

Synthesis, Spectroscopic Characterization and Electrochemistry of Mixed Ligand Complexes of Copper (I) Halide with PPh₃ and 2-Arylazo Imidazole

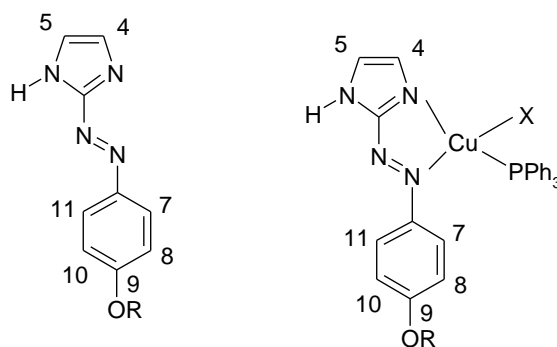
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Abstract

The reaction of CuX (X = Cl, I) with a mixture of PPh₃ and 2-arylazo imidazole has synthesized mixed ligand complexes of the composition, [Cu(HaaiOR)(PPh₃)X]. The composition is supported by microanalytical data. The structure has been established by spectroscopic (UV-Vis, IR, NMR) studies. Cyclic voltammograms of the complexes show a high potential Cu(II)/Cu(I) couple and azo reductions. The [Cu(HaaiOR)(PPh₃)I] complexes show an additional additional oxidation peak due to I/I couple.



Introduction

Azo dyes, an important class of chemicals in pigment industries, have been used in coordination chemistry as a target to synthesise photostable and weather stable pigments¹. Recently, some metal complexes of dyes have found applications in high-technology realm such as photoelectronic devices, optical recording media², light emitting diodes³, field effect transistors⁴, photovoltaic cells (PVCs)⁵ etc. Studies have been made on different organic dyes for efficient dye sensitized solar cells⁶⁻¹⁴. Azo dyes are interesting materials for solar batteries and non-linear optical appliances¹⁵. Chelating property of azo dyes has been utilized in a number of analytical methods¹⁶, including sensors^{17, 18}, to determine metal ions.

Metal complexes containing azo groups have aroused great interest due to the possibility of conformational modification under UV light irradiation¹⁹. 1-Alkyl-2-(arylo)imidazole (RaaiR') exhibits photochromism^{20, 21}, a reversible photo-induced transformation between *cis* and *trans* states whose absorption spectra differ²²⁻²⁷. This molecule has been used as ligand for some transition and nontransition metal complexes by us²⁸⁻³⁴ and others³⁵⁻³⁸

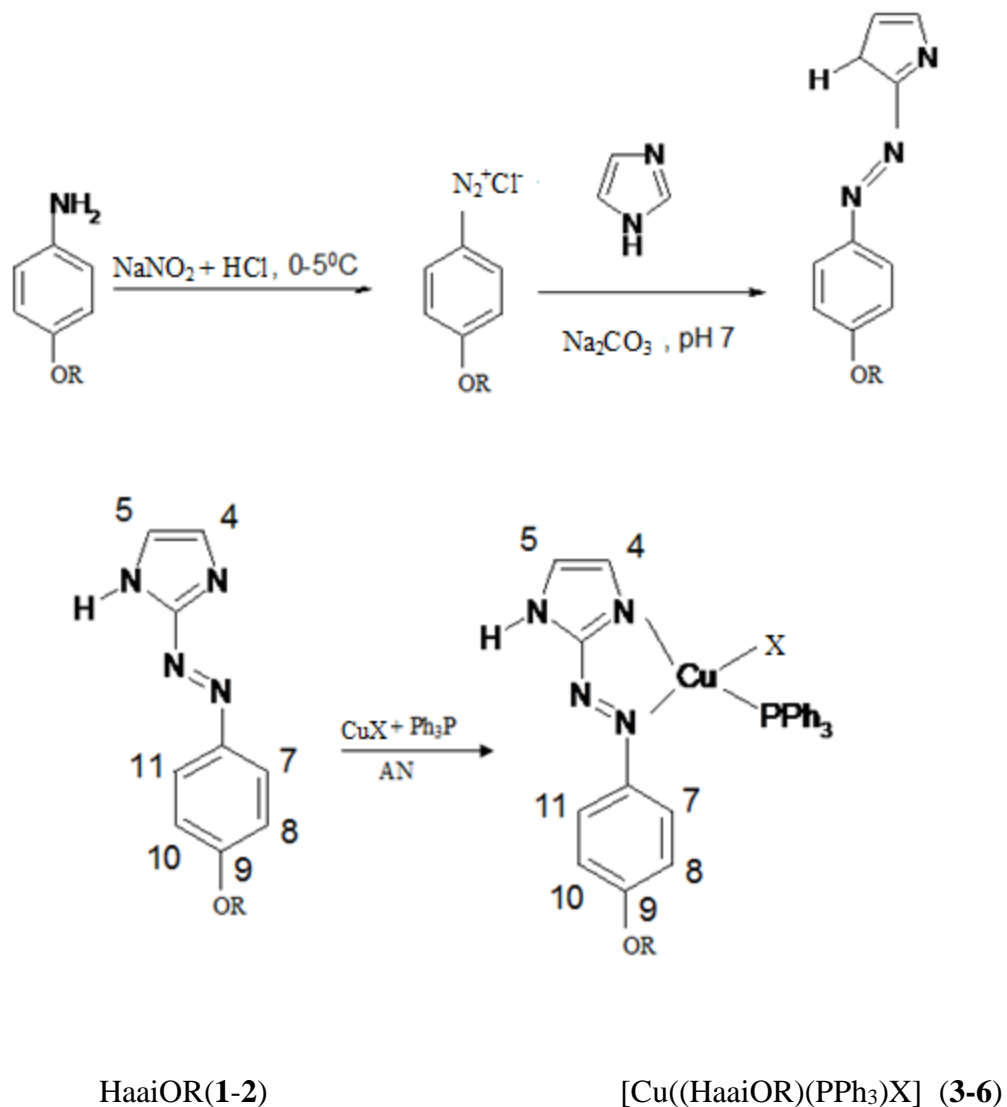
Halide compounds of the metals with d¹⁰ configuration show various coordination numbers and configuration³⁹⁻⁴³. The chemistry of Group 11 metals (Cu, Ag, Au) has been of considerable attention⁴⁴ because of their interesting electronic, optical, structural, biological and catalytic properties⁴⁵⁻⁴⁷. Azoimidazole carries π -acidic azoimine (-N=N-C=N-) chelating group and stabilizes low valent metal redox state. The presence of other π -acidic molecules like, PPh₃, CO, NO cooperates the azoimine function to stabilize low redox state like Cr(0), Mo(0), W(0), Ru(0)⁴⁸⁻⁵⁰, Cu(I) etc.^{51, 52}. This article describes synthesis, spectroscopic characterization and electrochemistry of mixed ligand complexes of copper(I) halide with PPh₃ and 2-arylo)imidazole.

Results and Discussion

III.2.1 Synthesis and formulation

2-(p-methoxyphenylazo)imidazole, 2-(p-ethoxyphenylazo)imidazole, (HaaiOR) have been used in this work **Scheme 1** to prepare copper(I) complexes. The reaction of CuX and PPh₃ forms the tetramer [Ph₃PCuX]₄⁵³ which upon reaction *in situ* with HaaiOR in MeCN has yielded

the complexes of composition $[\text{Cu}(\text{HaaiOR})(\text{PPh}_3)\text{Cl}]$. The compounds are non-conducting and their composition has been supported by microanalytical data (**Table 1**).



$\text{R} = \text{CH}_3$ (1), $\text{R} = \text{C}_2\text{H}_5$ (2)

$\text{R} = \text{CH}_3, \text{X} = \text{Cl}$ (3), $\text{R} = \text{C}_2\text{H}_5, \text{X} = \text{Cl}$ (4)

$\text{R} = \text{CH}_3, \text{X} = \text{I}$ (5), $\text{R} = \text{C}_2\text{H}_5, \text{X} = \text{I}$ (6)

Scheme 1: Synthesis of ligands and complexes

Table 1. Microanalytical data^a

Compounds	Microanalytical data Found(calc.)%		
	C	H	N
[Cu(HaaiOCH ₃)(PPh ₃)Cl] (3)	53.32(53.34)	4.18(4.17)	8.61(8.58)
[Cu(HaaiOC ₂ H ₅)(PPh ₃)Cl] (4)	62.06(62.03)	4.83(4.85)	9.95(9.98)
[Cu(HaaiOCH ₃)(PPh ₃)I] (5)	52.61(52.63)	3.95(3.94)	8.79(8.77)
[Cu(HaaiOC ₂ H ₅)(PPh ₃)I] (6)	61.43(61.42)	4.62(4.60)	10.24(10.23)

Spectroscopic studies

IR Spectra

IR spectra of the complexes show moderately intense stretching at 1595-1600 and 1435-1445 cm⁻¹ and are assigned to $\nu(\text{C}=\text{N})$ and $\nu(\text{N}=\text{N})$, respectively (Fig.1). Other vibration are shifted to lower energy in the copper complexes (3-6) compared to the free ligand values ^[57] which are in support of coordination of azo -N and imine -N to Cu(I).

The spectral data are shown in **Table 2**.

UV-Vis Spectra

The solution electronic spectra of the complexes, **3-6**, are recorded in MeCN in 200-900 nm, **Table 2**. The bands in the UV region are intense ($\epsilon \sim 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) at 240-255, 365-380 nm and are referred to ligand centred charge transitions⁵⁷. A weak band is observed at 550-600 nm ($\epsilon \sim 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) which is characteristic to MLCT transition of tetrahedral [Cu(azoimidazole)]⁺.

Table 2. IR^a and UV-Vis^b spectral data of the complexes.

Compounds	IR in KBr disc(cm ⁻¹)		UV-VIS spectral data $\lambda_{\max}(\text{nm})(10^{-3}\epsilon(\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}))$
	$\nu(\text{N}=\text{N})$	$\nu(\text{C}=\text{N})$	
(3)	1427	1599	266(13.26), 362(15.11), 433(3.86), 558 (0.41)
(4)	1424	1599	267(13.34), 364(15.21), 432(3.97), 560 (0.45)
(5)	1435	1598	262(7.4), 360(16.30), 425(4.62), 564 (0.52)
(6)	1427	1600	264(14.52), 370(17.6), 434(4.49), 580 (0.46)

NMR Spectra

The ¹H NMR spectra of the complexes are recorded in CDCl₃ (**Fig.3**) and the signals are assigned unambiguously by spin-spin interaction, the effect of substitution therein and on comparing with previously reported compounds⁵⁴⁻⁵⁷. The atom numbering pattern is shown in the **Scheme.1**. Data **Table 3** reveals that the signals in the spectra of the complexes in general are shifted downfield compared to the spectra of free ligand⁵⁷. Signals of imidazole protons, 4- and 5-H, shift significantly ($\Delta\delta$, 0.2 – 0.5 ppm) whereas shifting for aryl protons 7,11-H is in the range 0.06-0.15 ppm. 8-10-H remains almost unshifted. This supports the chelation by N(imidazole) and N(azo).

Table 3 ¹H NMR spectral data of [Cu(HaaiOR)(PPh₃)(X)] (X = Cl, I) complexes in CDCl₃ at 300 K

Comp	δ (ppm) (J (Hz))							
	4-H ^a	5-H ^a	7, 11-H ^b	8,10-H ^b	O- CH ₃ ^e	O-CH ₂ ^g	(O-CH ₂) CH ₃ ^h	PPh ₃
(3)	7.24	7.20	8.08 (7.6)	7.04 (7.6)	4.02			7.28-7.44
(4)	7.19	7.08	7.50 (8.0)	7.29 (7.6)		4.51 (9.0)	1.57 (7.0)	7.31-7.44
(5)	7.25	7.23	8.14 (8.0)	7.09 (8.0)	4.01			7.26-7.41
(6)	7.19	7.11	7.55 (7.6)	7.32 (8.0)		4.52 (9.0)	1.63 (7.0)	7.30-7.43

Electrochemistry and Redox interconversion, Cu^{II} ↔ Cu^I

Cyclic voltammogram (CV) of copper(I) complexes, [Cu((Haa)X)(PPh₃)Cl], are recorded in MeCN at a Pt-disk milli electrode in the potential range +1.5 to -2.0 V versus SCE reference electrode (**Table 4**). Complexes show a quasireversible oxidative response ~1 V. On scanning to -ve direction up to -2.0 V we observe a sharp anodic signal at ~ -0.2, an irreversible response, E_{pc} at ~ -0.9 V and a quasireversible couple at -1.2 V (ΔE_p > 150 mV) **Fig.4** The sharp anodic signal at ~ -0.2 V, possibly the Cu(I)/Cu(0) couple. The reduced Cu(0) is absorbed on the electrode surface as evident from the narrow width of the anodic response with a large peak current.

Table 4. Cyclic voltammetric data^a

Complex	Metal redox couple			Ligand redox couple	
	E, V (ΔE _p , mV)			E, V (ΔE _p , mV)	
	X/X ⁻	Cu ^{II} /Cu ^I	Cu ^I /Cu ⁰	azo/azo ⁻	azo ⁻ /azo ⁻
3		1.03	-0.21	-0.89	-1.24
4		1.04	-0.22 ^b	-0.90 ^b	-1.25
5		1.03	-0.21 ^b	-0.89 ^b	-1.26
6		1.06	-0.21 ^b	-0.88 ^b	-1.25

^a Solvent: MeCN, Pt-disk working electrode, supporting electrolyte, TBAP (0.01 M); reference, SCE; solute concentration, 10⁻³ M; scan rate, 0.05 V s⁻¹; ΔE_p = |E_{pa} - E_{pc}|, mV; E_{pa} = anodic peak potential, E_{pc} = cathodic peak potential, V; E_{1/2} = 0.5(E_{pa} + E_{pc}), V. ^b E_{pc}

Experimental

Materials

Imidazole, different aromatic amines, CuCl and CuI and triphenyl phosphine were purchased from E. Merck India. All other chemicals and solvents were of reagent grade and used as received. 2-(aryloxy)imidazole (HaaiOR) were prepared by reported procedure^{51, 52}.

Physical measurements

Microanalytical (C,H,N) data (**Table 1**) were obtained from a Perkin-Elmer 2400 CHNS/O elemental analyzer. Spectroscopic data were obtained using the following instruments: UV-Vis, Perkin-Elmer Lambda-25; IR (KBr disk, 4000-200 cm^{-1}), Perkin- Elmer RX-1 spectrophotometer, and ^1H NMR, Bruker 300 MHz FT-NMR spectrometer. Electrochemical measurements were performed using computer-controlled PAR model 250 VersaStat electrochemical instruments with Pt-disk electrodes. All measurements were carried out under nitrogen environment at 298 K with reference to SCE in acetonitrile using $[\text{nBu}_4\text{N}][\text{ClO}_4]$ as supporting electrolyte. The reported potentials are uncorrected for junction potential. Room temperature (298 K) magnetic susceptibility was measured using Sherwood Scientific Cambridge, UK at 298 K. EPR spectra were recorded in MeCN solution at room temperature (298 K) and liquid nitrogen temperature (77 K) using Bruker ESR spectrometer model EMX 10/12, X-band ER 4119 HS cylindrical resonator.

Preparation of compounds

Synthesis of $[\text{Cu}(\text{HaaiOC}_2\text{H}_5)(\text{PPh}_3)\text{Cl}]$ (4)

To methanol solution (25 ml) of 2-(aryloxy)imidazole (HaaiOR) (65 mg, 0.35 mmol) acetonitrile solution of CuCl (45 mg, 0.35 mmol) and triphenyl phosphine (92 mg, 0.35 mmol) were added, stirred and refluxed for 3 h. The solution was filtered through G4 crucible and was allowed to evaporate slowly in air. Block shaped dark micro crystals deposited on the wall of beaker. These were collected by filtration. X-ray quality block shaped crystals were obtained by recrystallising from DMF-MeOH solution (1:2 v/v). Yield, 0.15 g (71%).

Conclusion

Mixed ligand complexes of $[\text{Cu}(\text{HaaiOR})(\text{PPh}_3)\text{X}]$ are described in this work. The composition is supported by microanalytical data. The structure has been established by spectroscopic (UV-Vis, IR, NMR) data. IR spectra of the complexes show moderately intense stretching at 1595-1600 and 1435-1445 cm^{-1} and are assigned to $\nu(\text{C}=\text{N})$ and $\nu(\text{N}=\text{N})$, respectively. The solution electronic spectra of the complexes show π , π^* and N , π^* transitions. Cyclic voltammograms of the complexes show a high potential $\text{Cu}(\text{II})/\text{Cu}(\text{I})$ couple and azo reductions.

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