



# Synthesis, spectroscopic properties, structural characterization and electrochemistry of mixed ligand complexes of copper(I) halide with PPh<sub>3</sub> and naphthylazoimidazole

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## ABSTRACT

The reaction of CuX (X = Cl, Br, I) with a mixture of PPh<sub>3</sub> and 1-alkyl-2-(naphthyl- $\alpha/\beta$ -azo)imidazole has synthesized mixed ligand complexes of the composition, [Cu( $\alpha/\beta$ -NaiR)(PPh<sub>3</sub>)X]. The spectroscopic characterization (IR, UV–Vis, <sup>1</sup>H NMR) supports this formulation. The single crystal X-ray diffraction study of [Cu(( $\alpha$ -NaiMe)(PPh<sub>3</sub>))I] (**7a**) ( $\alpha$ -NaiMe = 1-methyl-2-(naphthyl- $\alpha$ -azo)imidazole) shows a distorted tetrahedral geometry about Cu(I). Cyclic voltammograms of the complexes show a high potential Cu(II)/Cu(I) couple and azo reductions. The [Cu( $\alpha/\beta$ -NaiR)(PPh<sub>3</sub>)I] complexes show an additional oxidative response at 0.4 V that is assigned to I/I<sup>-</sup>. A sharp anodic peak at  $\sim$ -0.2 V is assigned to the oxidation of metallic Cu, deposited on electrode surface upon scanning to the negative side of the SCE. DFT and TD-DFT computations of [Cu(( $\alpha$ -NaiMe)(PPh<sub>3</sub>))I] (**7a**), [Cu(( $\alpha$ -NaiMe)(PPh<sub>3</sub>))I]<sup>+</sup> (**7a\***) and [Cu(( $\alpha$ -NaiMe)(PPh<sub>3</sub>))I]<sup>-</sup> (**7a<sup>-</sup>**) were carried out to examine the electronic configuration and to explain the spectral and redox properties of the complexes.

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## 1. Introduction

Imidazole is ubiquitous in chemistry and biology [1]. The synthesis of polydentate ligands using imidazole and their metal complexes are of interest [2–4]. We have been engaged in the synthesis of azo functionalized imidazoles such as 1-alkyl-2-(arylo)imidazole for several years [5–12]. The arylazoheterocycle stabilizes metals in their lower oxidation state [8–12], such as Cu(I), Ag(I), Fe(II), Co(II), Ru(II), Os(II). The azoimine function, –N=N–C=N– is the chelating group contributing to the chemical, spectral and electrochemical properties of the molecules. It has been proposed that the stability, visible spectra and Cu(II)/Cu(I) redox potential of Cu(I)-arylazoheterocycles are due to  $d\pi(\text{Cu(I)}) \rightarrow \pi^*(\text{ligand orbital})$  transitions [10–12]. The presence of  $\pi$ -acidic co-ligands, like PPh<sub>3</sub> and CO, may assist the azoimine function to stabilize the lower oxidation state more efficiently [8,9] compared to the azoimine function alone. In this work, we report mixed ligand complexes of copper(I) halide with PPh<sub>3</sub> and 1-alkyl-2-(naphthyl- $\alpha/\beta$ -azo)imidazoles ( $\alpha/\beta$ -NaiR). The complexes are oxidized by chlorine in

methanol and the copper(II) complexes thus obtained are reduced by ascorbic acid to the copper(I) derivatives. A theoretical calculation using the DFT computation technique is used to define the electronic configuration of the molecules and to give an explanation of their electronic properties. We have attempted this procedure to correlate the electronic and redox properties of the complexes. The calculation was carried out using the neutral, oxidized and reduced compound.

## 2. Experimental

### 2.1. Materials

Imidazole, naphthyl amines, CuX (X = Cl, Br, I) and triphenyl phosphine were purchased from E. Merck India. All other chemicals and solvents were of reagent grade and were used as received. The 1-alkyl-2-(naphthyl-azo)imidazoles were prepared by the reported procedure [10].

### 2.2. Physical measurements

Microanalytical (C,H,N) data 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 disc, 4000–200 cm<sup>-1</sup>), Perkin–Elmer RX-1

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spectrophotometer, and  $^1\text{H}$  NMR, Bruker 300 MHz FT NMR spectrometer. Electrochemical measurements were performed using computer-controlled PAR model 250 VersaStat electrochemical instruments with Pt-disc electrodes. All measurements were carried out under a nitrogen environment at 298 K with reference to SCE in acetonitrile using  $[\text{nBu}_4\text{N}][\text{ClO}_4]$  as a supporting electrolyte. The reported potentials are not corrected further for junction potentials. Room temperature (298 K) magnetic susceptibility was measured using Sherwood Scientific Cambridge, UK at 298 K. ESR spectra were recorded in MeCN solution at room temperature (298 K) and at liquid nitrogen temperature (77 K) using a Bruker ESR spectrometer model EMX 10/12, X-band ER 4119 HS cylindrical resonator.

### 2.3. Synthesis $[\text{Cu}(\alpha\text{-NaiMe})(\text{PPh}_3)]$ (**7a**) and analytical data

To a methanol solution (25 ml) of 1-methyl-2-(naphthyl- $\alpha$ -azo)imidazole ( $\alpha\text{-NaiMe}$ ) (0.09 g, 0.38 mmol), CuI (0.07 g, 0.37 mmol) in acetonitrile (25 ml) and  $\text{PPh}_3$  (0.1 g, 0.38 mmol) were added, stirred and refluxed for 3 h. The solution was filtered under hot conditions through a G4 crucible and was allowed to evaporate slowly in air. Microcrystals, deposited on the wall of beaker, were collected by filtration. These crystals were ground and a DMF solution was prepared. Methanol (2 volumes) was added to this solution. After a week X-ray quality crystals separated out at the bottom of the beaker. These were collected and dried over  $\text{CaCl}_2$  in a desiccator. The yield was 0.15 g (71%).

All the other complexes were prepared by the same procedure. In all cases, crystalline products were obtained. The yield varied from 70–80%. Microanalytical data of the complexes are as follows:  $[\text{Cu}(\alpha\text{-NaiMe})(\text{PPh}_3)\text{Cl}]$  (**3a**): *Anal. Calc.* for  $\text{C}_{32}\text{H}_{27}\text{CuClN}_4\text{P}$ : C, 64.32; H, 4.50; N, 9.30. Found: C, 64.35; H, 4.54; N, 9.37%. FT-IR (KBr disc,  $\text{cm}^{-1}$ ):  $\nu(\text{N}=\text{N})$ , 1365;  $\nu(\text{C}=\text{N})$ , 1580. UV-VIS spectral data in  $\text{CH}_3\text{CN}$  ( $\lambda_{\text{max}}$  (nm) ( $\epsilon$ ,  $10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ )): 375 (5.08), 393 (4.01), 580 (0.81).  $[\text{Cu}(\alpha\text{-NaiEt})(\text{PPh}_3)\text{Cl}]$  (**3b**): *Anal. Calc.* for  $\text{C}_{33}\text{H}_{29}\text{CuClN}_4\text{P}$ : C, 64.81; H, 4.78; N, 9.16. Found: C, 64.79; H, 4.73; N, 9.10%. FT-IR (KBr disc,  $\text{cm}^{-1}$ ):  $\nu(\text{N}=\text{N})$ , 1350;  $\nu(\text{C}=\text{N})$ , 1577. UV-Vis spectral data in  $\text{CH}_3\text{CN}$  ( $\lambda_{\text{max}}$  (nm) ( $\epsilon$ ,  $10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ )): 371 (6.01), 394 (4.38), 575 (0.89).  $[\text{Cu}(\beta\text{-NaiMe})(\text{PPh}_3)\text{Cl}]$  (**4a**): *Anal. Calc.* for  $\text{C}_{32}\text{H}_{27}\text{CuClN}_4\text{P}$ : C, 64.32; H, 4.55; N, 9.38. Found: C, 64.35; H, 4.50; N, 9.31%. FT-IR (KBr disc,  $\text{cm}^{-1}$ ):  $\nu(\text{N}=\text{N})$ , 1355;  $\nu(\text{C}=\text{N})$ , 1571. UV-Vis spectral data in  $\text{CH}_3\text{CN}$  ( $\lambda_{\text{max}}$  (nm) ( $\epsilon$ ,  $10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ )): 376 (5.06), 395 (4.86), 590 (0.55).  $[\text{Cu}(\beta\text{-NaiEt})(\text{PPh}_3)\text{Cl}]$  (**4b**): *Anal. Calc.* for  $\text{C}_{33}\text{H}_{29}\text{CuClN}_4\text{P}$ : C, 64.81; H, 4.78; N, 9.16. Found: C, 64.73; H, 4.72; N, 9.13%. FT-IR (KBr disc,  $\text{cm}^{-1}$ ):  $\nu(\text{N}=\text{N})$ , 1345;  $\nu(\text{C}=\text{N})$ , 1573. UV-Vis spectral data in  $\text{CH}_3\text{CN}$  ( $\lambda_{\text{max}}$  (nm) ( $\epsilon$ ,  $10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ )): 379 (5.85), 396 (4.38), 590 (0.76).  $[\text{Cu}(\alpha\text{-NaiMe})(\text{PPh}_3)\text{Br}]$  (**5a**): *Anal. Calc.* for  $\text{C}_{32}\text{H}_{27}\text{CuBrN}_4\text{P}$ : C, 59.87; H, 4.21; N, 8.73. Found: C, 59.82; H, 4.26; N, 8.71%. FT-IR (KBr disc,  $\text{cm}^{-1}$ ):  $\nu(\text{N}=\text{N})$ , 1340;  $\nu(\text{C}=\text{N})$ , 1540. UV-Vis spectral data in  $\text{CH}_3\text{CN}$  ( $\lambda_{\text{max}}$  (nm) ( $\epsilon$ ,  $10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ )): 378 (5.26), 391 (4.81), 570 (0.95).  $[\text{Cu}(\alpha\text{-NaiEt})(\text{PPh}_3)\text{Br}]$  (**5b**): *Anal. Calc.* for  $\text{C}_{33}\text{H}_{29}\text{CuBrN}_4\text{P}$ : C, 60.42; H, 4.46; N, 8.54. Found: C, 60.43; H, 4.41; N, 8.50%. FT-IR (KBr disc,  $\text{cm}^{-1}$ ):  $\nu(\text{N}=\text{N})$ , 1325;  $\nu(\text{C}=\text{N})$ , 1550. UV-Vis spectral data in  $\text{CH}_3\text{CN}$  ( $\lambda_{\text{max}}$  (nm) ( $\epsilon$ ,  $10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ )): 379 (5.31), 394 (4.31), 580 (0.80).  $[\text{Cu}(\beta\text{-NaiMe})(\text{PPh}_3)\text{Br}]$  (**6a**): *Anal. Calc.* for  $\text{C}_{32}\text{H}_{27}\text{CuBrN}_4\text{P}$ : C, 59.87; H, 4.21; N, 8.73. Found: C, 59.83; H, 4.24; N, 8.70%. FT-IR (KBr disc,  $\text{cm}^{-1}$ ):  $\nu(\text{N}=\text{N})$ , 1331;  $\nu(\text{C}=\text{N})$ , 1555. UV-Vis spectral data in  $\text{CH}_3\text{CN}$  ( $\lambda_{\text{max}}$  (nm) ( $\epsilon$ ,  $10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ )): 380 (5.19), 395 (4.37), 590 (0.87).  $[\text{Cu}(\beta\text{-NaiEt})(\text{PPh}_3)\text{Br}]$  (**6b**): *Anal. Calc.* for  $\text{C}_{33}\text{H}_{29}\text{CuBrN}_4\text{P}$ : C, 60.42; H, 4.46; N, 8.54. Found: C, 60.40; H, 4.40; N, 8.50%. FT-IR (KBr disc,  $\text{cm}^{-1}$ ):  $\nu(\text{N}=\text{N})$ , 1335;  $\nu(\text{C}=\text{N})$ , 1550. UV-Vis spectral data in  $\text{CH}_3\text{CN}$  ( $\lambda_{\text{max}}$  (nm) ( $\epsilon$ ,  $10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ )): 374 (5.43), 396 (4.21), 588 (0.75).  $[\text{Cu}(\alpha\text{-$

$\text{NaiMe})(\text{PPh}_3)]$  (**7a**): *Anal. Calc.* for  $\text{C}_{32}\text{H}_{27}\text{CuClN}_4\text{P}$ : C, 55.78; H, 3.92; N, 8.13. Found: C, 55.72; H, 3.90; N, 8.14%. FT-IR (KBr disc,  $\text{cm}^{-1}$ ):  $\nu(\text{N}=\text{N})$ , 1345;  $\nu(\text{C}=\text{N})$ , 1557. UV-Vis spectral data in  $\text{CH}_3\text{CN}$  ( $\lambda_{\text{max}}$  (nm) ( $\epsilon$ ,  $10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ )): 376 (4.99), 394 (4.11), 585 (0.85).  $[\text{Cu}(\alpha\text{-NaiEt})(\text{PPh}_3)]$  (**7b**): *Anal. Calc.* for  $\text{C}_{33}\text{H}_{29}\text{CuClN}_4\text{P}$ : C, 56.38; H, 4.13; N, 7.97. Found: C, 56.32; H, 4.17; N, 7.96%. FT-IR (KBr disc,  $\text{cm}^{-1}$ ):  $\nu(\text{N}=\text{N})$ , 1342;  $\nu(\text{C}=\text{N})$ , 1552. UV-Vis spectral data in  $\text{CH}_3\text{CN}$  ( $\lambda_{\text{max}}$  (nm) ( $\epsilon$ ,  $10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ )): 379 (5.47), 398 (4.20), 570 (0.89).  $[\text{Cu}(\beta\text{-NaiMe})(\text{PPh}_3)]$  (**8a**): *Anal. Calc.* for  $\text{C}_{32}\text{H}_{27}\text{CuClN}_4\text{P}$ : C, 55.78; H, 3.92; N, 8.13. Found: C, 55.72; H, 4.00; N, 8.10%. FT-IR (KBr disc,  $\text{cm}^{-1}$ ):  $\nu(\text{N}=\text{N})$ , 1335;  $\nu(\text{C}=\text{N})$ , 1555. UV-Vis spectral data in  $\text{CH}_3\text{CN}$  ( $\lambda_{\text{max}}$  (nm) ( $\epsilon$ ,  $10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ )): 375 (5.61), 393 (4.49), 595 (0.77).  $[\text{Cu}(\beta\text{-NaiEt})(\text{PPh}_3)]$  (**8b**): *Anal. Calc.* for  $\text{C}_{33}\text{H}_{29}\text{CuClN}_4\text{P}$ : C, 56.38; H, 4.13; N, 7.97. Found: C, 56.33; H, 4.10; N, 7.92%. FT-IR (KBr disc,  $\text{cm}^{-1}$ ):  $\nu(\text{N}=\text{N})$ , 1340;  $\nu(\text{C}=\text{N})$ , 1554. UV-Vis spectral data in  $\text{CH}_3\text{CN}$  ( $\lambda_{\text{max}}$  (nm) ( $\epsilon$ ,  $10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ )): 375 (5.29), 396 (4.19), 582 (0.90).

### 2.4. X-ray crystal structure analyses **7a**

Crystals suitable for an X-ray diffraction study of  $[\text{Cu}(\alpha\text{-NaiMe})(\text{PPh}_3)]$  (**7a**) (0.38  $\times$  0.28  $\times$  0.06 mm) were prepared by slow evaporation of a N,N-dimethylformamide–methanol (1:2 v/v) solution of the compound under ambient conditions. Diffraction data were collected with a Bruker SMART 1 K CCD area-detector diffractometer using fine focused sealed tube graphite-monochromatized Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Unit cell parameters were determined by the least-squares method with the data in the range  $-11 \leq h \leq 11$ ,  $-23 \leq k \leq 22$ ,  $-18 \leq l \leq 22$  and angles  $3.30^\circ < 2\theta < 52.10^\circ$  for **7a**. The crystallographic data and structural refinement parameters are given in Table 1. Data were corrected for Lorentz and polarization effects. Data reduction was carried out by using the SAINT program [13]. The structure was solved by direct methods using SHELXS-97 [14] and successive difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically. Full matrix least-squares refinements on  $F_o^2$  were carried out using SHELXL-97 [15] with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were constrained to ride on their respective carbon or nitrogen atoms with anisotropic displacement parameters equal to 1.2 times the equivalent isotropic displacement

**Table 1**  
Summarized crystallographic data for  $[\text{Cu}(\alpha\text{-NaiMe})(\text{PPh}_3)]$  (**7a**).

	$[\text{Cu}(\alpha\text{-NaiMe})(\text{PPh}_3)]$ ( <b>7a</b> )
Empirical formula	$\text{C}_{32}\text{H}_{27}\text{N}_4\text{PCu}$
Formula weight	688.99
Temperature (K)	298(2)
Crystal system	monoclinic
Space group	$P2_1/c$
<i>Unit cell dimensions</i>	
<i>a</i> (Å)	9.395(2)
<i>b</i> (Å)	19.268(4)
<i>c</i> (Å)	18.435(3)
$\beta$ ( $^\circ$ )	119.445(8)
<i>V</i> (Å $^3$ )	2906.1(10)
<i>Z</i>	4
$\lambda$ (Å)	0.71073
$\mu$ (Mo K $\alpha$ ) ( $\text{mm}^{-1}$ )	1.897
$D_{\text{calc}}$ ( $\text{Mg m}^{-3}$ )	1.575
Refine parameters	354
Total reflection	5438
$R_1^a$ [ $I > 2\sigma(I)$ ]	0.0665
$wR_2^b$	0.1198
Goodness-of-fit (GOF)	1.283

<sup>a</sup>  $R = \sum |F_o - F_c| / \sum F_o$ .

<sup>b</sup>  $wR = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$  where  $w = 1 / [\sigma^2(F^2) + (0.0212P)^2 + 6.3126P]$  where  $P = (F_o^2 + 2F_c^2)/3$ .

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