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Chemistry of azoimidazoles: synthesis, spectral characterization and redox properties of *bis*(N(1)-alkyl-2-(arylazo)imidazole) copper(I) and silver(I) complexes

Tarun K. Misra, Debasis Das and Chittaranjan Sinha*

Department of Chemistry, The University of Burdwan, Burdwan 713 104, India

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Abstract—N(1)-Alkyl-2(arylazo)imidazoles *p*-$C_6H_4N{=}NC_3H_2N$ N(1)R′, RaaiR′, R′ = Me (**2**), Et (**3**); R = H(**a**), Me(**b**), OMe(**c**), Cl(**d**), NO_2(**e**) yield catonic *bis*-chelated complexes with both copper(I) (**4,5**) and silver(I) (**6,7**). These were isolated as perchlorate salts and the composition is supported by elemental analyses. The complexes are 1:1 electrolytes in methanol. The N=N stretch in copper(I) complexes shows a large shift to lower frequency (*ca* 1335 cm^{-1}) from the free ligand value (*ca* 1400 cm^{-1}) due to $d(Cu) \rightarrow \pi^*$ (RaaiR′) back bonding. This effect is much less pronounced in silver(I) complexes indicating a negligible $d\pi$–π^* (RaaiR′) interaction. The complexes show highly resolved symmetrical ^1H NMR spectra. The copper(I) complexes exhibit intense MLCT transitions in the visible region. In methanol the $Cu(RaaiR')_2^{2+}/Cu(RaaiR')_2^{+}$ couple has $E_{1/2}$ *ca* 0.45 V *vs* SCE at 298 K. The high positive potential may be due to the distortion in the geometry of $Cu(RaaiR)_2^{+}$. © 1997 Elsevier Science Ltd

Keywords: azoimidazoles; high potential copper(I) complex; silver(I) complex; MLCT; distorted tetrahedral.

Heterocyclic nitrogens play an important role in coordination chemistry [1]. Imidazole is a ubiquitous ligand [2] in chemical and biological systems as it appears as such in proteins, nucleic acids etc. This has stimulated the synthesis of imidazole containing ligands and their metal complexes in order to understand the role of the ligand in biological systems [3].

To explore the transition metal chemistry of the azoimine system [4], —N=N—C=N—, we have synthesized a ligand incorporating the arylazo group in the imidazole heterocycle known as 2-(arylazo) imidazole (**1**) [5]. The exobidentate [6] character of the imidazole moiety is restricted by N(1)-alkylation and the ligands (**2,3**) become N,N-chelating types [7].

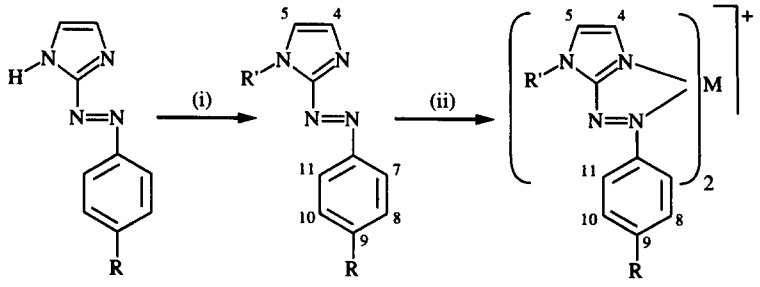
The ubiquity of copper–imidazole bonding in copper metallo-proteins has encouraged the development of the copper chemistry of imidazole and its derivatives [2,3,8]. The monovalent copper (d^{10}) chemistry of heterocyclic N-donor systems has drawn attention [9,10] because of its instability, unusual structural features, utility in solar energy and supramolecular devices, catalytic activity in photo-redox reactions and the biological relevance of high potential copper complexes. The richness of the copper chemistry has encouraged research on the chemistry of the heavier congener of the family, silver [11,12]. The stability of copper(I) systems having CuN_4 environment is due to the π-acidity of the ligands and their steric accessibility to attain distorted tetrahedral coordination sphere. Herein we report a high-potential CuN_4 system using an electronic control *via* ligand π-acidity which preferentially stabilizes cuprous state along with silver(I) complexes; the ligand concerned is N(1)-alkyl-2-(arylazo)imidazole (**2,3**).

RESULTS AND DISCUSSION

Synthesis and formulation

The ligands and complexes presented in this work are described in Scheme 1. The ligands are N(1)-alkyl-2-(arylazo)imidazoles, *p*-$RC_6H_4N{=}NC_3H_2N$ N(1)R′, and abbreviated as RaaiR′ (**2,3**). They were synthesized by the alkylation of corresponding 2-(ary-

* Author to whom correspondence should be addressed.



1 *2 / 3* *4 / 5* or *6 / 7*

R'	CH_3	CH_3CH_2
	2	*3*
	4	*5*
	6	*7*

R'	H	CH_3	OCH_3	Cl	NO_2
	a	*b*	*c*	*d*	*e*

M = Cu(I) (*4*, *5*); Ag(I) (*6*, *7*)

Scheme 1.

lazo)imidazole (**1**) with alkyliodide in dry THF in presence of NaH [13]. They are N,N-chelators and react smoothly with $Cu(CH_3CN)_4ClO_4$ or $AgNO_3$ in boiling methanol in the ratio of 1:2 to yield cationic $[M(RaaiR')_2]^+$ (M = Cu (**4,5**); Ag (**6,7**)).

The complexes were isolated as their perchlorate salt. In an alternate synthetic process [10(b)] Ag complexes (**6,7**) were used to synthesize the copper complexes (**4,5**). The reaction of $[Ag(RaaiR')_2]^+$ $[ClO_4]^-$ in boiling ethanol with hydrated $CuCl_2$ in a 1:2 mole proportion afforded dark crystals of $[Cu(RaaiR')_2][ClO_4]$. The mechanism and the byproducts of the reduction are not yet known. However, the complex formation followed by reduction would be a plausible path for the direct formation [10] of the cuprous complex. The silver(I) complexes are obtained as orange or orange-brown crystals and can be stored for a long time.

The complexes were characterized by elemental analyses (Table 1) which confirmed that metal–ligand maintains 1:2 ratio. The composition has also been studied by Job's method for copper(I) complexes at *ca* 570 nm spectrophotometrically and support the 1:2 metal–ligand ratio. Magnetic susceptibility measurements showed that the compounds are diamagnetic (d^{10}) in nature, as expected. They are soluble in common polar organic solvents and insoluble in nonpolar benzene, hexane etc. The molar conductance (Λ_M) of complexes lies between 100 and 120 Ω^{-1} cm^2 mol^{-1} suggesting a 1:1 type electrolytic nature of the compounds [10]. These results collectively conform to the formulation of the compounds as $[M(RaaiR')_2][ClO_4]$.

Bonding and structure assessment

(*i*) *IR and UV–vis spectra.* The alkylation is supported by the elimination of a broad medium intense N—H stretch centred at *ca* 3350 cm^{-1} in parent azoimidazoles (**1**). The ν(N=N) and endocyclic ν(C=N) appear at *ca* 1400 and 1600 cm^{-1}, respectively. Imidazole ring stretching modes appear at 1500–1400, 780–790, 740–750 and 660–600 cm^{-1} in the compounds [14]. In $[Ag(RaaiR')_2][ClO_4]$ (**6,7**) the ν(N=N) is red shifted by 10–15 cm^{-1} and the corresponding $[Cu(RaaiR')_2]ClO_4$ exhibit sharp stretch 1325–1340 cm^{-1} and has been assigned to ν(N=N) [10(a),12]. The ν(N=N) is considerably lowered in copper(I) complexes ($\Delta\nu$ = 60–75 cm^{-1}) compared to silver(I) complexes ($\Delta\nu$ = 10–15 cm^{-1}) and has been attributed to the presence of d(Cu)–π^* (RaaiR') backbonding in the copper complexes [10(a)]. All the complexes exhibit a structureless band *ca* 1090 cm^{-1} correspond to $\nu(ClO_4)$ suggesting lack of significant perchlorate coordination in the solid state [10,15].

The solution electronic spectra of the complexes were recorded in the range 900–220 nm in methanol. The spectral data are collected in Table 1. The visible range of the spectrum is dominated by metal-to-ligand charge transfer (MLCT) which is a characteristic feature of the copper(I) complexes when bonded with conjugated organic chromophore [9,10]. The MLCT transitions of $[Cu(NN)_2]^+$ have been modelled using D_{2d} symmetry in which the ligands possess low lying ψ^* and χ^* orbitals [16]. Herein the copper(I) complexes (**4,5**) exhibit the absorptions at *ca* 700, 570 and 425 nm those are assigned to MLCT transitions. In silver(I) complexes (**6,7**) the absorption bands show small bathochromic shift relative to free ligands indicating weak interaction between ligand and Ag^+ [11(b)]. The difference in solution electronic spectra between silver(I) and copper(I) complexes is consistent with the IR data (*vide supra*). Both the complexes obey Beer's Law in methanol and hence $[M(RaaiR')_2]^+$ is stable in this solvent. A similar situation appears in the *bis*-arylazopyridine copper(I) [10(a)] and silver(I) [11(b)] complexes. It is reasonable on comparing the reported results, to assume a grossly tetrahedral structure with MN_4 coordination sphere.

Table 1. Microanalytical and UV–vis spectral data of the complexes

Compd.	Elemental analysis[a] (%) C	H	N	M	UV–vis data[b] λ_{max}[nm, $\varepsilon(M^{-1}\,cm^{-1})$]
(**4a**)	44.7	3.7	21.1	12.0	698(1718), 569(8956), 434(23,064)[c],
	(44.9)	(3.7)	(20.9)	(11.9)	384(40,065), 284(6757)
(**4b**)	47.0	4.3	19.8	10.8	710(1275), 574(7735), 427(20,540)[c],
	(46.9)	(4.3)	(19.9)	(11.3)	390(41,688), 277(5790)
(**4c**)	44.3	4.1	18.9	10.5	711(967), 572(6926), 426(16,462)[c],
	(44.4)	(4.0)	(18.8)	(10.7)	408(39,341), 269(6569)
(**4d**)	39.7	3.1	18.6	10.4	722(621), 571(2548), 430(18,340)[c],
	(39.7)	(3.0)	(18.5)	(10.5)	380(34,600), 286(3520)
(**4e**)	38.5	3.0	22.3	10.0	714(740), 589(2117), 442(17,142)[c],
	(38.4)	(2.9)	(22.4)	(10.2)	391(33,036), 282(6440)
(**5a**)	46.9	4.3	19.8	11.1	692(1260), 565(5832), 424(18,601)[c],
	(46.9)	(4.3)	(19.9)	(11.3)	380(20,525), 280(5948)
(**5b**)	48.8	4.8	19.0	10.6	701(807), 568(4552), 445(13,815)[c],
	(48.7)	(4.7)	(19.0)	(10.7)	386(25,707), 278(6731)
(**5c**)	46.3	4.4	18.0	10.0	705(1022), 560(4971), 422(15,779)[c],
	(46.2)	(4.5)	(18.0)	(10.2)	400(27,812), 274(4213)
(**5d**)	41.6	3.4	17.8	9.9	714(1102), 570(3842), 425(15,830)[c],
	(41.8)	(3.5)	(17.7)	(10.0)	390(23,081), 290(3410)
(**5e**)	40.4	3.3	21.5	9.6	703(760), 565(4567), 435(12,445)[c],
	(40.4)	(3.4)	(21.4)	(9.7)	380(22,794), 284(5924)
(**6a**)	41.3	3.6	19.3	18.4	376(43,192), 281(6973)
	(41.4)	(3.5)	(19.3)	(18.6)	
(**6b**)	43.4	4.0	18.4	17.5	379(53,873), 287(14,316)
	(43.5)	(3.9)	(18.4)	(17.8)	
(**6c**)	41.2	3.6	17.6	16.6	393(60,273), 280(11,905)
	(41.3)	(3.8)	(17.5)	(16.9)	
(**6d**)	37.1	2.7	17.4	16.5	379(47,352), 287(12,457)
	(37.0)	(2.8)	(17.3)	(16.7)	
(**6e**)	35.8	2.8	20.8	16.3	396(40,304), 282(13,105)
	(35.9)	(2.7)	(20.9)	(16.1)	
(**7a**)	43.5	4.1	18.4	17.6	366(18,960), 277(1886)
	(43.5)	(3.9)	(18.4)	(17.8)	
(**7b**)	45.5	4.3	17.7	16.8	380(43,260), 288(10,955)
	(45.3)	(4.4)	(17.6)	(17.0)	
(**7c**)	43.1	4.3	16.7	16.4	390(12,087), 272(2280)
	(43.2)	(4.2)	(16.8)	(16.2)	
(**7d**)	38.9	3.4	16.4	16.2	385(37,613), 280(4059)
	(39.0)	(3.3)	(16.6)	(16.0)	
(**7e**)	38.2	3.0	20.2	15.3	386(39,147), 282(15,659)
	(38.0)	(3.2)	(20.1)	(15.5)	

[a] Calculated values are in parentheses.
[b] The solvent was MeOH.
[c] Shoulder.

Magnetic resonance spectra

All the chelates show highly resolved ^{1}H NMR spectra in $CDCl_3$. The spectral data are collected in Table 2. The proton numbering pattern is shown in Scheme 1. Assignment of individual proton resonances are made by spin–spin splitting, comparative integration, chemical shift and changes therein on substitution. 2-(arylazo)imidazoles (**1**) exhibit N—H resonance at 10.4 ppm [7] which is eliminated on alkylation. The methyl signal in N(1)-methylated derivatives (**2**) appears as a sharp singlet at *ca* 4.00 ppm and ethylated products (**3**) show a quartet and a triplet at *ca* 4.3 and 1.4 ppm for $—CH_2—$ and $—CH_3$ protons, respectively. In copper(I) and silver(I) chelates all these signals are shifted downfield by 0.2–0.3 ppm (Table 3) indicating metal–ligand binding. Imidazolic protons 4- and 5-H appear at the upfield position *ca* 7.25 and 7.15 ppm, respectively, and are almost insensitive to the substituents in 2-aryl ring. In complexes (**4**–**7**) these two signals are significantly shifted downfield by *ca* 0.4 and 0.1 ppm, respectively. The aromatic protons in azoaryl ring are assigned on the basis of the substitution effect. On $—CH_3$ (**b**) and $—OCH_3$ (**c**) sub-

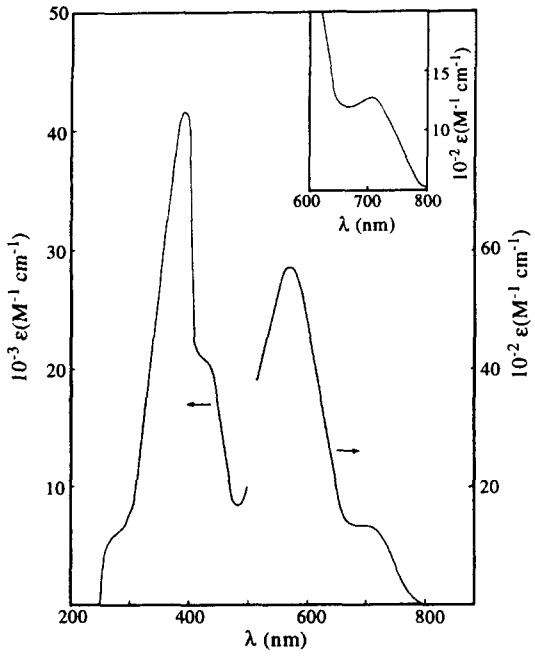


Fig. 1.

stitution at 9th position 8,10-H signals are upfield shifted and —Cl (**d**) and —NO_2 (**e**) substitution shift the signals in reverse direction. This is expected in view of inductive and electromeric effect [17]. The 9-CH_3 and 9-OCH_3 signals appear as a single band in all the compounds at *ca* 2.4 and 3.8 ppm, respectively. Representative spectra are shown in Fig. 2.

It is noted that all the protons in the aliphatic and aromatic regions exhibit only one signal (singlet or multiplet) for each proton. This suggests that both the chelate rings in the complexes are magnetically equivalent at least on the NMR time scale and complexes contain the effective C_2- axis which is also in agreement with the proposed tetradentate structure of the complexes.

Redox properties

The results of cyclic voltammetric scans for $Cu(RaaiR')_2^+$ are shown in Fig. 3 and data are given in Table 3. In methanol with TBAP as the supporting electrolyte in complexes **4,5** undergo quasi-reversible oxidation-reduction reaction at *ca* 0.4–0.5 V *vs* SCE (at 50 mV s^{-1} scan rate) at a Pt-bead working electrode. The response is attributed to copper(II)/copper(I) couple (eq. 1).

$$Cu(RaaiR')_2^{2+} + e \rightleftharpoons Cu(RaaiR')_2^+ \qquad (1)$$

The quasi-reversible character is accounted from the ΔE_p (E_{pa}–E_{pc}) values under the conditions of measurements [10(a)].

The controlled potential coulometry at 0.7 V fully corroborates the one electron stoichiometry of the couple. The copper(II) congener, formed by electrolysis, shows an identical response but reductive in nature. The $E_{1/2}$ data reveals that the redox process occurs at a moderately high positive potential. The oxidation potential of copper(I) systems are sensitive to the steric crowding, low symmetry environment, tetrahedral distortion about the metal centre [9,10,18,19] but examples are very limited. The role of the azoimine function in bringing about the high copper(II)/copper(I) potential is well established [10(a),11]. The present example shows slightly lower potential (0.5 V *vs* SCE) than that of arylazopyridine copper(I) complexes (0.65 V *vs* SCE). This may be due to less π-acidity of imidazole than that of pyridine ring [1(d)]. The use of electron deficient ligands in copper(I) complexes may be a strategy in developing model compounds which possess the redox properties of many copper containing biological systems [20].

The electroactivity of copper(I) complexes (**4,5**) was examined at potentials negative to the SCE. A single multielectron quasi-reversible (E_{pc} = −0.9 to −1.2 V *vs* SCE, ΔE_p = 320–370 mV, at scan rate 50 mV s^{-1}) response was observed. It is believed that this response arises from reduction of the azoimine function [10(a)].

The electrochemistry of silver complexes are not very informative. The cathodic progress followed by scan reversal in anodic side gives an irreversible oxidative response on the positive side to SCE. The reason is unknown and may be due to the oxidation of adsorbed silver on the electrode bed [21] which is produced on the cathodic scan because no such response is found on first anodic scan.

EXPERIMENTAL

Materials

2-(Arylazo)imidazoles (**1**) were synthesized as reported earlier [5]. The complex $[Cu(MeCN)_4]ClO_4$ was prepared by following a known procedure [10(a)]. The purification/preparation of solvents and supporting electrolyte were carried out as previously reported [10]. The salts, $CuCl_2 \cdot 2H_2O$ and $AgNO_3$ were obtained, respectively from E. Merck and Glaxo, Bombay. Dinitrogen was purified by bubbling through an alkaline pyrogallol solution. All other chemicals and solvents were reagent grade and were used as received.

Physical measurements

UV–vis spectra were recorded by Shimadzu UV160A spectrophotometer. IR spectra were obtained using Perkin–Elmer 783 and 883 spectrophotometers. ^1H NMR spectra were collected in $CDCl_3$ using JEOL, JNM-GX270 and Bruker 300 MHz FTNMR spectrometers; solution electrical conductivity was measured using Systronics 304 digital conductivity meter with a solution concentration of *ca* 10^{-3} mol dm^{-3}. Magnetic susceptibilities were

Table 2. ^{1}H NMR spectral data for RaaiR′ (**2,3**) and [M(RaaiR′)$_2$]-ClO$_4$ (M = Cu^I (**4,5**); Ag^I (**6,7**) in $CDCl_3$)

Compound	δ, ppm						
	4-H[a]	5-H[a]	7,11-H[b]	8,10-H	—CH_3	—CH_2—	R
(**2a**)	7.26	7.13	7.94	7.32[c]	4.06	—	—
(**2b**)	7.22	7.10	7.90	7.10[b]	4.04	—	2.35
(**2c**)	7.20	7.10	7.85	7.00[b]	4.03	—	3.85
(**2d**)	7.29	7.15	7.91	7.38[b]	4.07	—	—
(**2e**)	7.32	7.18	7.96	8.14[b]	4.09	—	—
(**3a**)	7.23	7.10	7.93	7.30[c]	1.45[c]	4.37[d]	—
(**3b**)	7.20	7.08	7.85	7.06[b]	1.44[c]	4.35[d]	2.32
(**3c**)	7.15	7.07	7.80	6.98[b]	1.42[c]	4.33[d]	3.85
(**3d**)	7.20	7.13	7.90	7.49[b]	1.47[c]	4.41[d]	—
(**3e**)	7.24	7.16	8.00	8.18[b]	1.50[c]	4.44[d]	—
(**4a**)	7.65	7.31	7.80	7.51[c]	4.18	—	—
(**4b**)	7.63	7.28	7.77	7.38[b]	4.17	2.41	—
(**4c**)	7.58	7.23	7.71	7.30[b]	4.18	3.80	—
(**4d**)	7.66	7.33	7.84	7.64[b]	4.20	—	—
(**4e**)	7.70	7.34	8.12	8.40[b]	4.20	—	—
(**5a**)	7.72	7.34	7.84	7.55[c]	1.71[c]	4.70[d]	—
(**5b**)	7.70	7.32	7.80	7.41[b]	1.70[c]	4.68[d]	2.42
(**5c**)	7.66	7.28	7.76	7.30[b]	1.68[c]	4.69[d]	3.81
(**5d**)	7.74	7.35	7.87	7.68[b]	1.71[c]	4.71[d]	—
(**5e**)	7.79	7.37	8.14	8.45[b]	1.72[c]	4.73[d]	—
(**6a**)	7.62	7.24	7.72	7.41[c]	4.20	—	—
(**6b**)	7.60	7.21	7.68	7.26[b]	4.18	—	3.39
(**6c**)	7.55	7.19	7.64	7.20[b]	4.18	—	3.80
(**6d**)	7.62	7.23	7.70	7.53[b]	4.20	—	—
(**6e**)	7.64	7.25	7.75	7.97[b]	4.23	—	—
(**7a**)	7.68	7.23	7.75	7.45[c]	1.66[c]	4.63[d]	—
(**7b**)	7.67	7.21	7.71	7.29[b]	1.64[c]	4.62[d]	2.39
(**7c**)	7.65	7.18	7.66	7.21[b]	1.64[c]	4.61[d]	3.80
(**7d**)	7.70	7.23	7.71	7.55[b]	1.66[c]	4.63[d]	—
(**7e**)	7.72	7.26	7.77	8.00[b]	1.66[c]	4.65[d]	—

[a] In most cases as unsplit band.
[b] Doublet.
[c] Triplet and includes 9-H signal.
[d] Quartet.

Table 3. Cyclic voltammetric data[a,b] for the complexes [Cu(RaaiR′)$_2$]ClO$_4$ (**4,5**) in MeOH at 298 K

Compound	E_{pa} (V)	E_{pc} (V)	ΔE_p (mv)	$E_{1/2}$ (V)	n[c]
(**4a**)	0.503	0.393	110	0.448	0.92
(**4b**)	0.496	0.391	105	0.444	1.04
(**4c**)	0.486	0.368	118	0.427	1.02
(**4d**)	0.519	0.416	103	0.468	1.05
(**4e**)	0.554	0.436	118	0.495	0.98
(**5a**)	0.514	0.400	114	0.457	0.94
(**5b**)	0.510	0.388	122	0.449	1.01
(**5c**)	0.494	0.368	126	0.431	0.98
(**5d**)	0.534	0.417	117	0.478	1.03
(**5e**)	0.557	0.450	107	0.504	1.02

[a] All values of E are quoted *vs* the SCE; supporting electrolyte TBAP (0.1 mol); solute concentration *ca* 10^{-3} mol; scan rate 0.05 V s^{-1}.
[b] The responses are oxidative in nature.
[c] $n = Q/Q'$; where Q' is the calculated coulomb count after exhaustive electrolysis; oxidations were performed at 0.70 V *vs* SCE in CH_3OH (0.10 M [N Bu$_4$][ClO$_4$]).

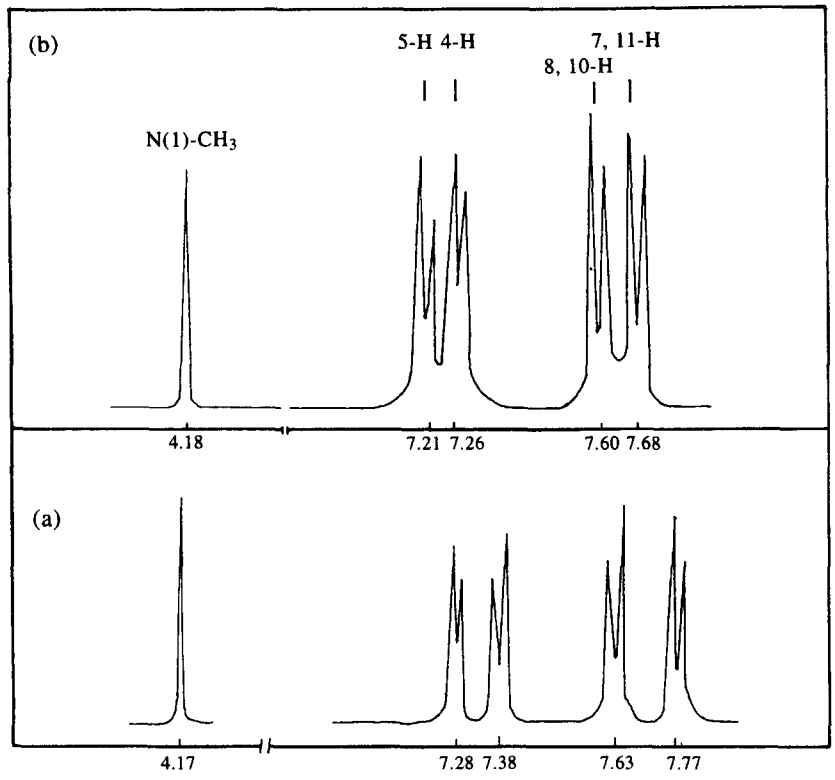


Fig. 2.

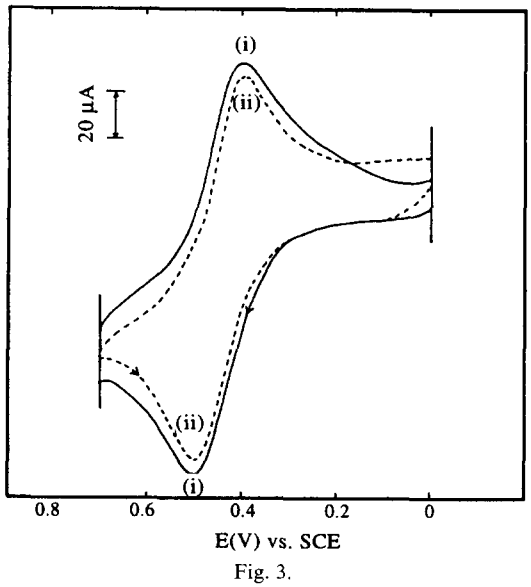


Fig. 3.

obtained from vibrating sample magnetometer PAR-155 model; C, H, N results were collected from Perkin–Elmer 240 C elemental analyser. Copper and silver were estimated respectively by iodometric titration [22(a)] and gravimetrically [22(b)]. Voltammetric measurements were done with use of computer controlled PAR model 270 VERSTAT electrochemical instrument. All experiments were done at 298 K under dinitrogen with a three electrode system platinum as working electrode. All potentials are referenced to the saturated calomel electrode (SCE) and are uncorrected for the junction contributions with tertrabutyl ammonium perchlorate (TBAP) as supporting electrolyte.

Preparation of compounds. Alkylation of 2-*(arylazo)imidazoles* (**1**). *Synthesis of N*(1)*-methyl* 2-(((9-*methyl*)*phenyl*)*azo*)*imidazole* (**2**)

To dry THF solution (20 cm^3) of 2-(((9-methyl) phenyl)azo)imidazole (**1b**) (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 then warmed at 60°C for an additional 1 h. The solution was evaporated, extracted with $CHCl_3$ (2×10 cm^3), washed with 10% NaOH (3×10 cm^3) and finally with distilled water (3×20 cm^3). It was chromatographed over silica gel prepared in benzene and the desired compound was eluted by acetonitrile-benzene (1:19 v/v). The orange crystalline needles were separated on slow evaporation (0.48 g, 45%).

Other ligands were performed by identical procedure. For N(1)-ethyl derivatives ethyl iodide is used instead of methyl iodide. The yield was 30–50%. The mps of the compounds are: **2a**, $100+2$; **2b**, 115 ± 2; **2c**, gum; **2d**, 160 ± 1; **2e**, decomposed above

250°C; **3a**, 78±1; **3b**, 96±1; **3c**, gum; **3d**, 130±1 and **3e**, 154±1°C. Found: C, 64.7; H, 5.2; N, 30.1. Calc. for $C_{10}H_{10}N_4$ (**2a**): C, 64.5; H, 5.4; N, 30.1%. Found: C, 65.9; H, 5.9; N, 28.1. Calc. for $C_{11}H_{12}N_4$ (**2b**): C, 66.0; H, 6.0; N, 28.0%. $C_{11}H_{12}N_4O$ (**2c**): gum. Found: C, 54.6; H, 3.9; N, 25.3. Calc. for $C_{10}H_9H_4Cl$ (**2d**): C, 54.4; H, 4.1; N, 25.4%. Found: C, 51.8; H, 3.8; N, 30.2. Calc. for $C_{10}H_9N_5O_2$ (**2e**): C, 52.0; H, 3.9; N, 30.3%. Found: C, 66.1; H, 6.2; N, 27.8. Calc. for $C_{11}H_{12}N_4$ (**3a**): C, 66.0; H, 6.0; N, 28.0%. Found: C, 67.5; H, 6.3; N, 26.3. Calc. for $C_{12}H_{14}N_4$ (**3b**): C, 67.3; H, 6.5; N, 26.2%. $C_{12}H_{14}N_4O$ (**3c**): gum. Found: C, 56.0; H, 4.9; N, 24.1. Calc. for $C_{11}H_{11}N_4Cl$ (**3d**): C, 56.3; H, 4.7; N, 23.9%. Found: 54.1; H, 4.4; N, 28.8. Calc. for $C_{11}H_{11}N_5O_2$ (**3e**): C, 53.9; H, 4.5; N, 28.6%. UV–vis in MeOH (λ_{max}, nm(ε, M^{-1} cm^{-1})): (**2a**) 360 (17,000), 280 (4100); (**2b**) 362 (24,500), 270 (3800); (**2c**) 368 (22,800), 275 (4050); (**2d**) 380 (25,700), 280 (4450); (**2e**) 390 (26,400), 280 (7840); (**3a**) 375 (15,400), 360 (16,650), 272 (2000); (**3b**) 376 (18,320), 355 (20,800), 270 (3300); (**3c**) 380 (17,520), 362 (19,600), 275 (2930); (**3d**) 383 (35,300), 370 (36,930), 270 (4020); (**3e**) 385 (30,600), 280 (9350).

Synthesis of bis[N(1)-methyl-2-(((9-methyl)phenyl) azo)imidazole] silver(I) perchlorate, [Ag(Me aai Me)$_2$]ClO_4 (**6b**)

A solution of $AgNO_3$ (0.085 g, 0.5 mmol) in methanol (10 cm^3) was added slowly to the stirred solution of **2b** (0.2 g, 1 mmol) and the mixture was heated to reflux for 2 h. On cooling, orange–yellow precipitate appeared. It was further heated to redissolve the precipitate and filtered hot through G-4 sintered glass crucible. To this an aqueous $NaClO_4$ (1 g in 5 cm^3) was added with constant stirring. Dark orange–brown compound was collected by filtration, washed with water and recrystallised from methanol-water (3:1 v/v). It was dried in vacuo and preversed in dark. The yield was 75%.

All other silver compounds were prepared similarly and the yield was 65–80%.

Synthesis of bis[N(1)-methyl 2-(((9-methyl)phenyl) azo)imidazole] copper(I) perchlorate, [Cu(Me aai Me)$_2$]ClO_4 (**4b**)

(*i*) *From* [Cu(MeCN)$_4$]ClO_4. The ligand **2b** (0.2 g, 1 mmol) in dry MeOH (10 cm^3) was added dropwise to stirred methanolic solution (10 cm^3) of [Cu(MeCN)$_4$]ClO_4 (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%).

(*ii*) *From* [Ag(Me aai Me)$_2$]ClO_4 *and* $CuCl_2 \cdot 2H_2O$. $CuCl_2 \cdot 2H_2O$ (0.1 g, 0.59 mmol) was dissolved in 20 cm^3 of 1:1 methanol–water and [Ag(Me aai Me)$_2$]ClO_4 (**6b**) (0.72 g, 1.19 mmol) was added and the mixture was heated to reflux for 1 h. The dark brown solution was cooled and filtered through a G-4 sintered glass funnel. The filtrate was then concentrated to 10 cm^3 and left for crystallization. The dark crystals, thus deposited, were filtered and washed with hexane and dried *in vacuo*, yield 0.25 g (76%).

All other copper(I) complexes were prepared similarly. The silver assisted route (process (ii)) gave better yields than the direct synthetic path (process (i)) and was followed. The yield of other complexes was 70–85%.

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REFERENCES

1. (a) Inoue, M. and Kubo, M., *Coord. Chem. Rev.*, 1976, **21,** 1; (b) Raper, E. S., *Coord. Chem. Rev.*, 1985, **61,** 115; (c) Reedijk, J., *Comprehensive Coordination Chemistry*, G. Wilkinson, R. D. Gillard and J. A. McCleverty (eds), Vol. 2, p. 73, Pergamon Press, Oxford (1987); (d) Constable, E. C. and Steel, P. J., *Coord. Chem. Rev.*, 1989, **93,** 205; (e) Steel, P. J., *Coord. Chem. Rev.*, 1990, **106,** 227.
2. Street, J. P., Skorey, K. I., Brown, R. S. and Ball, R. G., *J. Am. chem. Soc.*, 1985, **107,** 7669; Guss, J. M., Merritt, E. A., Phizackerley, R. P., Hedman, B., Murata, M., Hodgson, K. O. and Freeman, H. C., *Science*, 1988, **241,** 806; Baker, E. N., *J. Mol. Biol.*, 1988, **203,** 1071; Godden, J. W., Turley, S., Teller, D. C., Adman, E. T., Liu, M.-Y., Payne, W. J. and LeGall, J., *Science*, 1991, **253,** 438; Mao, Z. W., Yu, K. B., Chen, D., Han, S. Y., Sui, Y. X. and Tang, W. X., *Inorg. Chem.*, 1993, **32,** 3104.
3. Tejel, C., Villarroya, B. E., Ciriano, M. A., Oro, L. A., Lanfranchi, M., Piripicchio, A. and -Camellini, M. T., *Inorg. Chem.*, 1996, **35,** 4360; Higgs, T. C., Helliwell, M. and Garner, C. D., *J. Chem. Soc., Dalton Trans.*, 1996, 2101 and references therein.
4. Pal, C. K., Chattopadhyay, S., Sinha, C., Bandyopadhyay, D. and Chakravorty, A., *Polyhedron*, 1994, **13,** 999; Pal, C. K., Chattopadhyay, S., Sinha, C. and Chakravorty, A., *Inorg. Chem.*, 1994, **33,** 6140 and references therein; Roy, R., Chattopadhyay, P., Sinha, C. and Chattopadhyay, S., *Polyhedron*, 1996, **15,** 3361.
5. Mohamoud, M., Hamman, A. H., El-Gyar, S. A. and Ibrahim, S. A., *Mont. Chem.*, 1986, **117,** 313.
6. Masciocchi, N., Moret, M., Cairati, P., Sironi, A., Ardizzoia, G. A. and La Monica, G., *J. Chem. Soc., Dalton Trans.*, 1995, 1671; -Wan, M. Z.,

Qui-Wei, H., -Xia, T. W., -Xiaung, L. S., Ze-Min, W. and -Ling, H. J., *Polyhedron*, 1996, **15,** 321; Shyu, H. L., Wei, H. H., Lee, G. H. and Wang, T., *Inorg. Chem.*, 1996, **35,** 5396.
7. Das, D., Nayak, M. K. and Sinha, C., *Trans. Met. Chem.*, in press.
8. Schugar, H. J., *Copper Coordination Chemistry: Biochemical Inorganic Perspectives*, K. D. Karlin and J. Zubieta (eds), p. 43, Adenine Press, New York (1983).
9. (a) Malmstrom, B. G. in *New Trends in Bioinorganic Chemistry*, R. J. P. Williams, J. R. R. F. De Silva (eds), p. 59, Academic Press, New York (1978); (b) McMillin, D. R., Kirchhoff, J. R. and Goodwin, K. V., *Coord. Chem. Rev.*, 1985, **64,** 83; (c) Sakaki, S., Koga, G. and Ohkubo, K., *Inorg. Chem.*, 1986, **25,** 2330; (d) Baker, L. J., Bowmaker, G. A., Hart, R. D., Harvey, P. J., Healy, P. C. and White, A. H., *Inorg. Chem.*, 1994, **33,** 3925; (e) Scott, S. M., Gordon, K. C. and Burell, A. K., *Inorg. Chem.*, 1996, **35,** 2452.
10. (a) Datta, D. and Chakravorty, A., *Inorg. Chem.*, 1983, **22,** 1085; (b) Goswami, S., Kharmawphlang, W., Deb, A. K. and Peng, S.-M., *Polyhedron*, 1996, **15,** 3635.
11. (a) Wilkinson, G., *Comprehensive Coordination Chemistry*, Vol. 5, p. 775, Pergamon Press, Oxford (1987); (b) Deb, A. K., Choudhury, S. and Goswami, S., *Polyhedron*, 1990, **9,** 2251.
12. Kakoti, M., Deb, A. K. and Goswami, S., *Inorg. Chem.*, 1992, **31,** 1302; Choudhury, S., Deb, A. K. and Goswami, S., *Polyhedron*, 1994, **13,** 1063.
13. Lockhart, J. C. and Rushton, D. J., *J. Chem. Soc., Dalton Trans.*, 1991, 2633.
14. Rout, K. C., Mohanty, R. R., Jena, S. and Dash, K. C., *Polyhedron*, 1996, **15,** 1023.
15. Elder, R. C., Hegg, M. J. and Deutsch, E., *Inorg. Chem.*, 1978, **17,** 427.
16. Phifer, C. C., McMillin, D. R., *Inorg. Chem.*, 1986, **25,** 1329.
17. Chattopadhyay, P. and Sinha, C., *Polyhedron*, 1994, **13,** 2689.
18. Patterson, G. H. and Holm, R. H., *Bioinorg. Chem.*, 1975, **4,** 257; Sorell, T. N. and Jameson, D. L., *Inorg. Chem.*, 1982, **21,** 1014.
19. Gordon, R. C., Al-obaidi, A. H. R., Jayaweera, P. M., McGarvey, J. H., Malone, J. F. and Bell, S. E. J., *J. Chem. Soc., Dalton Trans.*, 1996, 1591; Uma, R., Palaniandavar, M. and Butcher, R. J., *J. Chem. Soc., Dalton Trans.*, 1996, 2061; Keung-Ito, P. K., Peng, S. M., Wong, K. Y. and Che, C. M., *J. Chem. Soc., Dalton Trans.*, 1996, 1929.
20. Robandt, P. V., Schoeder, R. R., Rorabacher, D. B., *Inorg. Chem.*, 1993, **32,** 3957.
21. Matsubayashi, G., Maikawa, T., Tamura, H., Nakano, M. and Arakawa, R., *J. Chem. Soc., Dalton Trans.*, 1996, 1539.
22. Vogel, A. I., *A Text Book of Quantitative Inorganic Analyses*, 3rd edn., ELBS, Longman (1975). (a) p. 358; (b) p. 486.