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Structure, electrochemistry and photochromism of $[Cu(RaaiR')(PPh_3)X]$ (RaaiR' = 1-alkyl-2-(arylazo)imidazole; X = Cl, Br, I) and correlation with theoretical calculations

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ABSTRACT

The reaction between CuX (X = Cl, Br, I), PPh₃ and 1-alkyl-2-(arylazo)imidazole (RaaiR') has synthesized [Cu(RaaiR')(PPh₃)X]. The composition has been established by spectroscopic (UV–Vis, IR, ¹H NMR) data and the single crystal X-ray diffraction study of [Cu(MeaaiH)(PPh₃)Cl] and [Cu(MeaaiH)(PPh₃)Br] (MeaaiH = 2-(*p*-tolylazo)imidazole) have confirmed the structures. These complexes show *trans*-to-*cis* (E-to-Z) photoisomerisation upon UV light irradiation. Quantum yields ($\phi_{E\rightarrow Z}$) of [Cu(RaaiR')(PPh₃)X] are lower than the free ligand values. The rate of isomerisation follows the sequence [Cu(RaaiR')(PPh₃)Cl] < [Cu(RaaiR')(PPh₃)Br] < [Cu(RaaiR')(PPh₃)I]. The *cis*-to-*trans* (Z-to-E) isomerisation is very slow upon light irradiation and has been achieved by a thermal route. The activation energy (*E*_a) of the Z-to-E isomerisation has been calculated by a controlled temperature reaction. DFT calculations of the optimized geometry of representative complexes have been used to determine the composition and energy of the molecular levels.

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1. Introduction

Azo dyes, an important class of chemicals in pigment industries, have been used in coordination chemistry as a target to synthesize photostable and weather stable pigments [1]. Recently, some metal complexes of dyes have found applications in the high-technology realm, for example as photoelectronic devices, optical recording media [2], light emitting diodes [3], field effect transistors [4], photovoltaic cells (PVCs) [5] etc. Studies have been made on different organic dyes for efficient dye sensitized solar cells [6–14]. Azo dyes are interesting materials for solar batteries and non-linear optical appliances [15]. The chelating property of azo dyes has been utilized in a number of analytical methods [16], 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 irradiation [19]. 1-Alkyl-2-(arylazo)imidazole (RaaiR') exhibits photochromism [20,21], a reversible photo-induced transformation between *cis* and *trans* geometries, whose absorption spectra differ [22–27] significantly. This molecule has been used as a ligand for the synthesis of some transition and non-transition metal complexes [28–38]. The photochromic behavior of 1-alkyl-2-(arylazo)imidazole (RaaiR') [20,21] and some complexes like Hg(II)-[39], Cd(II)- [40] and Pd(II)-azoimidazoles [41] has inspired us to examine the photochromic property of copper(I) halide complexes.

Halide compounds of metals with a d^{10} configuration show various coordination numbers and configurations [42,43]. The chemistry of group 11 metals (Cu, Ag, Au) has been given considerable attention [44] because of their interesting electronic, optical, structural, biological and catalytic properties [45–47]. Azoimidazole carries a π -acidic azoimine (-N=N-C=N-) chelating group and stabilizes low valent metal redox states. The presence of other π -acidic molecules, like PPh₃, CO and NO, cooperates with the azoimine function to stabilize low redox states like Cr(0), Mo(0), W(0), Ru(0) [48–50], Cu(1) [51,52] etc. Herein we report Cu(1)–halide–PPh₃ complexes of RaaiR'. The complexes are oxidized by chlorine in methanol and the copper(II) complexes so obtained are reduced by ascorbic acid to precursor copper(I) derivatives. This work describes the structures, redox and photochromism of Cu(1)–PPh₃–RaaiR'. Theoretical calculations using the DFT



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computation technique for the optimized geometries of the compounds has been used to define the electronic configuration and to explain the spectroscopic and redox properties of the molecules.

2. Experimental

2.1. Materials

Imidazole, different aromatic 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 used as received. The 1-alkyl-2-(arylazo)imidazoles (RaaiR') were prepared by a reported procedure [51,52].

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 disk, 4000-200 cm⁻¹), Perkin-Elmer RX-1 spectrophotometer; 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 a nitrogen environment at 298 K with reference to SCE in acetonitrile using [nBu₄N][ClO₄] as the 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 a Bruker ESR spectrometer model EMX 10/12, X-band ER 4119 HS cylindrical resonator.

2.3. Synthesis

2.3.1. [Cu(PPh₃)(MeaaiH)Cl] (4b)

To a methanol solution (25 ml) of 2-(*p*-tolyl-azo)imidazole (MeaaiH) (65 mg, 0.35 mmol), an acetonitrile solution of CuCl (45 mg, 0.35 mmol) and PPh₃ (92 mg, 0.35 mmol) were added, stirred and refluxed for 3 h. The solution was filtered through a G4 crucible and allowed to evaporate slowly in air. Block shaped dark micro crystals deposited on the wall of the beaker. These were collected by filtration and washed with cold methanol. X-ray quality block shaped crystals were obtained by recrystallising from a DMF–MeOH solution (1:2 v/v). Yield: 0.15 g (71%).

2.3.2. [Cu(PPh₃)(MeaaiH)I] (10b)

To a methanol solution (25 ml) of 2-(*p*-tolyl-azo)imidazole (MeaaiH) (65 mg, 0.35 mmol), an acetonitrile solution of Cul (70 mg, 0.35 mmol) and PPh₃ (92 mg, 0.35 mmol) were added, stirred and refluxed for 3 h. The solution was filtered through a G4 crucible and allowed to evaporate slowly in air. Block shaped black micro crystals deposited on the wall of the beaker and were washed with cold methanol. These were collected by filtration. X-ray quality block shaped crystals were obtained by recrystallsing from a DMF–MeOH solution (1:2 v/v). Yield: 0.15 g (71%).

All other complexes were prepared by the same procedure. In all cases, crystalline products were obtained. The yields varied from 70% to 80% and microanalytical data of the complexes are as follows: [Cu(HaaiH)(PPh₃)Cl] (**4a**) *Anal.* Calc. for C₂₇H₂₃CuClN₄P: C, 60.79; H, 4.60; N, 10.50. Found: C, 60.81; H, 4.59; N, 10.53%. FT-IR (KBr disc, cm⁻¹): v(N=N) 1424; v(C=N) 1599; v (PPh₃) 520, 474, 420. UV–Vis (CH₃CN) λ_{max} (nm) (10⁻³ ϵ (dm³ mol⁻¹ cm⁻¹)): 267(13.34), 364(15.21), 432(3.97), 560(0.45). [Cu(Mea-

159

aiH)(PPh₃)Cl] (**4b**) Anal. Calc. for C₂₈H₂₅CuClN₄P: C, 61.42; H, 4.60; N, 10.23. Found: C,61.44; H, 4.63; N, 10.20%. FT-IR (KBr disc, cm⁻¹): v (N=N) 1435; v (C=N) 1598; v (PPh₃) 516, 470, 416. UV-Vis (CH₃CN) λ_{max} (nm) (10⁻³ ϵ (dm³ mol⁻¹ cm⁻¹)): 262(7.4), 360(16.30), 425(4.62), 564(0.52). [Cu(HaaiMe)(PPh₃)Cl] (5a) Anal. Calc. for C₂₈H₂₅CuClN₄P: C, 61.42; H, 4.60; N, 10.23. Found: C, 61.43; H, 4.62; N, 10.24%. FT-IR (KBr disc, cm⁻¹): v (N=N) 1427; v (C=N) 1600; v (PPh₃) 525, 476, 416. UV-Vis (CH₃CN) λ_{max} (nm) $(10^{-3} \epsilon (dm^3 mol^{-1} cm^{-1}))$: 264(14.52), 370(17.6), 434(4.49), $[Cu(MeaaiMe)(PPh_3)Cl]$ (5b) Anal. 580(0.46). Calc for C29H27CuClN4P: C, 62.03; H, 4.85; N, 9.98. Found: C, 62.05; H, 4.81; N, 10.01%. FT-IR (KBr disc, cm⁻¹): v (N=N) 1429; v (C=N) 1597; ν (PPh₃) 507, 474, 425. UV-Vis (CH₃CN) λ_{max} (nm) $(10^{-3} \epsilon (dm^3 mol^{-1} cm^{-1}))$: 275(6.95), 373(14.35), 436(3.88), 482(0.62). [Cu(HaaiEt)(PPh₃)Cl] (**6a**) Anal. Calc. for C₂₉H₂₇CuClN₄P: C. 62.03; H. 4.85; N. 9.98. Found: C, 62.06; H, 4.83; N, 9.95%. FT-IR (KBr disc, cm^{-1}): v (N=N) 1435: v (C=N) 1599: v (PPh₃) 522, 473. 420. UV–Vis (CH₃CN) λ_{max} (nm) (10⁻³ ϵ (dm³ mol⁻¹ cm⁻¹)): 279(7.86), 372(11.45), 420(6.32), 574(0.45). [Cu(MeaaiEt)(PPh₃)Cl] (6b) Anal. Calc. for C₃₀H₂₉CuClN₄P: C, 62.60; H, 5.07; N, 9.73. Found: C, 62.63; H, 5.03; N, 9.77%. FT-IR (KBr disc, cm⁻¹ (N=N): 1434; v (C=N): 1598; v (PPh₃): 522, 475, 424. UV-Vis $\lambda_{\rm max}$ (nm) (10⁻³ ϵ (dm³ mol⁻¹ cm⁻¹)): 263(3.92), (CH₃CN) 379(10.13), 441(3.43), 580(0.60). [Cu(HaaiH)(PPh₃)Br] (7a) Anal. Calc. for C₂₇H₂₃CuBrN₄P: C, 56.11; H, 4.01; N, 9.69. Found: C, 56.14; H, 3.98; N, 9.71%. FT-IR (KBr disc, cm⁻¹): v (N=N) 1423; v (C=N) 1597; v (PPh₃) 524, 470, 420. UV–Vis (CH₃CN) λ_{max} (nm) $(10^{-3} \epsilon (dm^3 mol^{-1} cm^{-1}))$: 271(7.25), 364(13.39), 443(5.49), 566(0.52). [Cu(MeaaiH)(PPh₃)Br] (7b) Anal. Calc. for C₂₈H₂₅CuBrN₄P: C, 56.81; H, 4.25; N, 9.46. Found: C, 56.84; H, 4.24; N, 9.43%. FT-IR (KBr disc, cm⁻¹): v (N=N) 1436; v (C=N) 1596; v (PPh₃) 521, 470, 422. UV–Vis (CH₃CN) λ_{max} (nm) $(10^{-3} \epsilon (dm^3 mol^{-1} cm^{-1})): 265(5.38), 358(16.97), 440(5.31),$ 550(0.48). [Cu(HaaiMe)(PPh₃)Br] (8a) Anal. Calc. for C₂₈H₂₅CuBrN₄P: C, 56.81; H, 4.25; N, 9.46. Found: C, 56.84; H, 4.22; N, 9.51%. FT-IR (KBr disc, cm⁻¹): v (N=N) 1432; v (C=N) 1594; v 466, 424, UV–Vis (CH₃CN) (PPh₃) 516. $\lambda_{\rm max}$ (nm) $(10^{-3} \epsilon (dm^3 mol^{-1} cm^{-1}); 278(8.47), 376(13.57), 423(6.23),$ 578(0.91). [Cu(MeaaiMe)(PPh₃)Br] (8b) Anal. Calc. for C₂₉H₂₇CuBrN₄P: C, 57.47; H, 4.49; N, 9.24. Found: C,57.51; H, 4.63; N, 9.20%. FT-IR (KBr disc, cm⁻¹): v (N=N) 1431; v (C=N) 1598; v (PPh₃) 534, 478, 426. UV–Vis (CH₃CN) $\lambda_{\rm max}$ (nm) $(10^{-3} \epsilon (dm^3 mol^{-1} cm^{-1})):$ 275(6.64), 379(17.3), 437(5.94). 575(0.67). [Cu(HaaiEt)(PPh₃)Br] (**9a**) Anal. Calc. for C₂₉H₂₇CuBrN₄P: C, 57.47; H, 4.49; N, 9.24. Found: C, 57.49; H, 4.52; N, 9.24%. FT-IR (KBr disc, cm⁻¹): v (N=N) 1434; v (C=N) 1599; v (PPh₃) 536, 470, 428. UV–Vis (CH₃CN) λ_{max} (nm) (10⁻³ ϵ (dm³ mol⁻¹ cm⁻¹)): 282(6.89), 375(12.80), 423(5.37), 578(0.80). [Cu(MeaaiEt)(PPh₃)Br] (**9b**) Anal. Calc for C₃₀H₂₉CuBrN₄P: 58.12; H, 4.71; N, 9.03. Found: C, 58.13; H, 4.76; N, 9.00%. FT-IR (KBr disc, cm⁻¹): v (N=N) 1431; v (C=N) 1598; v (PPh₃) 516, 470, 416. UV-Vis (CH₃CN) λ_{max} (nm) $(10^{-3} \epsilon (dm^3 mol^{-1} cm^{-1}))$: 278(6.34), 375(15.36), 433(5.93), 580(0.66). [Cu(HaaiH)(PPh₃)I] (**10a**) Anal. Calc. for C₂₇H₂₃CuIN₄P: C, 51.89; H, 3.71; N, 8.97. Found: C, 51.90; H, 3.70; N, 8.98%. FT-IR (KBr disc, cm⁻¹): v (N=N) 1423; v (C=N) 1595; v (PPh₃) 530, 470, 420. UV–Vis (CH₃CN) λ_{max} (nm) (10⁻³ ϵ (dm³ mol⁻¹ cm⁻¹)): 261(5.93), 367(11.77), 441(4.71), 470(0.54). [Cu(MeaaiH)(PPh₃)I] (10b) Anal. Calc. for C₂₈H₂₅CuIN₄P: C, 52.63; H, 3.94; N, 8.77. Found: C, 52.60; H, 3.93; N, 8.79%. FT-IR (KBr disc, cm⁻¹): v (N=N) 1433; v (C=N) 1595; v (PPh₃) 525, 470, 425. UV-Vis (CH₃CN) λ_{max} (nm) (10⁻³ ϵ (dm³ mol⁻¹ cm⁻¹)): 245(6.46), 362(10.72), 433(5.32), 545(0.65). [Cu(HaaiMe)(PPh₃)I] (11a) Anal. Calc. for C₂₈H₂₅CuIN₄P: C, 52.63; H, 3.94; N, 8.77. Found: C, 52.61; H, 3.95; N, 8.79%. FT-IR (KBr disc, cm⁻¹): v (N=N) 1422; v (C=N) 1600; v (PPh₃) 524, 474, 416. UV-Vis (CH₃CN) λ_{max} (nm) $(10^{-3} \epsilon (dm^3 mol^{-1} cm^{-1})): 282(8.77), 370(15.42), 426(5.04),$

576(0.60). $[Cu(MeaaiMe)(PPh_3)I]$ (11b) Anal. Calc. for C₂₉H₂₇CuIN₄P: C, 53.34; H, 4.17; N, 8.58. Found: C, 53.31; H, 4.16; N, 8.60%. FT-IR (KBr disc, cm⁻¹): v (N=N) 1432; v (C=N, 1599; v (PPh₃) 525, 472, 420. UV-Vis (CH₃CN) λ_{max} (nm) $(10^{-3} \epsilon (dm^3 mol^{-1} cm^{-1})): 281(5.38), 381(11.20), 440(5.14),$ 581(0.75). [Cu(HaaiEt)(PPh₃)I] (**12a**) Anal. Calc. for C₂₉H₂₇CuIN₄P: C, 53.34; H, 4.17; N, 8.58. C, 52.63; H, 3.94; N, 8.77. Found: C, 53.32; H, 4.18; N, 8.61%. FT-IR (KBr disc, cm⁻¹): v (N=N) 1436; v (C=N) 1597; ν (PPh₃) 527, 467, 420. UV-Vis (CH₃CN) λ_{max} (nm) $(10^{-3} \epsilon (dm^3 mol^{-1} cm^{-1})): 282(8.52), 374(17.18), 426(6.43),$ 578(0.75). [Cu(MeaaiEt)(PPh₃)I] (**12b**) Anal. Calc. for C₃₀H₂₉CuIN₄P: C, 54.02; H, 4.38; N, 8.39. Found: C, 54.04; H, 4.36; N, 8.40%. FT-IR (KBr disc, cm⁻¹): v (N=N) 1432; v (C=N) 1596; v (PPh₃) 536, 476, 430. UV–Vis (CH₃CN) λ_{max} (nm) (10⁻³ ϵ (dm³ mol⁻¹ cm⁻¹)): 273(13.32), 378(16.37), 435(5.93), 584(0.67).

2.4. Cu(II)-Cu(I) interconversion

$[Cu(MeaaiH)(PPh_3)Cl](4b) \xrightarrow{Cl_2 \text{ solution}} [Cu(MeaaiH)(PPh_3)Cl_2](13b)$

[Cu(MeaaiH)(PPh₃)Cl] (**4b**) (120 mg, 0.220 mmol), was dissolved in CH₃CN and chlorine saturated methanol was added in drops. The resultant brown solution was stirred for 6 h at room temperature with time-to-time addition of chlorine saturated methanol. The solution color turned permanently to deep brown. A methanol solution of LiCl (2 ml, 0.2 mmol) was added and stirred for a few minutes. It was then filtered and allowed to evaporate in air. The solid mass so obtained was washed with a profuse amount of water, recrystallised from methanol and then dried in a CaCl₂ desiccator. Yield 74 mg (58%).

$[Cu(MeaaiH)(PPh_3)Cl_2](\textbf{13b}) \rightarrow [Cu(MeaaiH)(PPh_3)Cl](\textbf{4b})$

To a stirred dry methanol solution of $[Cu(MeaaiH)(PPh_3)Cl_2]$ (13b) (50 mg, 0.09 mmol), ascorbic acid (20 mg, 0.11 mmol) was added pinchwise in excess. The resultant dark brown–red solution was stirred for 3 h at room temperature and then filtered. The filtrate was left for slow evaporation at room temperature in a beaker. A dark crystalline compound was deposited on the wall of container after a week. The product was then washed with water and dried in a CaCl₂ desiccator. Recrystallisation was carried out by diffusion of a CH_2Cl_2 solution of the compound into hexane. Yield 31 mg (66%).

2.5. X-ray diffraction study

The crystallographic data are shown in Table 5. Suitable single crystals of complexes **4b** $(0.10 \times 0.15 \times 0.28 \text{ mm})$ and **7b** $(0.14 \times 0.20 \times 0.23 \text{ mm})$ were mounted on a Siemens CCD diffractometer equipped with graphite monochromated Mo Ka $(\lambda = 0.71073 \text{ Å})$ radiation. The unit cell parameters and crystal-orientation matrices were determined for the two complexes by least squares refinements of all reflections. The intensity data were corrected for Lorentz and polarization effects, and an empirical absorption correction was also employed using the SAINT program [53]. Data were collected applying the condition $I > 2\sigma(I)$. All these structures were solved by direct methods and followed by successive Fourier and difference Fourier syntheses. Full matrix least squares refinements on F² were carried out using SHELXL-97 with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were constrained to ride on their respective carbon or nitrogen atoms with isotropic displacement parameters equal to 1.2 times the equivalent isotropic displacement of their parent atom in all cases. Complex neutral atom scattering factors were used throughout in all cases. All calculations were carried out using SHELXS 97 [54], SHELXL97 [55], PLATON 99 [56] and ORTEP-3 [57] programs.

2.6. Photometric measurements

Absorption spectra were taken with a PerkinElmer Lambda 25 UV–Vis spectrophotometer in a 1×1 cm quartz optical cell maintained at 25 °C with a Peltier thermostat. The light source of a PerkinElmer LS 55 spectrofluorimeter was used as the excitation light,



RaaiR[/] (1-3)

 $[Cu((RaaiR')(PPh_3)X]$ (4-12)

R = H, R' = H (1a), R = Me, R' = H (1b); Abbreviations of a, b remain the same.

 $R=H,\,R'=Me\;({\bf 2a}),\,R=Me,\,R'=Me\;({\bf 2b});\quad X=-Cl-({\bf 4},-{\bf 5},-{\bf 6});\quad Br-({\bf 7},-{\bf 8},-{\bf 9});$

R = H, R' = Et (3a), R = Me, R' = Et (3b), I (10, 11, 12)

[Cu(HaaiH)(PPh ₃)Cl]	(4 a),	[Cu(MeaaiH)(PPh3)Cl]] (4b),	[Cu(HaaiMe)(PPh ₃)Cl]	(5a),
[Cu(MeaaiMe)(PPh ₃)Cl] (5b),	[Cu(HaaiEt)(PPh3)C	[1] (6a),	[Cu(MeaaiEt)(PPh ₃)Cl]	(6b),
[Cu(HaaiH)(PPh3)Br]	(7a),	[Cu(MeaaiH)(PPh3)Br] (7b),	[Cu(HaaiMe)(PPh3)Br]	(8 a),
[Cu(MeaaiMe)(PPh ₃)Br] (8b),	[Cu(HaaiEt)(PPh3)Br]	(9 a),	[Cu(MeaaiEt)(PPh3)Br]	(9b),
[Cu(HaaiH)(PPh ₃)I] ((10a),	[Cu(MeaaiH)(PPh3)]	(10b),	[Cu(HaaiMe)(PPh ₃)I]	(11a),
[Cu(MeaaiMe)(PPh ₃)I]	(11b), [(Cu(HaaiEt)(PPh ₃)I] (12	2a), [Cu(MeaaiEt)(PPh ₃)I (12b).	



Fig. 1. Molecular structures of (a) [Cu(MeaaiH)(PPh₃)Cl] (4b) and (b) [Cu(MeaaiH)(PPh₃)Br] (7b).

Table 1

Selected bond distances (Å) and angles (°) for [Cu(PPh₃)(MeaaiH)Cl] (4b) and [Cu(PPh₃)(MeaaiH)Br] (7b), and the structures generated from DFT calculations for 4b, 7b and [Cu(PPh₃)(MeaaiH)I] (10b).

Bond distances (Å)			Bond angles (°)		
	X-ray	DFT/B3LYP		X-ray	DFT/B3LYP
[Cu(PPh3)(MeaaiH)Cl] (4b)					
Cu–Cl	2.3127(6)	2.322	Cl(1)-Cu-P	117.34(2)	118.7
Cu–P	2.2001(6)	2.268	Cl(1)-Cu-N(1)	105.32(5)	108.1
Cu-N(1)	2.0997(1)	2.123	Cl(1)-Cu-N(4)	101.23(5)	102.6
Cu-N(4)	2.1352(16)	2.140	P-Cu-N(1)	119.61(5)	116.9
N(3)-N(4)	1.269(2)	1.277	P-Cu-N(4)	128.45(5)	126.5
N(3)-C(3)	1.381(3)	1.373	N(1)-Cu-N(4)	76.95(6)	75.68
N(4)-C(4)	1.430(3)	1.408			
[Cu(PPh ₃)(MeaaiH)Br] (7b)					
Cu–Br	2.436(6)	2.449	Br(1)-Cu-P	117.573(17)	117.6
Cu–P	2.202(3)	2.254	Br(1)-Cu-N(1)	105.31(5)	105.6
Cu-N(1)	2.1037(17)	2.131	Br(1)-Cu-N(4)	101.95(4)	102.0
Cu-N(4)	2.1320(16)	2.151	P-Cu-N(1)	119.43(5)	118.9
N(3)-N(4)	1.266(2)	1.277	P-Cu-N(4)	127.69(5)	127.8
N(3)-C(3)	1.345(3)	1.374	N(1)-Cu-N(4)	76.90(7)	76.77
N(4)-C(4)	1.432(3)	1.415			
[Cu(PPh ₃)(MeaaiH)I] (10b)					
Cu–I	-	2.654	I-Cu-P	-	121.2
Cu–P	-	2.271	I-Cu-N(1)	-	105.0
Cu-N(1)	-	2.140	I-Cu-N(4)	-	102.9
Cu-N(4)	-	2.160	P-Cu-N(1)	-	116.6
N(3)-N(4)	-	1.277	P-Cu-N(4)	-	125.3
N(3)-C(3)	-	1.371	N(1)-Cu-N(4)	-	75.9
N(4)-C(4)	-	1.410			

with a slit width of 10 nm. An optical filter was used to cut off overtones when necessary. The absorption spectra of the *cis* isomers were obtained by extrapolation of the absorption spectra of a *cis*-rich mixture for which the composition was known from ¹H NMR integration. Quantum yields () were obtained by measuring the initial *trans*-to-*cis* isomerization rates (ν) in a well-stirred solution within the above instrument using the equation,

$$v = (\phi I_0 / V)(1 - 10^{-\text{ADS}})$$

where I_0 is the photon flux at the front of the cell, *V* is the volume of the solution, and Abs is the initial absorbance for the azobenzene ($\phi = 0.11$ for $\pi - \pi^*$ excitation [58]) under the same irradiation conditions.

The thermal *cis*-to-*trans* isomerisation rates were obtained by monitoring absorption changes intermittently for a *cis*-rich solution kept in the dark at a constant temperature in the range from 298 to 313 K. The activation energy (E_a) and the frequency factor (A) were obtained from the Arrhenius plot,

$$\ln k = \ln A - E_a/RT$$

where k is the measured rate constant, R is the gas constant, and T is the absolute temperature. The values of activation free energy (ΔG^*) and activation entropy (ΔS^*) were obtained through the relationships,

$$\Delta G^* = E_a - RT - T\Delta S^*$$
 and $\Delta S^* = [\ln A - 1 - \ln(k_B T/h)/R$



Scheme 2. Photochromism of free and coordinated RaaiR'.

where $k_{\rm B}$ and h are Boltzmann's and Plank's constants, respectively.

2.7. DFT calculations

The density functional theory (DFT) calculations on the crystal structures of **4b** and **7b** were carried out using the GAUSSIAN 03w program package [59] with the aid of the GAUSSVIEW visualization program [60] The hybrid functional by Becke, B3LYP [61], was used, which included a mixture of Hartree–Fock exchange with DFT exchange–correlation. For C, H, N and I, we used MIDI! basis functions [62] as this basis set is applicable to all these elements and includes polarization functions. For Cu, we used the LanL2DZ basis set, including Los Alamos Effective Core Potentials [63–65].

3. Results and discussion

3.1. Synthesis of complexes

1-Alkyl-2-(arylazo)imidazoles (RaaiR'), like 2-(phenylazo)imidazole (HaaiH) (**1a**), 2-(p-tolylazo)imidazole (MeaaiH) (**1b**), 1-methyl-2-(phenylazo)imidazole (HaaiMe, **2a**), 1-methyl-2-(p-tolylazo)imidazole (MeaaiMe, **2b**), 1-ethyl-2-(phenylazo)imidazole

(HaaiEt, **3a**) and 1-ethyl-2-(*p*-tolylazo)imidazole (MeaaiEt, **3b**), are used in this work (Scheme 1) to prepare copper(I) complexes. The reaction of CuX and PPh₃ forms the tetramer $[Ph_3PCuX]_4$ [66], which upon reaction *in situ* with RaaiR' in MeCN has yielded complexes of the composition [Cu(RaaiR')(PPh₃)X] (X = Cl (**4**, **5**, **6**), Br (**7**, **8**, **9**), I (**10**, **11**, **12**)). We have also isolated $[Ph_3PCuX]_4$ and have reacted it with RaaiR' under the same reaction conditions, and this gives complexes of the same composition. However, the reactions have been carried out *in situ* as this is more economic in terms of time. The compounds are non-conducting and their composition has been supported by microanalytical data. The structures have been established in representative cases by a single-crystal X-ray diffraction study.

$$CuX + PPh_3 \xrightarrow[reflux]{MeCN-MeOH} 1/4 [Ph_3PCuX]_4 \xrightarrow[reflux, RaaiR]{MeCN-MeOH} [Cu(RaaiR)(PPh_3)X]$$

3.2. Molecular structures

The molecular structures of $[Cu(MeaaiH)(PPh_3)Cl]$ (**4b**) and $[Cu(MeaaiH)(PPh_3)Br]$ (**7b**) are shown in Fig. 1a and b, respectively. Bond parameters are listed in Table 1. Each discrete molecular unit



Fig. 2. C–H··· π (a) and π – π (b) interactions in [Cu(MeaaiH)(PPh₃)Cl] (**4b**).



Fig. 3. Surface plots of some selected MOs of [Cu(MeaaiH)(PPh₃)X] (X = Cl (4b), Br (7b), I (10b)).

consists of the coordination unit CuN₂PX. The chelating ligand, MeaaiH acts as a N,N'-donor (N refers to N(imidazole) and N' refers to N(azo)). The atomic arrangements Cu, N(4), N(3), C(3) and N(1), constitute a chelate plane with a deviation of <0.04 Å in 4b and 0.035 Å in **7b**. The pendant aryl ring makes a dihedral angle of $9.82(10)^{\circ}$ for **4b** and $8.76(10)^{\circ}$ for **7b** with the respective chelated azoimidazole ring. The acute bite angle, Cu(N,N'), 76.95(6)° (4b) and 76.90(7)° (7b), is extended by MeaaiH on coordination to Cu(I) and is comparable with reported results in the series of chelated arylazoimidazole complexes of d^{10} metal complexes [51,52,67,68]. The small chelate angle may be one of the reasons for geometrical distortion. The ligand (MeaaiH) is planar (maximum deviation ~ 0.08 Å). The Cu–N(imidazole) bond length (2.0997(1) Å, 4b 2.1037(17)) Å, 7b) is shorter than that of Cu(I)-N(azo) (2.1352(16) Å, 4b and 2.1320(16) Å, 7b), which reflects the stronger interaction of Cu(I) with N(imidazole) compared to N(azo). Because of the long Cu(I)–N(azo) distance, the molecule may exhibit photoactivation *via* cleavage of this bond followed by rotation to introduce photoisomerisation (Scheme 2, vide infra). The N=N distance is 1.269(2) Å in **4b** and 1.266(2) Å in **7b**. These are elongated by a small amount compared to that of the free ligand value (1.250(1) Å) [20], which supports $d(Cu) \rightarrow \pi$ (azoimine) charge transfer.

A π - π interaction is observed between the chelate plane of Cu(N,N') and the imidazole ring of two adjacent molecules (Cg(1) (chelated Cu(N,N') plane)-Cg(1)(imidazole), 3.79(1)Å) in **4b** and 3.86(4)Å (Cg(1) (Cu(N,N') plane)-Cg(2) (imidazole)) in **7b**. The phenyl rings of PPh₃ interact with the partners of a neighboring molecule and the C-H··· π distance is 2.89(3)Å (symmetry, 1+X, Y, Z) in **4b** and 2.86(4)Å (symmetry, 1+X, Y, Z) in **7b**. These two interactions increase the intermolecular attraction to generate a

 π -network, while the slippage between both imidazole rings is too large (ca. 4.32(5) Å) to establish effective interactions (Fig. 2). These two interactions (π - π and C-H··· π) have endowed a 1D chain to the solid state geometry of this molecule.

DFT calculations have been performed for three complexes to establish the structural relationship between the crystal structures of **4b** and **7b** (Fig. 1) and the theoretically generated optimized geometry. The structure of **10b** was generated by using DFT calculations only. The structural agreement has been observed from a



Fig. 4. Correlation amongst calculated energy levels of [Cu(MeaaiH)(PPh₃)X] (X = Cl (4b), Br (7b), I (10b)).

comparison of bond distances and angles between the calculated and X-ray determined structures of **4b** and **7b** (Table 1). The theoretical bond distances are longer by 0.01–0.07 Å compared to those obtained from the X-ray determined structures (Fig. 1).

3.3. Spectroscopic studies

IR spectra of the complexes show moderately intense stretching bands at 1595–1600 and 1435–1445 cm⁻¹ which are assigned to v (C=N) and v (N=N), respectively. Other vibrations are shifted to a lower energy in the copper complexes (4–12) compared to the free ligand values [69].

The solution UV-Vis spectra of the complexes 4-12 are recorded in MeCN in the range 200-900 nm. The bands in the UV region are intense ($\epsilon \sim 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) at 240–255 and 365– 380 nm, and are referred to intramolecular charge transfer transitions $(n-\pi^*, \pi -\pi^*)$ [69]. A band at 550–600 nm ($\epsilon \sim 10^3$ mol⁻¹ dm³ cm⁻¹) is characteristic of a MLCT transition of tetrahedral [Cu(azoimidazole)₂]⁺. The electronic configuration of the three representative complexes 4b, 7b and 10b are used to explain the origin of the transitions. The selected MOs of the complexes are shown in Fig. 3. The HOMOs of these three complexes are composed of copper (25%), PPh₃ (10%) and halogen (30% of Cl in 4b, 65% of Br in 7b and 83% of I in 10b) (Supplementary Material, Table S1). Other occupied MOs (HOMO-1, HOMO-2 etc.) are composed of Cu and X (halogen). The LUMO is a π^* orbital delocalized over the entire arylazoimidazole moiety (90%), while LUMO+1, LUMO+2 etc. are dominated by PPh₃. As a consequence, a significant mixing of orbitals of MeaaiH and PPh3 may be considered. The energies of the MOs are correlated in Fig. 4. The calculated transitions are given as Supplementary Material (Table S2). The intensity of these transitions has been assessed from oscillator strengths (f). The calculated bands are of MLCT, XLCT, YLCT and ILCT types (MLCT, metal-to-ligand charge transfer; XLCT, halide-to-ligand charge transfer, YLCT, phosphine-to-ligand charge transfer; ILCT, intra-ligand charge transfer where the ligand refers to MeaaiH). The transitions in UV region (<400 nm) are a mixture of ILCT and YLCT $(Y = PPh_3)$. The observed transitions appear closer to the calculated wavelength in the complexes. The transitions appearing in the region >600 nm are described as an admixture of MLCT and XLCT.

The ¹H NMR spectra of the complexes are recorded in CDCl₃ and the signals are assigned (Supplementary Material, Table S1) unambiguously by spin-spin interactions, the effect of substitution therein and on comparing with previously reported compounds [67–69]. The atom numbering pattern is shown in the structure (Scheme 1). Data reveal that the signals in the spectra of the complexes in general are shifted downfield compared to the spectra of the free ligands [69]. The signals of the imidazole protons, 4 and 5H, shift significantly (Δ , 0.2–0.5 ppm), whereas shifting for the aryl protons, 7 and 11H, is in the range 0.06-0.15 ppm. Protons 8–10H remain almost unshifted. This supports chelation by N(imidazole) and N(azo) in which the imidazole-N binds more effectively than the azo-N to Cu(I) (vide supra, X-ray structures). The electron donating effect of the (Ar-)Me group in the Cu(I) complexes of MeaaiR' shifts aryl protons (7-11H) to the upfield side compared to Cu(I)-HaaiR'.

3.4. Photochromism of [Cu(RaaiR')(PPh₃)X]

The chelated ligands RaaiR' in the complexes [Cu(R-aaiR')(PPh₃)X] undergo photo-induced *trans*(*E*)-*to-cis*(*Z*) isomerisation. The effect of light irradiation on [Cu(RaaiR')(PPh₃)X] (**5**, **6**, **8**, **9**, **11** and **12**) in acetonitrile solution was investigated by UV–Vis spectroscopy (Fig. 5). The complexes, [Cu(RaaiH)(PPh₃)X] (**4**, **7** and **10**) show very slow spectral change upon UV light irradiation and have not been used further. The metal ion and its oxidation

state, nature of the ligand, presence of other coordinating ligand(s) etc. play an important role in the photoisomerisation of the coordinated ligand in the complexes [23,70–72]. Upon UV light irradiation the *trans* structure of RaaiR' changes to the *cis* structure about the azo (–N=N–) function and the *cis* molar ratio reaches >95% (Scheme 2).

The complexes are resistant to photo degradation upon repeated irradiation at least up to 15 cycles in each case.

UV-light irradiation of a solution of [Cu(RaaiR')(PPh₃)X] may cleave the Cu-N(azo) bond and make the ligand free to rotate about the azo-aryl group (-N=N-Ar), which isomerizes it from the *trans*(E) to the *cis* (Z) form. This is apprehended on considering the longer Cu(I)-N(azo) bond length than Cu-N(imidazole) distance in the complexes (Table 1). The rates of photoisomerisation and also the quantum yields (*trans*-to-*cis* (E–Z), $_{t\rightarrow c}$) increase with the decreasing electronegativity of X in the complexes: the rate follows $[Cu(RaaiR')(PPh_3)Cl]$ (5, 6) < $[Cu(RaaiR')(PPh_3)Br]$ (8) 9 < [Cu(RaaiR')(PPh₃)I] (11, 12) (Table 2). It is observed that the HOMO-LUMO energy difference (ΔE) decreases with decreasing electronegativity of X: 2.3 eV ([Cu(MeaaiH)(PPh₃)Cl], 4b), 2.25 eV $([Cu(MeaaiH)(PPh_3)Br], 7b)$ and 1.75 eV $([Cu(MeaaiH)(PPh_3)I],$ **10b**) (Fig. 4, correlation diagram). The composition of the MOs



Fig. 5. Spectroscopic changes of (i) [Cu(MeaaiMe)(PPh3)Br] (8b) and (ii) [Cu(Haai-Me)(PPh3)I] (11a) in MeCN upon repeated irradiation at 380 nm at 3 min intervals at 25 °C. Inset figure shows spectra of the *cis* and *trans* isomers of the complex.

Table 2 Excitation wavelength ($\lambda \pi$, π^*), rate of *trans* (t) \rightarrow *cis* (c) conversion and quantum yield ($_{t\rightarrow c}$) in MeCN.

Compounds	$\lambda \pi_{,} \pi^{*} (\mathrm{nm})$	Isosbestic point (nm)	Rate of $t \rightarrow c$ conversion x 10 ⁸ (s ⁻¹)	t→c
[Cu(HaaiMe)(PPh ₃)Cl] (5a)	377	335, 466	2.64	0.1731
[Cu(MeaaiMe)(PPh ₃)Cl] (5b)	382	334, 462	2.61	0.1639
[Cu(HaaiEt)(PPh ₃)Cl] (6a)	376	331, 464	2.64	0.1678
[Cu(MeaaiEt)(PPh ₃)Cl] (6b)	381	330, 474	2.56	0.1581
[Cu(HaaiMe)(PPh3)Br] (8a)	375	336, 468	2.71	0.1863
[Cu(MeaaiMe)(PPh ₃)Br] (8b)	380	331, 460	2.67	0.1754
[Cu(HaaiEt)(PPh ₃)Br] (9a)	377	335, 474	2.69	0.1782
[Cu(MeaaiEt)(PPh ₃)Br] (9b)	381	334, 473	2.62	0.1629
[Cu(HaaiMe)(PPh ₃)I] (11a)	374	332, 463	2.82	0.1972
[Cu(MeaaiMe)(PPh ₃)I] (11b)	381	333, 463	2.71	0.1816
[Cu(HaaiEt)(PPh ₃)I] (12a)	375	332, 462	2.74	0.1865
[Cu(MeaaiEt)(PPh ₃)I] (12b)	380	331, 472	2.65	0.1769

Table 3

Rate and activation parameters for $cis(c) \rightarrow trans(t)$ thermal isomerisation.

Compound	Temp (K)	Rate of thermal $c \rightarrow t$ conversion $\times 10^4$ (s ⁻¹)	E _a kJ mol ⁻¹	ΔH^* kJ mol $^{-1}$	ΔS^* J mol $^{-1}$ K $^{-1}$	∆G* ^c kJ mol ^{−1}
[Cu(HaaiMe)(PPh ₃)Cl] (5a)	298 303 308 313	1.3215 2.1958 2.9726 3.6825	52.52	49.98	-150.83	94.93
[Cu(MeaaiMe)(PPh ₃)Cl] (5b)	298 303 308 313	1.703 2.5955 3.4167 4.5429	49.98	47.44	-157.56	94.39
[Cu(HaaiEt)(PPh ₃)Cl] (6a)	298 303 308 313	1.2196 1.9864 2.672 3.3164	51.27	48.74	-155.73	95.14
[Cu(MeaaiEt)(PPh ₃)Cl] (6b)	298 303 308 313	1.654 2.3965 3.281 3.9973	46.0107	43.47	-171.13	94.47
[Cu(HaaiMe)(PPh ₃)Br] (8a)	298 303 308 313	0.9524 1.8479 2.6884 3.7925	59.29	56.75	-131.05	95.81
[Cu(MeaaiMe)(PPh ₃)Br] (8b)	298 303 308 313	1.5462 2.6486 3.7173 4.6894	57.028	54.49	-134.40	94.54
[Cu(HaaiEt)(PPh ₃)Br] (9a)	298 303 308 313	0.7973 1.2529 1.8136 2.4310	57.68	55.14	-138.04	96.28
[Cu(MeaaiEt)(PPh ₃)Br] (9b)	298 303 308 313	1.5023 2.4351 3.3351 4.2243	53.099	50.56	-147.94	94.65
[Cu(HaaiMe)(PPh ₃)I] (11a)	298 303 308 313	1.0573 1.8479 2.6884 3.7925	65.35	62.81	-109.79	95.53
[Cu(MeaaiMe)(PPh ₃)l] (11b)	298 303 308 313	0.8945 1.41 2.154 3.076	64.19	61.6484	-115.42559	96.05
[Cu(HaaiEt)(PPh ₃)I] (12a)	298 303 308 313	1.2928 2.4373 3.5326 4.4931	63.91	61.37	-112.60	94.93
[Cu(MeaaiEt)(PPh ₃)I] (12b)	298 303 308 313	0.8729 1.2629 1.9974 2.6149	58.20	55.66	-135.79	96.13



Fig. 6. Eyring plots of Z-to-E thermal isomerisation of (a) [Cu(MeaaiMe)(PPh₃)Cl] (5b, ▲); slope, -7415.01126; intercept, 9.87672; R^2 , 0.998. (b) [Cu(MeaaiMe)(PPh₃)Br] (8b, ●) slope, -6553.86192; intercept, 7.595; R^2 , 0.968. (c) [Cu(MeaaiMe)(PPh₃)I] (11b, ■); slope, -6441.33079; intercept, 7.3841; R^2 , 0.969 at different temperatures.



Fig. 7. Cyclic voltammogram of $[Cu(MeaaiEt)(PPh_3)I]$ in MeCN using a Pt-disk working electrode, Pt-wire auxiliary and SCE reference electrode in the presence of $[n-Bu_4N](ClO_4)$ supporting electrolyte at 50 mV S⁻¹ scan rate, at 300 K.

may be used to explain this effect. The HOMO is composed of 31% Cl in **4b**; 65% Br in **7b** and 83% I in **10b** and the LUMO is mainly dominated by MeaaiH (90%). The bonded X may serve as an antenna to receive a photon and to transfer energy to the participating groups. Thus, a function of higher X contribution and of lower ΔE may act as an efficient energy acceptor and communicator [71,72]. Once the energy is transferred to the LUMO, the long Cu–N(azo) bond may cleave (possibly the rate controlling factor) to initiate photoisomerisation. This indeed happens. The $_{t \rightarrow c}$ values of the complexes are lower than that of the free ligand $(t_{t \to c} = 0.25 \pm 0.03)$ [20,21]. The presence of the coordinated {Cu(PPh₃)X} motif may increase the molar mass and rotor volume of the complexes and severely interfere with the motion of the -N=N-Ar moiety. The rotor volume has a significant influence on the isomerisation rate and quantum yields [23,73,74]. The complexation increases the rotor volume, leading to less efficient isomerisation.

The *cis*-to-*trans* (Z-to-E) isomerisation of the complexes has been carried out by UV–Vis spectroscopy at various temperatures, 298–313 K. The Eyring plots in the range 298–313 K are used to

calculate the activation energies (Table 3, Fig. 6). In the complexes the E_{as} are severely reduced, which means faster *cis*-to-*trans* (Z-to-E) thermal isomerisation of the complexes. The entropies of activation (ΔS_*) are highly negative in the complexes compared to the free ligand. This is also in support of an increase in rotor volume in the complexes.

3.5. Electrochemistry and redox interconversion, $Cu^{II} \leftrightarrow Cu^{I}$

The cyclic voltammograms of the copper(I) complexes [Cu((RaaiR')(PPh₃)X] are recorded in MeCN at a Pt-disk milli electrode in the potential range +1.5 to -2.0 V versus the SCE reference electrode (Fig. 7; Table 4). [Cu((RaaiR')(PPh₃)Cl] (4-6) and [Cu((RaaiR')(PPh₃)Br] (**7–9**), show a quasireversible oxidative response of $\sim 1 \text{ V}$ while the complexes $[Cu((RaaiR')(PPh_3)I]$ (10–12) show two quasireversible redox responses at \sim 0.4 and \sim 1 V. A significant observation is the appearance of a quasireversible redox couple at 0.4 V for [Cu((RaaiR')(PPh₃)I] (10-12) which may be assigned to the I^{-}/I response. $[Cu(RaaiR')_{2}](ClO_{4})$ shows a Cu(II)/Cu(I) couple at 0.5–0.6 V [51,52,69], and in [Cu((RaaiR')(PPh₃)X] this redox couple shifts to a more positive redox value which may be due to the π -acidity of the coordinated PPh₃. On scanning to the –ve direction up to -2.0 V, we observed a sharp anodic signal at -0.2, an irreversible response, E_{pc} at -0.9 V and a quasireversible couple at $-1.2 \text{ V} (\Delta E_{\text{P}} > 150 \text{ mV})$ (Fig. 7). The sharp anodic signal at -0.2 Vis possibly the Cu(I)/Cu(0) couple. The reduced Cu(0) is absorbed on the electrode surface as is evident from the narrow width of the anodic response with a large peak current. To account for the Cu(I)/Cu(0) redox response we carried out a few more experiments with varying scan rates (20-500 mV/s at 20 mV interval) and end potential to back scan. A well defined sharp cathodic current is observed at 20–150 mV/s, while broadening of the cathodic peak is observed at a higher scan rate. This observation suggests that the heterogeneous electron transfer rate is influenced by the applied potential [74,75]. An interesting observation is recorded on changing the back scan potential: no cathodic signal is observed at a potential above -0.4 V. On decreasing the back scan potential (-0.4to -1.3 V), it is recorded that the intensity of the cathodic peak at -0.2 V increases. It is quite obvious that the rate of reduction, $Cu(I) \rightarrow Cu(0)$, increases with decreasing back scan potential and the amount of deposited Cu(0) increases. It is reoxidised on scan reversal and shows a sharp peak. The reductive responses at -0.9and -1.2 V may be assigned to reduction of the azo group [azo/ azo⁻; azo⁻/azo⁼] of the chelated ligands. The free ligand does not show any oxidation, but irreversible reductive responses appear at <-1.0 V.

The DFT calculations of three representative complexes, **4b**, **7b** and **10b**, suggest that the HOMO is composed of Cu and X (*vide su-pra*). Because of the higher iodide contribution to the HOMO (83%), the redox response may be assigned to the I/I^- couple at 0.4 V, followed by the metal oxidation Cu(II)/Cu(I). The unoccupied MOs are significantly dominated by the azoimine function of the chelated ligand MeaaiH; thus the reduction is rightly referred to electron accommodation at the azo dominated orbital of the ligand.

The [Cu(RaaiR')(PPh₃)Cl] complexes are oxidized to the Cu(II) complexes by chlorine and are characterized by spectroscopic and magnetic measurements as [Cu(RaaiR')(PPh₃)Cl₂] (**13**, **14**). Again, the Cu(II) complexes are reduced by ascorbic acid to the Cu(I) complexes. The Cu(II)–Cu(I) inter-conversion has been carried out with [Cu(MeaaiMe)(PPh₃)Cl] (**5b**) and [Cu(Meaai-Et)(PPh₃)Cl] (**6b**). Magnetic moment (room temperature) data (**13b**, 1.83 BM; **14b**, 1.88 BM) indicates a Cu(II) (d^9) redox state, which supports the composition [Cu(HaaiMe)(PPh₃)Cl₂] (**13b**) and Cu(MeaaiMe)(PPh₃)Cl₂] (**14b**) at 300 K, and the complexes are EPR active. The EPR spectra were recorded at liquid N₂ temperature

Complex	Metal redox cou	ple <i>E</i> , $V(\Delta E_{\rm p}, {\rm mV})$		Ligand redox couple B	$E, V (\Delta E_{\rm p}, {\rm mV})^{\rm c}$
	X/X ^{-b}	Cu ^{II} /Cu ^I	Cu ^I /Cu ^{0b}	azo/azo ⁻	azo=/azo-
4a		1.04	-0.22	-0.90	-1.25
4b		1.03	-0.21	-0.89	-1.26
5a		1.06	-0.21	-0.88	-1.25
5b		1.05	-0.22	-0.89	-1.26
6a		1.06	-0.21	-0.88	-1.25
6b		1.05	-0.22	-0.89	-1.26
7a		1.00	-0.22	-0.90^{b}	-1.25
7b		1.06	-0.21	-0.89	-1.26
8a		1.07	-0.21	-0.88	-1.25
8b		1.05	-0.22	-0.89	-1.26
9a		1.07	-0.24	-0.83	-1.23
9b		1.02	-0.26	-0.84	-1.23
10a	0.39	1.00	-0.28	-0.85	-1.24
		(150)			
10b	0.40	1.06	-0.24	-0.84	-1.24
		(150)			
11a	0.41	1.10	-0.24	-0.79	-1.18
		(150)			
11b	0.33	1.07	-0.23	-0.79	-1.15
		(160)			
12a	0.30	1.09	-0.24	-0.79	-1.16
		(130)			
12b	0.32	1.07	-0.28	-0.79	-1.18
		(140)			

^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; $\Delta E_p = E_{pa} - E_{pc}$, mV; E_{pa} = anodic peak potential, E_{pc} = cathodic peak potential, V; $E_{1/2}$ = 0.5($E_{pa} + E_{pc}$), V.

^b E_{pa}. ^c E_{pc}.



Fig. 8. EPR spectrum of $[Cu(MeaaiMe)(PPh_3)Cl_2]$ (13b) in MeOH at 77 K (the complex is obtained by the reaction of $[Cu(MeaaiMe)(PPh_3)Cl]$ with Cl_2 in MeOH).

(77 K). The four line (⁶³Cu, I = 3/2) EPR spectra are anisotropic at higher magnetic field (Fig. 8). Three peaks are of low intensity in the weaker field and are considered to originate from the $g_{||}$ (2.240) component and g_{\perp} is 2.032. The relation $g_{||} > g_{\perp} > 2.0023$ agrees with the ground state configuration of $d_x^2 - y^2$. The solution spectrum (Fig. 9) shows two additional weak bands at 730–740



Fig. 9. Uv–Vis spectrum of [Cu(MeaaiMe)(PPh₃)Cl₂] (13b) in MeCN.

and 620–630 nm, which are referred to as *d*–*d* transitions of Cu(II) complexes, and the higher energy bands correspond to $n-\pi^*$ (380–390 nm) and $\pi-\pi^*$ (280–300 nm) transitions. An intense band at 445–450 nm is assigned to a MLCT ($d \pi$ (Cu) $\rightarrow \pi^*$ (azoimine)) transition.

The copper(II) complexes $[Cu(HaaiMe)(PPh_3)Cl_2]$ (**13b**) and $Cu(MeaaiMe)(PPh_3)Cl_2]$ (**14b**) are reduced by ascorbic acid and are identified by matching the spectroscopic and cyclic voltammetric results. The compounds are diamagnetic. The structures of the coordinated Cu(I) compounds have been established by their ¹H NMR spectra and a comparison with the spectra of the directly synthesized complexes. Microanalytical data (C, H, N) also confirm the composition of the compounds.



Table 5

Summarized crystallographic data for [Cu(MeaaiH)(PPh₃)Cl] (4b) and [Cu(MeaaiH) (PPh3)Br] (7b).

$\begin{array}{ccccc} & \mbox{Empirical formula} & \mbox{C_{28}H_{25}$ClCuN_4P$} & \mbox{C_{28}H_{25}$BrCuN_4P$} \\ & \mbox{Formula weight} & 547.48 & 591.94 \\ & \mbox{$T(K)$} & 290(2) & 273(2) \\ & \mbox{λ} & \mbox{λ} & 0.71073 & 0.71073 \\ & \mbox{C_{70}stal system} & triclinic & triclinic \\ & \mbox{$Space group$} & $p$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$
Formula weight547.48591.94 T (K)290(2)273(2) λ (Å)0.710730.71073Crystal systemtriclinictriclinicSpace group $p\bar{1}$ $p\bar{1}$ Unit cell dimensionsa9.0911(2)9.0953(2) b (Å)9.6045(2)9.6363(2) c (Å)14.9520(4)15.2467(3) α (°)98.6060(12)98.9030(12) β (°)93.5880(11)93.8130(11) γ (°)92.5750(10)93.9290(10) V (Å3)1286.36(5)1313.06(5) Z 2 2 μ (Mo K α) (mm ⁻¹)1.0392.438 D_{calc} (Mgm ⁻³)1.4131.497
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$\begin{array}{cccc} \dot{\lambda} (\dot{\rm A}) & 0.71073 & 0.71073 \\ \mbox{Crystal system} & triclinic & triclinic \\ \mbox{Space group} & p\bar{1} & p\bar{1} \\ \mbox{Unit cell dimensions} & & & \\ a (\dot{\rm A}) & 9.0911(2) & 9.0953(2) \\ b (\dot{\rm A}) & 9.6045(2) & 9.6363(2) \\ c (\dot{\rm A}) & 14.9520(4) & 15.2467(3) \\ \alpha (^{\circ}) & 98.6060(12) & 98.9030(12) \\ \beta (^{\circ}) & 93.5880(11) & 93.8130(11) \\ \gamma (^{\circ}) & 92.5750(10) & 93.9290(10) \\ V (\dot{\rm A}^3) & 1286.36(5) & 1313.06(5) \\ Z & 2 & 2 \\ \mu ({\rm Mo} \ {\rm K}\alpha) ({\rm mm}^{-1}) & 1.039 & 2.438 \\ D_{\rm calc} ({\rm Mgm}^{-3}) & 1.413 & 1.497 \\ \end{array}$
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$\begin{array}{ccccc} \alpha \left(^{\circ} \right) & 98.6060(12) & 98.9030(12) \\ \beta \left(^{\circ} \right) & 93.5880(11) & 93.8130(11) \\ \gamma \left(^{\circ} \right) & 92.5750(10) & 93.9290(10) \\ V \left(^{A} \right) & 1286.36(5) & 1313.06(5) \\ Z & 2 & 2 \\ \mu \left(\text{Mo K} \alpha \right) \left(\text{mm}^{-1} \right) & 1.039 & 2.438 \\ D_{\text{calc}} \left(\text{Mgm}^{-3} \right) & 1.413 & 1.497 \end{array}$
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Z 2 2 μ (Mo K α) (mm ⁻¹) 1.039 2.438 D_{calc} (Mgm ⁻³) 1.413 1.497
$D_{\text{calc}} (\text{Mgm}^{-3})$ 1.413 1.497
Crystal size (mm ³) $0.10 \times 0.15 \times 0.28$ $0.14 \times 0.20 \times 0.23$
hkl range $-13 \le h \le 13$, $-14 \le h \le 14$,
$-13 \le k \le 13$, $-15 \le k \le 15$,
$-21 \le l \le 21$ $-23 \le l \le 23$
<i>θ</i> range (°) 1.38–31.16 2.15–34.01
Refine parameters 316 317
Total reflection 8052 10705
Unique data 4525 5492
$[I > 2\sigma(I)]$
$R_1^a [I > 2\sigma(I)]$ 0.0361 0.0354
wR ₂ ^b 0.0762 0.0954
Goodness of fit 0.965 0.925
$\Delta_{\rm max} (e {\rm \AA}^{-3}) $ 0.460 0.611
$\Delta_{\min} (e \AA^{-3}) -0.693 -0.770$

^a $R = \Sigma F_0 - F_c / \Sigma F_0$.

^b $wR = [\Sigma w(F_0^2 - F_c^2)/\Sigma wF_0^4]^{1/2}$ are general but w are different, w = 1/2 $[^{2}(F^{2}) + (0.0400P)^{2}]$ for (**4b**); $w = 1/[^{2}(F^{2}) + (0.0600P)^{2}]$ for (**7b**) where $P = (F_0^2 + 2Fc^2)/3.$

4. Conclusion

The mixed ligand complexes $[Cu((RaaiR')(PPh_3)X]$ (RaaiR' = 1alkyl-2-(arylylazo)imidazole) are described. Some of the complexes have been structurally confirmed by single crystal X-ray diffraction measurements. The complexes show a trans-to-cis (E-to-Z) isomerisation of the coordinated azoimidazole upon light irradiation in the UV range. Quantum yields $(t \rightarrow c)$ of photoisomerisation were calculated. The cis-to-trans (Z-E) isomerisation is a thermally induced process. The activation energy (E_a) of isomerisation was calculated by a controlled temperature experiment. An increase in electronegativity of X decreases the rate of isomerisation. Upon treatment with a chlorine saturated alcohol solution, the Cu(I) complexes are oxidized to the respective Cu(II) complexes, which then can be further reduced by ascorbic acid back to the precursor Cu(I) complexes. DFT and TD-DFT calculations have been used to determine the electronic structures, and these support the spectra and cyclic voltammetric properties of the complexes.

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Appendix A. Supplementary data

CCDC 654254 and 654255 contain the supplementary crystallographic data for [Cu(MeaaiH)(PPh3)Cl] (4b) and [Cu(MeaaiH)(PPh3)Br] (7b). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/ 10.1016/j.poly.2012.07.039.

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