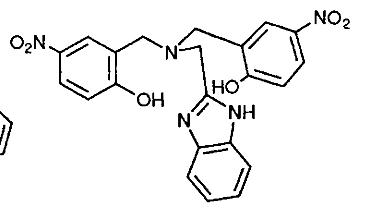
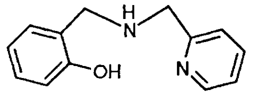
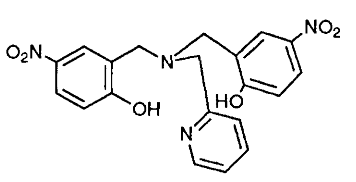


H$_2$L^7



HL^4



H$_2$L^8

the same procedure used for HL^1. To a thf solution (40 cm^3) of 2-(2-aminoethyl)benzimidazole dihydrochloride (0.94 g, 4 mmol) was added dropwise a solution of 2-chloromethyl-4-nitrophenol (0.75 g, 4 mmol) in MeOH (30 cm^3) followed by NEt$_3$ (0.41 g, 4 mmol). The mixture was heated under reflux for 2 h. Charcoal was then added, the solution filtered and the filtrate rotaevaporated to obtain a syrup. The latter was dissolved in methanol (25 cm^3) and NEt$_3$ (0.41 g, 4 mmol) was added followed by Cu(ClO$_4$)$_2$•6H$_2$O (1.48 g, 4 mmol) in methanol (4.4 cm^3). The green precipitate formed immediately was filtered off, washed with methanol and dried under vacuum over P$_4$O$_{10}$.

[CuL^3(Cl)]•H$_2$O. (2-Hydroxy-5-nitrobenzyl)(2-pyridylmethyl)amine (HL^3) was obtained as a syrup by the method employed for HL^1, using 2-aminomethylpyridine (0.43 g, 4 mmol), 2-chloromethyl-4-nitrophenol (0.75 g, 4 mmol) and NEt$_3$ (0.41 g, 4 mmol). The syrup obtained was dissolved in methanol (25 cm^3) and NEt$_3$ (0.41 g, 4 mmol) was added followed by CuCl$_2$•2H$_2$O (0.85 g, 5 mmol) in methanol (5 cm^3). The green precipitate formed immediately was filtered off, washed with methanol and dried under vacuum over P$_4$O$_{10}$.

[CuL^4(Cl)]•H$_2$O. (2-Hydroxybenzyl)(2-pyridylmethyl)amine (HL^4) was prepared as follows. To 2-aminomethylpyridine (0.43 g, 4 mmol) in methanol (20 cm^3), was added salicylaldehyde (0.49 g, 4 mmol) followed by NEt$_3$ (0.41 g, 4 mmol) dropwise. The solution was refluxed for 0.5 h and cooled. With cooling in ice, NaBH$_4$ (0.15 g, 4 mmol) in methanol (10 cm^3) was added. Charcoal was then added, the solution filtered and the filtrate rotaevaporated to obtain a syrup as for HL^1. The compound thus obtained was dissolved in methanol (25 cm^3) and NEt$_3$ (0.41 g, 4 mmol) was added followed by CuCl$_2$•2H$_2$O (0.68 g, 4 mmol) in methanol (4 cm^3). The green precipitate formed immediately was filtered off, washed with methanol and dried under vacuum over P$_4$O$_{10}$.

[CuL^5(Cl)]•4H$_2$O. Bis(benzimidazol-2-ylmethyl)(2-hydroxy-5-nitrobenzyl)amine (HL^5) was obtained as a syrup by the method employed for HL^1, using 2-chloromethyl-4-nitrophenol (0.75 g, 4 mmol), 2-aminomethylbenzimidazole dihydrochloride (1.76 g, 8 mmol) and NEt$_3$ (2.45 g, 24 mmol). The syrup obtained was dissolved in methanol (25 cm^3) and NEt$_3$ (0.41 g, 4 mmol) was added followed by CuCl$_2$•2H$_2$O (0.68 g, 4 mmol) in methanol (4 cm^3). The green precipitate formed immediately was filtered off, washed with methanol and dried under vacuum over P$_4$O$_{10}$.

[CuL^6(Cl)]. (2-Hydroxy-5-nitrobenzyl)bis(2-pyridylmethyl)amine (HL^6) was obtained as a syrup[8] by the method employed for HL^1, using bis(2-pyridylmethyl)amine (0.80 g, 4 mmol), 2-chloromethyl-4-nitrophenol (0.75 g, 4 mmol) and NEt$_3$ (0.41 g, 4 mmol). The syrup obtained was dissolved in methanol (25 cm^3) and NEt$_3$ (0.41 g, 4 mmol) was added followed by CuCl$_2$•2H$_2$O (0.68 g, 4 mmol) in methanol (4 cm^3). The green precipitate formed immediately was filtered off, washed with methanol and dried under vacuum over P$_4$O$_{10}$. A solution of this complex in methanol on standing at room temperature gave crystals suitable for X-ray analysis.

[CuL^6(H$_2$O)]ClO$_4$•H$_2$O. This complex was prepared following the procedure used for [CuL^6(Cl)] but by using Cu(ClO$_4$)$_2$•6H$_2$O (1.48 g, 4 mmol) in methanol (4.4 cm^3) instead of CuCl$_2$•2H$_2$O.

[CuL^6(NCS)]. A saturated solution of ammonium thiocyanate in methanol (7.5 cm^3) was added to a solution of [Cu(L^6)Cl] in MeOH–MeCN (1 : 1, 20 cm^{-3}). The solution was stirred well for 15 min and filtered. The filtrate was allowed to stand for 2 d. Dark green crystals were filtered off, washed with a small amount of methanol and dried under vacuum over P$_4$O$_{10}$.

[CuL^6(N$_3$)]•H$_2$O. A saturated solution of sodium azide in MeOH (7.5 cm^3) was added to a solution of [Cu(L^6)Cl] in MeOH–MeCN (1 : 1, 15 cm^3). The solution was stirred well for 15 min and the green crystalline product formed was filtered off, washed with a small amount of methanol and dried under vacuum over P$_4$O$_{10}$.

[CuL^7(H$_2$O)]•2H$_2$O. (Benzimidazol-2-ylmethyl)bis(2-hydroxy-5-nitrobenzyl)amine (H$_2$L^7) was obtained as a syrup by the method employed for HL^1, using 2-aminomethylbenzimidazole dihydrochloride (0.88 g, 4 mmol), 2-chloromethyl-4-nitrophenol (0.75 g, 8 mmol) and NEt$_3$ (1.63 g, 16 mmol). The syrup obtained was dissolved in methanol (25 cm^3) and NEt$_3$ (0.82 g, 8 mmol) was added followed by CuCl$_2$•2H$_2$O (0.68 g, 4 mmol) in methanol (4 cm^3). The green precipitate formed immediately was filtered off, washed with methanol and dried under vacuum over P$_4$O$_{10}$.

[CuL^8(H$_2$O)]. Bis(2-hydroxy-5-nitrobenzyl)(2-pyridylmethyl)amine (H$_2$L^8) was obtained as a syrup by the method employed for HL^1, using 2-aminomethylpyridine (0.43 g, 4 mmol) and 2-chloromethyl-4-nitrophenol (1.5 g, 8 mmol) and NEt$_3$ (0.82 g, 8 mmol). The syrup obtained was dissolved in methanol (25 cm^3) and NEt$_3$ (0.82 g, 8 mmol) was added followed by CuCl$_2$•2H$_2$O (0.68 g, 4 mmol) in methanol (4 cm^3). The green precipitate formed immediately was filtered off, washed with methanol and dried under vacuum over P$_4$O$_{10}$.

All the complexes were isolated in good yield (70–80%) and their elemental analyses are collected in Table 1.

Physical Measurements.—Elemental analyses for the complexes were done at Central Drug Research Institute, Lucknow, India. Infrared spectra were recorded as KBr discs and Nujol mulls on a Shimadzu 400–4000 spectrophotometer, reflectance and solution spectra on a Hitachi U-3400 double-beam UV/VIS/NIR spectrophotometer, and EPR spectra on a Varian E-112 X-band spectrometer, the field being calibrated with diphenylpicrylhydrazyl (dpph). The values of g_0 and A_0 were measured at ambient temperature and $g_{\parallel}$ and $A_{\parallel}$ at 77 K.

Cyclic voltammetry and differential pulse voltammetry at a platinum-sphere electrode were performed at 25.0 ± 0.2 °C. A three-electrode cell configuration was used. The reference electrode was Ag(s)–$AgNO_3$ (0.01 mol dm^{-3}), $N(C_6H_{13})_4ClO_4$ (0.1 mol dm^{-3}) in acetonitrile. The temperature of the electrochemical cell was maintained by a cryocirculator (Haake D8 G). The solutions were deoxygenated by bubbling research-grade nitrogen. The instruments utilised included a EG & G PAR 273 potentiostat/galvanostat and an IBM PS-2 computer; EG & G M270 software was employed to carry out the experiments and to acquire the data. A Hewlett-Packard plotter (DMP 40) was used for the voltammograms.

Crystallographic Data Collection and Structure Analysis for [CuL^6(Cl)].—A crystal showing nice extinction under a polarising microscope was used for data collection with an Enraf-Nonius CAD4 diffractometer using Mo-Kα radiation. The triclinic cell obtained with randomly chosen reflections in the range of $9 < \theta < 12°$ did not show any higher symmetry with the usual transformation techniques. These reflections were centred and the cell parameters refined by the least-squares method. The intensities of three reflections were monitored every 100. Over the entire period of data collection the variation of these intensities was much less than 10%. Finally, the intensity data set was subjected to Lorentz polarisation and absorption corrections. For the latter a FORTRAN program (ABSORPTION.FOR)[9] based on the method of North *et al.*[10] was used. The details regarding the data collection and processing are presented in Table 2.

The statistical analysis of the data showed that the crystal was centric. The absence of any systematic absences led to the determination of the space group as $P\bar{1}$. The coordinates of the copper atom were determined from the strongest peak and by analysing the Patterson vectors the chloride and a few nitrogen atoms were determined. The Fourier difference synthesis done with these atoms revealed all the non-hydrogen atoms. Further refinement of these atoms also revealed all the hydrogens. The latter were refined isotropically and the non-hydrogen atoms anisotropically till convergence of the shift/e.s.d. to 10^{-3}. All the electron densities were accounted for and the *R* factor was 0.048. The SHELX 400 program[11] was used for structure solution and refinement and a DEC 1090 computer for calculations. The molecular structure was drawn using ORTEP II.[12] The final atomic coordinates are given in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Table 1 Elemental analyses for the copper(II) complexes with calculated values in parentheses

	Analysis (%)		
Compound	C	H	N
[CuL^1(Cl)(H_2O)]·3H_2O	34.20	4.40	10.85
	(33.85)	(4.00)	(10.55)
[CuL^1(H_2O)]ClO_4·3H_2O	38.20	4.55	11.75
	(38.45)	(4.50)	(11.95)
[CuL^2(H_2O)]ClO_4·2H_2O	36.35	4.00	10.70
	(36.35)	(4.00)	(10.60)
[CuL^3(Cl)]·H_2O	41.50	3.55	11.20
	(41.60)	(3.75)	(11.20)
[CuL^4(Cl)]·H_2O	47.55	4.30	9.10
	(47.25)	(4.60)	(8.50)
[CuL^5(Cl)]·4H_2O	46.35	4.20	41.20
	(46.15)	(4.55)	(14.05)
[CuL^6(Cl)]	50.60	3.45	12.45
	(50.90)	(3.80)	(12.50)
[CuL^6(H_2O)]ClO_4·H_2O	41.55	3.75	10.40
	(41.60)	(3.85)	(10.20)
[CuL^6(N_3)]·H_2O	48.40	3.95	21.40
	(48.25)	(4.05)	(20.75)
[CuL^6(NCS)]	51.35	3.60	14.50
	(51.00)	(3.65)	(14.85)
[CuL^7(H_2O)]·2H_2O	46.90	4.30	12.60
	(46.75)	(4.10)	(12.40)
[CuL^8(H_2O)]	49.50	4.20	11.90
	(49.05)	(3.70)	(11.45)

Table 2 Crystallographic data for [CuL^6(Cl)]

Formula	$C_{19}H_{17}ClCuN_4O_3$
M	448.36
Crystal symmetry	Triclinic
Space group	$P\bar{1}$
a/Å	6.938(1)
b/Å	11.782(6)
c/Å	12.678(3)
α/°	114.56(3)
β/°	92.70(2)
γ/°	95.36(2)
U/Å^3	934.23
F(000)	458
Z	2
μ(Mo-Kα)/cm^{-1}	13.87
Crystal dimensions/mm	0.23 × 0.31 × 0.68
D_c/g cm^{-3}	1.59
λ(Mo-Kα)/Å	0.7107
T/K	293
Scan type	ω–2θ
θ-Range/°	1.0–27.5
No. of reflections measured	4836
No. of observed reflections	3824 [$I_o \geqslant 3.0\sigma(I_o)$]
Weighting scheme	$1/[\sigma^2(F) + 0.005\,877F^2]$
R	0.048

Table 3 Atomic coordinates (×10^4, ×10^5 for Cu) of the non-hydrogen atoms of [CuL^6(Cl)] with estimated standard deviations (e.s.d.s) in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu(1)	48 922(3)	19 406(3)	4 966(3)
N(2)	3 943(3)	1 207(2)	−1 182(2)
C(3)	2 163(4)	586(3)	−1 653(3)
C(4)	1 650(5)	77(3)	−2 830(3)
C(5)	3 000(6)	190(4)	−3 558(3)
C(6)	4 815(6)	816(3)	−3 088(3)
C(7)	5 251(4)	1 315(3)	−1 884(2)
C(8)	7 254(4)	1 919(3)	−1 321(2)
N(9)	7 233(3)	2 686(2)	−53(2)
C(10)	8 988(4)	2 623(3)	621(2)
C(11)	8 546(4)	2 836(2)	1 827(2)
C(12)	9 974(5)	3 285(3)	2 750(3)
C(13)	9 463(5)	3 424(3)	3 842(3)
C(14)	7 567(6)	3 098(4)	3 965(3)
C(15)	6 217(5)	2 639(4)	3 006(3)
N(16)	6 699(3)	2 497(2)	1 942(2)
C(17)	7 031(4)	4 014(2)	142(2)
C(18)	6 722(4)	4 875(2)	1 363(2)
C(19)	8 139(4)	5 820(3)	2 062(2)
C(20)	7 775(5)	6 650(3)	3 179(3)
C(21)	5 941(6)	6 556(3)	3 563(3)
C(22)	4 516(5)	5 632(3)	2 871(3)
C(23)	4 859(4)	4 714(2)	1 762(2)
O(24)	3 591(3)	3 780(2)	1 131(2)
N(25)	9 275(4)	7 608(3)	3 921(2)
O(26)	10 890(4)	7 667(3)	3 588(3)
O(27)	8 881(5)	8 351(3)	4 884(2)
Cl(28)	2 623(1)	818(1)	1 015(1)

Results and Discussion

Description of Structure of [CuL^6(Cl)].—An ORTEP plot of the complex is illustrated in Fig. 1, and selected bond lengths and angles are given in Table 4. The compound crystallises in the triclinic space group $P\bar{1}$. The crystal structure reveals that the copper atom is co-ordinated to two pyridine nitrogens, the tertiary amine nitrogen, the phenolate oxygen and the chloride ion. The geometry around copper(II) is best described as square pyramidal with a very small trigonal-bipyramidal component,[13] $\tau = 0.16$ [$= (\beta - \alpha)/60$, where β = Cl–Cu–N(9) 169.6° and α = N(2)–Cu–N(16) 160.1°]; for perfect tetragonal and trigonal-bipyramidal geometries the values of τ are zero and unity respectively.[13] The basal plane is comprised of two pyridine and tertiary amine nitrogen atoms and a chloride ion. The copper is 0.223 Å above the plane and axially co-ordinated to the phenolate oxygen.

The axial co-ordination of the phenolate ion is in contrast to the equatorial co-ordination encountered in all the salicylaldehyde-derived copper(II) complexes[14,15] and in the analogous [CuL^9(N$_3$)] {HL^9 = 2-[methylbis(2-pyridylethyl)-amino]phenol}.[16] Obviously, it is the introduction of the electron-withdrawing NO$_2$ group *para* to the phenolic group which brings about a change in the site of co-ordination of the phenolate ion, *viz.* equatorial to axial, even though both [CuL^6(Cl)] and [CuL^9(N$_3$)][16] ($\tau = 0$) possess approximately the same co-ordination geometry. This is reminiscent of compounds of non-transition elements, where the most electronegative element occupies the axial position. However, crystal-packing forces could be equally responsible for the axial co-ordination. Whereas one of the pyridines in the azide[16] complex takes up the axial position, both the pyridine-nitrogen donors in [CuL^6(Cl)] occupy equatorial sites. Consequently, the N$_{py}$–Cu–N$_{py}$ angle changes from 95.5° in the azide to 160.1° in the present complex. However, this angle is less than that for other copper(II) complexes containing two co-ordinating pyridine moieties (168–178°) and adopting a square-pyramidal geometry[17] in a binuclear environment. The weak co-ordination of the chloride ion in the equatorial position is evident from the long Cu–Cl bond [2.256(1) Å], longer than the axial Cu–Cl bond in [CuL^{10}(Cl)]$^+$ [L^{10} = tris(2-pyridylmethyl)amine],[18] [CuL^{11}(Cl)]$^+$ [L^{11} = bis(1-methylimidazol-2-ylmethyl)(2-pyridylmethyl)amine],[19] and [CuL^{12}(Cl)]$^+$ [L^{12} = tris(1-methylimidazol-2-ylmethyl)amine].[19] Though there are mononuclear complexes with other types of oxygen donors, for example ether oxygen in the axial position[20] of Cu^{II}, there seems to be no report of phenolate co-ordinating to mononuclear copper(II). The only such bonds reported so far are in binuclear[21] compounds. Further, the crystal structure[22] of a tyrosylhistidinate complex of Cu^{II} reveals a long axial Cu^{II}–O(phenol) bond [2.601(4) Å], formed by the phenolic hydroxyl group but from a neighbouring molecule.

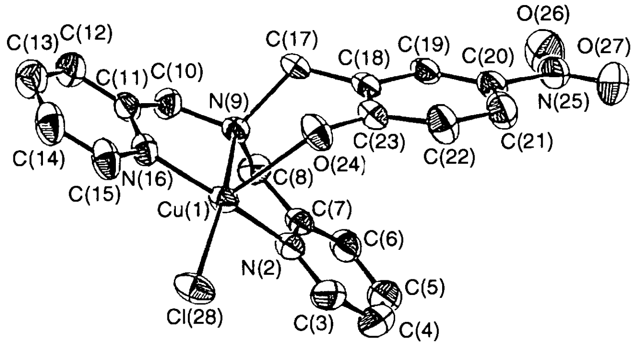


Fig. 1 An ORTEP drawing of [CuL^6(Cl)] showing the atom numbering and the thermal motion ellipsoids (50% probability level) for non-hydrogen atoms

Table 4 Bond lengths (Å) and angles (°) involving non-hydrogen atoms of [CuL^6(Cl)] with e.s.d.s in parentheses

Cu(1)–N(2)	1.986(1)	Cu(1)–N(9)	2.060(1)
Cu(1)–N(16)	1.997(1)	Cu(1)–O(24)	2.268(1)
Cu(1)–Cl(28)	2.256(1)	N(2)–C(3)	1.374(1)
N(2)–C(7)	1.334(1)	C(8)–N(9)	1.483(1)
N(9)–C(10)	1.480(1)	N(9)–C(17)	1.501(1)
C(11)–N(16)	1.339(1)	C(15)–N(16)	1.361(1)
C(23)–O(24)	1.283(1)		
O(24)–Cu(1)–Cl(28)	98.7(1)	N(16)–Cu(1)–Cl(28)	95.9(1)
N(16)–Cu(1)–O(24)	93.5(1)	N(9)–Cu(1)–Cl(28)	169.6(1)
N(9)–Cu(1)–O(24)	91.7(1)	N(9)–Cu(1)–N(16)	82.3(1)
N(2)–Cu(1)–Cl(28)	96.4(1)	N(2)–Cu(1)–O(24)	100.1(1)
N(2)–Cu(1)–N(16)	160.1(1)	N(2)–Cu(1)–N(9)	82.9(1)
Cu(1)–N(2)–C(7)	115.1(2)	Cu(1)–N(2)–C(3)	125.9(2)
N(2)–C(7)–C(8)	116.5(2)	C(7)–C(8)–N(9)	111.3(2)
Cu(1)–N(9)–C(8)	107.8(2)	C(8)–N(9)–C(17)	108.3(2)
C(8)–N(9)–C(10)	112.0(2)	Cu(1)–N(9)–C(17)	110.6(2)
Cu(1)–N(9)–C(10)	106.6(2)	C(10)–N(9)–C(17)	111.4(2)
N(9)–C(10)–C(11)	110.3(2)	Cu(1)–N(16)–C(15)	126.8(2)
Cu(1)–N(16)–C(11)	114.5(2)	N(9)–C(17)–C(18)	114.9(2)
Cu(1)–O(24)–C(23)	111.4(2)		

IR Spectra.—The presence of co-ordinated and/or lattice water[23] in all the complexes, except [CuL^6(Cl)] and [CuL^6(NCS)], is shown by a broad medium-intensity band in the range 3400–3600 cm^{-1}. For [CuL^1]ClO$_4$ and [CuL^2]ClO$_4$ the sharp bands observed in the region 3200–3300 cm^{-1} may be attributed to ν(N–H). The strong unsplit band around 1150 cm^{-1} for the perchlorate complexes of L^1 and L^6 suggests no co-ordination of perchlorate ion.[24] The complexes [CuL^6(N$_3$)] and [CuL^6(NCS)] exhibit bands around 2040 and 2090 cm^{-1} respectively, characteristic of co-ordinated[16,25] azide and NCS$^-$ (N).

Electronic Absorption Spectra.—The low values of $\tilde{\nu}_{max}$ (12 500–14 900 cm^{-1}, Table 5) observed in the reflectance spectra of all the present complexes suggest the possibility of an anion[26] or oxygen[27] co-ordinated to Cu^{II} and/or the presence of some trigonal element[23] in the geometry around Cu^{II}. Thus [CuL^6]ClO$_4$ and [CuL^6(N$_3$)] display spectral features different from those of [CuL^6(Cl)] suggesting substantial changes in the geometry[28,29] around Cu^{II}. All the other complexes exhibit spectra similar to that of [CuL^6(Cl)], suggesting a square-based geometry. The data in Table 5 reveal that the structure in the solid state undergoes changes on dissolution for [CuL^6]ClO$_4$ and other compounds. In dmf solution all the copper complexes exhibit a broad ligand-field band with a weak low-energy shoulder (Fig. 2) suggestive of a square-pyramidal geometry.[30] However, [CuL^6]ClO$_4$ again shows spectral features different from those of [CuL^6(Cl)], suggesting a substantially different geometry[31] in solution as well. The high-energy band of

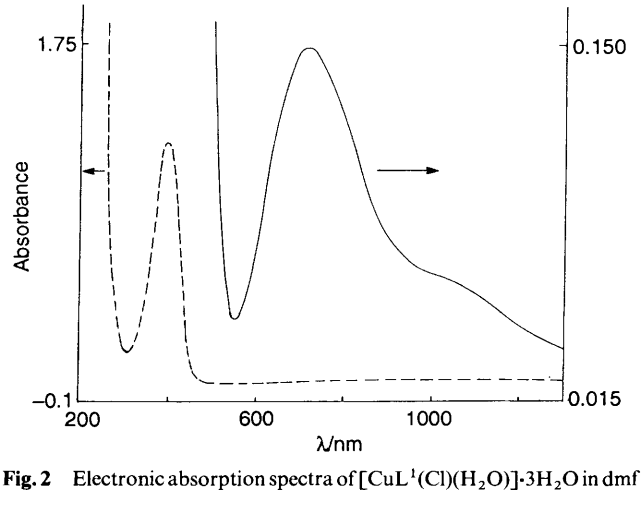


Fig. 2 Electronic absorption spectra of [CuL^1(Cl)(H$_2$O)]·3H$_2$O in dmf

Table 5 Electronic spectral data ($\tilde{\nu}_{max}$/cm^{-1}, ε/dm^3 mol^{-1} cm^{-1}, in parentheses) for the copper(II) complexes

Compound	Medium	Ligand field[a]	Charge transfer[b]	Ligand based[b]
$[CuL^1(Cl)]_4$	Solid	12 700	24 300	35 200
	dmf	13 900 (110)	25 200 (13 500)	36 600 (19 700)
		10 200s (40)		
$[CuL^1ClO_4]$	Solid	14 200	26 500	34 600
	dmf	14 200 (230)	25 400 (18 900)	36 700 (12 600)
		9 700s (70)		
$[CuL^2]ClO_4$	Solid	13 200	24 200	33 800
	dmf	14 500 (230)	25 300 (18 100)	36 800 (11 300)
		10 500s (65)		
$[CuL^3(Cl)]$	Solid	14 300	—	—
	dmf	14 500 (150)	25 500 (24 850)	37 500 (11 700)
		10 400s (75)		
$[CuL^4(Cl)]$	Solid	15 600	—	—
	MeOH	15 700 (165)	26 800 (6550)	37 300 (19 200)
$[CuL^5(Cl)]$	Solid	12 800	26 400	33 600
	dmf	13 900 (115)	24 300 (6200)	35 800 (17 800)
		8 900s (70)		31 400 (9900)
$[CuL^6]ClO_4$	Solid	15 700s,		
		12 500s	26 100	34 000
	dmf	13 500 (140)	25 600 (16 400)	37 300 (9800)
		11 800 (150)		35 100 (4970)
$[CuL^6(Cl)]$	Solid	13 700	22 700	33 600, 27 400
	dmf	14 000 (240)	24 600 (36 200)	37 500 (19 800)
		10 200 (160)	20 600 (345)	
	MeOH	14 500 (260)	26 700 (27 860)	40 300 (24 100)
$[CuL^6(N_3)]$	Solid	14 900, 13 300	—	—
	MeOH	15 100 (280)	25 900 (16 590)	40 300 (9300)
		10 000 (75)		31 500 (26 100)
$[CuL^6(NCS)]$	Solid	14 900	—	—
	MeOH	15 000 (225)	26 100 (26 100)	39 800 (17 200)
$[CuL^7]$	Solid	12 500	26 600	35 000
	dmf	14 000 (150)	25 300 (35 250)	36 600 (19 600)
		10 200 (75)		33 400 (9900)
$[CuL^8]$	Solid	14 000	26 600	33 500
	dmf	14 600 (180)	25 400 (30 800)	36 900 (15 800)
		10 200s (95)		42 000 (22 600)

[a] Concentration $\approx 1 \times 10^{-3}$ mol dm^{-3}. [b] Concentration $\approx 9 \times 10^{-5}$ mol dm^{-3}.

$[CuL^2]ClO_4$ is blue-shifted, compared to $[CuL^1]ClO_4$, suggesting that six-membered chelate rings involving σ donors[32] favour Cu^{II}. The lower $\tilde{\nu}_{max}$ value of $[CuL^3(Cl)]$ compared to that for $[CuL^4(Cl)]$ shows the weaker co-ordination of nitrophenolate ion. The replacement of the bulky bzim pendant in $[CuL^5(Cl)]$ and $[CuL^7]$ by the more basic py as in $[CuL^6(Cl)]$ and $[CuL^8]$ blue-shifts the higher-energy ligand-field bands, as expected.

The highly intense band observed for the present complexes around 25 500 cm^{-1} may be due to a $Cu^{II} \rightarrow O^-$ (axial) and/or equatorial $O^- \rightarrow Cu^{II}$ charge-transfer (c.t.) transition. For complexes with axial phenolate co-ordination the charge transfer from the filled d orbitals (d_{xz},d_{yz}) of copper(II) to the antibonding orbitals of the phenolic residue[33] would constitute a major source of intensity of this band and may be facilitated by the strongly electron-withdrawing NO_2 group. Molecular orbital calculations[34] show that both the highest-occupied molecular orbitals π_1 and π_2 levels as well as the n(σ) level lying close to π_2 would participate in c.t. transitions.

EPR Spectra.—The frozen-solution spectra of all the complexes (Table 6), except $[CuL^6(N_3)]$ and $[CuL^6(Cl)]$ in MeOH and MeCN, are axial (Fig. 3).[35] The spectra of $[CuL^6(N_3)]$ in MeOH and $[CuL^6(Cl)]$, both in MeOH and MeCN, show rhombic features. For the present complexes the $g_{\parallel}$ values lie in the range 2.20–2.28, consistent with the presence of CuO_2N_2 or CuO_3N chromophores. Further, the $g_{\parallel}$ and $A_{\parallel}$ values of most of the complexes lie in the region for CuN_2O_2 chromophores in the $g_{\parallel}$ *vs.* $A_{\parallel}$ plot[36] and are interestingly close to those of galactose oxidase.[37]

The $g_{\parallel}$ values of the bzim-incorporated complexes of L^1 and L^2 are lower than that for the py-incorporated $[CuL^3(Cl)]$; this is because of the lower positive charge[36] on Cu^{II} in the latter. On the other hand, the $g_{\parallel}$ value of $[CuL^3(Cl)]$ is lower than that of $[CuL^4(Cl)]$ on account of the electron-withdrawing *p*-nitro group in $[CuL^3(Cl)]$ which increases the net positive charge[34] on Cu^{II}.

The lower $g_{\parallel}/A_{\parallel}$ quotient[36] and the higher $\tilde{\nu}_{max}$ value for $[CuL^4(Cl)]$ compared to complexes of L^2–L^3 suggests a preference for planarity[38] in the former. The replacement of pendant bzim in $[CuL^5(Cl)]$ by nitrophenolate as in $[CuL^7]$ leads to an increase in $g_{\parallel}$, due to the decrease in positive charge[36] on Cu^{II}. In contrast, the $g_{\parallel}$ value decreases when the py pendant in $[CuL^6(Cl)]$ is replaced by nitrophenolate as in $[CuL^8]$; this suggests the importance of changes in geometry caused by different donors. Thus, $[CuL^7]$ exhibits higher $g_{\parallel}$ and lower $\tilde{\nu}_{max}$ values compared to $[CuL^8]$.

Redox Chemistry.—For the complexes of tridentate ligands (L^2–L^4) the $Cu^{II} \rightarrow Cu^{I}$ reduction process occurs in the range -0.11 to -0.21 V and $Cu^{I} \rightarrow Cu^{0}$ around -1.0 V (Table 7). The ΔE_p values for the former couple decrease in the order $[CuL^4(Cl)] > [CuL^3(Cl)] > [CuL^2(Cl)] > [CuL^1(Cl)] > [CuL^1]ClO_4$. This reveals that the stereochemical reorganisation accompanying the redox change is more facile[39] for the NO_2-substituted and for bzim rather than py-incorporated complexes; this may be due to the bulky bzim favouring[32] a distorted geometry, and NO_2 π delocalisation. The $E_{\frac{1}{2}}$ values of these complexes follow the order $[CuL^4(Cl)] > [CuL^3(Cl)] > [CuL^1]ClO_4 > [CuL^1(Cl)] \approx [CuL^2]ClO_4$. This suggests that the enhanced π-back-bonding involving py rings[32] compared to bzim raises $E_{\frac{1}{2}}$. The decrease in electron density on

Table 6 The EPR spectral data for the copper(II) complexes[a]

Compound	Medium	g_0	A_0[b]	$g_\parallel$	$A_\parallel$	$g_\perp$[c]	$A_\perp$[d]	G[e]	$g_\parallel/A_\parallel$
$[CuL^1]ClO_4$	Powder	2.100	56	—	—	—	—	—	—
	dmf–Me_2CO	2.134	65	2.285	181	2.059	7	4.8	126
$[CuL^1(Cl)]$	Powder	2.110	66	—	—	—	—	—	—
	dmf–Me_2CO	2.136	65	2.285	173	2.062	11	4.6	132
$[CuL^2]ClO_4$	Powder	—	78	2.275	—	2.079	—	—	—
	dmf–Me_2CO	2.144	70	2.285	181	2.074	15	3.9	126
$[CuL^3(Cl)]$	Powder	2.088	75	—	—	—	—	—	—
	dmf–Me_2CO	2.110	80	2.245	176	2.043	32	5.6	127
$[CuL^4(Cl)]$	Powder	—	—	2.173	—	2.076	—	—	—
	MeOH	2.131	70	2.249	193	2.072	9	3.5	116
$[CuL^5(Cl)]$	Powder	2.114	50	—	—	—	—	—	—
	dmf–Me_2CO	2.129	74	2.262	174	2.063	24	4.1	130
$[CuL^6]ClO_4$	Powder[f]	2.229 2.141 2.048	92	—	—	—	—	—	—
	dmf	2.139	55	2.276	185	2.071	−10	3.9	123
$[CuL^6(Cl)]$	Powder	—	13	2.269	—	2.073	—	—	—
	dmf[g]	2.124	71	2.244	179	2.064	17	3.8	127
	MeCN[f]	2.106	79	2.218	174	2.050	32	4.3	127
	MeOH[f]	2.138	78	2.217	173	2.098	31	2.2	128
$[CuL^6(NCS)]$	MeOH[g]	2.110	86	2.227	187	2.052	36	4.3	119
$[CuL^6(N_3)]$	Solid[f]	2.057 2.096 2.155	35	—	—	—	—	—	—
	MeOH[f]	2.163	65	2.327	187	2.081	4	4.0	124
$[CuL^7]$	Powder	2.119	78	—	—	—	—	—	
	dmf–Me_2CO	2.132	65	2.285	174	2.056	11	5.0	131
$[CuL^8]$	Powder	2.101	73	—	—	—	—	—	—
	dmf–Me_2CO	2.127	65	2.274	172	2.054	12	5.0	132

[a] All hyperfine coupling constants in units of 10^{-4} cm^{-1}. [b] For polycrystalline samples one third of the width between the first-derivative spectrum's maximum and minimum. [c] $g_\perp = \frac{1}{2}(3g_0 - g_\parallel)$. [d] $A_\perp = \frac{1}{2}(3A_0 - A_\parallel)$. [e] $G = (g_\parallel - 2)/(g_\perp - 2)$. [f] Shows rhombic features. [g] Five N-superhyperfine lines observed.

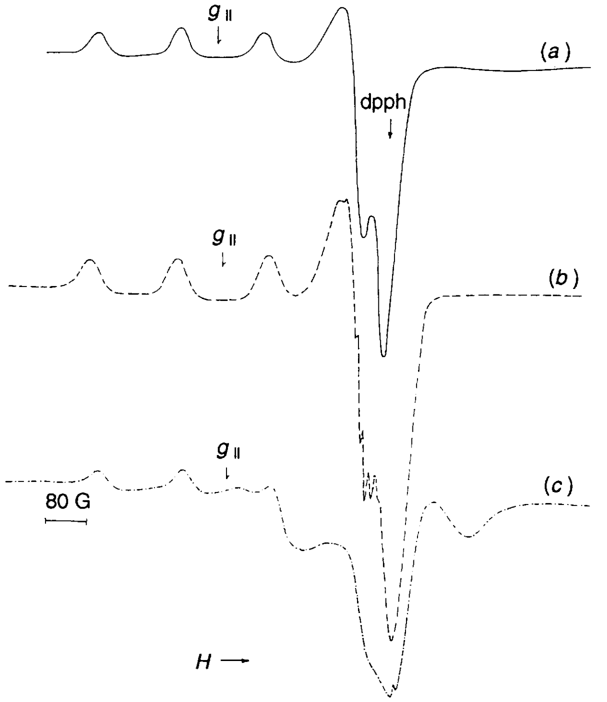


Fig. 3 The EPR spectra of (a) $[CuL^3(Cl)]$ in dmf, (b) $[CuL^6(NCS)]$ and (c) $[CuL^6(Cl)]$ in MeOH at 77 K (G = 10^{-4} T)

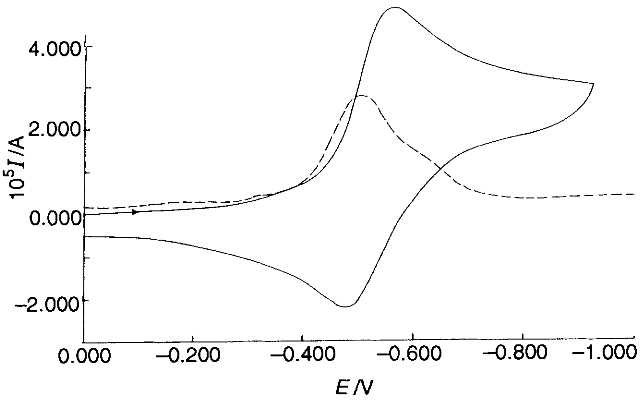


Fig. 4 Cyclic (——) and differential pulse (– – –) voltammograms of 0.001 mol dm^{-3} $[CuL^6(Cl)]$ in MeCN at 25 °C at 0.05 and 0.01 V s^{-1} scan rates respectively; pulse height for differential pulse voltammogram 0.05 V

Cu^{II} upon introduction of a NO_2 group is expected to elevate $E_{\frac{1}{2}}$. However, the $E_{\frac{1}{2}}$ of $[CuL^3(Cl)]$ is found to be lower than that of $[CuL^4(Cl)]$ and may be due to the comparatively weak Cu–O(phenolate) bond in the former, which dictates the co-ordination of ClO_4^- {from $N(C_6H_{13})_4ClO_4$} as well as Cl^- to Cu^{II}.

The $Cu^{II} \rightarrow Cu^I$ reduction process for the complexes of the tripodal ligands with one nitrophenolate pendant (L^5 and L^6) occurs at a potential more negative than those for the tridentate ligands (Table 7). Though the process for $[CuL^6(Cl)]$ is more reversible (Fig. 4) than that for $[Cu(L^5)Cl]$, the $E_{\frac{1}{2}}$ of the latter is more positive than that of the former and this may be due to the formation of a strong σ bond by the more basic py.[32] The redox behaviour of $[CuL^6(X)]$ complexes is dependent on the X^- and the solvents used (Table 7) in line with their spectral behaviour. Thus, the comparatively more negative potential of $[CuL^6(N_3)]$ in MeOH is consistent with the stronger co-ordination of N_3^- ion than of the Cl^- in $[CuL^6(Cl)]$. The $E_{\frac{1}{2}}$ values of the $[CuL^6(X)]$ complexes in MeCN decrease in the

Table 7 Redox data[a] for the copper(II) complexes at 50 mV s^{-1} scan rate

Compound	Solvent	E_{pc}	E_{pa}	ΔE_p	$E_{\frac{1}{2}}$	$E_{\frac{1}{2}}$[b]	i_{pa}/i_{pc}	$10^{-6} D$
$[CuL^1]ClO_4$ + mim[c]	dmf–NBu_4ClO_4	−0.21	0.06	146	−0.07	−0.07	1.7	2.56
		−1.11	—	—	—	—	—	—
		−0.22	−0.04	177	−0.13	−0.10	1.9	—
		−1.13	−0.73	400	−1.00	−1.00	1.2	—
$[CuL^1(Cl)]$ + mim	dmf–NBu_4ClO_4	−0.19	0.06	180	−0.10	−0.09	3.9	0.23
		−1.04	—	—	—	−0.97	—	—
		−0.30	−0.16	146	−0.23	−0.17	1.5	—
		−1.16	−0.77	384	−0.97	−1.05	1.1	—
$[CuL^2]ClO_4$ + mim	dmf–NBu_4ClO_4	−0.17	0.02	190	−0.07	−0.1	2.6	0.19
		−0.99	—	—	−0.69	−0.90	—	—
		−0.39	−0.23	154	−0.04	−0.31	1.0	—
		−1.19	−0.72	470	−0.96	−1.09	1.5	—
$[CuL^3(Cl)]$	dmf–$N(C_6H_{13})_4ClO_4$	−0.20	−0.03	231	−0.08	−0.03	1.0	0.34
		−1.16	—	—	—	−1.06	—	—
$[CuL^4(Cl)]$	MeOH–NBu_4ClO_4	−0.11	0.22	330	0.05	0.03	1.1	2.18
		−0.88	−0.36	520	—	−0.86	—	—
$[CuL^5(Cl)]$ + mim	dmf–NBu_4ClO_4	−0.68	—	—	—	−0.61		10.80
		−1.11	—	—	—	−1.03	—	—
		−1.17	−0.80	368	−0.99	−1.07	1.1	—
$[CuL^6]ClO_4$ + mim	MeCN–$N(C_6H_{13})_4ClO_4$	−0.70	−0.59	108	−0.64	−0.58	—	16.15
						−0.82[d]		
		−1.02	−0.59	—	—	−1.16	—	—
		−0.75[e]	−0.54	212	−0.60	−0.58	—	—
		−1.19[e]	−0.78	414	−0.98	—	—	—
		−0.85	−0.67	180	−0.77	−0.76	1.0	—
		−1.03	—	—	—	—	—	—
$[CuL^6(Cl)]$	dmf–NBu_4ClO_4	−0.88	−0.76	114	−0.82	−0.82	1.0	13.25
		−1.64	—	—	—	−1.40		
$[CuL^6(Cl)]$ + mim	MeCN–$N(C_6H_{13})_4ClO_4$	−0.56	−0.48	86	−0.52	−0.53	0.8	11.0
		−0.76	−0.63	134	−0.48	−0.69	0.3	—
			−0.19					
$[CuL^6(Cl)]$	MeOH–NEt_4BF_4	−0.63	−0.42	210	−0.53	−0.56	1.0	7.88
		−1.35						
$[CuL^6(N_3)]$	MeOH–NEt_4BF_4	−0.73	—	—	—	−0.71	—	6.76
$[CuL^6(NCS)]$	MeCN–$N(C_6H_{13})_4ClO_4$	−0.73	−0.43	292	−0.63	−0.72	1.0	17.25
						−0.65[d]		
$[CuL^7]$ + mim	dmf–NBu_4ClO_4	−1.04	—	—	—	−0.95	—	22.00
		−1.45	—	—	—	−1.25	—	—
		−1.14	—	—	—	−1.07	—	—
$[CuL^8]$ + mim	dmf–NBu_4ClO_4	−0.75	—	—	—	−0.89	—	25.50
		−1.27	—	—	—	−1.17	—	—
		−1.24	—	—	—	−1.09	1.9	—
		−1.51	−0.75	—	—	−1.42		

Reference electrode Ag–$AgNO_3$ (0.01 mol dm^{-3}), $N(C_6H_{13})_4ClO_4$ 0.1 mol dm^{-3} in MeCN: add 544 mV to convert into NHE.

[a] At 25 °C. [b] Differential pulse voltammetry at 0.01 V s^{-1} scan rate, pulse height = 0.05 V. [c] *N*-Methylimidazole. [d] Appears as a shoulder. [e] At 1 V s^{-1} scan rate.

order $Cl^- \approx ClO_4^- > NCS^-$, suggesting the presence of MeCN and nitrogen of NCS^- in the co-ordination sphere.

The redox behaviours of $[CuL^7]$ and $[CuL^8]$, both with two phenolate donors, are similar in that they exhibit two irreversible cathodic waves. The high diffusion coefficient (*D* value) for the more positive cathodic peak (Table 7) and the absence of the stripping peak for the more negative cathodic peak lead us to suggest that these processes correspond to $Cu^{II} \rightarrow Cu^0$ and $NO_2 \rightarrow NO_2^-$ respectively.

Thus the spectral and electrochemical studies suggest that the donor strength in the complexes follows the order nitrophenolate < py < bzim with tridentate ligands and nitrophenolate < bzim < py with tripodal tetradentate ligands. Though a tripodal ligand is expected to elevate[40] the $E_{\frac{1}{2}}$ of a copper(II) complex by 0.24 V by imposing a trigonal geometry, the present complexes of tripodal ligands (except $[CuL^7]$ and $[CuL^8]$) exhibit values in the range 0.50–0.25 V *vs.* normal hydrogen electrode (NHE) in spite of the square-pyramidal geometry stabilising Cu^{II}. On the addition of *N*-methylimidazole (mim) to all the complexes, the $E_{\frac{1}{2}}$ of the Cu^{II}–Cu^I couple shifts to a more negative value indicating a decrease in Lewis acidity of Cu^{II}.

Conclusion

It is well known that tripodal ligands tend to impose a trigonal geometry[19,23] around Cu^{II}. However, they do not exhibit any restraint[18,41] on rearrangement to a square-based geometry when (*a*) one of the three five-membered chelate rings in a tripodal complex is substituted[17] by a six-membered one, (*b*) a sterically hindered pendant such as 3-methyl-2-pyridyl is incorporated[42] or (*c*) a stronger monodentate ligand like N_3^- is added[16] to the complex. The geometry around Cu^{II} in the present tripodal complexes may be assigned as square-based, on the basis of the crystal structure[4] of $[CuL^6(Cl)]$ and spectral and electrochemical properties. This geometry is obviously a result of the factors (*a*) and (*c*) mentioned above and/or due to the presence of pendant donor atoms dissimilar in donor strength and type as in L^6. However, each of the present ligands, owing to their flexibility, can exist in a range of conformations.

Owing to the plasticity effect[26] of copper(II) and the formation of structural pathways,[30] each ligand L^n can exist as a series of complexes of the type $[CuL^n(X)]$ with a range of stereochemistries. Obviously, crystal structures of these complexes are essential to establish them and also to distinguish the axial or equatorial co-ordination of phenolate oxygens, especially in the case of complexes with two such donors.

The spectral and electrochemical properties of $[CuL^6(X)]$ complexes are interestingly anion and solvent dependent. The complex $[CuL^6(Cl)]$ which exhibits electrochemical reversibility and EPR parameters similar to those of galactose oxidase seems to be suitable for mimicking the catalytic activity of the latter. The substitution of Cl^- by mim is relevant to the suggestion by Knowles and co-workers[2] that O^6 of galactose would directly co-ordinate to copper at the equatorial site occupied by acetate.

Acknowledgements

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