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Copper coordination compounds of chelating imidazole-azo-aryl ligand. The molecular structures of bis[1-ethyl-2-(*p*-tolylazo) imidazole]-bis-(azido)copper(II) and bis[1-methyl-2-(phenylazo) imidazole]-bis(thiocyanato)copper(II)†

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Reaction of $Cu(ClO_4)_2\ 6H_2O$ with 1-alkyl-2-(arylazo)imidazole [RaaiR′ where R = H (**a**), Me (**b**); R′ = Me (**1**), Et (**2**)] and NaN_3/NH_4SCN (1 : 2 : 2 mole ratio) form mononuclear complexes $[Cu(RaaiR')_2(N_3)_2]$ (**3,4**) and $[Cu(RaaiR')_2(SCN)_2]$. DMF (**5,6**). The complexes are characterized by elemental, spectral, electrochemical and other physicochemical results. The structures of both the complexes are confirmed by the single crystal X-ray diffraction studies of $[Cu(MeaaiEt)_2(N_3)_2]$ (**4b**) and $[Cu(HaaiMe)_2(SCN)_2]$. DMF (**5a**). The complexes are reduced to $[Cu(RaaiR')_2]^+$ by ascorbic acid. However, air oxidation of $[Cu(MeaaiEt)_2](ClO_4)$ in presence of N_3^-/SCN^- produces $[Cu(MeaaiEt)_2(N_3/NCS)_2]$.

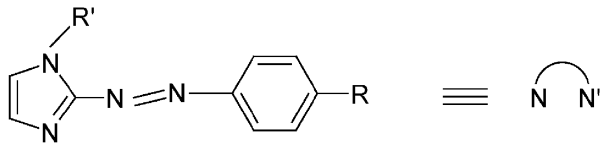
Introduction

Copper complexes are of considerable interest mainly due to their variety in coordination geometry, exquisite colors, technical application dependent molecular structures and spectroscopic properties and their biochemical significance.[1] Hexacoordinated copper(II) complexes exhibit tetragonal distortion because of the Jahn Teller effect[2] and the tetrahedral geometry is generally preferred in the copper(I) state. The π-acidic chelating function with N-heterocycle donor group, azoimine (–N=N–C=N–)[3–7] is an efficient agent to stabilize the copper(I) state. A large number of copper(I) complexes of azoimine function have been reported recently.[5–7] Arylazoimidazole has a π-acidic azoimine function and a stabilized low valence metal redox state like, Cu(I),[6,7] Fe(II),[8] Ru(II),[9] Os(II).[10] However, the reaction condition, choice of solvent, counter ion and the structure, denticity, nature of donor centres of ligands may regulate the oxidation state and geometry of the metal ion.[2–7] The reaction of copper(II) salts with 1-alkyl-2-(arylazo)imidazole in hydroxy solvents, even in air, has synthesized copper(I) complexes. Under the identical reaction conditions addition of NaN_3 or NH_4SCN to the mixture of copper(II) perchlorate and RaaiR′ has isolated $[Cu(RaaiR')_2(X)_2]$ (X = N_3, SCN). The molecular structure of representative complexes of bis-(azido)-copper(II) and bis-(thiocyanato)-copper(II) have been characterized by X-ray crystallography. The spectroscopic and structural characterizations are detailed below.

Results and discussion

The complexes

Four ligands belonging to the azoimine family (–N=N–C=N–) of 1-alkyl-2-(arylazo)imidazole (RaaiR′) are used in this work.



RaaiR′

R = H (**a**), Me (**b**); R′ = Me (**1**), Et (**2**)

Methanolic solutions of $Cu(ClO_4)_2.6H_2O$ and the appropriate ligand in 1 : 2 mole ratio have been reacted followed by the addition of aqueous solution of NaN_3 or NH_4SCN (2 equiv.). The slow evaporation of the solution isolates dark colored crystalline compounds. The complexes have been characterized as $[Cu(RaaiR')_2(X)_2]$ [X = N_3^- (**3,4**); SCN^- (**5,6**)]. The ligands are unsymmetric N,N′-chelator [N = N(imidazole); N′ = N(azo)] and the pseudooctahedral $M(N,N')_2X_2$ may exist in five stereoisomeric forms. In Ru(II)-complexes $Ru(N,N')_2Cl_2$ we have isolated and characterized four isomers.[9,10] With reference to coordination pairs of Cl,Cl; N,N; N′,N′; the isomers are abbreviated as *trans-cis-cis* (*tcc*); *trans-trans-trans* (*ttt*); *cis-trans-trans* (*ctc*); *cis-cis-trans* (*cct*) and *cis-cis-cis* (*ccc*).

The cobalt(II) complexes, $[Co(N,N')_2(N_3)_2]$ have been characterized as *ccc* isomer.[11] The present series of complexes, $Cu(RaaiR')_2(X)_2$ shows *cct* coordination sequence. We have been failed to isolate dihalo or diaqueo complexes

† Electronic supplementary information (ESI) available: tables of UV-Vis spectral, voltammetric and ESR data and UV-Vis, ESR spectra. See http://www.rsc.org/suppdata/nj/b4/b406445c/
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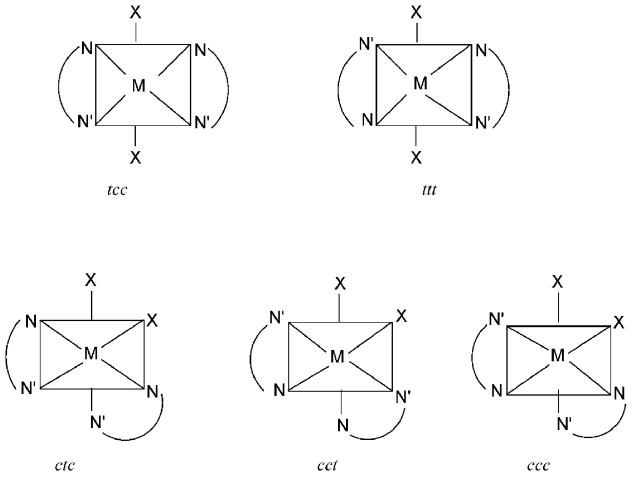


$[Cu(RaaiR')_2(H_2O)_2](ClO_4)_2$. Mixtures of $CuCl_2$ or $CuBr_2$ or $Cu(ClO_4)_2.6H_2O$ and ligands in methanol do not synthesize copper(II) complexes, rather the Cu(I)-complex $[Cu(RaaiR')_2]^+$ has been separated.[6c]

The complexes $Cu(RaaiR')_2X_2$ (**3–6**) are sufficiently soluble in alcohol, chloroform, dichloromethane, acetonitrile but insoluble in hydrocarbons (hexane, benzene, toluene). They are non-conducting in methanol/acetonitrile solution. The microanalytical data and copper estimation (idometric method) support the composition of the complexes. At room temperature their effective magnetic moments lie 1.8–1.9 B.M., typical of $S = 1/2$ (Cu(II)).

Crystal structures

Complexes $[Cu(MeaaiEt)_2(N_3)_2]$ (**4b**) and $[Cu(HaaiMe)_2(NCS)_2]$ (**5a**) were characterized by single crystal X-ray crystallography. Perspective views of the molecules are shown in Figs. 1 and 2. Selected bond lengths and angles are given in Tables S1 and S2 in the supplementary data.† In the discrete molecule copper(II) is surrounded by two ligands and two pseudohalides. The ligand serves as an unsymmetric N,N′-chelating agent (N refers to imidazole-N and N′ refers to azo-N donor centres) and two ligands chelate in an arrangement to give *cis*-N,N and *trans*-N′,N′ stereochemistry. Pseudohalides (N_3^- or NCS^-) coordinate in a *cis*-fashion around Cu(II). Thus, the coordination sequence of pseudohalides, imidazole-N(N) and azo-N(N′) describe *cis-cis-trans* stereochemical orientation.[9,10] The geometry of the copper ion is elongated

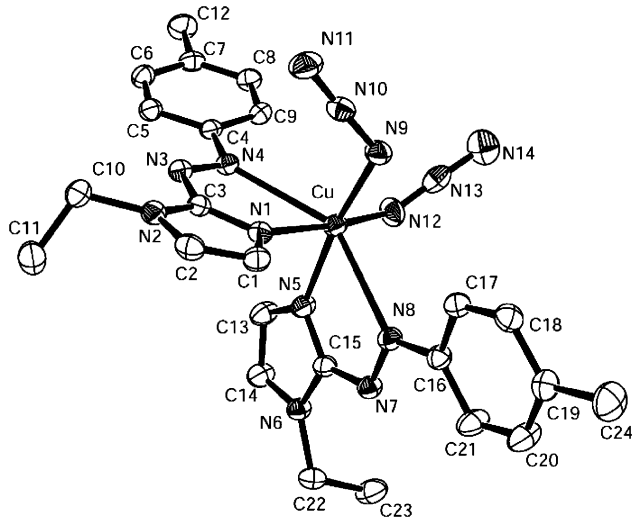


Fig. 1 Ortep view of $[Cu(MeaaiEt)_2(N_3)_2]$ (**4b**).

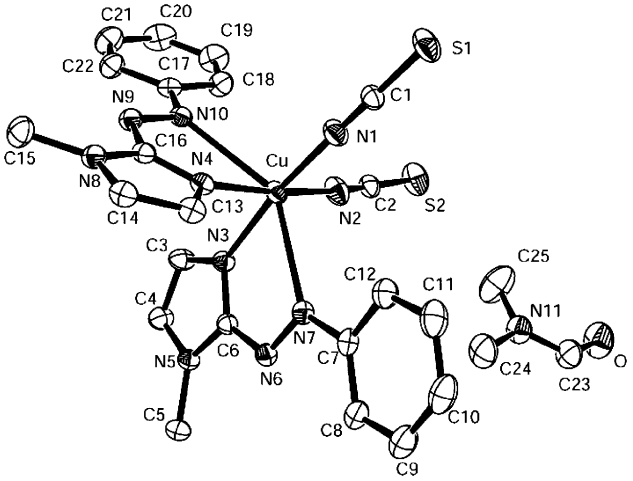


Fig. 2 Ortep view of $[Cu(HaaiMe)_2(NCS)_2]$.DMF (**5a**).

octahedral; the equatorial plane is formed by the two imidazole nitrogens (each from an individual ligand) and two pseudohalide N donor centres. Two axial positions are occupied by two azo-N donor centres of two HaaiMe. Thiocyanate (–NCS) is an ambidentate ligand. However, in the present example it coordinates as an N-donor ligand. Although N_3^- and NCS^- are versatile bridging agents,[11] in the present case they are behaving as unidentate ligands. In **4b** the N–Cu–N bond angles subtended by the chelating ligands are N(1)–Cu–N(4), 68.70(8)°; N(5)–Cu–N(8), 68.05(8)°. Similarly, in $[Cu(HaaiMe)_2(NCS)_2]$ (**5a**) the chelate angles are N(3)–Cu–N(7) 69.61(9)° and N(4)–Cu–N(10) 69.12(9)°. The deviation of the angle from the ideal 90° for a regular octahedron is the result of steric requirements of the bidentate ligands. Other angles in the chelated motif also deviate in either direction from the regular five membered ring. Arylazoimidazole moiety is almost planar with deviation from the least square plane <0.04 Å. The chelate rings constitute good planes (mean deviation ~ 0.03 Å). The pendant aryl ring makes a small dihedral with the chelate plane and lies in the range 8–11°. The proposed molecular planes in an octahedral geometry are found to be heavily distorted in these structures. The distortion in CuN_6 coordination is supported from the bond parameters of the structures.

There are three types of N-donor centres: N(imidazole), N(azo) and N(azido)/N(thiocyanato). N(azo) requires considerably more room than the other two N-donor types.[12] There are at least two steric reasons for this. First, the N(azo) belongs to exocyclic N=N along with a pendant aryl group; thus the van der Waals repulsion will be greater than for N(imidazole). Secondly, the N(azido) has larger s-character compared to N(azo) (because the resonating structure of N_3^- carries triple bonded nitrogens of sp hybridization while N=N in azo carries sp^2 hybridisation) and thus N(azo) is more space demanding. The same argument may be extended to the N(thiocyanato) group. Distortion is not only of electronic origin (Jahn–Teller distortion for d,[9] $Cu(II))^2$ but also arises from the steric effect of N-donor centres. The lowering in overall symmetry is manifested by the elongation of axial bonds and two N(azo) donor centres occupy two axial positions. The Cu–N(azo) distances lie in the range of 2.6–2.7 Å. The longest Cu–N distance in the series is the Cu–N(azo) distance. However, The Cu–N(azo) distances are less than that of the sum of the van der Waals radii of Cu(II) (1.40 Å) and N(azo) (1.55 Å).[13] This implies covalent interaction of N(azo) and Cu(II). The Cu(II) has some preferential binding to N(imidazole)[1b]compared to N(azo). The Cu–N(imidazole) distances are equal in the square plane of $[Cu(MeaaiEt)_2(N_3)_2]$ (**4b**) [Cu–N(1)/N(5); 2.011(2)] and lie in the reported range (1.96–2.15 Å).[14] However, Ru(II),[9] and Os(II)[10] show higher

affinity to N(azo) than to the N(imidazole) centre. Pd(II)[15] and Pt(II)[16] prefer the imidazole-N center due to the better retro-donation offered by azo-N compared to the imidazolyl-N system. This indirectly supports the chemical preference for the Cu(II) to the imidazole group. The structural studies of Co(II),[11] Zn(II),[17] Cd(II)[18] and Hg(II)[19] complexes of arylazoimidazoles show schizophrenic affinity to imidazole-N. The sum of the equatorial bond angles (plane is constituted by two imidazole-N and two pseudohalide-N donor centres) at Cu is 358.58° in $[Cu(MeaaiEt)_2(N_3)_2]$ or 361.14° in $[Cu(HaaiMe)_2(NCS)_2]$. It shows that the metal ion is essentially in the mean plane. A significant deviation from the trans angle is observed for two axial N-donors over that of equatorial N-donors in the chelated fragment Cu(HaaiMe) and Cu(MeaaiEt). In the equatorial plane the trans angles are about 170° [N(1)–Cu–N(12), 170.23(12)°; N(5)–Cu–N(9), 170.38(10)°] in $Cu(MeaaiEt)_2(N_3)_2$; N(2)–Cu–N(4), 172.14(11); N(1)–Cu–N(3), 171.59(10)° in $Cu(HaaiMe)_2(NCS)_2$. The axial ∠N–Cu–N is <150° [N(4)–Cu–N(8), 146.92(7)° in $[Cu(MeaaiEt)_2(N_3)_2]$ and N(7)–Cu–N(10), 143.38(8)° in $[Cu(HaaiMe)_2(NCS)_2]$]. The large deviation (~35°) from the trans angle (180°) is undoubtedly from the combined contribution of short chelate angle, removing inherent degeneracy of d^9 configuration and steric requirement of azo-N centres. The azido and thiocyanato bond lengths and angles are within reported data.[20] The azo, N=N, distances in both the complexes lie within 1.26–1.27 Å which is longer than the free ligand value (1.250(1) Å).[21] The small extension of the azo bond may be due to the manifestation of structural strain arising out of the small chelate bite angle and the steric requirement of the chelated azoimine fragment as well as weak d(Cu)→π*(azo) back donation.

Spectral studies

Infrared spectra show characteristic strong transmission at 2031–2039 cm^{-1} along with a weak band at 2045–2047 cm^{-1} for $[Cu(RaaiR')_2(N_3)_2]$ (**3/4**). These correspond to $\nu_{asym}(N_3)$. This supports mononuclear mono-dentate N_3^- bonding in **3/4**. The $[Cu(RaaiR')_2(SCN)_2]DMF$ (**5/6**) complexes show characteristic strong transmission at 2098–2105 cm^{-1} along with a weak band at 2090–2093 which correspond to $\nu_{asym}(NCS^-)$. The chelated ligand RaaiR′ shows characteristic transmission at 1600–370 cm^{-1}. Moderately intense stretching at 1585–1600 and 1435–1440 cm^{-1} is due to ν(C=N) and ν(N=N) respectively.

The solution spectra of these complexes are recorded in MeCN at 200–1100 nm. To test the solution stability of the complexes the solution is left overnight and it is observed whether the spectral profile pattern and intensity has remained unchanged. The visible region shows two weak shoulders and these are of d-d origin, as revealed by their low intensities (see supplementary data†). The d-d absorptions of $[Cu(RaaiR')_2(NCS)_2]$ (**5,6**) are blue shifted by 10–20 nm compared to those of $[Cu(RaaiR')_2(N_3)_2]$ (**3,4**). High intense transition of 400–475 nm may be assigned to metal-to-ligand charge transfer transitions; the enhanced intensity of thiocyanato derivatives, **5,6**, may be suggestive of stronger distortion compared to azido complexes (**3,4**). The distortion may be indicated by the deviation of axial N–Cu–N bond angles from 180°. In $[Cu(HaaiMe)_2(NCS)_2]$ the angle is 143.30(8)° which is 146.92(7)° in $[Cu(MeaaiEt)_2(N_3)_2]$ (Tables S1 and S2 in the supplementary data†). It may also be argued that redox orbitals composed of both Cu and N_3/NCS are involved in the MLCT processes. Other transitions below 400 nm may be assigned to intraligand charge transfer transitions. The reflectance spectra of the complexes show almost similar spectral pattern and symmetry as in solution, implying that the solid-state structures are retained in solution. The shift of the band in the visible region to lower energy on going from solution to the solid state is consistent with increased interaction in solution. The d-d bands are shifted to longer wavelength on going from thiocyanato (700–705 nm) to azido (710–720 nm) complexes. This is consistent with a higher ligand field factor of N-coordinated –NCS than $–N_3$.[12]

Electrochemistry

Fig. 3 shows the cyclic voltammetric response exhibited by the complexes in MeCN at a Pt-disk milli-electrode in the potential range +1.6 to −1.6 V *versus* Ag/AgCl, Cl^- reference electrode. A reductive response is observed at ~0.4 V and the quasi-reversibility has been assessed from the large peak-to-peak separation (ΔE_P > 180 mV). The ratio of ip_c/ip_a remains near to 1 at the scan rate 0.05 to 0.2 V s^{-1}. The one-electron nature of the redox process is estimated on comparing with the current height of the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ couple. The redox response is referred to Cu(II)/Cu(I). On scanning the programme in the –ve direction to −1.4 V two quasi-reversible couples are observed at −0.5 to −0.6 V ($\Delta E_P \geq 160$ mV) and −0.9 to −1.0 V (ΔE_P > 180 mV) (Fig. 3). They may be assigned to reduction of the azo group [(–N=N–)/(–N=N–)$^-$] of the chelated ligands. The voltammogram also shows a broad cathodic peak at −1.1 V with an anodic counter part at −0.1 V, possibly due to the Cu(I)/Cu(0) couple.[22] The reduced Cu(0) is absorbed on the electrode surface as evidenced from the narrow width of the anodic response with a large peak current. On carrying out the experiment with back scan going to negative potential to −0.6 V does not observe such large anodic current at −0.1 V. Redox potentials are shifted to less positive values on going from $[Cu(MeaaiEt)_2(N_3)_2]$ to $[Cu(HaaiMe)_2(NCS)_2]$ (data are available from electronic supplementary information†). On the electrode surface Cu(II) is reduced to Cu(I) and is stabilized by coordinated arylazoimidazole which may be reduced further to the Cu(0) state on scanning to the cathodic side. $Cu(RaaiR')_2^+$ exhibit Cu(II)/Cu(I) oxidation couple at 0.4–0.5 V. Coulometric oxidation of $Cu(RaaiR')_2^+$ has generated stable $Cu(RaaiR')_2^{+2}$ at least on the electrochemical time scale.[6] The present series of complexes also exhibit quasi-reversible Cu(II)/Cu(I) couples at ~0.4 V.

EPR studies

The EPR spectra of the polycrystalline powdered complexes recorded at room temperature (298 K) are identical to those at liquid N_2 temperature (77 K). The low resolution of polycrystalline spectra is usual where copper centres are relatively closer together, the hyperfine splittings are poor due to paramagnetic exchange narrowing. However, the resolution is better in the solution, therefore, spectra (77 K) were used to determine the EPR parameters. The frozen solution spectra show better signal resolution that can be attributed to a single species. The EPR spectra of Cu(II) complexes provide information about hyperfine and superhyperfine structures which helps in defining the geometry and distortion of the complexes. The complexes show usual four line (^{63}Cu, $I = 3/2$) EPR spectra

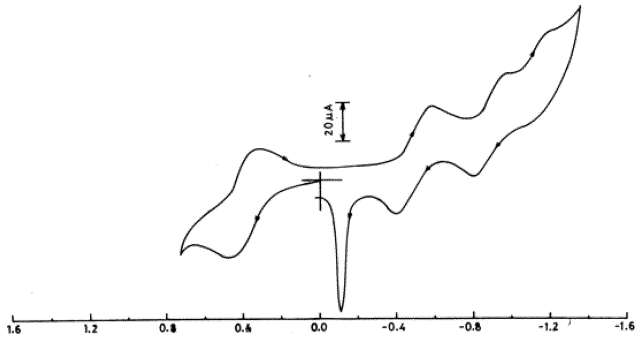


Fig. 3 Cyclic voltammogram of $[Cu(MeaaiEt)_2(N_3)_2]$ (**4b**).

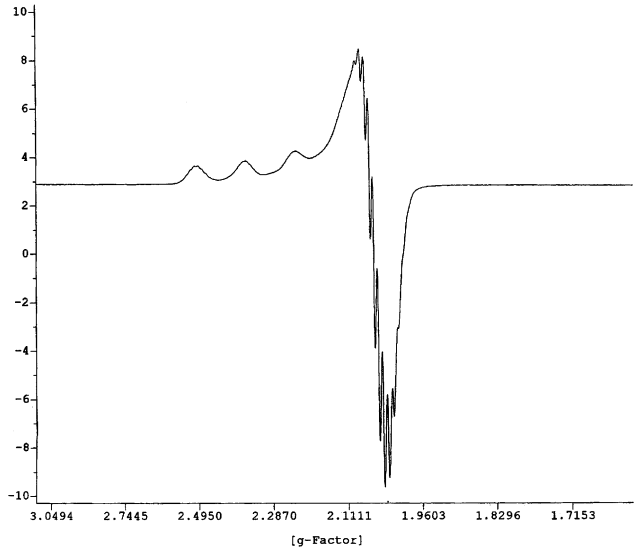
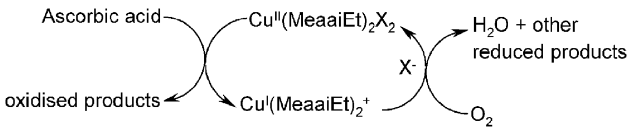


Fig. 4 ESR spectrum of $[Cu(HaaiMe)_2(SCN)_2]$ (**5a**).

and are anisotropic at higher magnetic field (data may be obtained from electronic supplementary information†). The three peaks of low intensity in the weaker field are considered to originate from the $g_{\|}$ component and $A_{\|}$ lies 150–160 $\times$ $10^{-4}cm^{-1}$. The calculated $g_{\|}$ and $g_{\perp}$ values for these complexes were 2.25 and 2.05 respectively. The relation $g_{\|} > g_{\perp} > 2.0023$ agrees with the ground state configuration of $d_{x^2-y^2}$. The axial symmetry parameter $G > 4$ $[G = (g_{\|} - 2)/(g_{\perp} - 2)]$ indicates there is no exchange interaction between copper centre.[14] This is in support of axially elongated octahedral geometry. The superhyperfine coupling constant $A_{\perp}$ average to 15 $\times$ 10^{-4} cm^{-1} and is in the range of Cu–N interaction.[14] For CuN_6 coordination there will be (2.6 + 1) 13 responses and they are observed, indeed (Fig. 4).

Redox interconversion, $Cu^{II} \leftrightarrow Cu^{I}$

The Cu(II)– Cu(I) interconversion is readily displaced in either direction depending on the nature of donor centres in complexing agent, anions and solvents. The ligand geometry, conjugated chelating function control the Cu(II)/Cu(I) redox potential.[22] The experiment has been carried out using two representative compounds of the series, $[Cu(MeaaiEt)_2X_2]$ where, $X^- = N_3^-$ (**4b**); NCS^- (**6b**). The complexes react with ascorbic acid in aqueous-methanol suspension and brown-red copper(I) complexes are precipitated as perchlorate salt upon addition of $NaClO_4$. Identity of reduced product has been established by matching the spectroscopic and cyclic voltammetric results of $[Cu(MeaaiEt)_2](ClO_4)$, reported earlier.[6] The compound is diamagnetic. The microanalytical data of the complex supports identity of the compounds (Anal. Found: C, 48.63; H, 4.65; N, 19.07; Cu, 10.80. Calc. for $C_{24}H_{28}N_8ClO_4Cu$: C, 48.73; H, 4.73; N, 18.95; Cu, 10.74%. The identity of Cu(I) compound has also been established by ^1H NMR spectrum and on comparing with the spectrum of directly synthesised $Cu(MeaaiEt)_2(ClO_4)$.)[6] However, we did not characterize ascorbic acid oxidized product. This proves that a reduction of Cu(II) to Cu(I) is associated with dissociation of Cu–N_3 (azido)/NCS(thiocyanato) bond along with stereochemical conversion to Td geometry. In a second experiment, to a methanolic suspension of $[Cu(HaaiMe)_2(N_3)_2]$ a solution of $NaNO_2$ (aqueous) was added and refluxed for 1 h in air. The solution color changed to deep red-brown. A crystalline compound was precipitated by reducing the volume of the solution to half of the original followed by the addition of $NaClO_4$. The compound so obtained was purified by crystallisation from CH_2Cl_2–MeOH. The spectroscopic (IR and UV-VIS), magnetic and voltammetric identification support the formation of the copper(I) complex $[Cu(HaaiMe)_2](ClO_4)$. The microanalytical data of the complex are as follows: *Anal.* Found: C, 44.78 H, 3.85; N, 20.75; Cu, 11.78. Calc. for $C_{20}H_{20}N_8ClO_4Cu$: C, 44.94; H, 3.74; N, 20.97; Cu, 11.89%. In another experiment, air was passed through the methanol–water suspension of $[Cu(MeaaiEt)_2](ClO_4)$ in the presence of excess NaN_3. A sparingly soluble compound in MeOH was isolated and spectral examination showed the presence of strong $\nu(N_3)$ at 2045 along with a weak signal at 2031 cm^{-1}. The spectral and magnetism study suggest the formation of $[Cu(MeaaiEt)_2(N_3)_2]$ complex. (Identity of the compound has been tested with microanalytical data: *Anal.* Found: C, 50.12; H, 4.91; N, 34.13; Cu, 10.89. Calc. for $C_{24}H_{28}N_{14}Cu$: C, 50.03; H, 4.86; N, 34.05; Cu, 11.04%.) Similar reaction with $Cu(MeaaiEt)_2(NCS)_2$ has yielded an insoluble product. We did not proceed further. However, $[Cu(MeaaiEt)_2](ClO_4)$ can not be oxidized to Cu(II)-complex upon exposure to air.



Conclusion

This paper describes the mononuclear azido and thiocyanato Cu(II) complexes of 1-alkyl-2-(arylazo)imidazole. The complexes are characterized by different physicochemical methods and single crystal X-ray study. The complexes show redox interconversion of Cu(II) $\leftrightarrow$ Cu(I).

Experimental

Materials

$Cu(ClO_4)_2.6H_2O$, NaN_3, NH_4SCN were purchased from Loba Chemi, Bombay and 1-alkyl-2-(arylazo)imdazoles (RaaiR′) were prepared following the literature procedures.[11] All other chemicals and solvents are reagent grade. Solvents were used after drying.

CAUTION! Azido and perchlorate complexes of transition metal ions containing organic ligands are potentially explosive. Only a small amount of material should be prepared, and it should be handled with care.

Measurements

Microanalyses (C, H, N) were performed using a Perkin-Elmer 2400 CHNO/S elemental analyzer. Spectroscopic measurements were carried out using the following instruments: UV-VIS spectra, reflectance spectra, JASCO UV-VIS/NIR model V-570; IR spectra (KBr disk, 4000–200 cm^{-1}), JASCO FT-IR model 420. Room temperature magnetic moment was measured using vibrating sample 155 magnetometer at 298 K. Molar conductances (Λ_M) were measured in a Systronics conductivity meter 304 model using *ca.* 10^{-3} M solutions in MeCN. Electrochemical measurements were carried out with the use of computer controlled EG & G PARC VersaStat model 250 Electrochemical instrument using a Pt-disk working electrode. The solution was IR compensated and the results were collected at 298 K. The reported results are referenced to $Ag/AgCl,Cl^-$ in acetonitrile and are uncorrected for junction potential. ESR spectra were measured in MeCN solution at room temperature (298 K) and liquid nitrogen temperature (77 K) using Bruker ESR spectrometer model EMX 10/12, X-band ER 4119 HS cylindrical resonator.

Synthesis of mononuclear azido complex

[Cu(MeaaiEt)$_2$(N$_3$)$_2$] (4b). 1-Ethyl-2-(*p*-tolylazo)imidazole (MeaaiEt) (**2b**) (0.11 g, 0.50 mmol) in 2-methoxy ethanol (10 ml) was added dropwise to a stirred solution of Cu(ClO$_4$)$_2$.6H$_2$O (0.092 g, 0.25 mmol) in MeOH (10 ml) at 298 K. The greenish brown solution was stirred for 15 min. Then NaN$_3$ (0.03 g, 0.50 mmol) in MeOH (10 ml) was added to the brown solution. The color changed from greenish brown to red brown. The solution was filtered and then left undisturbed for a week. Dark brown crystals were obtained. The crystals were washed with water, methanol and ether and finally dried *in vacuo*. Yield was 0.10 g, (70%).

The microanalytical data of the complex are as follows, [Cu(MeaaiEt)$_2$(N$_3$)$_2$] (**4b**): *Anal.* Found: C, 50.15; H, 4.76; N, 34.16; Cu, 10.62. Calc. for C$_{24}$H$_{28}$N$_{14}$Cu: C, 50.03; H, 4.86; N, 34.05; Cu, 11.04%.

All other complexes were prepared by the same procedure. In all cases, crystalline products were obtained. The yield varied from 70–75% and microanalytical data of the complexes are as follows. [Cu(HaaiMe)$_2$(N$_3$)$_2$] (**3a**): *Anal.* Found: C, 46.08; H, 3.91; N, 37.60; Cu, 12.21. Calc for C$_{20}$H$_{20}$N$_{14}$Cu: C, 46.19; H, 3.85; N, 37.73; Cu, 12.23%; [Cu(HaaiEt)$_2$(N$_3$)$_2$](**4a**) *Anal.* Found: C, 48.31; H, 4.29; N, 35.85; Cu, 11.44. Calc. for C$_{22}$H$_{24}$N$_{14}$Cu: C, 48.22; H, 4.38; N, 35.79; Cu, 11.58%; [Cu(MeaaiMe)$_2$(N$_3$)$_2$] (**3b**): *Anal.* Found: C, 48.30; H, 4.31; N, 35.84; Cu, 11.44. Calc. For C$_{22}$H$_{24}$N$_{14}$ Cu: C, 48.22; H, 4.38; N, 35.79; Cu, 11.60%.

Synthesis of mononuclear thiocyanato complexes

[Cu(HaaiMe)$_2$(SCN)$_2$].DMF (5a). 1-Methyl-2-(phenylazo) imidazole (HaaiMe) (**1a**) (0.094 g, 0.50 mmol) was dissolved in *N*,*N*-dimethylformamide (10 ml) and added dropwise to the stirred solution of Cu(ClO$_4$)$_2$.6H$_2$O (0.092 g, 0.25 mmol) in MeOH (10 ml) at 298 K. NH$_4$SCN (0.033 g, 0.50 mmol) in MeOH (10 ml) was added dropwise to the greenish brown solution and stirred for 15 min. The solution was then filtered and left undisturbed for a week. The dark brown crystals were collected by filtration, washed with aqueous methanol (1 : 1, v/v) and finally with ether and then dried in *vacuo*. Yield was 0.11 g, (70%).

The microanalytical data of the complex are as follows, [Cu(HaaiMe)$_2$(SCN)$_2$].DMF (**5a**) *Anal.* Found: C, 48.10; H, 4.38; N, 24.59; Cu, 10.01. Calc. for C$_{25}$H$_{27}$N$_{11}$S$_2$OCu: C, 48.02; H, 4.32; N, 24.63; Cu, 10.16%.

All other complexes were prepared by the same procedure. In all cases, crystalline products were obtained. The yield varied from 70–75% and microanalytical data of the complexes are as follows. [Cu(HaaiEt)$_2$(SCN)$_2$].DMF (**6a**) *Anal.* Found: C, 49.71; H, 4.79; N, 23.65; Cu, 9.34. Calc. for C$_{27}$H$_{31}$N$_{11}$S$_2$OCu: C, 49.66; H, 4.74; N, 23.58; Cu, 9.73%; [Cu(MeaaiMe)$_2$(SCN)$_2$].DMF (**5b**): *Anal.* Found: C, 49.74; H, 4.81; N, 23.67; Cu, 9.48. Calc. For; C$_{27}$H$_{31}$N$_{11}$S$_2$OCu: C, 49.66; H, 4.74; N, 23.58; Cu, 9.73%; [Cu(MeaaiEt)$_2$(SCN)$_2$].DMF (**6b**): *Anal.* Found: C, 51.09; H, 5.19; N, 22.69; Cu, 9.12. Calc. for C$_{29}$H$_{35}$N$_{11}$S$_2$OCu: C, 51.15; H, 5.14; N, 22.62; Cu, 9.33%.

Copper(II)–copper(I) interconversion

[Cu(MeaaiEt)$_2$(N$_3$)$_2$] → [Cu(MeaaiEt)$_2$] (ClO$_4$). To methanolic suspension (15 ml) of [Cu(MeaaiEt)$_2$(N$_3$)$_2$] (0.14 g, 0.25 mmol) ascorbic acid (0.09 g, 0.50 mmol) in water (5 ml) was added with stirring. The brown suspension quickly changed to deep red-brown and stirring was continued for 30 min. To this solution NaClO$_4$ (2 ml, saturated) was added and the precipitated mass was filtered and washed with water and cold methanol. The residue was dried over CaCl$_2$ in a desiccator and subjected to column chromatography in a silica gel column prepared in CHCl$_3$. A brownish-red band was eluted by CHCl$_3$–MeOH (4 : 1, V/V) mixture and dried in air. Crystals were obtained by diffusion of CH$_2$Cl$_2$ solution of the complex to a hexane layer. Yield of [Cu(MeaaiEt)$_2$](ClO$_4$), 0.08 g, 57%. The microanalytical data of the complex are as follows: *Anal.* Found: C, 48.65; H, 4.69; N, 19.01; Cu, 10.81. Calc. for C$_{24}$H$_{28}$N$_8$ClO$_4$Cu: C, 48.73; H, 4.73; N, 18.95; Cu, 10.74%.

[Cu(MeaaiEt)$_2$] (ClO$_4$) → [Cu(MeaaiEt)$_2$(N$_3$)$_2$]. To a methanolic suspension of [Cu(MeaaiEt)$_2$] (ClO$_4$) (0.15 g, 0.25 mmol) an aqueous solution of NaN$_3$ (0.03 g, 0.50 mmol) was added and air was passed for 30 min and from time-to-time methanol was added to maintain the volume of the solution at 25 ml. The mixture was filtered and kept in freeze for 4 h. A brown precipitate was filtered and washed with water, and cold methanol. The compound was soluble in a mixture of 2-methoxyethanol and methanol (1 : 5, v/v) and was crystallized by evaporation in air for a week. Yield of [Cu(MeaaiEt)$_2$(N$_3$)$_2$], 0.08 g, 60%. The microanalytical data of the complex are as follows: *Anal.* Found: C, 50.11; H, 4.79; N, 34.11; Cu, 10.69. Calc. for C$_{24}$H$_{28}$N$_{14}$Cu: C, 50.03; H, 4.86; N, 34.05; Cu, 11.04%.

A similar reaction of [Cu(MeaaiEt)$_2$](ClO$_4$) with NH$_4$CNS was carried out and the product [Cu(MeaaiEt)$_2$(NCS)$_2$] was isolated in 35% yield. The microanalytical data of the complex are as follows: *Anal.* Found: C, 51.22; H, 4.53; N, 22.99; Cu, 10.38. Calc. for C$_{26}$H$_{28}$N$_{10}$S$_2$Cu: C, 51.36; H, 4.61; N, 23.04; Cu, 10.45%.

Table 1 Summarised crystallographic data for [Cu(MeaaiEt)$_2$(N$_3$)$_2$] and [Cu(HaaiMe)$_2$(SCN)$_2$].DMF

	[Cu(MeaaiEt)$_2$(N$_3$)$_2$] (**4b**)	[Cu(HaaiMe)$_2$(SCN)$_2$]. DMF (**5a**)
Empirical formula	C$_{24}$H$_{28}$N$_{14}$Cu	C$_{22}$H$_{20}$N$_{10}$S$_2$Cu, C$_3$H$_7$NO
Formula weight	576.15	625.27
Space group	Orthorhombic, *Pbca*	Triclinic, $P\bar{1}$
Unit cell dimensions		
a/(Å)	11.8632(8)	8.7294(7)
b/(Å)	17.6782(13)	12.1861(10)
c/(Å)	26.703(2)	15.3426(12)
α	90	72.435(1)
β(°)	90	79.6680(10)
ϒ	90	89.855(2)
V/Å^3	5600.2(7)	1528.5(2)
Z	8	2
λ/Å	0.71073	0.71073
μ (Mo-Kα)/mm^{-1}	0.821	0.889
D$_{calc}$/kg m^{-3}	1367	1359
Refine parameters	352	361
Observed data [$I > 2\sigma(I)$]	3521	4303
Reflection number get	6480	6765
$R_1[I > 2\sigma(I)]$	0.0546	0.0474
WR_2	0.1076	0.1369
Goodness of fit	0.99	0.89

X-Ray structure determination of [Cu(MeaaiEt)$_2$(N$_3$)$_2$] (4b) and [Cu(HaaiMe)$_2$(SCN)$_2$] DMF (5a) complexes

Data were collected with Siemens SMART CCD diffractometer using graphite-monochromatized Mo-Kα radiation (λ = 0.71073 Å) at 293 K for both **4b** and **5a**. Unit cell parameters were determined from least-squares refinement of setting angles with 2θ in the range $4.0 \leq 2\theta \leq 56.6°$ and $2.8 \leq 2\theta \leq 56.6°$ for 4b and **5a** respectively. Total data collected are 31899 (**4b**) and 15128 (**5a**) out of which unique data are 6480 (**4b**) and 6765 (**5a**). The *hkl* range are $-15 \leq h \leq 11$, $-23 \leq k$

≤ 23, $-29 \leq l \leq 33$ for **4b** and $-11 \leq h \leq 11$, $-15 \leq k \leq 16$, $-20 \leq l \leq 19$ for **5a**. A summary of the crystallographic data and structure refinement parameters are given in Table 1. Reflection data were recorded using the ω scan technique. Data were corrected for Lorentz polarization effects and for linear decay. Semi-empirical absorption corrections based on ψ-scans were applied. The structure was solved by heavy atom methods using SHELXS-97 and successive difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were fixed geometrically and refined using the riding model. In the final difference Fourier map the residual minima and maxima were [−0.28, 0.45 and −0.27, 0.42 (e/Å^3) for **4b** and **5a** respectively] carried out using SHELXL-97.

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