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Chemistry of azopyrimidines
Synthesis, spectral characterization, electrochemistry and X-ray crystal structure of bis[2-(arylazo)pyrimidine] complexes of copper(I)

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Abstract

2-(Arylazo)pyrimidines (aapm, **3**) have been synthesized by condensing nitrosoaromatics with 2-aminopyrimidine. They yield cationic bis-chelated complexes with copper(I), $Cu(aapm)_2^+$ and are isolated as perchlorate salts. The complexes are 1:1 electrolytes in MeOH and exhibit intense MLCT transitions in the visible region. The N=N stretch in copper(I) complexes shows a large shift to lower frequency (approx. 1315 cm^{-1}) from the free ligand value (approx. 1425 cm^{-1}) due to $d(Cu)\rightarrow\pi^*$(aapm) back bonding. The complexes show highly resolved symmetrical ^1H NMR spectra. In MeOH the $Cu(aapm)_2^{2+}/Cu(aapm)_2^+$ couple appears at $E_{1/2}$ at approx. 0.7 V versus SCE at 298 K. The structure has been confirmed by X-ray crystallography.

Keywords: Azopyrimidines; High potential copper(I) complexes; Distorted tetrahedral structure

1. Introduction

Recent years have witnessed a great deal of interest in the synthesis of the complexes of copper with α-diimine type ligands because of interdependence of their coordination geometry and their redox and photochemical behaviour [1–5]. Copper can adopt variable valence states and the ability is reflected in its redox properties [6–10]. The monovalent copper (d^{10}) chemistry has drawn special attention 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 [6–22].

Proper combination of the steric crowding and π-acidity in a well designed ligand are the most important prerequisites for high stability of copper(I) complexes [7–10,18–21]. The use of heterocyclic *N*-donor ligands to stabilize low valent metal-redox states is widely studied in coordination chemistry [23–26]. The number of hetero atoms, ring size and the substituents in the heterocyclic ring significantly modify the π-acidity and regulate the physical and chemical properties of the compounds [27–29]. Ligands consisting of one *N*-heterocyclic ring with a pendant nitrogen donor from azo function, known as (arylazo)heterocycles have been used to stabilize low oxidation states [7–10,30–41] like Cu(I), Ru(II), Os(II), Re(II),Co(II), Fe(II), etc.

There are two studies available in the literature on the stabilization of copper(I) by azoheterocycles; the first study appeared in 1983 from Datta and Chakravorty [7] which looked at copper(I) complexes of 2-(arylazo)pyridine (aap, **1**); the second study has appeared recently from our group [8–10], which looked at copper(I) complexes of *N*(I)-alkyl-2-(arylazo)imidazoles (RaaiX, **2**). Anchoring of the azo function in a heterocycle backbone is interesting because of the photochromatic, redox active, pH responsive and photo-redox activity of this functional group [42,43]. With this background we have initiated to search for new azoheterocycles of pyrimidine (**3**). It is chosen because of its higher π-acidity [27–29] than conventional widely used pyridine bases and its biochemical importance [44–47]. In coordination chemistry the *meta*-related nitrogen in pyrimidine has played an important role for connecting different metals, transmitting

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anti-ferromagnetic interactions and for obtaining magnetic systems of high nuclearity [48–51].

In this report we describe the synthesis, spectral, redox studies and single crystal X-ray structure of copper(I)complexes of 2-(arylazo)pyrimidine.

2. Experimental

2.1. Materials

2-Aminopyrimidine was obtained from Aldrich. $[Cu(MeCN)_4](ClO_4)$ was prepared as previously described [7]. Propylene carbonate (AR) was purchased from Aldrich. All other chemicals and solvents were used as previously described [8–10].

2.2. Instrumentation

Microanalytical (C,H,N) data were obtained from a Perkin Elmer 2400 CHNS/O elemental analyzer. Spectroscopic data were obtained with the use of the following instruments: UV–Vis spectra, Shimadzu UV-160A; IR spectra (KBr disk, 4000–200 cm^{-1}), JASCO 420 FT-IR; ^1H NMR spectra, Brucker 300 MHz FT-NMR spectrometers. Electrochemical measurements were carried out with the use of a computer controlled PAR model 270 VERSASTAT, using a platinum disk working electrode. The solution was iR compensated and the results were collected at 298 K. The reported results are referenced to the saturated calomel electrode (SCE) in acetonitrile.

2.3. Synthesis of ligands

2-(Arylazo)pyrimidines (aapm, **3**) were synthesized by condensing 2-aminopyrimidine with nitrosoaromatics. A representative case is detailed in Section 2.4. Available information [32–38] on 2-(arylazo)pyridine was served as a guideline for setting experimental conditions.

2.4. 2-(Phenylazo)pyrimidine (papm)

To a nitrogen flushed solution of 2-aminopyrimidine (2.0 g, 2.1 mmol) in dry benzene (30 ml) in the presence of molecular sodium (1 g), nitrosobenzene (2.5 g, 2.3 mmol) was added in small portions for 2 h under refluxing conditions. The reaction was further continued for 3 h and cooled to room temperature. A dark red solution was then filtered and the filtrate was water washed (20 ml×3). It was then evaporated to reduce the volume to 5 ml and chromatographed on silica gel (60–120 mesh) column (30×1 cm). A light yellow band was eluted by petroleum-spirit (60–80) and rejected. A red band was then eluted with benzene and collected. Evaporation of solvent gave a 'gummy' mass of the ligand. The yield was 1.2 g (31%).

2-(*o*-Tollylazo)pyrimidine (*o*-tapm) (30%, gummy mass), 2-(*m*-tollylazo)pyrimidine (*m*-tapm) (35%, gummy mass), 2-(*p*-tollylazo)pyrimidine (*p*-tapm) (28%, gummy mass) and 2-(*p*-chloroazo)pyrimidine (*p*-Clpapm) (40%, semi solid) were prepared similarly.

2.5. Preparation of complexes

2.5.1. Bis[2-(phenylazo)pyrimidine]copper(I) perchlorate ($Cu(papm)_2(ClO_4)$) (**4**)

Nitrogen gas was bubbled through an orange red solution of the ligand papm (0.2 g, 1.09 mmol) in dry MeOH and $[Cu(MeCN)_4](ClO_4)$ (0.4 g, 1.22 mmol) was added at room temperature. The solution color turned to violet and was stirred for 2 h. The solution volume was then reduced to half by nitrogen bubbling. The dark crystalline mass that separated was filtered off and was recrystallized from methanol. The crystals were dried in vacuo and the yield was 0.18 g (68%).

All other complexes were prepared similarly and the yield ranged from 62–75%.

2.6. X-ray crystal structure and analysis

Single crystals of $[Cu(papm)_2]ClO_4$ (**4**), suitable for X-ray diffraction were grown by slow diffusion of hexane into dichloromethane solution at 298 K (Table 1). The crystal size was 0.15×0.40×0.50 mm^3. Diffraction measurements were carried out on a Nonius CAD-4 fully automated four circle diffractometer with graphite-monochromated (Mo Kα) radiation (λ=0.7107 Å) at 298 K.

Table 1
Crystallographic data for $[Cu(papm)_2](ClO_4)$ (**4**)

Empirical formula	$C_{20}H_{16}N_8ClO_4Cu$
f_w	531.39
Crystal system	Monoclinic
Space group	*C* 2/*c*
a, Å	20.541 (2)
b, Å	19.012(7)
c, Å	11.893(2)
β, °	106.58(1)
V, $Å^3$	4451.3(19)
Z	8
T, K	298
λ, Å	0.7107
ρ_{calcd} g cm^{-3}	1.586
μ(Mo Kα), cm^{-1}	11.473
Transm coeff.[a]	0.884
Params refined	308
R_f[b] %	6.0
R_w[c] %	5.3
GOF[d]	2.31

[a] Maximum value normalized to 1.

[b] $R_f = \Sigma(|F_0| - |F_c|/\Sigma|F_0|$.

[c] $R_w = \Sigma \quad W(|F_0| - |F_c|)^2/\Sigma \quad W/|F_0|^2$; $\quad W^{-1} = \sigma^2(|F_0| + g|F_0|^2$; $\quad g =$ 0.000100.

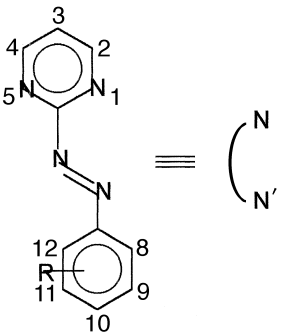
[d] The goodness-of-fit is defined as $[\Sigma W(|F_0| - |F_c|)^2/(n_0 - n_v]$, where n_o and n_v denote the numbers of data and variables, respectively.

The unit cell was determined and refined using setting angles of 25 reflections with 2θ angles in the range of 19.00–30.26°. The unit cell dimensions are listed in Table 4. Data were collected by $\theta-2\theta$ scans in the angular range of 2.0–50.0°. Three check reflections were measured after every hour during data collections to monitor crystal stability and showed no significant intensity variation. Of the 3910 unique reflections 2518 with $I>2\sigma(I)$ were used for the structure solution. Data reductions and structure refinement were performed using NBCVAX packages. The structure was solved by the Patterson method. All non-hydrogen atoms were located from subsequent difference Fourier maps. Tables containing full listings of atom coordinates, anisotropic thermal parameters and hydrogen atom locations are available as Supplementary data.

3. Results and discussion

3.1. Ligands and complexes

2-(Arylazo)pyrimidines (aapm, **3**) are used as ligands. These were synthesized by condensing nitrosoaromatics with 2-aminopyrimidine. The ligands are new and act as *N*,*N*′-chelating molecules. The donor centres are abbreviated as *N*(1)(pyrimidine),*N*. and *N*(azo),*N*′. The atom numbering scheme is shown in the structure of aapm (**3**).



≡

R	abbreviation
H	papm
8-Me	*o*-tapm
9-Me	*m*-tapm
10-Me	*p*-tapm
10-Cl	*p*-Clpapm

aapm

3

The ligands react smoothly with $[Cu(MeCN)_4ClO_4]$ in boiling MeOH in the ratio 1:2 to yield cationic $[Cu(aapm)_2]^+$ (**4**–**8**). The complexes were isolated as their perchlorate salt.

Microanalytical data and iodometric determination of copper support the ligand to metal in a 2:1 ratio. The composition has also been confirmed by a previously published method [52] at 560 nm spectrophotometrically. Magnetic susceptibility measurements showed that the compounds are diamagnetic (d^{10}) in nature. They are soluble in polar organic solvents. The molar conductance (Λ_M) of the complexes lies between 90 and 110 $\Omega^{-1}\,cm^2\,mol^{-1}$ suggesting a 1:1 ratio type electrolytic nature of the compounds.

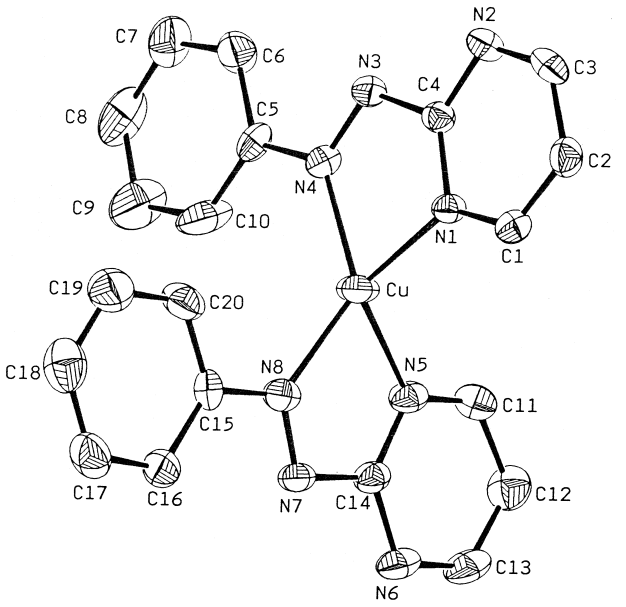


Fig. 1. Single crystal structure of $[Cu(papm)_2]^+$ showing the atom numbering scheme. For clarity, all hydrogen atoms have been omitted.

3.2. Structural studies

X-ray quality crystals were obtained by slow diffusion of hexane into a CH_2Cl_2 solution of complex (**4**). The solid state structure of the $[Cu(aapm)_2]^+$ complex cation is shown in Fig. 1. The bond lengths and angles within the coordination sphere of the copper ion are listed in Table 2. The asymmetric unit contains one complex cation, $[Cu(aapm)_2]^+$. The molecular packing diagram along the *c*-axis (Fig. 2) shows that ClO_4^- is shared by two unit cells. Two chelate rings Cu, N(1), C(4), N(3), N(4) and Cu, N(5), C(14), N(7), N(8) separately constitute two

Table 2
Selected bond distances (Å) and angles (°) and their estimated standard deviations for $[Cu(papm)_2]ClO_4$ (**4**)

Distances (Å)		Angles (°)	
Cu–N (1)	2.010(4)	N(1)–Cu–N(4)	79.06(19)
Cu–N (5)	2.038(4)	N(5)–Cu–N(8)	79.20(20)
Cu–N (4)	2.000(4)	N(4)–Cu–N(8)	131.93(20)
Cu–N (8)	1.981(5)	N(1)–Cu–N(5)	119.13(18)
N(3)–N(4)	1.257(7)	N(1)–Cu–N(8)	127.65(18)
N(7)–N(8)	1.260(6)	N(4)–Cu–N(5)	126.25(18)
–	–	Cu–N(4)–C(5)	125.5(4)
–	–	Cu–N(1)–C(1)	133.3(4)
–	–	Cu–N(4)–N(3)	118.7(4)
–	–	Cu–N(8)–N(7)	119.5(4)
–	–	Cu–N(5)–C(11)	132.6(4)
–	–	Cu–N(5)–C(14)	109.1(4)
–	–	Cu–N(8)–C(15)	126.7(4)
–	–	Cu–N(1)–C(4)	111.0(4)

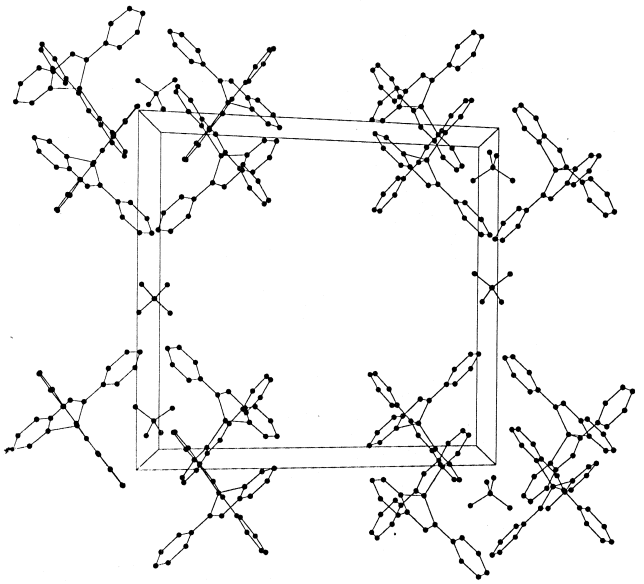


Fig. 2. Packing in the unit cell viewed along the *c*-axis.

planes (mean deviation 0.009 and 0.037 Å, respectively) and the dihedral angle is 87°. This suggests distorted tetrahedral CuN_4 coordination. Pendant phenyl rings are individually planar and slightly deviated from the planarity of the respective chelate rings (dihedral angle 3.0° for C_5–C_{10} ring with first chelate ring and 6.8° for C_{15}–C_{20} ring with the second chelate ring). These two pendant phenyl rings are inclined at an angle of 84.1°. Each ligand coordinates in a bidentate fashion with Cu–N(pym) (Cu–N(1)/Cu–N(5)) bond lengths comparable to other Cu^I-complexes of heterocyclic *N*-donor ligands [53–55]. The N=N bond distance (N(3)–N(4), 1.257(7); N(7)–N(8), 1.260(6) Å) are crystallographically indistinguishable. The N–N distance is not available in the free ligand, however, data available in some free azo ligands suggest that it is nearly 1.25 Å [32–38]. Thus, the N–N distance is slightly elongated and may be due to coordination of the azo–N function. The Cu–N(azo) (N(azo): N(4), N(8); 2.000(4), 1.981(5)Å) is shorter than the Cu–N(pym) (N(pym): N(1), N(5); 2.010(4), 2.038(4) Å) bond distances. The shortening may be due to greater π-back bonding, $d\pi(Cu)\rightarrow\pi^*$(azo) [32–38]. The average chelate [N(1)–Cu–N(4), N(5)–Cu–N(8)] angle is 79.1° and is the origin of the structural distortion from tetrahedral geometry. This is also reflected by other angular parameters around Cu(I) in the coordination sphere. N(1)–Cu–N(8) and N(4)–Cu–N(5) are 127.65(18) and 126.65(18)°, respectively. These are certainly closer to the tetrahedral value (109.8°) and expectedly deviated from the square planar angle (180°). Therefore, the overall coordination geometry about Cu(I) is corroborated with the distorted tetrahedral structure.

3.3. Spectral studies

Arylazopyrimidines exhibit $\nu_{(N=N)}$ and $\nu_{(C=N)}$ at 1420–1430 and 1600–1610 cm^{-1}, respectively. Pyrimidine ring stretching modes appear at the usual position [47]. $[Cu(aapm)_2](ClO_4)$, the $\nu_{(N=N)}$ appears at 1310–1325 cm^{-1} and is red shifted by 60–70 cm^{-1}. This has been attributed to the presence of $d(Cu)\rightarrow\pi^*$(aapm) back bonding [7–10]. All the complexes exhibit a structureless band approx. 1090 cm^{-1} corresponding to $\nu_{(ClO_4)}$ suggesting lack of significant perchlorate coordination in the solid state [53–55].

The electronic spectra of the complexes were recorded in MeOH solution in the range 900–220 nm. The spectral data are given in Table 3. The absorptions below 400 nm are due to intraligand charge transfer transitions (in comparison to free ligand values) and are not considered further. The visible range of the spectrum is dominated by metal-to-ligand charge transfer (MLCT) transition which is a characteristic feature of the copper(I) complexes when

Table 3
Microanalytical, UV–Vis and redox data

Compound	Elemental analyses[a]				UV–VIS spectral data[b]	Cyclic voltammetric data[c], E^0, V(ΔE_p, mV)	
	C	H	N	Cu	λ_{max}/nm ($10^3\varepsilon/M^{-1}\,cm^{-1}$)	Cu(II)/Cu(I)	Ligand reductions
$[Cu(papm)_2](ClO_4)$ (**4**)	45.11 (45.20)	3.09 (3.01)	20.96 (21.09)	12.10 (11.96)	708(0.87), 560(3.35), 362(12.56)	0.69(100)	−0.35(100), −0.81(120), −1.21(130)
$[Cu(o\text{-}tapm)_2](ClO_4)$ (**5**)	47.17 (47.23)	3.52 (3.58)	20.14 (20.04)	11.07 (11.36)	800(2.49), 635(5.21), 572(14.18), 370(18.74)	0.66(90)	−0.41(80), −0.88(110), −1.34(140)
$[Cu(m\text{-}tapm)_2](ClO_4)$ (**6**)	47.08 (47.23)	3.64 (3.58)	20.12 (20.04)	11.74 (11.36)	790(2.22), 630(4.11), 567(15.79), 368(16.66)	0.63(100)	−0.38(75), −0.77(100), −1.40(150)
$[Cu(p\text{-}tapm)_2](ClO_4)$ (**7**)	47.31 (47.23)	3.62 (3.58)	19.92 (20.04)	11.78 (11.36)	713(0.47), 564(1.59), 377(6.91)	0.64(100)	−0.34(68), −0.72(120), −1.38(140)
$[Cu(p\text{-}Clpapm)_2](ClO_4)$ (**8**)	39.91 (40.00)	2.38 (2.33)	18.73 (18.67)	10.65 (10.58)	720(1.05), 556(3.40), 381(9.68)	0.76(90)	−0.24(70), −0.58(80), −1.21(140)

[a] Calculated values are in parentheses.
[b] Solvent: MeOH.
[c] Solvent: propylene carbonate; supporting electrolyte TBAP (0.1 M), solute concentration ~10^{-3} M, Pt-bead working electrode, scan rate 0.05 V s^{-1}, SCE reference and Pt-wire auxiliary electrode.

bonded with a conjugated organic chromophore [6–21]. A similar situation is observed [7–10] in $Cu(aap)_2^+$ and $Cu(aai)_2^+$ complexes. This is likely for a tetrahedrally distorted CuN_4^+ coordination sphere. A single crystal X-ray structural study supports this behavior (vide supra). The spectral data in Table 3 reveal that $[Cu(o\text{-tapm})_2](ClO_4)$ (**5**) and $[Cu(m\text{-tapm})_2](ClO_4)$ (**6**) exhibit three MLCT transitions of high intensity while others show two observable transitions of relatively low intensity. This may be due to the steric effect provided by *o*-Me/*m*-Me in the aryl ring leading to stronger tetrahedral distortion and improved stabilization of copper(I).

All the chelates display highly resolved ^1H NMR spectra in $CDCl_3$. The spectral data are collected in Table 4. The proton numbering pattern is shown in structure **3**. Assignment of individual proton resonance are made by spin–spin interaction, comparative integration, chemical shift and changes therein on substitution.

The spectra of the ligand is clearly divided into two portions; the downfield part is due to pyrimidine protons [47] (4–6-H) and the upfield signals refer to azoaryl protons (8–12-H). Aryl protons are affected by substitution; for 10-methyl substitution (*p*-tapm) the signals are shifted upfield owing to inductive electron release by the methyl group and the reverse effect is seen for 10-Cl substitution in *p*-Clpapm due to the electron withdrawing effect of the –Cl group with respect to papm. The signal movement is corroborated with the electronic effect of the substituents. 8-Me in *o*-tapm appears at 2.7 ppm whereas 9-Me and 10-Me in *m*-tapm and *p*-tapm appear at 2.5 and 2.4 ppm, respectively. The characteristic signal in *m*-tapm is the appearance of a singlet for 8-H.

In complexes the protons are perturbed irregularly. The data in Table 3 reveal that the pyrimidine protons are mostly affected compared to aryl protons. The 6-H signal is downfield shifted by approx. 1 ppm while 4- and 5-H are upfield shifted. Aryl protons (8–11-H) remain almost undisturbed with a small upfield shifting of the 12-H signal. It is noted that all the protons 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 supported by tetrahedral CuN_4 geometry from the solid state structural study.

3.4. Redox studies

The redox behavior of the complexes in propylene carbonate solution was examined under a nitrogen environment cyclic voltammetrically at a platinum disk working electrode using tetrabutylammonium perchlorate (NBu_4ClO_4) as a supporting electrolyte and the potentials are reported with reference to the SCE. The results were collected and are given in Table 2. The complexes $[Cu(aapm)_2](ClO_4)$ undergo a quasi-reversible oxidation–reduction reaction at approx. 0.63–0.76 V versus SCE (at 50 mV s^{-1} scan rate). The response is attributed to the copper(II)/copper(I) couple (Eq. (1)). The quasi-reversible character is

$$[Cu(aapm)_2]^{2+} + e^- \rightleftharpoons [Cu(aapm)_2]^+ \quad (1)$$

accounted from the ΔE_P ($E_{pa} - E_{pc}$) values under the conditions of measurements [7–10]. The redox data is correlated with the electron donating and withdrawing effects of the substituents in the azopyrimidine backbone. Ligand reductions are observed as negative to SCE; three consecutive reduction waves are observed at the negative side to SCE. These potentials may be due to reductions of azoimine functions in the ligand frame [7] analogous to azopyridine systems. The LUMO of the ligand can accommodate up to two electrons and the reduction may be represented by Eq. (2)

Table 4
^1H NMR spectra[a] of aapm and $[Cu(aapm)_2](ClO_4)$

Compound	δ, ppm (*J*, Hz)								
	4-H[b]	5-H	6-H[b]	8-H	9-H	10-H	11-H	12-H[b]	R
papm	8.24(7.0)	8.10[d]	8.24(7.0)	7.83[b](9.0)	7.45[d]	7.45[d]	7.45[d]	7.83(9.0)	–
o-tapm	8.18(7.0)	8.09[d]	8.18[b](7.0)	–	7.20[b](8.0)	7.50[c](8.0)	7.50[c](8.0)	7.75(8.0)	2.61
m-tapm	8.20(8.0)	8.11[d]	8.20(8.0)	7.58[d]	–	7.32[b](8.0)	7.32[c](8.0)	7.72(8.0)	2.54
p-tapm	8.20(7.4)	8.10[d]	8.20(7.4)	7.80[b](9.0)	7.31[b](8.0)	–	7.31[b](8.0)	7.80[b](9.0)	2.43
p-Clpapm	8.30(7.8)	8.14[d]	8.30(7.8)	7.88[b](8.0)	7.54[b](8.0)	–	7.54[b](8.0)	7.88[b](8.0)	–
(**4**)	8.11(7.0)	7.85[c](9.0)	9.20(7.0)	7.63[b](8.0)	7.50[d]	7.50[d]	7.50[d]	7.63(8.0)	2.64
(**5**)	7.98(8.0)	7.72[c](8.0)	9.15(8.0)	–	7.28[b](7.0)	7.38[c](8.0)	7.42[c](8.0)	7.63(8.0)	2.64
(**6**)	8.00(7.0)	7.72[c](8.0)	9.11(7.0)	7.43[e]	–	7.21[b](8.0)	7.38[c](8.0)	7.60(8.0)	2.51
(**7**)	7.95(7.4)	7.74[c](7.0)	9.04(8.0)	7.54[b](8.0)	7.17[b](8.0)	–	7.17[b](8.0)	7.54(8.0)	2.45
(**8**)	8.12(8.0)	7.85[c](7.0)	9.22(8.0)	7.70[b](7.4)	7.58[b](8.0)	–	7.58[b](8.0)	7.70(7.4)	–

[a] In $CDCl_3$, temp. 295 K.
[b] Doublet.
[c] Triplet.
[d] Multiplet.
[e] Singlet.

$$-N{=}N- \overset{+e^-}{\rightleftharpoons} [-N\cdots N-]^- \overset{+e^-}{\rightleftharpoons} [-N-N-]^{=} \quad (2)$$

In principle, four electrons will enter into two chelated ligand systems. The difference in the potential of the first two successive reduction couples is 0.4–0.5 V whereas the third couple appears at a more negative position; the difference between the second and the third couple is 0.7–0.8 V. This is expected as the first two electrons may accommodate at two π^*(azo) orbitals of the chelated azopyrimidine fragment and the third one will enter into the singly occupied π^* orbital.

The potential is sensitive to the substituents in the azoaryl fragment. A decrease in σ-donor capacity of the substituent in the ligand frame increases both the Cu(II)/Cu(I) and the bound-ligand reduction potentials.

An observable deviation is observed for [Cu(*o*-tapm)$_2$]ClO$_4$ (**5**) where the Cu(II)/Cu(I) couple appears at a higher potential than [Cu(*m*/*p* tapm)$_2$]ClO$_4$ (**6**/**7**). This may be due to steric crowding provided by the *o*-Me group leading to a more tetrahedral distortion and hence better stabilization of the copper(I) system.

The controlled potential coulometry of **4** at 0.9 V fully corroborates the one electron stoichiometry of the couple. The copper(II) congener, formed by electrolysis, shows an identical response but is reductive in nature. There are two other studies available on the stabilization of copper(I) by azoimine function; 2-(arylazo)pyridines (aap) [7], $[Cu(aap)_2]^+$, $E_{1/2}=0.61$–0.63 V versus SCE and 2-(arylazo)imidazoles (aai) [8–10] $[Cu(aai)_2]^+$, $E_{1/2}=0.4$–0.5 V versus SCE. The potential of the present series of complexes are highest amongst the reported values. This may be due to the highest π-acidity of the pyrimidines which follows the order pyrimidine>pyridine>imidazole [27–29]. 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.

Supplementary data

Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request and the deposition number is 103230.

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