

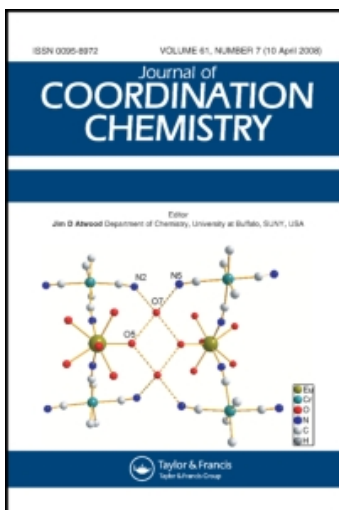
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### Synthesis, characterization and comparative studies of mono- and dimeric copper(II) complexes containing tripodal ligands

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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  $[\text{CuBr}_2(\text{L})]$  and  $[\text{Cu}_2\text{Br}_2(\text{L})_2](\text{ClO}_4)_2$  containing nitrogen donor tripodal ligands  $\text{L} = 2,6\text{-bis}(\text{pyrazol-1-yl})\text{pyridine}$  (bppy) or  $2,6\text{-bis}(3,5\text{-dimethylpyrazol-1-yl})\text{pyridine}$  (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.*  $2,6\text{-bis}(\text{pyrazol-1-yl})\text{pyridine}$  (bppy) and  $2,6\text{-bis}(3,5\text{-dimethylpyrazol-1-yl})\text{pyridine}$  (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.*  $[\text{CuBr}_2(\text{bppy})]$  and  $[\text{Cu}_2\text{Br}_2(\text{bppy})_2](\text{ClO}_4)_2$  have been reported from our laboratory [19].  $[\text{CuBr}_2(\text{bppy})]$  has a distorted square-pyramidal structure whereas  $[\text{Cu}_2\text{Br}_2(\text{bppy})_2](\text{ClO}_4)_2$  is a di-bromo bridged Cu(II) dinuclear complex stabilized by weak interaction of  $\text{ClO}_4^-$  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.*  $[\text{CuBr}_2(\text{dmbppy})]$  and  $[\text{Cu}_2\text{Br}_2(\text{dmbppy})_2](\text{ClO}_4)_2$  and their comparative studies with copper(II) complexes of bppy.

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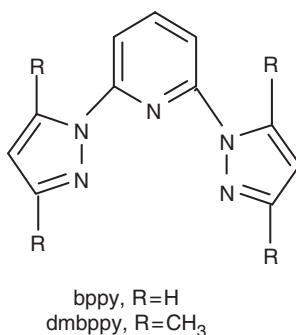


Figure 1. Structure of the tripodal ligands, when R=H, 2,6-bis(pyrazol-1-yl)pyridine (bppy), or R=CH<sub>3</sub>, 2,6-bis(3,5-dimethylpyrazol-1-yl)pyridine (dmbppy).

## 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<sub>2</sub> 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<sub>2</sub>Br<sub>2</sub>(dmbppy)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>

Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (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<sup>3</sup>) 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<sub>30</sub>H<sub>34</sub>N<sub>10</sub>Br<sub>2</sub>Cu<sub>2</sub>Cl<sub>2</sub>O<sub>8</sub> (%), C, 35.3; H, 3.3; N, 13.7. Found: C, 35.2; H, 3.1; N, 13.9. IR(cm<sup>-1</sup>, 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<sub>max</sub>, MeCN): 314 nm, Δ<sub>M</sub> (MeCN) = 245 Ω<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>, μ<sub>eff</sub> at 25°C = 1.25 BM.

## 2.2. Preparation of $[\text{Cu}_2\text{Br}_2(\text{bpppy})_2](\text{ClO}_4)_2$

$[\text{Cu}_2\text{Br}_2(\text{bpppy})_2](\text{ClO}_4)_2$  was prepared according to the reported method [19]. Anal. Calcd for  $\text{C}_{22}\text{H}_{18}\text{N}_{10}\text{Br}_2\text{Cl}_2\text{O}_8\text{Cu}_2$  (%): C, 29.1; H, 2.0; N, 15.4. Found: C, 28.8; H, 1.8; N, 14.9. IR( $\text{cm}^{-1}$  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 ( $\lambda_{\text{max}}$ , MeCN): 324 nm,  $\Lambda_{\text{M}}(\text{MeCN}) = 235 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ ,  $\mu_{\text{eff}}$  at  $25^\circ\text{C} = 1.31 \text{ BM}$ .

## 2.3. Preparation of $[\text{CuBr}_2(\text{dmbppy})]$

A mixture of  $\text{CuBr}_2$  (0.223 g, 1 mmol) and dmbppy (0.267 g, 1 mmol) in acetonitrile ( $20 \text{ cm}^3$ ) 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  $\text{C}_{15}\text{H}_{17}\text{N}_5\text{CuBr}_2$  (%): C, 36.7; H, 3.5; N, 14.3. Found: C, 36.4; H, 3.7; N, 13.9. IR( $\text{cm}^{-1}$ , 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 ( $\lambda_{\text{max}}$ , MeCN): 319 nm,  $\Lambda_{\text{M}}(\text{MeCN}) = 12 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ ;  $\mu_{\text{eff}}$  at  $25^\circ\text{C} = 1.75 \text{ BM}$ .

## 2.4. Preparation of $[\text{CuBr}_2(\text{bpppy})]$

To a solution of  $\text{CuBr}_2$  (0.223 g, 1 mmol) in acetonitrile ( $10 \text{ cm}^3$ ), a solution of bpppy (0.211 g, 1 mmol) in acetonitrile ( $10 \text{ cm}^3$ ) 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  $\text{C}_{11}\text{H}_9\text{N}_5\text{CuBr}_2$  (%): C, 30.4; H, 2.1; N, 16.1. Found: 30.1; H, 2.0; N, 15.9. IR( $\text{cm}^{-1}$ , 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 ( $\lambda_{\text{max}}$ , MeCN): 315 nm;  $\Lambda_{\text{M}}(\text{MeCN}) = 10 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ ;  $\mu_{\text{eff}}$  at  $25^\circ\text{C} = 1.80 \text{ BM}$ .

*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 = bpppy or dmbppy) in acetonitrile yielded monomeric complexes  $[\text{CuBr}_2(\text{L})]$ , whereas copper(II) perchlorate in presence of KBr with L in acetonitrile gave bromo-bridged dinuclear complexes of the type  $[\text{Cu}_2\text{Br}_2(\text{L})_2](\text{ClO}_4)_2$ . 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  $[\text{CuBr}_2(\text{L})]$  and  $[\text{Cu}_2\text{Br}_2(\text{L})_2](\text{ClO}_4)_2$

(L = bppy or dmbppy). Conductivity measurements of the monomeric complexes *viz.*  $[\text{CuBr}_2(\text{L})]$  in acetonitrile showed molar conductance values in the range  $10\text{--}12\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ , confirming the covalent nature of the bromo groups bonded to copper. The molar conductance of  $[\text{Cu}_2\text{Br}_2(\text{L})_2](\text{ClO}_4)_2$  (L = bppy, dmbppy) is observed in the range  $235\text{--}245\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ , confirming 1 : 2 electrolytes [22]. The IR spectra of Cu(II) complexes showed absorption bands attributable to the tridentate ligands:  $3070\text{--}3145\ \text{cm}^{-1}$ , C–H stretching;  $1480\text{--}1490$  and  $1315\text{--}1325\ \text{cm}^{-1}$ , ring stretching;  $1045\text{--}1060\ \text{cm}^{-1}$ , in plane C–H bending;  $825\text{--}875\ \text{cm}^{-1}$  out of plane C–H bending [23]. The dinuclear Cu(II) complexes showed a very strong absorption in the region  $1080\text{--}1090\ \text{cm}^{-1}$  and a medium sharp absorption at  $908\ \text{cm}^{-1}$  characteristic of  $\nu_3$  and  $\nu_4$  modes of ionic perchlorate [24]. Due to the presence of some ligand vibrational modes in the region  $500\text{--}250\ \text{cm}^{-1}$ , assignments due to  $\nu_{\text{Cu-N}}$  and  $\nu_{\text{Cu-Br}}$  cannot be made unambiguously. However, a band of medium intensity at  $380\ \text{cm}^{-1}$  for  $\nu_{\text{Cu-N}}$  and at  $310\ \text{cm}^{-1}$  for  $\nu_{\text{Cu-Br}}$  may be assigned [24]. The electronic absorption spectra of monomeric and dimeric Cu(II) complexes in acetonitrile showed a strong absorption band in the  $315\text{--}325\ \text{nm}$  range, which may be assigned to the metal-ligand charge transfer transition [25]. Two or three bands in the region  $225\text{--}275\ \text{nm}$  ( $E = 104\text{--}105$ ) may be due to intraligand transitions. One broad band between  $650\text{--}730\ \text{nm}$  ( $E = 200$ ) 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  $E_{1/2} = 0.44\ \text{V}$  ( $\Delta E_p = 140\ \text{mV}$ ) (figure 2) and  $E_{1/2} = 0.55\ \text{V}$  ( $\Delta E_p = 220\ \text{mV}$ ) for  $[\text{CuBr}_2(\text{bppy})]$  and  $[\text{CuBr}_2(\text{dmbppy})]$  complexes, respectively. The dinuclear complexes in acetonitrile showed a reversible couple at  $E_{1/2} = 0.02\ \text{V}$  ( $\Delta E_p = 65\ \text{mV}$ ) (figure 3) for  $[\text{Cu}_2\text{Br}_2(\text{bppy})_2](\text{ClO}_4)_2$  and a quasi reversible couple at positive potential  $E_{1/2} = 0.13\ \text{V}$  ( $\Delta E_p = 220\ \text{mV}$ ) for  $[\text{Cu}_2\text{Br}_2(\text{dmbppy})_2](\text{ClO}_4)_2$ . On varying scan rate from  $0.02$  to  $0.20\ \text{V s}^{-1}$ , a change of  $\Delta E_p = 140\text{--}220\ \text{mV}$  is obtained, where  $E_{1/2}$  remains constant confirming quasi-reversibility of the system [26].

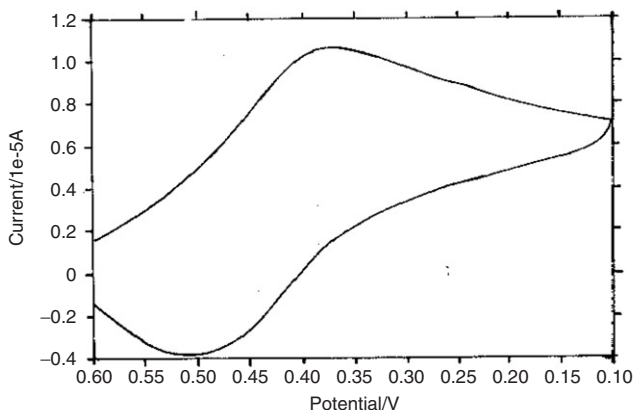


Figure 2. C.V. of  $[\text{CuBr}_2(\text{bppy})]$  in MeCN at room temperature at a scan rate of  $0.05\ \text{V s}^{-1}$  using TBAP as supporting electrolyte.

Magnetic susceptibility measurements for the monomeric copper(II) complexes at room temperature showed  $\mu_{\text{eff}}$  at  $25^\circ\text{C} = 1.80$  BM indicating one unpaired electron in the mononuclear copper(II) complex. The bromo-bridged dinuclear copper(II) compounds showed magnetic moments in the range  $\mu_{\text{eff}} = 1.25$  BM to  $1.31$  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  $[\text{CuBr}_2(\text{bppy})]$  in acetonitrile as frozen glass showed axial distortion with  $g_{\perp} = 2.064$ ,  $g_{\parallel} = 2.306$  and  $A_{\parallel} = 150$  G. Single crystal X-ray studies show a pseudo square pyramid where the axial bromide makes an angle of  $89^\circ$  with the bppy ligand plane [19]. The ESR spectrum of the dimeric complex  $[\text{Cu}_2\text{Br}_2(\text{bppy})_2](\text{ClO}_4)_2$  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  $\text{ClO}_4^-$  group in axial positions, giving a pseudo-octahedral geometry [19]. ESR spectrum of  $[\text{CuBr}_2(\text{dmbppy})]$  at liquid nitrogen temperature for the powder form and in acetonitrile frozen solution showed  $g_{\perp} = 2.050$ ,  $g_{\parallel} = 2.302$  and  $A_{\parallel} = 148$  G; and at  $g_{\perp} = 2.053$ ,  $g_{\parallel} = 2.294$ , and  $A_{\parallel} = 140$  G, respectively. This observation is similar to that of  $[\text{CuBr}_2(\text{bppy})]$  (*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  $[\text{Cu}_2\text{Br}_2(\text{dmbppy})_2](\text{ClO}_4)_2$  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  $A_{\parallel} = 137$  G, whereas acetonitrile frozen solution showed  $g_{\perp} = 2.439$ ,  $g_{\parallel} = 2.168$  and  $A_{\parallel} = 131$  G. These features are similar to its monomeric counterpart. The structure of the complex is very similar to  $[\text{Cu}_2\text{Br}_2(\text{bppy})_2](\text{ClO}_4)_2$  except lacking coordination of  $\text{ClO}_4^-$  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

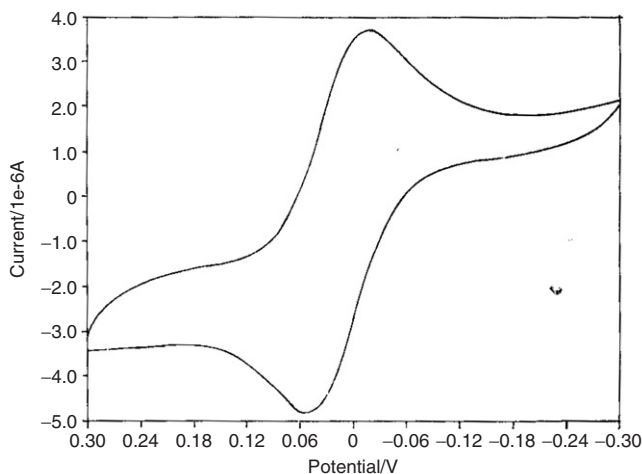


Figure 3. C.V. of  $[\text{Cu}_2\text{Br}_2(\text{bppy})_2](\text{ClO}_4)_2$  in MeCN at room temperature at a scan rate of  $0.1 \text{ V s}^{-1}$  using TBAP as supporting electrolyte.

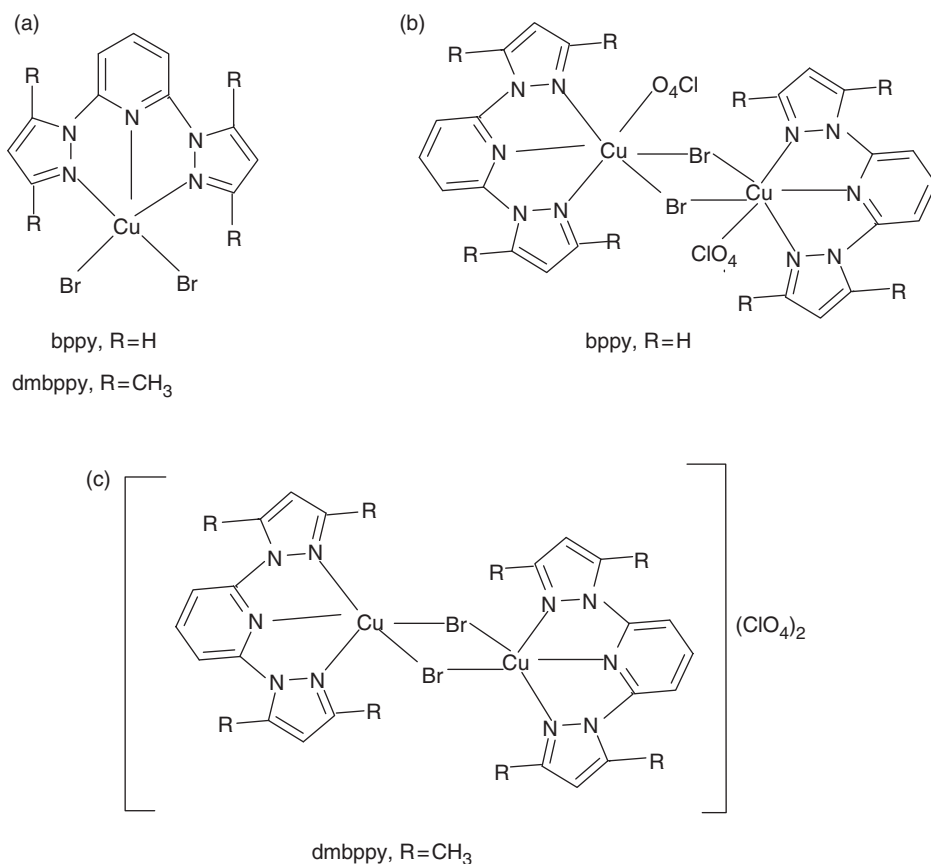


Figure 4. Structure of (a)  $[\text{CuBr}_2(\text{L})]$  where  $\text{L}=\text{bppy}$  or  $\text{dmbppy}$ ; (b)  $[\text{Cu}_2\text{Br}_2(\text{bppy})_2](\text{ClO}_4)_2$ ; and (c)  $[\text{Cu}_2\text{Br}_2(\text{dmbppy})_2](\text{ClO}_4)_2$ .

$[\text{CuBr}_2(\text{bppy})]$  and  $[\text{Cu}_2\text{Br}_2(\text{bppy})_2](\text{ClO}_4)_2$  were reported [19]. The structure of  $[\text{CuBr}_2(\text{dmbppy})]$  is proposed to be similar to that of its bppy analogue. On the basis of various physical studies including ESR,  $[\text{Cu}_2\text{Br}_2(\text{dmbppy})_2](\text{ClO}_4)_2$  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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