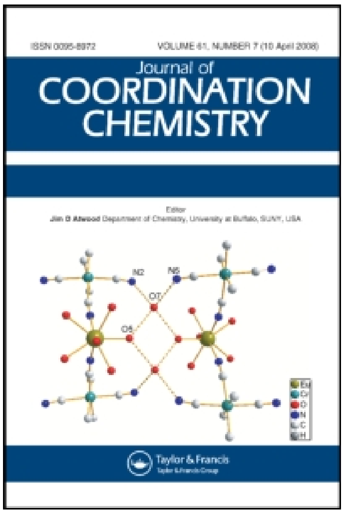

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Synthesis, characterization and comparative studies of mono- and dimeric copper(II) complexes containing tripodal ligands

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Synthesis, characterization and comparative studies of mono- and dimeric copper(II) complexes containing tripodal ligands

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Mono and dimeric bromo-bridged copper(II) complexes of the type [$CuBr_2$(L)] and [$Cu_2Br_2(L)_2$]$(ClO_4)_2$ containing nitrogen donor tripodal ligands L = 2,6-*bis*(pyrazol-1-yl) pyridine (bppy) or 2,6-*bis*(3,5-dimethylpyrazol-1-yl)pyridine (dmbppy) have been synthesized. All complexes have been characterized by elemental analysis, IR, ESR and electronic spectra and magnetic susceptibility and cyclic voltammetry measurements.

Keywords: Copper(II); Tripodal; Monomeric; Dimeric; Cyclic voltammetry; ESR

1. Introduction

Tripodal ligands are of interest due to coordination ability towards metal ions [1–9]. Transition metal complexes with tripodal ligands *viz*. 2,6-bis(pyrazol-1-yl)pyridine (bppy) and 2,6-*bis*(3,5-dimethylpyrazol-1-yl)pyridine (dmbppy) (figure 1) display interesting physical, chemical, magnetic and structural behaviors, generally showing high thermodynamic stability and kinetic inertness and forming supramolecular complexes [10–18]. There is considerable interest in the photophysical, photochemical and redox properties of these complexes [10, 13, 14, 16].

Present work describes the synthesis and characterization of complexes containing bppy or dmbppy. Single crystal X-ray structures of two of the complexes *viz*. [$CuBr_2$(bppy)] and [$Cu_2Br_2(bppy)_2$]$(ClO_4)_2$ have been reported from our laboratory [19]. [$CuBr_2$(bppy)] has a distorted square-pyramidal structure whereas [$Cu_2Br_2(bppy)_2$]$(ClO_4)_2$ is a di-bromo bridged Cu(II) dinuclear complex stabilized by weak interaction of ClO_4^- with Cu(II), exhibiting a pseudo-octahedral geometry around each copper center [20]. In this manuscript, we report synthesis and characterization of two new copper(II) complexes *viz*. [$CuBr_2$(dmbppy)] and [$Cu_2Br_2(dmbppy)_2$]$(ClO_4)_2$ and their comparative studies with copper(II) complexes of bppy.

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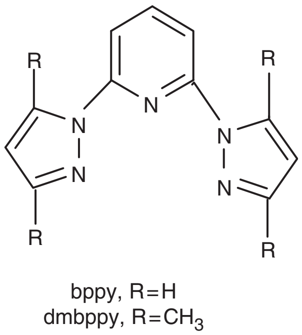

Figure 1. Structure of the tripodal ligands, when R=H, 2,6-*bis*(pyrazol-1-yl)pyridine (bppy), or R=CH_3, 2,6-*bis*(3,5-dimethylpyrazol-1-yl)pyridine (dmbppy).

2. Experimental

All chemicals used are of AR or chemically pure grade. Solvents were purified prior to use by standard methods. 2,6-Dibromopyridine, pyrazole and $CuBr_2$ were purchased from Merck. 3,5-Dimethylpyrazole was prepared by condensation of acetylacetone and hydrazine hydrate. The ligands bppy and dmbppy were prepared according to the published procedure [21]. Molar conductivity measurements of millimolar acetonitrile solutions were made on a Wayne-Kerr Automatic Precision B905 conductometer. IR spectra were recorded as KBr pellets using a Perkin-Elmer 983 or 410 Nicolet spectrophotometer. C, H and N analyses were carried out at SAIF, NEHU, Shillong. Spectroscopic grade solvents were used for cyclic voltammetry and UV–Vis measurements. UV–Vis spectra were recorded on a Beckman DU 650 spectrophotometer. Cyclic voltammetry experiments were recorded on a CH instruments electrochemical analyzer CHI 620B under nitrogen. Room temperature magnetic susceptibility measurements were carried out on a Sherwood Scientific magnetic susceptibility balance. ESR spectra were obtained from SAIF, IIT Chennai.

2.1. *Preparation of* $[Cu_2Br_2(dmbppy)_2](ClO_4)_2$

$Cu(ClO_4)_2 \cdot 6H_2O$ (0.370 g, 1 mmol), dmbppy (0.267 g, 1 mmol) and KBr (0.27 g, 0.25 mmol) were taken in acetonitrile (20 cm^3) and stirred for 4 h at room temperature. During the stirring, the color changed from blue to greenish blue. The solution was slowly evaporated at room temperature giving a green crystalline solid which was separated by filtration, washed with diethylether several times and dried *in vacuo*. Yield: 0.260 g (53%). Anal. Calcd for $C_{30}H_{34}N_{10}Br_2Cu_2Cl_2O_8$ (%), C, 35.3; H, 3.3; N, 13.7. Found: C, 35.2; H, 3.1; N, 13.9. IR(cm^{-1}, KBr pellets): 3134(w), 3107(w), 2982(w), 2923(w), 2851(w), 1616(s), 1564(s), 1488(s), 1475(s), 1391(m), 1321(s), 1144(s), 1112(s), 1087(s), 1056(s), 989(m), 841(w), 786(m), 742(m), 624(s), 576(w); UV–Vis (λ_{max}, MeCN): 314 nm, Λ_M (MeCN) = 245 $\Omega^{-1}cm^2mol^{-1}$, μ_{eff} at 25°C = 1.25 BM.

2.2. *Preparation of [$Cu_2Br_2(bppy)_2$](ClO_4)$_2$*

[Cu_2Br_2(bppy)$_2$](ClO_4)$_2$ was prepared according to the reported method [19]. Anal. Calcd for $C_{22}H_{18}N_{10}Br_2Cl_2O_8Cu_2$ (%): C, 29.1; H, 2.0; N, 15.4. Found: C, 28.8; H, 1.8; N, 14.9. IR(cm^{-1} KBr pellets): 3073(s, sh), 1624(s), 1591(s), 1499(m), 1483(s), 1403(s), 1349(s), 1314(m), 1210(m), 1150–1050(s, br), 971(m), 908(w), 805(m), 774(s), 625(s), 589(w); UV–Vis (λ_{max}, MeCN): 324 nm, Λ_M(MeCN) = 235 $\Omega^{-1}cm^2mol^{-1}$, μ_{eff} at 25°C = 1.31 BM.

2.3. *Preparation of [$CuBr_2$(dmbppy)]*

A mixture of $CuBr_2$ (0.223 g, 1 mmol) and dmbppy (0.267 g, 1 mmol) in acetonitrile (20 cm^3) was stirred for 1 h at room temperature. A yellowish green compound obtained was separated by filtration, washed with diethylether several times and dried *in vacuo*. Yield: 0.200 g (74%). Anal. Calcd for $C_{15}H_{17}N_5CuBr_2$ (%): C, 36.7; H, 3.5; N, 14.3. Found: C, 36.4; H, 3.7; N, 13.9. IR(cm^{-1}, KBr pellets): 3142(m), 3108(m), 2979(w), 2925(w), 1620(s), 1567(s), 1490(s), 1476(s), 1414(w), 1390(m), 1363(m), 1321(s), 1284(w), 1143(w), 992(m), 927(m), 826(w), 782(s), 769(s), 741(s), 616(m), 576(w); UV–Vis (λ_{max}, MeCN): 319 nm, Λ_M(MeCN) = 12 $\Omega^{-1}cm^2mol^{-1}$; μ_{eff} at 25°C = 1.75 BM.

2.4. *Preparation of [$CuBr_2$(bppy)]*

To a solution of $CuBr_2$ (0.223 g, 1 mmol) in acetonirile (10 cm^3), a solution of bppy (0.211 g, 1 mmol) in acetonitrile (10 cm^3) was added and the mixture was stirred at room temperature for 3 h. The solution was slowly evaporated at room temperature giving green crystalline compound which was separated by filtration, washed with diethylether several times and dried *in vacuo*. Yield: 0.160 g (71.7%). Anal. Calcd for $C_{11}H_9N_5CuBr_2$ (%): C, 30.4; H, 2.1; N, 16.1. Found: 30.1; H, 2.0; N, 15.9. IR(cm^{-1}, KBr pellets): 3129(m), 3118(m), 3086(m), 3071(m), 1620(s), 1589(s), 1519(s), 1481(s), 1400(s), 1351(s), 1314(m), 1176(m), 1072(m), 1058(s), 970(s), 843(w), 798(m), 775(s), 675(m), 636(m), 621(m), 597(w). UV–Vis (λ_{max}, MeCN): 315 nm; Λ_M(MeCN) = 10 $\Omega^{-1}cm^2mol^{-1}$; μ_{eff} at 25°C = 1.80 BM.

Caution: Perchlorate salts are potentially explosive. Suitable care should be taken while handling such compounds which should not be stored in large quantity.

3. Results and discussion

Copper(II) bromide complexes with tripodal ligands(L) (L = bppy or dmbppy) in acetonitrile yielded monomeric complexes [$CuBr_2$(L)], whereas copper(II) perchlorate in presence of KBr with L in acetonitrile gave bromo-bridged dinuclear complexes of the type [$Cu_2Br_2(L)_2$](ClO_4)$_2$. These compounds are air stable and soluble in various polar solvents *viz*. acetonitrile, alcohols *etc*. Microanalytical data of the monomeric and dimeric complexes suggested compositions [$CuBr_2$(L)] and [$Cu_2Br_2(L)_2$](ClO_4)$_2$

(L = bppy or dmbppy). Conductivity measurements of the monomeric complexes *viz.* [$CuBr_2(L)$] in acetonitrile showed molar conductance values in the range $10–12\,\Omega^{-1}\,cm^2\,mol^{-1}$, confirming the covalent nature of the bromo groups bonded to copper. The molar conductance of [$Cu_2Br_2(L)_2$](ClO_4)$_2$ (L = bppy, dmbppy) is observed in the range $235–245\,\Omega^{-1}\,cm^2\,mol^{-1}$, confirming 1 : 2 electrolytes [22]. The IR spectra of Cu(II) complexes showed absorption bands attributable to the tridentate ligands: $3070–3145\,cm^{-1}$, C–H stretching; 1480–1490 and $1315–1325\,cm^{-1}$, ring stretching; $1045–1060\,cm^{-1}$, in plane C–H bending; $825–875\,cm^{-1}$ out of plane C–H bending [23]. The dinuclear Cu(II) complexes showed a very strong absorption in the region $1080–1090\,cm^{-1}$ and a medium sharp absorption at $908\,cm^{-1}$ characteristic of ν_3 and ν_4 modes of ionic perchlorate [24]. Due to the presence of some ligand vibrational modes in the region $500–250\,cm^{-1}$, assignments due to $\nu_{Cu–N}$ and $\nu_{Cu–Br}$ cannot be made unambiguously. However, a band of medium intensity at $380\,cm^{-1}$ for $\nu_{Cu–N}$ and at $310\,cm^{-1}$ for $\nu_{Cu–Br}$ may be assigned [24]. The electronic absorption spectra of monomeric and dimeric Cu(II) complexes in acetonitrile showed a strong absorption band in the 315–325 nm range, which may be assigned to the metal-ligand charge transfer transition [25]. Two or three bands in the region 225–275 nm ($E = 104–105$) may be due to intraligand transitions. One broad band between 650–730 nm ($E = 200$) observed for the Cu(II) complexes may be assigned to d–d transitions [25].

The cyclic voltammetric behavior of the mononuclear complexes in acetonitrile using tetrabutylammonium perchlorate (TBAP) as supporting electrolyte is characterized by a quasi-reversible wave at $E_{1/2} = 0.44\,V$ ($\Delta E_p = 140\,mV$) (figure 2) and $E_{1/2} = 0.55\,V$ ($\Delta E_p = 220\,mV$) for [$CuBr_2$(bppy)] and [$CuBr_2$(dmbppy)] complexes, respectively. The dinuclear complexes in acetonitrile showed a reversible couple at $E_{1/2} = 0.02\,V$ ($\Delta E_p = 65\,mV$) (figure 3) for [$Cu_2Br_2(bppy)_2$](ClO_4)$_2$ and a quasi reversible couple at positive potential $E_{1/2} = 0.13\,V$ ($\Delta E_p = 220\,mV$) for [$Cu_2Br_2(dmbppy)_2$](ClO_4)$_2$. On varying scan rate from 0.02 to $0.20\,V\,s^{-1}$, a change of $\Delta E_p = 140–220\,mV$ is obtained, where $E_{1/2}$ remains constant confirming quasi-reversibility of the system [26].

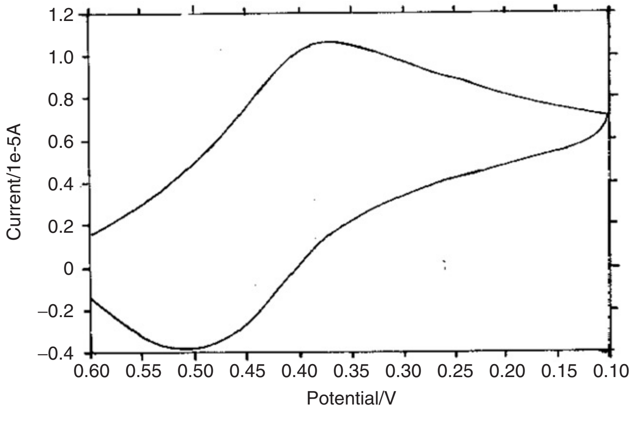

Figure 2. C.V. of [$CuBr_2$(bppy)] in MeCN at room temperature at a scan rate of $0.05\,V\,s^{-1}$ using TBAP as supporting electrolyte.

Magnetic susceptibility measurements for the monomeric copper(II) complexes at room temperature showed μ_{eff} at $25^\circ\mathrm{C} = 1.80\,\mathrm{BM}$ indicating one unpaired electron in the mononuclear copper(II) complex. The bromo-bridged dinuclear copper(II) compounds showed magnetic moments in the range $\mu_{\mathrm{eff}} = 1.25\,\mathrm{BM}$ to $1.31\,\mathrm{BM}$ at room temperature. Lowering in the magnetic moments from that of monomeric Cu(II) indicate weak antiferromagnetic interaction between the two copper(II) centers.

ESR spectrum of [CuBr$_2$(bppy)] in acetonitrile as frozen glass showed axial distortion with $g_\perp = 2.064$, $g_\parallel = 2.306$ and $A_\parallel = 150\,\mathrm{G}$. Single crystal X-ray studies show a pseudo square pyramid where the axial bromide makes an angle of 89° with the bppy ligand plane [19]. The ESR spectrum of the dimeric complex [Cu$_2$Br$_2$(bppy)$_2$](ClO$_4$)$_2$ at liquid nitrogen temperature in powder form and as frozen glass in acetonitrile showed only one *g* value, $g = 2.133$ and $g = 2.093$, respectively. Only one *g* value implies that $g_{xx} = g_{yy} = g_{zz}$ and the geometry around each of the two copper atoms is very close to octahedral. The above structural features are confirmed by single crystal X-ray studies where each copper has a tridentate bppy ligand and one bromo group in the square plane and a bridging bromo and a weakly coordinated $\mathrm{ClO_4^-}$ group in axial positions, giving a pseudo-octahedral geometry [19]. ESR spectrum of [CuBr$_2$(dmbppy)] at liquid nitrogen temperature for the powder form and in acetonitrile frozen solution showed $g_\perp = 2.050$, $g_\parallel = 2.302$ and $A_\parallel = 148\,\mathrm{G}$; and at $g_\perp = 2.053$, $g_\parallel = 2.294$, and $A_\parallel = 140\,\mathrm{G}$, respectively. This observation is similar to that of [CuBr$_2$(bppy)] (*vide supra*) and this complex is also proposed to have a square pyramidal structure with $d_{x^2-y^2}$ ground state. The ESR spectrum of [Cu$_2$Br$_2$(dmbppy)$_2$](ClO$_4$)$_2$ is different from its bppy analogue with well resolved $g_\perp$ and $g_\parallel$ signals at liquid nitrogen temperature in powder form and in acetonitrile frozen solution. The ESR in powder form showed $g_\perp = 2.456$, $g_\parallel = 2.165$ and $A_\parallel = 137\,\mathrm{G}$, whereas acetonitrile frozen solution showed $g_\perp = 2.439$, $g_\parallel = 2.168$ and $A_\parallel = 131\,\mathrm{G}$. These features are similar to its monomeric counterpart. The structure of the complex is very similar to [Cu$_2$Br$_2$(bppy)$_2$](ClO$_4$)$_2$ except lacking coordination of $\mathrm{ClO_4}^-$ in the axial position, thereby giving rise to a square pyramidal geometry with $d_{x^2-y^2}$ ground state and not a pseudo-octahedral geometry. The structures of

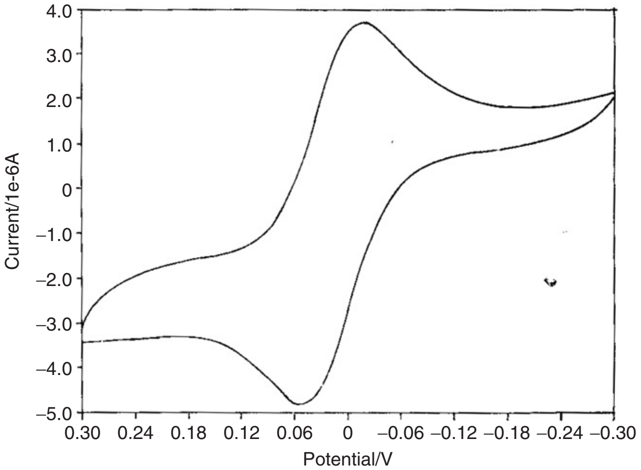

Figure 3. C.V. of [Cu$_2$Br$_2$(bppy)$_2$](ClO$_4$)$_2$ in MeCN at room temperature at a scan rate of $0.1\,\mathrm{V\,s^{-1}}$ using TBAP as supporting electrolyte.

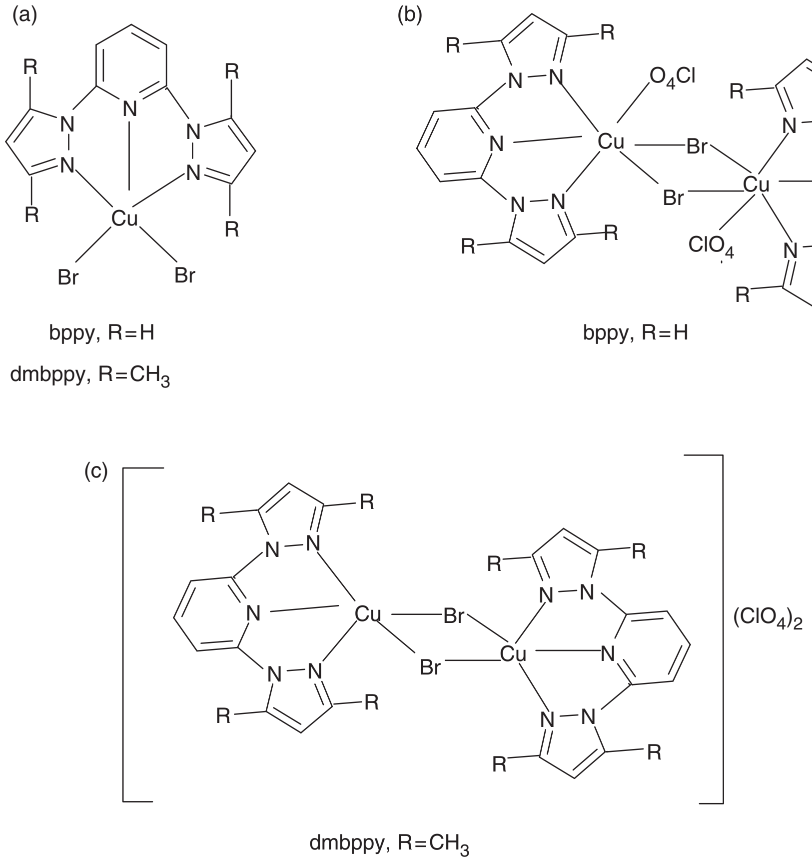

Figure 4. Structure of (a) [CuBr$_2$(L)] where L = bppy or dmbppy; (b) [Cu$_2$Br$_2$(bppy)$_2$] (ClO$_4$)$_2$; and (c) [Cu$_2$Br$_2$(dmbppy)$_2$](ClO$_4$)$_2$.

[CuBr$_2$(bppy)] and [Cu$_2$Br$_2$(bppy)$_2$](ClO$_4$)$_2$ were reported [19]. The structure of [CuBr$_2$(dmbppy)] is proposed to be similar to that of its bppy analogue. On the basis of various physical studies including ESR, [Cu$_2$Br$_2$(dmbppy)$_2$](ClO$_4$)$_2$ is proposed to be five coordinate with tridentate dmbppy and two bridging bromides [27, 28] with square pyramidal geometry. The structures are shown in figure 4.

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