

Studies on the chemistry of copper(I) with arylazoimidazoles

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Abstract. N(1)-alkyl-2-(arylo)imidazoles ($RC_6H_4N=NC_3H_2N N(1)X$; X=Me (a), Et (b); R = 7-Me(L¹), 7-OMe(L²), 7-Cl(L³), 7-NO₂(L⁴) and 8-Me(L⁵)) yield perchlorate salts of bis-chelated complexes with copper(I). The complexes are 1:1 electrolyte and the composition is supported by Jobs method of continuous variation. The N=N stretching is red shifted by 60–70 cm⁻¹ compared to free ligand values suggesting efficient charge delocalization from Cu(I) to ligand centre. This is supported by high intense MLCT transitions in the visible region. The complexes show highly resolved symmetrical ¹H NMR spectra exhibiting C₂-symmetry at least in the NMR time scale. In MeOH the complexes exhibit quasi-reversible CuL₂²⁺/CuL₂⁺ couple at 0.4–0.5 V vs SCE at 298 K. The high positive potential may be due to the distortion in the geometry of CuL₂⁺.

Keywords. Azoimidazoles; high potential copper(I) complex; MLCT; distorted tetrahedral.

1. Introduction

The studies on the complexation of imidazole and its derivatives have been an important area in the field of biochemical, analytical, industrial and anticancer reagents^{1–3}. The ubiquity of copper-imidazole bonding in copper metalloproteins has encouraged the development of copper chemistry of imidazole and derivatives^{4,5}. The monovalent copper (*d*¹⁰) chemistry of the heterocyclic-N donor systems has drawn special attention^{6,7} because of its instability, unusual structural features, utility in solar energy and supramolecular devices, catalytic activity in photoredox reactions and the biological relevance of high potential copper complexes^{8–10}. For the last couple of years we are engaged in the development of the coordination chemistry and analytical application of 2-(arylo)imidazols (1) and their N(1)-alkylated derivatives^{11–13}. The molecule includes two important functions; bioactive, imidazole and π -acidic azoimine, –N=N–C=N– moiety. The azoimine function has the speciality to stabilise copper (I) state^{9–12}. The stability of copper(I) systems having CuN₄ environment is due to the π -acidity of the ligands and their steric accessibility to attain distorted tetrahedral coordination sphere. To study the effect of steric crowding on the redox stability of copper(I) state we have synthesised {(ortho-substituted)arylo}imidazoles (L¹–L⁵) and we describe here the synthesis, spectral characterisation and electrochemical activity of copper(I) complexes.

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2. Experimental

2.1 Materials

o-Methyl-, *o*-methoxy- and *m*-methylanilines were purchased from SRL; *o*-chloro- and *o*-nitroanilines were E. Merck reagents. Imidazole was a Glaxo reagent, Bombay. NaClO₄ was obtained from E. Merck. The complexes [Cu(MeCN)₄](ClO₄) was prepared by following a known procedure¹². Purification of solvents were performed as reported procedure¹⁰. The parent ligands 2-(aryldiazonium chloride with imidazole in Na₂CO₃ solution (pH 7) and purified by reported procedures¹¹. Melting points of the compounds are 2-((7-methyl)phenylazo)imidazole (L¹), 162 ± 1; 2-((7-methoxy)phenylazo)imidazole (L²), 129 ± 1, 2-((7-chloro)phenylazo)imidazole (L³), 179 ± 2; 2-((7-nitro)phenylazo)imidazole (L⁴), 152 ± 2 and 2-((8-methyl)phenylazo)-imidazole (L⁵), 142 ± 2 °C. Copper was estimated iodometrically by a known procedure¹⁴.

2.2 Preparation of *N*(1)-methyl-2-((7-methyl)phenylazo)imidazole (L^{1a})

To dry THF solution of 2-((7-methyl)phenylazo)imidazole (L¹) (0.75 g, 4.03 mmol) NaH (50% paraffin)(0.35 g) was added in small portions and stirred at cold condition for 0.5 h. Methyl iodide was added slowly for a period of 1 h and warm at 60°C for another 1 h. The solution was evaporated, extracted with CHCl₃ and washed with 10% NaOH (10 ml × 3) and finally with distilled water (20 ml × 3). It was chromatographed over silica gel prepared in benzene and the desired compound was eluted by MeCN–C₆H₆ (1:19, v/v). The orange crystalline needles were separated on slow evaporation. The yield was 0.48 g, (45%).

Other alkylated products were prepared following the same general route and the yield varied 35 to 50%. Melting points, of the compounds: L^{1a}, 88 ± 1; L^{2a}, gum; L^{3a} 98 ± 2; L^{4a}, 118 ± 1; L^{5a}, gum; L^{1b}, gum; L^{2b}, gum; L^{3b}, gum; L^{4b}, 106 ± 2 °C; L^{5b} gum.

2.3 Preparation of bis[*N*(1)-methyl-2-((7-methyl)phenylazo)imidazole] copper (I) perchlorate, [Cu(L^{1a})₂](ClO₄) (2a)

The ligand L^{1a} (0.2 g, 1 mmol) in dry MeOH (10 ml) was added dropwise to stirred methanolic solution (10 ml) of [Cu(MeCN)₄](ClO₄) (0.4 g, 1.22 mmol) at room temperature under dinitrogen. The dark-brown solution was stirred for 2 h and the solution volume was reduced to half by nitrogen bubbling. The dark crystalline mass that separated was filtered off and was recrystallised from methanol, the crystals were dried *in vacuo*, yield 0.32 g (57%).

Other complexes were prepared following a similar procedure.

3. Results and discussion

The ligand used in the present work are *N*(1)-alkyl-2-(*ortho/meta*-substituted phenylazo)-imidazoles, (R–C₆H₄N=NC₃H₂H *N*(1)X; R = 7-Me (L¹); 7-OMe (L²), 7-Cl (L³), 7-NO₂ (L⁴) and 8-Me (L⁵)). The alkyl group X in *N*(1)-X are methyl (**a**), and ethyl (**b**). 2-(Arylazo)imidazoles are obtained by standard procedure and alkylated by adding alkyl halide in THF solution in presence of NaH. They are *N,N*-chelators and react smoothly with [Cu(MeCN)₄](ClO₄) in boiling methanol in the ratio of 1:2 to isolate (Cu(L)₂](ClO₄) (**2–6**) in presence of aqueous NaClO₄.

The complexes were characterised by elemental analysis (table 1) which confirmed the 1:2 metal/ligand ratio. The composition has also been supported by Job's method at

Table 1. Elemental analyses^a, UV-VIS spectral^b and cyclic voltammetric^c data of [Cu(L)₂](ClO₄)

Compound	Elemental analyses				UV-VIS spectral data		CV data	
	C	H	N	Cu	$\lambda_{\text{max}}/\text{nm}(10^{-3} \text{ L mol}^{-1} \text{ cm}^{-1})$	E_{298}^0	$V(\Delta E_p, \text{mV})$	
[Cu(L ^{1a}) ₂](ClO ₄)(2a)	46.7 (46.9)	4.4 (4.3)	19.8 (19.9)	11.4 (11.3)	786(0.30) ^d , 612(1.46), 447(6.41)		0.45(120)	
[Cu(L ^{1b}) ₂](ClO ₄)(2b)	47.0 (47.1)	5.3 (5.2)	18.2 (18.2)	10.5 (10.5)	792(0.64) ^d , 615(1.72), 443(9.27)		0.46(110)	
[Cu(L ^{2a}) ₂](ClO ₄)(3a)	44.4 (44.4)	4.1 (4.0)	18.7 (18.8)	10.8 (10.7)	807(1.14) ^d , 610(3.17), 413(25.0)		0.43(125)	
[Cu(L ^{2b}) ₂](ClO ₄)(3b)	46.2 (46.2)	4.5 (4.5)	18.0 (18.0)	10.0 (10.2)	814(0.53) ^d , 616(1.41), 418(18.0)		0.44(110)	
[Cu(L ^{3a}) ₂](ClO ₄)(4a)	39.7 (39.7)	3.0 (3.0)	18.6 (18.5)	10.5 (10.5)	807(0.56) ^d , 595(0.88), 402(11.98)		0.48(115)	
[Cu(L ^{3b}) ₂](ClO ₄)(4b)	41.9 (41.8)	3.4 (3.5)	17.8 (17.7)	10.0 (10.1)	808(0.78) ^d , 591(1.29), 403(17.56)		0.48(100)	
[Cu(L ^{4a}) ₂](ClO ₄)(5a)	38.5 (38.4)	2.9 (2.9)	22.3 (22.4)	10.2 (10.2)	755(0.28) ^d , 560(0.96), 395(17.03)		0.50(125)	
[Cu(L ^{4b}) ₂](ClO ₄)(5b)	40.5 (40.4)	3.4 (3.4)	21.5 (21.4)	9.8 (9.7)	757(0.63) ^d , 566(1.89), 398(23.68)		0.51(120)	
[Cu(L ^{5a}) ₂](ClO ₄)(6a)	46.9 (46.9)	4.2 (4.3)	19.9 (19.9)	11.1 (11.3)	780(1.1) ^d , 613(5.61), 437(16.68)		0.44(110)	
[Cu(L ^{5b}) ₂](ClO ₄)(6b)	47.0 (47.1)	5.3 (5.2)	18.4 (18.3)	10.2 (10.4)	778(0.92) ^d , 618(4.50), 442(13.27)		0.45(100)	

^a Calculated values are given in parentheses; ^b Solvent MeOH; ^c Pt-disk working electrode, SCE refers to solvent MeOH, supporting electrolyte Bu₄NClO₄, solute concentration $\sim 10^{-3}$, $E_{1/2} = (E_{pa} + E_{pc})/2$, $\Delta E_p = (E_{pa} - E_{pc})$, mV; ^d shoulder.

≈ 600 nm (studied in six cases (2–4)) spectrophotometrically. The compounds are diamagnetic in nature, as expected and are soluble in common polar organic solvents. The molar conductance (Λ_M) of complexes lies between 90 and $110 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ suggesting a 1:1 type electrolytic nature of the compound^{11,12}.

The solution electronic spectra of the complexes were drawn in the range 900 – 200 nm in MeOH. The spectral data are collected in table 1 and a representative spectrum is shown in figure 1. The transitions < 400 nm are due to intra-ligand charge transfer transition ($n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$) and are not considered further. The visible range of the spectrum exhibit three characteristic transitions. 760 – 810 , 560 – 620 , and 400 – 440 nm. A weaker band is observed at longer wavelength region. These transitions are not observed either in the free ligand or in the $(\text{Cu}(\text{MeCN})_4)(\text{ClO}_4)$ and are due to metal-to-ligand charge transfer (MLCT) transitions. This is a characteristic feature of the copper(I) complexes when bonded with conjugated organic chromophore^{8,10,12}. The complexes follow Beer's Law in MeOH and CHCl_3 and support the stability of $[\text{Cu}(\text{L})_2]\text{ClO}_4$ in these solvents. On comparing the reported results of similar type systems^{9,10,12}, it is reasonable to assume to grossly tetrahedral structure with MN_4 coordination sphere.

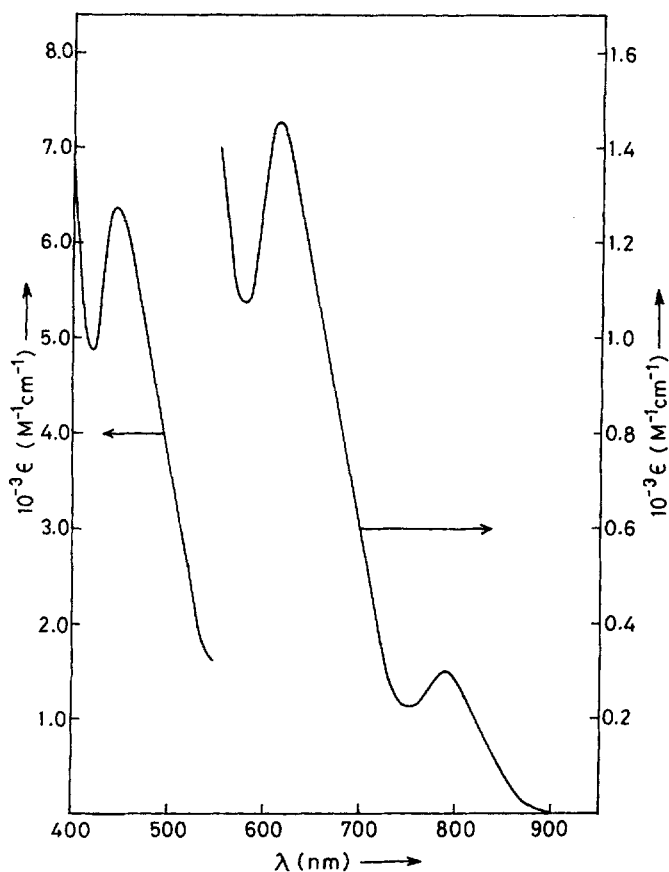
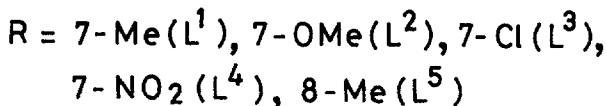
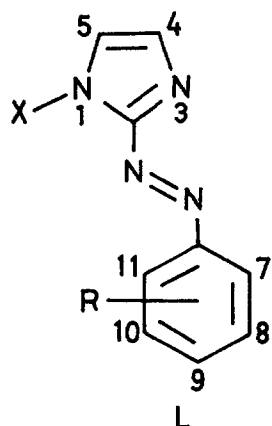


Figure 1. Electronic spectrum of $[\text{Cu}(\text{L}^{\text{1a}})_2](\text{ClO}_4)$ in CH_3OH .



Structures

In IR spectra of L exhibits $\nu_{(\text{N}=\text{N})}$ and endocyclic $\nu_{(\text{C}=\text{N})}$ appear at ≈ 1400 and 1600 cm^{-1} respectively. Imidazole ring stretching modes appear at $1500\text{--}1400$, $775\text{--}790$, $740\text{--}750$ and $650\text{--}600 \text{ cm}^{-1}$ in the compounds¹⁵. In the complexes $\nu_{(\text{N}=\text{N})}$ is considerably red shifted by $60\text{--}70 \text{ cm}^{-1}$ and has been attributed to the presence of $d(\text{Cu}) \rightarrow \pi^*(\text{L})$ back bonding. All the complexes exhibit a structureless band ≈ 1090 and 625 cm^{-1} which correspond to $\nu_{(\text{ClO}_4)}$ suggesting lack of significant perchlorate coordination in the solid state.

The bonding mode is established by ^1H NMR spectra. The spectra are recorded in CDCl_3 and data are given in table 2. The 7-Me and 7-OMe signals appear at 2.6 and 3.9 ppm respectively (free ligand values 2.4 and 3.8 ppm respectively) while 8-Me appears at 2.4 ppm (close to the free ligand value). The downfield shifting of former may be due to nearer position of electron withdrawing azo function. Other aryl protons are assigned on the basis of chemical shift, spin-spin splitting and changes therein on substitution. The 8-H is affected severely in (a–d) on substitution and the shifting is quite expected in view of the inductive and electronic effect of the substituents¹⁶. The 7-H signal appears as a singlet in (e). The signal 11-H appears relatively at downfield position followed by 10-H resonance. In complexes $[\text{CuL}_2]^+$ the protons suffer downfield shifting in irregular manner, 8-H and 9-H are shifted slightly ($\Delta\delta = 0.02\text{--}0.1$ ppm) while 10-H and 11-H are shifted by an appreciable amount ($\Delta\delta = 0.1\text{--}0.2$ ppm). The overall downfield shifting indicates the metal coordination. Imidazolic 4- and 5-H are shifted downfield by 0.2 and 0.1 ppm respectively, on complexation. Higher shifting in 4-H may be due to the coordination of N(3) to Cu^+ where 4-H is nearer than 5-H¹⁷. The N(1)-Me in copper(I) complexes (a) appears as singlet at 4.2 ppm (free ligand value 4.0 ppm) and N(1)- CH_2CH_3 in (b) shows a quartet at $\delta(\text{CH}_2)$, 4.7 ppm and a triplet $\delta(\text{CH}_3)$, 1.6 ppm compared to free ligand values 4.4 and 1.5 ppm respectively. All the protons (aliphatic and aromatic) exhibit only one signal (singlet or multiplet) for each proton and suggest that both the chelate rings in the complexes are magnetically equivalent at least on the NMR time-scale. This supports that an effective C_2 -axis is present which is in agreement with the CuN_4 tetrahedral coordination sphere.

The redox property of the complexes were carried out by cyclic voltammetry. The complexes exhibit quasi-reversible oxidation-reduction couple at ≈ 0.4 V versus SCE at a Pt-disk working electrode. The response is attributed to $\text{Cu(II)}/\text{Cu(I)}$ couple (1).

Table 2. ^1H NMR spectral data of L and $[\text{Cu}(\text{L}_2)](\text{ClO}_4)$ in CDCl_3 .

Compound	δ, ppm									
	4-H ^a	5-H ^a	7-H ^a	8-H ^b	9-H	10-H ^c	11-H ^b	12-H	13-H	R
L ^{1a}	7.22	7.09		7.24	7.32 ^c	7.25	7.65	4.00 ^a		2.73 ^e
L ^{1b}	7.24	7.11		7.26	7.35 ^c	7.28	7.65	4.43 ^d	1.52 ^c	2.76 ^e
L ^{2a}	7.20	7.06		7.02	7.21 ^c	7.12	7.58	4.02 ^a		3.91 ^f
L ^{2b}	7.23	7.09		7.05	7.21 ^c	7.10	7.60	4.40 ^d	1.58 ^c	3.90 ^f
L ^{3a}	7.25	7.13		7.48	7.40 ^c	7.32	7.72	4.08 ^a		
L ^{3b}	7.27	7.12		7.46	7.41 ^c	7.33	7.75	4.45 ^d	1.60 ^c	
L ^{4a}	7.30	7.15		7.72	7.61 ^c	7.68	7.92	4.11 ^a		
L ^{4b}	7.33	7.16		7.75	7.63 ^c	7.68	7.96	4.52 ^d	1.58 ^c	
L ^{5a}	7.22	7.11	7.74		7.35 ^b	7.35	7.80	4.00 ^a		2.44 ^e
L ^{5b}	7.25	7.16	7.76		7.38 ^c	7.38	7.79	4.43 ^d	1.51 ^c	2.44 ^e
(2a)	7.43	7.22		7.26	7.38 ^b	7.44	7.73	4.24 ^a		2.81 ^e
(2b)	7.45	7.24		7.28	7.41 ^c	7.47	7.75	4.68 ^d	1.61 ^c	2.82 ^e
(3a)	7.42	7.20		7.09	7.26 ^c	7.38	7.65	4.20 ^a		3.95 ^f
(3b)	7.44	7.20		7.10	7.25 ^c	7.40	7.68	4.70 ^d	1.60 ^c	3.95 ^f
(4a)	7.48	7.28		7.54	7.48 ^c	7.58	7.81	4.26 ^a		
(4b)	7.50	7.31		7.56	7.48 ^c	7.62	7.83	4.73 ^d	1.65	
(5a)	7.52	7.31		7.80	7.68 ^c	7.80	8.05	4.28 ^a		
(5b)	7.55	7.36		7.82	7.70 ^c	7.85	8.10	4.78 ^d	1.66 ^c	
(6a)	7.42	7.25	7.66		7.34 ^b	7.58	7.78	4.22 ^a		2.41 ^e
(6b)	7.49	7.24	7.62		7.27 ^b	7.62	7.70	4.61 ^d	1.66 ^c	2.35 ^e

^aSinglet; ^bdoublet ($J = 7.4\text{--}8.0\text{ Hz}$); ^ctriplet ($J = 7.6\text{--}8.0\text{ Hz}$); ^dquartet ($J = 9\text{--}10\text{ Hz}$); ^e $\delta_{(\text{Me})}$; ^f $\delta_{(\text{OMe})}$.

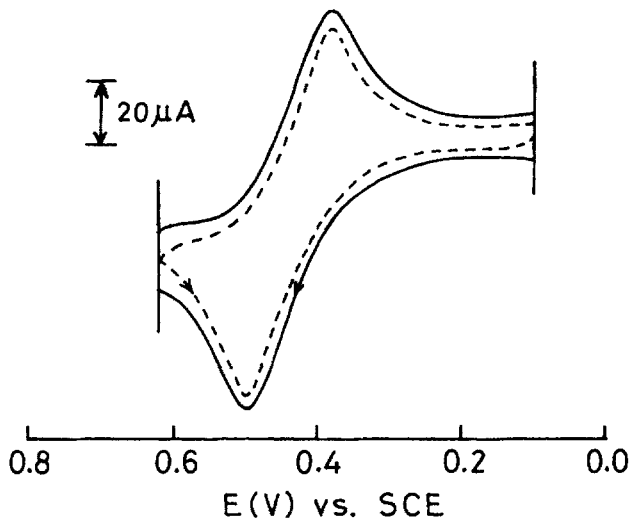
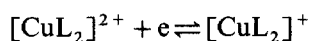


Figure 2. Cyclic voltammogram in CH_3OH $[\text{Cu}(\text{L}^{1a})_2](\text{ClO}_4)$ (—) and electrogenerated $[\text{Cu}(\text{L}^{1a})_2]^{2+}$ (---)

The peak-to-peak separation ($\Delta E_p = E_{pa} - E_{pc}$; $> 100\text{ mV}$) accounts for the quasi-reversible character of the couple. A representative voltammogram is shown in figure 2. The results are comparable with our previously reported results.



The $[\text{Cu}(\text{L}^1)_2]^+$ exhibit slightly higher redox value than $[\text{Cu}(\text{L}^5)_2]^+$ that may be due to greater steric crowding provided by 7-Me in L^1 than 8-Me in L^5 . The electronic effect of the substituents in aryl ring are also prominent in the potential values. Because of the electron donating effect of -OMe group (**3a**, **3b**), the π -acidity of azoimine function is reduced that stabilises Cu(I) less efficiently than that of $-\text{NO}_2$ substitution (**5a**, **5b**), the latter being an electron withdrawing group. The controlled potential coulometry at 0.62 V in one case $[\text{Cu}(\text{L}^{1a})_2](\text{ClO}_4)$ (**2a**) fully corroborates the one electron stoichiometry of the couple. The electrochemistry negative to SCE exhibit multielectron reduction response which may arise from the reduction of azoimine function¹⁰⁻¹².

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