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**Abstract**

One new N<sub>3</sub>S-coordinate tetradentate ligand *N,N*-bis((3,5-dimethyl-1*H*-pyrazol-1-yl)methyl)-2-(phenylthio)ethan-1-amine (bdmpe) has been synthesized and characterized. Two double end-on azide bridged copper(II) complexes [Cu(bdmpe)(μ<sub>1,1</sub>-N<sub>3</sub>)<sub>2</sub>(X)<sub>2</sub>] [X = ClO<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>] and two triple bridged copper(II) complexes [Cu<sub>2</sub>(dmpe)<sub>2</sub>(μ<sub>1,1</sub>-N<sub>3</sub>)<sub>2</sub>(Y)]PF<sub>6</sub> [where dmpe = *N*-((3,5-dimethyl-1*H*-pyrazol-1-yl)methyl)-2-(phenylthio)ethan-1-amine, Y = CH<sub>3</sub>COO<sup>-</sup> or HCOO<sup>-</sup>] have been synthesized and characterized. Ligand (dmpe) has been formed from ligand (bdmpe) during in situ complexation reaction. Crystal structures of the three complexes [Cu(bdmpe)(μ<sub>1,1</sub>-N<sub>3</sub>)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>], [Cu<sub>2</sub>(dmpe)<sub>2</sub>(μ<sub>1,1</sub>-N<sub>3</sub>)<sub>2</sub>(μ-CH<sub>3</sub>COO-*k-O*<sup>1</sup>,*O*<sup>1i</sup>)]PF<sub>6</sub> and [Cu<sub>2</sub>(dmpe)<sub>2</sub>(μ<sub>1,1</sub>-N<sub>3</sub>)<sub>2</sub>(μ-HCOO-*k-O*<sup>1</sup>,*O*<sup>1i</sup>)]PF<sub>6</sub> have been solved by single crystal X-ray diffraction studies and the structural data revealed that the complex [Cu<sub>2</sub>(bdmpe)<sub>2</sub>(μ<sub>1,1</sub>-N<sub>3</sub>)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> is binuclear and two copper(II) centres are bridged by a pair of (μ-1,1) N<sub>3</sub><sup>-</sup> ion whereas the structures of other two complexes are binuclear with triple bridged and two adjacent copper(II) centres are bridged by a pair of N<sub>3</sub><sup>-</sup> ions with end-on (μ-1,1) coordination mode and one acetate / formate group with *syn-syn* coordination mode, respectively. Variable temperature (4-273 K) magnetic measurement of the complexes show that complex [Cu(bdmpe)(μ<sub>1,1</sub>-N<sub>3</sub>)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>] has no magnetic interaction whereas other two triple bridged complexes have weak antiferromagnetic interactions with *J* values -15.3(1) cm<sup>-1</sup> for acetate bridged complex and -17.8(1) cm<sup>-1</sup> for formate bridged complex.

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## 2.1. Introduction

Polynuclear transition metal complexes with bridging ligands have received much attention to the coordination chemists for the development of magnetic material and to study the magneto-structural correlations [1-5]. Polynuclear copper(II) complexes have potential application not only for magnetic material but also for model study of metalloenzymes [6-7]. A large number of pseudohalides and many carboxylates have been used as bridging ligands for the synthesis of polynuclear copper(II) complexes and among the pseudohalides such as azide, thiocyanate and isocyanate etc, azide is the most versatile ligand and large number of polynuclear complexes have been synthesized with the bridging ligands [8-14]. In general, azide ion has two different modes of coordination as bridging ligand and they can coordinate to the metal centres either as end-to-end ( $\mu$ -1,3) or as end-on ( $\mu$ -1,1) coordination mode [15-17]. It is well established that the nature of magnetic interaction depends on the coordination mode of bridging azide group and it is reported that end-to-end coordination mode shows antiferromagnetic interaction whereas end-on gives ferromagnetic interaction [18-23].

Carboxylate group is also a versatile bridging ligand, bridge the metal centres via *syn-syn*, *syn-anti* and *anti-anti* coordination mode and take part in the magnetic exchange interaction between two metal centres [24-26]. It is reported that *syn-syn* conformation favours binuclear complexes with anti-ferromagnetic interaction while *syn-anti* conformation gives antiferromagnetic and *anti-anti* produce weak antiferromagnetic or ferromagnetic interactions [27-28]. There are only few copper(II) complexes with mixed end-on azide and *syn-syn* carboxylate bridged have been structurally and magnetically characterized [28-30].

In this chapter, synthesis and characterization of one new  $N_3S$  coordinate tripodal ligand *N,N*-bis((3,5-dimethyl-1*H*-pyrazol-1-yl)methyl)-2-(phenylthio)ethan-1-amine (bdmpe) and two binuclear double end-on azide bridged copper(II) complexes and two binuclear triple bridged copper(II) complexes containing double end-on azide and *syn-syn* carboxylate as co-ligands and bdmpe ligand have been discussed. Crystal structures of the complexes have been solved by single crystal X-ray diffraction studies. Variable temperature magnetic studies of the complexes have been discussed in detail.

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## 2.2. Experimental

### 2.2.1. Materials

The chemicals and solvents were analytical grade and purchased from commercial sources. Acetylacetone, paraformaldehyde, hydrazine hydrate,  $\text{NaN}_3$ , copper(II) nitrate hexahydrate, copper(II) acetate mono hydrate, (Loba, India), benzenethiol, 2-chloroethan-1-amine hydrochloride, copper(II) formate mono hydrate,  $\text{NH}_4\text{BF}_4$ ,  $\text{NH}_4\text{PF}_6$  (Aldrich) were reagent grade and used as received. 2-(arylsulfanyl)ethylamine [31] and 3,5-dimethyl-1H-pyrazole-1-yl)methanol [32] were synthesized by following the known procedures. Copper(II) perchlorate hexahydrate was prepared by reaction of copper carbonate with dilute  $\text{HClO}_4$  acid and followed by slow evaporation of the solution.

### 2.2.2. Physical Measurements

The IR spectra were recorded on a Perkin-Elmer FT-IR spectrometer RX1 spectrum using KBr pellets. The micro analysis (C, H and N) were carried out using a Perkin-Elmer IA 2400 series elemental analyzer.  $^1\text{H}$  NMR spectra were recorded on Bruker NMR AV400 spectrometer in  $\text{CDCl}_3$ . UV-Vis spectra (900 - 190 nm) were recorded on a Perkin-Elmer spectrophotometer model Lambda 35 in acetonitrile solution. Solution conductivity were measured in acetonitrile solution using Equip-Tronics conductivity meter (model no. EQ-660A).

The magnetic susceptibility measurements were obtained with the use of a Quantum Design SQUID magnetometer MPMS-XL. This magnetometer works between 1.8 and 400 K from dc applied ranging from -7 to 7 T. Measurements were performed on finely ground crystalline samples of 26.08 mg (complex **1**), 26.81 mg (complex **3**) and 26.08 mg (complex **4**). M vs H measurements have been performed at 100 K to check the presence of ferromagnetic impurities and that has been found absent completely for samples **3** and **4** and almost negligible quantity in complex **1**. The magnetic data were corrected for the sample holder and the diamagnetic correction of the complexes.

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### 2.2.3. Synthesis of Ligand

#### 2.2.3.1. Synthesis of *N,N*-bis((3,5-dimethyl-1*H*-pyrazol-1-yl)methyl)-2-(phenylthio)ethan-1-amine (bdmpe)

An acetonitrile solution (25 mL) of (3,5-dimethyl-1*H*-pyrazole-1-yl)methanol (1.0 g, 8 mmol) was added to a stirring solution of 2-(phenylthio)ethan-1-amine (0.685 g, 4 mmol) in same solvent (25 mL). The reaction mixture was stirred for two days at room temperature in closed vessel, finally refluxed for 3 h and dried over  $\text{Na}_2\text{SO}_4$  and solvent was evaporated under reduced pressure. Light yellow colour viscous liquid was obtained.

Yield. 1.53 g (92%). Found C = 65.75, H = 7.25, N = 18.78%, Elemental analysis Calc. for  $\text{C}_{20}\text{H}_{27}\text{N}_5\text{S}$ : C = 65.01, H = 7.37, N = 18.95%. IR (neat)  $\text{cm}^{-1}$ :  $\nu(\text{C}=\text{C})$ , 1583 s;  $\nu(\text{C}=\text{C}) + \nu(\text{C}=\text{N})/\text{pz ring}$ , 1553 s, 1462 s;  $\nu(\text{C}-\text{S})$ , 660 w.  $^1\text{H NMR}$ (400 MHz,  $\text{CDCl}_3$ , 20 °C).  $\delta/\text{ppm}$ : 7.2-7.5 (m, 5H, phenyl ring), 5.9 (s, 2H,  $-\text{CH}-/\text{pz ring}$ ), 4.9 (s, 4H,  $-\text{CH}_2-$ ), 2.89-2.93 (t, 2H,  $J_{\text{HZ}} = 7.6, 6.8 \text{ Hz}$ ,  $-\text{CH}_2-\text{CH}_2-\text{N}$ ), 2.72-2.76 (t, 2H,  $J_{\text{HZ}} = 6.8, 7.6 \text{ Hz}$ ,  $-\text{CH}_2-\text{NH}_2$ ), 2.20 (s, 6H,  $-\text{CH}_3/\text{pz ring}$ ), 2.18 (s, 6H,  $\text{CH}_3/\text{pz ring}$ ).

### 2.2.4. Syntheses of Complexes

*Caution!* Transition metal complexes with perchlorate ion and organic ligands are potentially explosive. Only a small amount of material should be synthesized and it should be handled with care.

#### 2.2.4.1. Synthesis of $[\text{Cu}(\text{bdmpe})(\mu_{1,1}-\text{N}_3)]_2(\text{ClO}_4)_2$ (1)

A methanol (10 mL) solution of ligand bdmpe (0.093 g, 0.25 mmol) was added to a stirring solution of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.095 g, 0.25 mmol) in methanol (10 mL) and color of the solution was changed to light green. A solution of sodium azide (0.017 g, 0.25 mmol) in methanol (10 mL) was added drop wise to above solution and light green color turned into dark green solution. This reaction mixture was stirred for 3h at room temperature, filtered and kept the filtrate for slow evaporation at room temperature. Dark green color crystals suitable for the X-ray structure were obtained after 4 days.

Yield: 0.075 g (52%). Found C = 41.81, H = 4.74, N = 19.50%, Elemental analysis  
 Calc. for  $C_{40}H_{54}Cl_2Cu_2N_{16}O_8S_2$ : C = 41.43, H = 4.71, N = 19.16%. IR (KBr,  $cm^{-1}$ ):  
 $\nu(N_3^-)$ , 2054;  $\nu(C = C)$ , 1583 s;  $\nu(C = C) + \nu(C = N)/pz$  ring, 1552 s, 1466 s;  $\nu(C-S)$ ,  
 648 w;  $\nu(ClO_4^-)$ , 1095 br;  $\delta(O-Cl-O)$ , 624 s. UV-Vis spectra:  $\lambda_{max}/nm$  ( $\epsilon_{max}/mol^{-1}cm^{-1}$ ).  
 642 (825), 420 (5137), 327 (1014).  $\Lambda_M$  ( $\Omega^{-1}cm^2 mol^{-1}$ ) = 122.

#### 2.2.4.2. Synthesis of $[Cu(bdmpe)(\mu_{1,1}-N_3)]_2(PF_6)_2$ (2)

To a stirring solution of copper(II) nitrate (0.060 g, 0.25 mmol) in methanol (10 mL) was added a solution of ligand bdmpe (0.093 g, 0.25 mmol) dissolved in the same solvent (10 mL). After 10 min, a solution of sodium azide (0.017 g, 0.25 mmol) in methanol (10 mL) was added drop wise to the above solution and light green color changed to dark green immediately. After 10 min, a solution of  $NH_4PF_6$  (0.042 g, 0.25 mmol) in MeOH (10 mL) was added drop by drop in above solution. Dark green colored solution was stirred for additional 3h, filtered and the filtrate was left to evaporate slowly at room temperature. After 4 days, dark green color compound was obtained.

Yield. 0.079 g (51%). Found C = 38.74, H = 4.39, N = 18.41%, Elemental analysis  
 Calc. for  $C_{40}H_{54}Cu_2F_{12}N_{16}P_2S_2$ : C = 38.51, H = 4.40, N = 18.35%. IR (KBr pellet)  
 $cm^{-1}$ :  $\nu(N_3^-)$ , 2048 vs ;  $\nu(C = C)$ , 1584 s;  $\nu(C = C) + \nu(C = N)/pz$  ring, 1555 s, 1466 s;  
 $\nu(C-S)$ , 656 w;  $\nu(PF_6^-)$ , 839 s. UV-Vis spectra:  $\lambda_{max}/nm$  ( $\epsilon_{max}/mol^{-1}cm^{-1}$ ). 640 (951),  
 420 (5728), 251 (15223).  $\Lambda_M$  ( $\Omega^{-1}cm^2 mol^{-1}$ ) = 118.

#### 2.2.4.3. Synthesis of $[Cu_2(dmpe)_2(\mu_{1,1}-N_3)_2(\mu-CH_3COO-k-O^1, O^{1i})]PF_6$ (3)

A solution of ligand bdmpe (0.093 g, 0.25 mmol) in methanol (10 mL) was added to a stirring solution of  $Cu(CH_3COO)_2 \cdot H_2O$  (0.050 g, 0.25 mmol) in methanol (10 mL). After 10 min, a solution of sodium azide (0.017 g, 0.25 mmol) in methanol (10 mL) was added slowly to the mixture. Finally, a solution of  $NH_4PF_6$  (0.042 g, 0.25 mmol) in methanol (10 mL) was added into the solution after 10 min. Dark green colored mixture was stirred for additional 3h, filtered and the filtrate was left to evaporate slowly. Dark green color crystals suitable for the X- ray analysis were obtained after 3 days.

Yield. 0.069 g (59%). Found C = 38.42 , H = 4.40, N = 17.92%, Elemental analysis  
 Calc. for  $C_{30}H_{41}Cu_2F_6N_{12}O_2PS_2$ : C = 38.49, H = 4.32, N = 17.73%. IR (KBr pellet)  
 $cm^{-1}$ :  $\nu(-NH)$ , 3329m;  $\nu(N_3)$ , 2059, 2045 vs ;  $\nu(C = C)$ , 1624 s;  $\nu(C = C) + \nu(C =$

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N)/pz ring, 1571 s, 1467 s;  $\nu(\text{C-S})$ , 656 w;  $\nu(\text{PF}_6^-)$ , 849 s. UV-Vis spectra:  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon_{\text{max}}/\text{mol}^{-1}\text{cm}^{-1}$ ). 644 (372), 402 (3603), 252 (20888).  $\Lambda_{\text{M}}$  ( $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ ) = 130.

#### 2.2.4.4. Synthesis of $[\text{Cu}_2(\text{dmpe})_2(\mu_{1,1}\text{-N}_3)_2(\mu\text{-HCOO-k-O}^1, \text{O}^{1i})]\text{PF}_6$ (**4**)

The complex was synthesized by following the same procedure as for complex **3** except copper (II) formate was used instead of copper(II) acetate.

Yield. 0.066 g (57%). Found C = 37.70, H = 4.25, N = 18.19%, Elemental analysis Calc. for  $\text{C}_{29}\text{H}_{39}\text{Cu}_2\text{F}_6\text{N}_{12}\text{O}_2\text{PS}_2$ : C = 37.85, H = 4.15, N = 18.31%. IR (KBr pellet)  $\text{cm}^{-1}$ :  $\nu(\text{-NH})$ , 3336 m;  $\nu(\text{N}_3)$ , 2051, 2046 vs;  $\nu(\text{C}=\text{C})$ , 1583 s;  $\nu(\text{C}=\text{C}) + \nu(\text{C}=\text{N})/\text{pz}$  ring, 1553 s, 1466 s;  $\nu(\text{C-S})$ , 656 w;  $\nu(\text{PF}_6^-)$ , 846 s. UV-Vis spectra:  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon_{\text{max}}/\text{mol}^{-1}\text{cm}^{-1}$ ). 644 (328), 402 (3159), 252 (17792).  $\Lambda_{\text{M}}$  ( $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ ) = 123.

### 2.3. X-ray Crystallography

The crystallographic data, details of data collection and some important features of the refinement for the compounds **1**, **3** and **4** are given in Table 2.1. Crystals of suitable size of the complexes were obtained by slow evaporation of methanol solution. The data were collected on Oxford X-CALIBUR-S diffractometer with Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 293 K for complexes **1** and **4** and with Cu-K $\alpha$  radiation ( $\lambda = 1.541841 \text{ \AA}$ ) at 150 K for complex **3**. The data interpretations were processed with CrysAlisPro, Agilent Technologies, Version 1.171.35.19 [33]. An absorption correction based on multi-scan method was applied [34]. All structures were solved by direct methods and refined by the full-matrix least-square based on  $F^2$  technique using SHELXL-97 program package [35]. All calculations were carried out using WinGX system Ver-1.64 [36]. All non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were located in their calculated position and treated as riding on the atoms to which they are attached.

Table 2.1. Crystal parameters of complexes 1, 3 and 4.

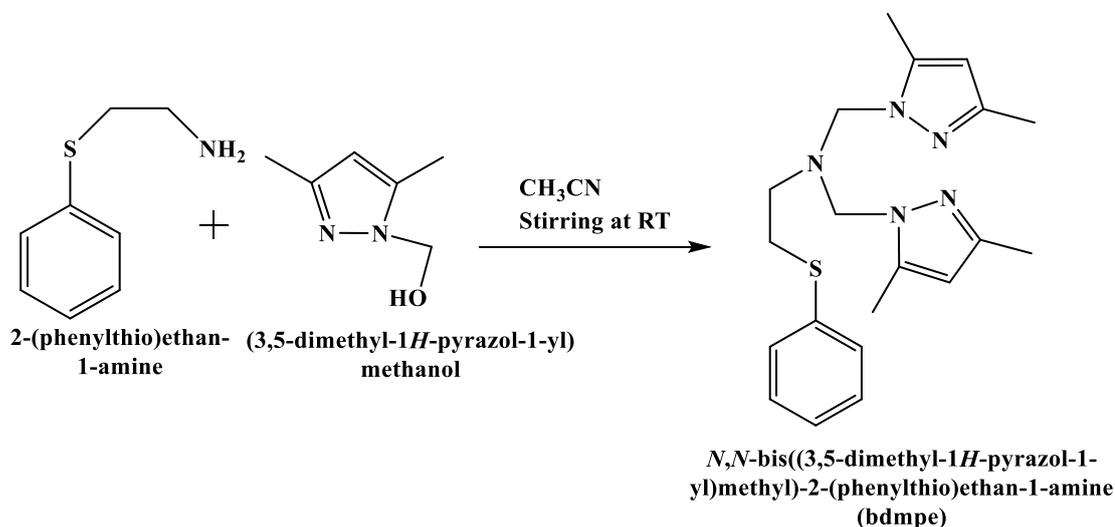
	[Cu(bdmpe)( $\mu_{1,1}$ - N <sub>3</sub> ) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> (1)	[Cu <sub>2</sub> (dmpe) <sub>2</sub> ( $\mu_{1,1}$ -N <sub>3</sub> ) <sub>2</sub> ( $\mu$ - CH <sub>3</sub> COO)]PF <sub>6</sub> (3)	[Cu <sub>2</sub> (dmpe) <sub>2</sub> ( $\mu_{1,1}$ -N <sub>3</sub> ) <sub>2</sub> ( $\mu$ - HCOO)]PF <sub>6</sub> (4)
Empirical formula	C <sub>40</sub> H <sub>54</sub> Cl <sub>2</sub> Cu <sub>2</sub> N <sub>16</sub> O <sub>8</sub> S <sub>2</sub>	C <sub>30</sub> H <sub>41</sub> Cu <sub>2</sub> F <sub>6</sub> N <sub>12</sub> O <sub>2</sub> PS <sub>2</sub>	C <sub>29</sub> H <sub>39</sub> Cu <sub>2</sub> F <sub>6</sub> N <sub>12</sub> O <sub>2</sub> PS <sub>2</sub>
Formula weight	1149.11	937.92	923.89
Temperature (K)	293(2)	150(2)	293(2)
Wavelength (Å)	0.71073	1.54184	0.71073
Crystal system	triclinic	orthorhombic	Orthorhombic
Space group	<i>P</i> - <i>I</i>	<i>Pbcn</i>	<i>Pbcn</i>
<i>a</i> (Å)	10.8018(5)	15.9281(6)	15.990(4)
<i>b</i> (Å)	11.2082(4)	17.8181(6)	17.502(5)
<i>c</i> (Å)	12.3181(5)	13.5289(5)	13.762(4)
$\alpha$ (°)	101.501(3)	90.00	90.00
$\beta$ (°)	112.501(4)	90.00	90.00
$\gamma$ (°)	101.129(3)	90.00	90.00
Volume (Å <sup>3</sup> )	1289.01(9)	3839.6(2)	3851.4(18)
<i>Z</i>	1	4	4

Density (gm/m <sup>3</sup> )	1.480	1.623	1.593
Absorption coefficient (mm <sup>-1</sup> )	1.480	1.623	1.593
F(000)	594.0	1920.0	1888.0
$\theta$ range for data collection (°)	6.16 to 58.1	7.44 to 146.72	3.46 to 52
Index ranges	-14 ≤ h ≤ 14, -15 ≤ k ≤ 15, -16 ≤ l ≤ 16	-14 ≤ h ≤ 19, -21 ≤ k ≤ 22, -16 ≤ l ≤ 12	-19 ≤ h ≤ 19, -21 ≤ k ≤ 21, -16 ≤ l ≤ 16
Reflections collected	27992	13926	29793
Independent reflections	6890 [Rint = 0.0410]	3833 [Rint = 0.0415]	3787 [Rint = 0.0694]
Data / restraints / parameters	6890/0/316	3833/61/288	3787/61/282
Goodness-of-fit on $F^2$	1.049	1.049	1.009
Final $R$ indices [ $I > 2\sigma(I)$ ]	$RI = 0.0436,$ $wR2 = 0.1071$	$RI = 0.0583,$ $wR2 = 0.1556$	$RI = 0.0357,$ $wR2 = 0.0765$
$R$ indices (all data)	$RI = 0.0536,$ $wR2 = 0.1128$	$RI = 0.0649,$ $wR2 = 0.1639$	$RI = 0.0652,$ $wR2 = 0.0897$
Largest diff. peak and hole (eA <sup>-3</sup> )	0.42 and -0.36	0.70 and -0.55	0.37 and -0.24
CCDC	981014	1493173	1493122

## 2.4. Results and Discussion

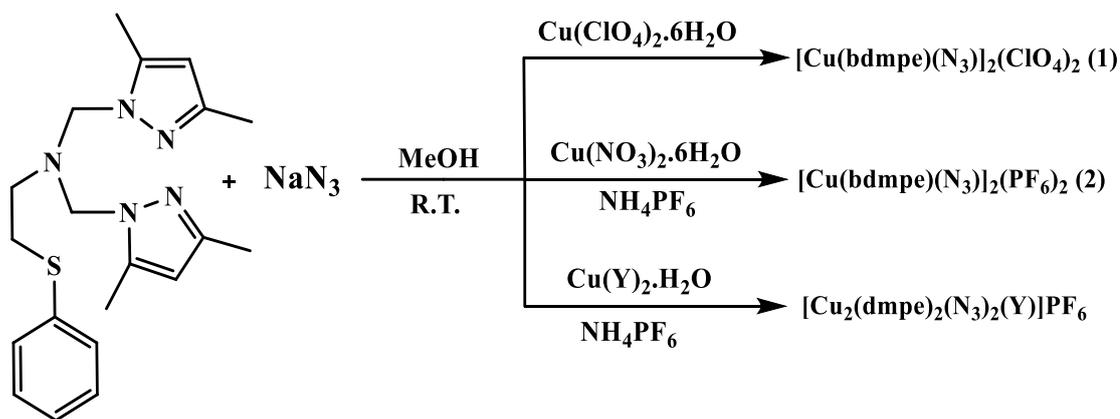
### 2.4.1. Syntheses

The ligand *N,N*-bis((3, 5-dimethyl-1*H*-pyrazol-1-yl)methyl)-2-(phenylthio)ethanamine (bdmpe) was synthesized as a viscous yellow liquid by the reaction of 2-(arylsulfanyl)ethylaniline and 3,5-dimethylpyrazol-1-methanol in acetonitrile (Scheme 2.1.) and characterized by spectroscopic methods.



**Scheme 2.1.** Synthesis of ligand (bdmpe).

The ligand possesses four potential donor sites- two nitrogen donor atoms from the two pyrazole rings, one nitrogen atom from the tertiary amine and one sulphur atom from the aryl sulphur. Binuclear double azide bridged copper(II) complexes  $[\text{Cu}(\text{bdmpe})(\mu_{1,1}\text{-N}_3)]_2(\text{X})_2$  [ $\text{X} = \text{ClO}_4^-$ ,  $\text{PF}_6^-$ ] were obtained as green compound with good yield (~50%) by the reaction of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  /  $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{NH}_4\text{PF}_6$ , ligand bdmpe and sodium azide in 1: 1: 1 mole ratio in methanol and binuclear triple bridge complexes  $[\text{Cu}_2(\text{dmpe})_2(\mu_{1,1}\text{-N}_3)_2(\text{Y})]\text{PF}_6$  [ $\text{Y} = \text{CH}_3\text{COO}^-$ ,  $\text{HCOO}^-$ ] were readily obtained with good yield (~60%) by the reaction of copper acetate/ formate, ligand bdmpe, sodium azide and  $\text{NH}_4\text{PF}_6$  in 1: 1: 1: 1 mole ratio in methanol at room temperature (scheme 2.2). There was no change in composition of the complexes even after addition of excess azide ions. The diffraction quality crystals for structural studies were obtained by slow evaporation of the methanol solution.



Where,  $\text{X} = \text{ClO}_4^-$ ,  $\text{PF}_6^-$

$\text{Y} = \text{CH}_3\text{COO}^-$ ,  $\text{HCOO}^-$

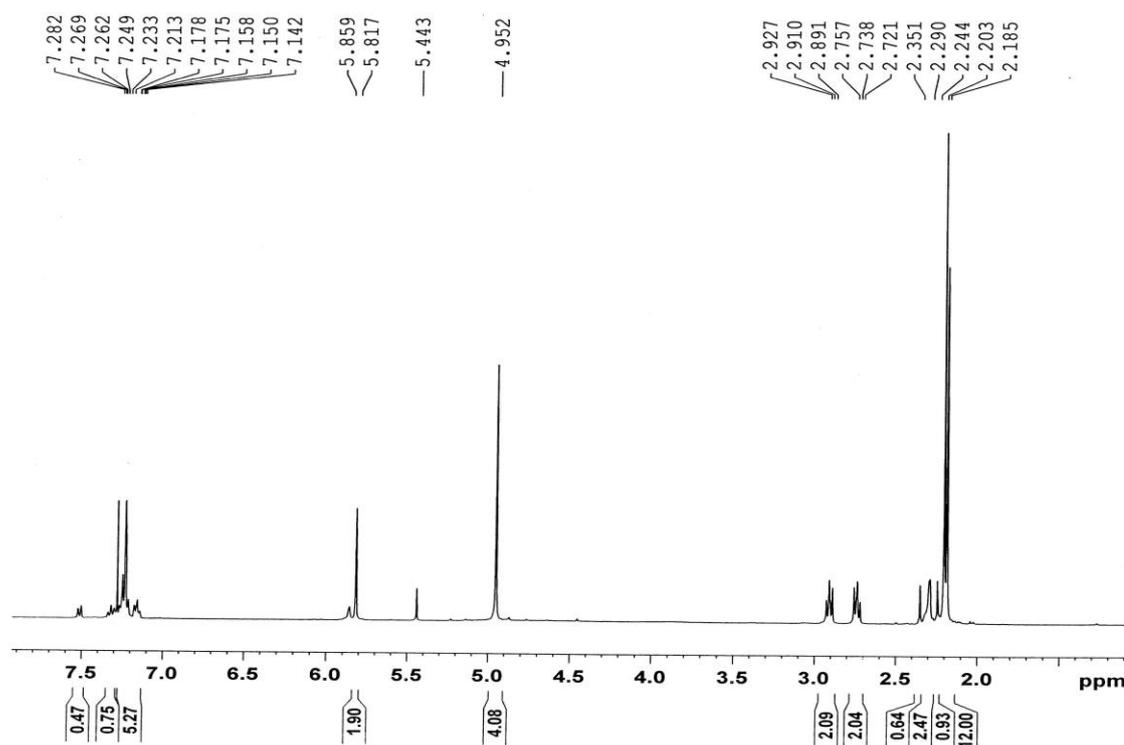
**Scheme 2.2.** Synthesis of complexes.

The important aspect of the reaction is that the ligand bdmpe acts as  $\text{N}_3\text{S}$ -donor tetradentate ligand in the complexes **1** and **2** whereas the ligand bdmpe has lost one pyrazolyl arm and transformed into  $\text{N}_2\text{S}$ -coordinate tridentate ligand dmpe during synthesis of complexes **3** and **4**. This transformation was confirmed by single crystal X-ray diffraction studies. This type of ligand transformations with pyrazolyl based ligand are already reported in the literature [37-39]. It is assumed that the pendant arm of ligand bdmpe was removed by cleaving two C-N bonds i.e. bond between  $\text{N}(\text{pyrazole})\text{-CH}_2$  and  $\text{CH}_2\text{-N}(\text{amine})$  of  $\text{N}(\text{pyrazole})\text{-CH}_2\text{-N}(\text{amine})$  moiety and form new  $\text{N}_2\text{S}$ -coordinated tridentate ligand [40-41].

The molecular compositions of the complexes were confirmed by microanalysis, IR, molar conductance and UV-Vis spectroscopy data. Molar conductivity measurement indicates that all the complexes 1:1 electrolyte [42]. The complexes are soluble in common organic solvents such as DCM, MeOH, EtOH and MeCN etc.

### 2.4.2. $^1\text{H}$ NMR, IR and UV-Visible spectral data

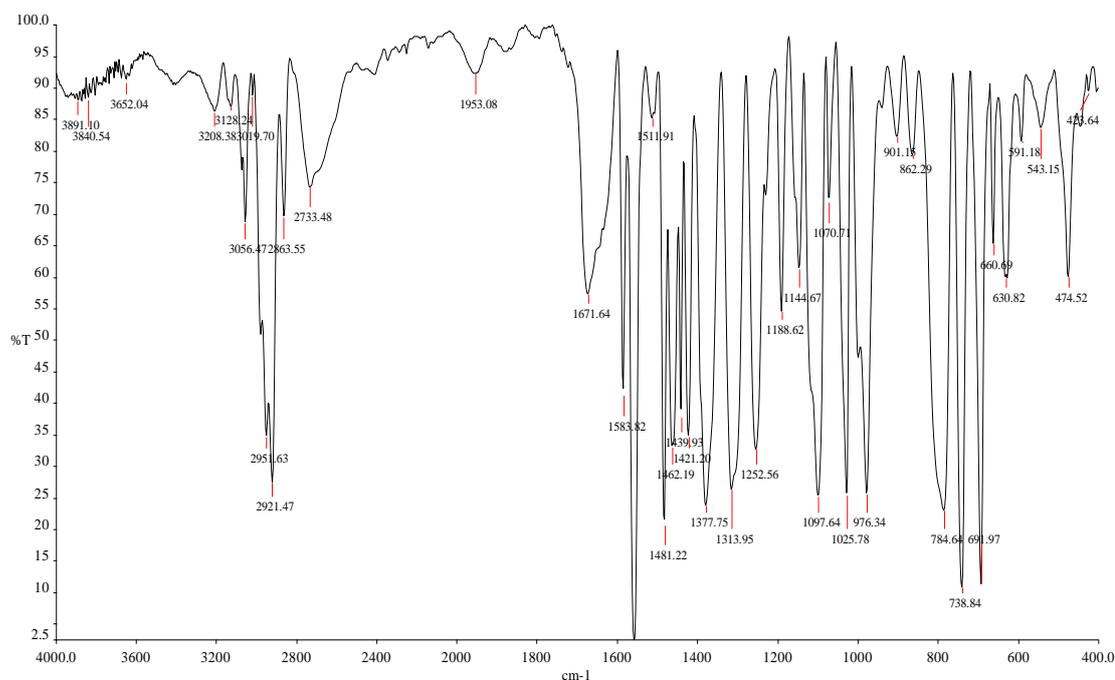
The  $^1\text{H}$  NMR spectrum of ligand bdmpe shows two singlets of six protons each at 2.185 and 2.203  $\delta$  ppm, confirming the presence of four methyl group of two pyrazole rings. Four protons from  $-\text{CH}_2-\text{CH}_2-$  appeared as two triplets in the region at 2.721-2.757 and 2.891-2.927  $\delta$  ppm, confirming the presence of  $\text{N}-\text{CH}_2-\text{CH}_2-\text{S}$  in the ligand. Four protons appeared as singlets at 4.952  $\delta$  ppm confirming the presence of two  $-\text{CH}_2-$  that are connected with pyrazole and tertiary amine moiety. Two protons from two pyrazole rings appeared as singlet at 5.817  $\delta$  ppm and five aromatic protons appeared as multiplet at 7.142-7.233 ppm.



**Fig.2.1.**  $^1\text{H}$ -NMR Spectrum of *N,N*-bis((3,5-dimethyl-1H-pyrazol-1-yl)methyl)-2-(phenylthio)ethanamine (bdmpe).

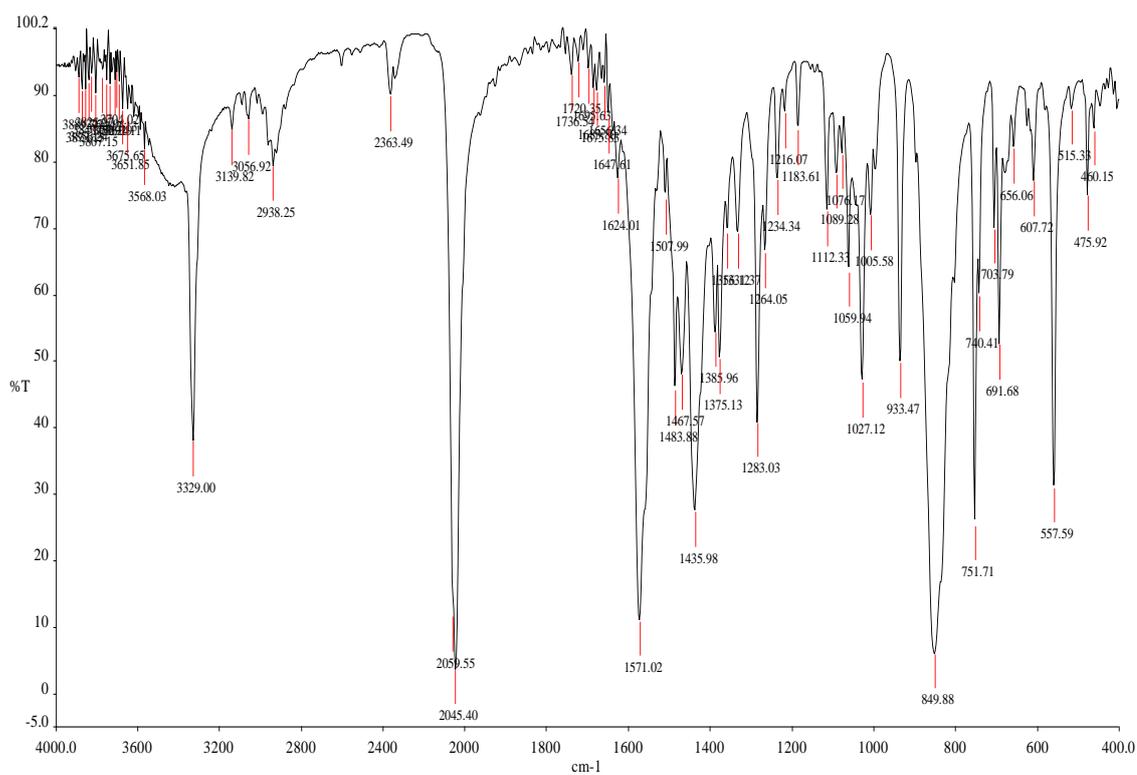
The IR spectrum of the ligand *N,N*-bis((3,5-dimethyl-1H-pyrazole-1-yl)methyl)-2-(phenylthio)ethanamine (bdmpe) and all the complexes have common absorption bands at  $\sim 1583\text{ cm}^{-1}$  for  $\nu(\text{C}=\text{C})$  of the phenyl rings, at  $\sim 1553$  and  $\sim 1467\text{ cm}^{-1}$  due to  $\nu(\text{C}=\text{N}) + \nu(\text{C}=\text{C})$  of the pyrazole ring and at  $\sim 654\text{ cm}^{-1}$  for  $\nu(\text{C}-\text{S})$  of thioether, indicating the co-ordination of the pyrazole groups and sulphur atom of ligand to the copper center in the complexes. In general, the end-on bridging vibration of the azide ( $\text{N}_3^-$ ) ion appears at  $2060\text{-}2070\text{ cm}^{-1}$  whereas the end-to-end

bridging mode appears at 2020-2040  $\text{cm}^{-1}$  [43]. All the complexes show two strong bands in the region of 2059 - 2045  $\text{cm}^{-1}$ , indicating end-on bridging coordination mode of the azide ion in all complexes. Complexes **3** and **4** exhibit one sharp band at  $\sim 3300 \text{ cm}^{-1}$  and this band is absent in IR spectra of ligand and also in complexes **1** and **2**, indicating the presence of -NH group in the complexes. Shifting of  $\nu(\text{C-S})$  from 660  $\text{cm}^{-1}$  to 654  $\text{cm}^{-1}$  in all complexes indicates the coordination of thioether (S) to copper(II) center. Complexes **3** and **4** show band at 1442  $\text{cm}^{-1}$  due to  $\nu_{\text{sym}}(\text{COO}^-)$  vibration of acetate and formate anion, respectively [44-45]. Complexes **2**, **3** and **4** have one strong band at 849  $\text{cm}^{-1}$  due to  $\nu(\text{PF}_6^-)$  ion and complex **1** has one broad band at  $\sim 1100 \text{ cm}^{-1}$  due to  $\nu_{\text{assy}}(\text{Cl-O})$  and a weak band at  $\sim 623 \text{ cm}^{-1}$  due to  $\delta(\text{O-Cl-O})$  of the  $\nu(\text{ClO}_4^-)$ , confirming the presence of the  $\text{PF}_6^-$  and  $\text{ClO}_4^-$  ion outside the coordination sphere [46]. All other bands of the ligands are also appeared in the IR spectra of the complexes. Nature of the co-ordination mode of azide and acetate ligand is also confirmed by the single crystal X-ray diffraction studies.

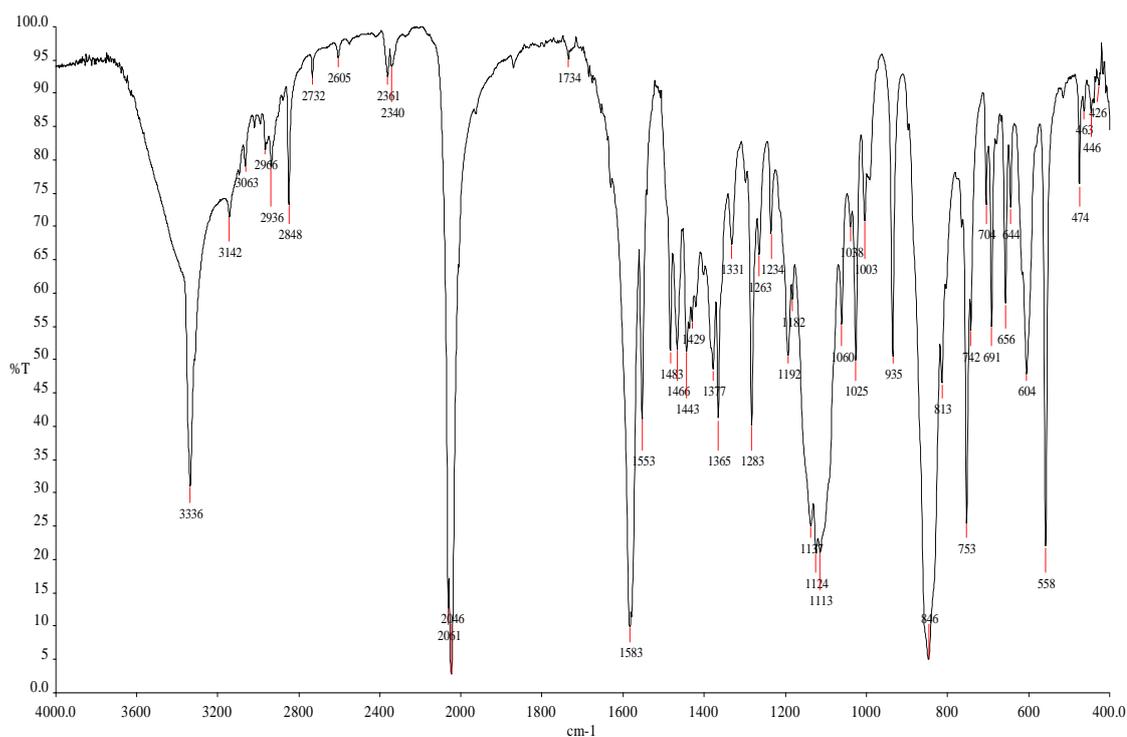


**Fig.2.2.** IR Spectrum of ligand *N,N*-bis((3, 5-dimethyl-1H-pyrazol-1-yl)methyl)-2-(phenylthio)ethanamine (bdmpe).





**Fig.2.5.** IR spectrum of  $[\text{Cu}_2(\text{dmpe})_2(\mu_{1,1}\text{-N}_3)_2(\mu\text{-CH}_3\text{COO-}k\text{-O}^1, \text{O}^{1i})]\text{PF}_6$  (3).



**Fig.2.6.** IR spectrum of  $[\text{Cu}_2(\text{dmpe})_2(\mu_{1,1}\text{-N}_3)_2(\mu\text{-HCOO-}k\text{-O}^1, \text{O}^{1i})]\text{PF}_6$  (4).

Electronic spectrum of all the complexes in acetonitrile solution at room temperature exhibit two bands at around  $\sim 640$  and  $\sim 410$  nm, which may be attributed to d-d transition [17]. Spectral bands below 400 nm are due to intraligand charge transitions.

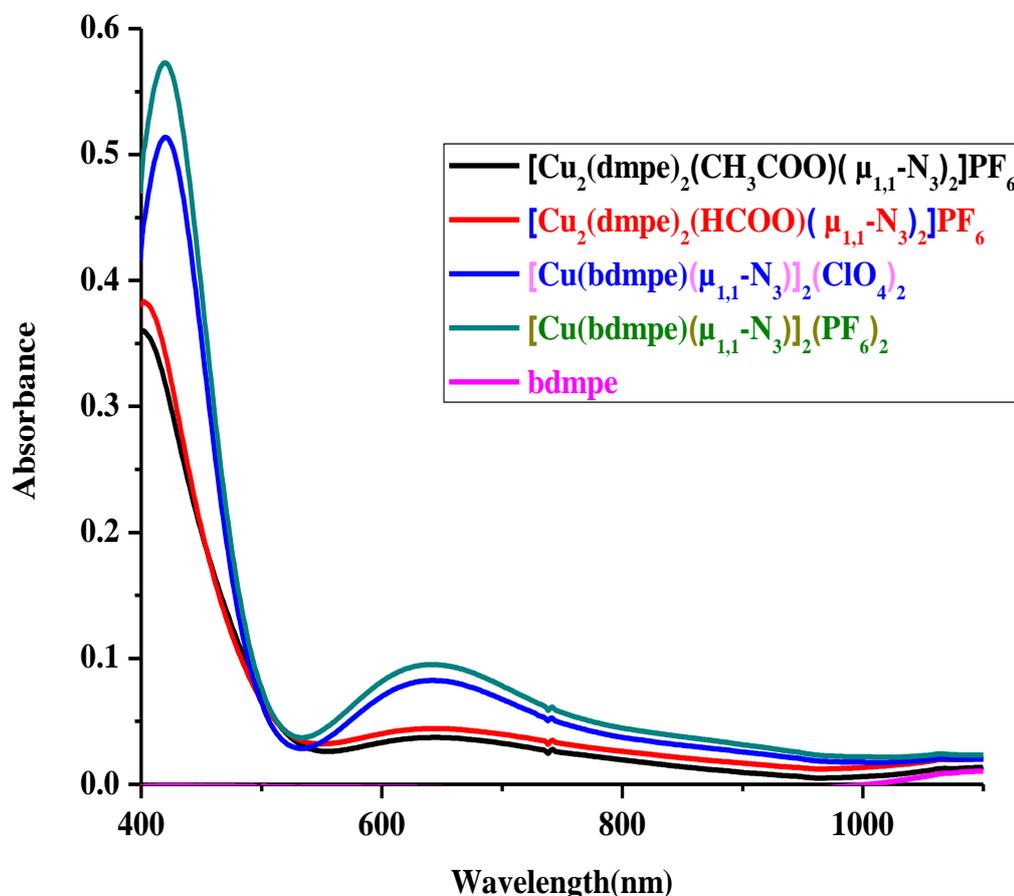


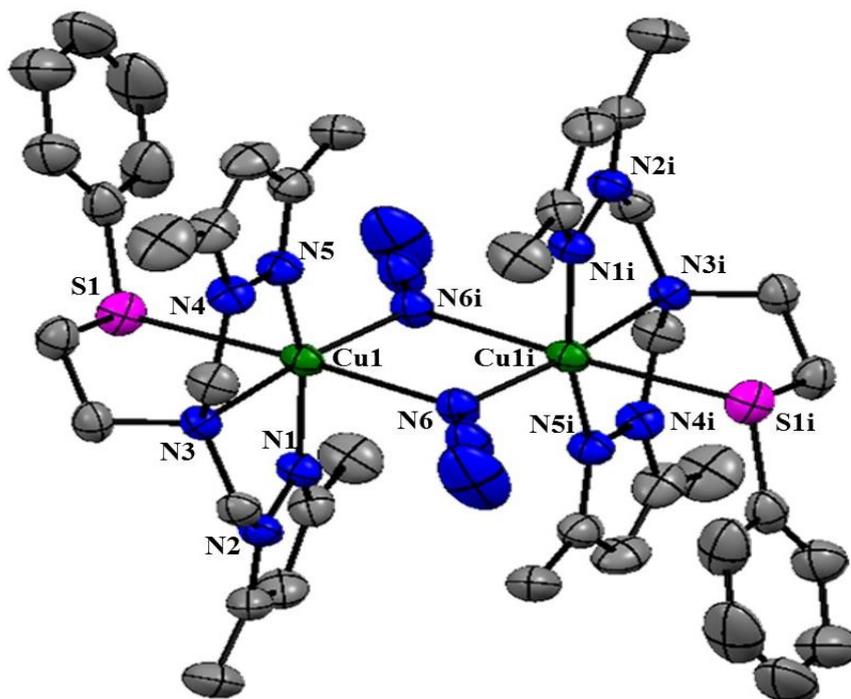
Fig.2.7. Electronic spectra of ligand bdmpe and complexes **1**, **2**, **3**, **4** in  $\text{CH}_3\text{CN}$  ( $10^{-3}$  M).

### 2.4.3. Description of Crystal Structures

#### 2.4.3.1. Crystal structure of $[\text{Cu}(\text{bdmpe})(\mu_{1,1}\text{-N}_3)]_2(\text{ClO}_4)_2$ (**1**)

An ORTEP diagram with the atom labeling scheme of complex **1** is shown in Fig.2.8(a). The unit cell contains two centro-symmetric binuclear  $[\text{Cu}(\text{bdmpe})(\text{N}_3)]_2^{2+}$  entities isolated by two perchlorate counter anions. Selected bond lengths and angles related to metal coordination sphere for the mononuclear unit are provided in Table 2.2, while crystallographic data are presented in Table 2.1. Each copper atoms is surrounded by six hetero atoms – three nitrogen atoms N(1), N(3), N(5) and one sulphur atom S(1) from ligand bdmpe and two nitrogen atoms N(6) and N(6i) from

two end-on azide bridging ligands. The coordination geometry around each copper center is distorted octahedral. The equatorial plane of each copper(II) centers is formed by N(1), N(3), N(5) and N(6i) atoms and the axial plane are occupied by N(6) and S(1) atoms. The equatorial bond distance of Cu-N(1)[1.983 Å], Cu-N(3)[2.103 Å], Cu-N(5)[1.982 Å] and Cu-N(6i)[1.955 Å] are much shorter than axial bond distances of Cu-S(1)[2.797Å] and Cu-N(6)[2.584 Å].



**Fig.2.8(a).** ORTEP diagram depicting the cationic part of the complex  $[\text{Cu}(\text{bdmpe})(\mu_{1,1}\text{-N}_3)]_2(\text{ClO}_4)_2$  (**1**) with atom numbering scheme (40% probability factor for the thermal ellipsoids).

**Table 2.2.** Bond lengths (Å) and bond angles (°) of Complexes **1**, **3** and **4**.

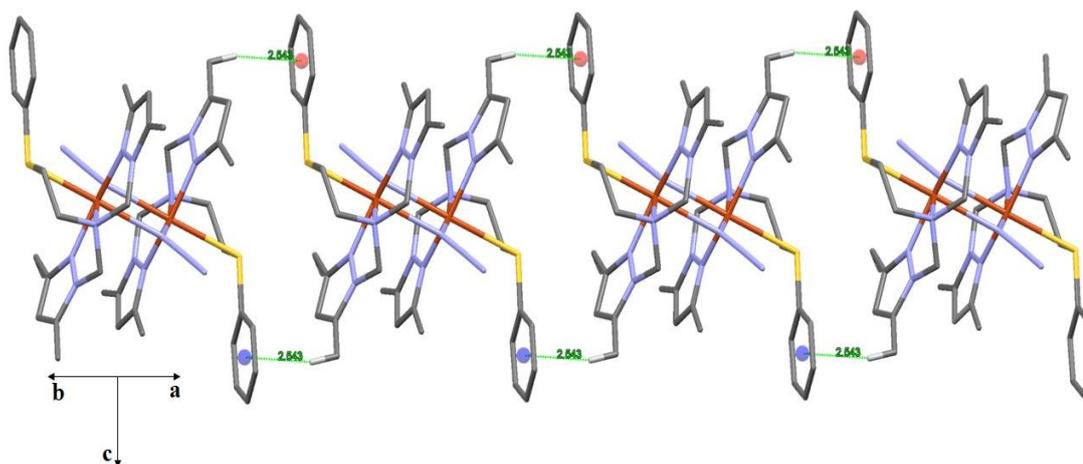
Bond lengths (Å)					
[Cu(bdmpe)( $\mu_{1,1}$ -N <sub>3</sub> )] <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>		[Cu <sub>2</sub> (dmpe) <sub>2</sub> ( $\mu_{1,1}$ -N <sub>3</sub> ) <sub>2</sub> ( $\mu$ -CH <sub>3</sub> COO)]PF <sub>6</sub>		[Cu <sub>2</sub> (dmpe) <sub>2</sub> ( $\mu_{1,1}$ -N <sub>3</sub> ) <sub>2</sub> ( $\mu$ -HCOO)]PF <sub>6</sub>	
(1)		(3)		(4)	
Cu(1)-N(6)	1.9548(19)	Cu(1)-N(4)	1.993(3)	Cu(1)-N(4)	1.983(2)
Cu(1)-N(5)	1.982(2)	Cu(1)-N(1)	1.996(3)	Cu(1)-N(1)	2.001(3)
Cu(1)-N(1)	1.983(2)	Cu(1)-N(3)	2.047(3)	Cu(1)-N(3)	2.047(3)
Cu(1)-N(3)	2.1027(19)	Cu(1)-N(4i)	2.523	Cu(1)-N(4i)	2.534
Cu(1)-S(1)	2.7970(7)	Cu(1)-S(1)	2.818	Cu(1)-S(1)	2.821
Cu(1)-N(6i)	2.584(4)	Cu(1)-O(1)	1.945(2)	Cu(1)-O(1)	1.959(2)
Cu(1)-Cu(1i)	3.494	Cu(1)-Cu(1i)	3.151	Cu(1)-Cu(1i)	3.199

Bond angles (°) of Complexes **1**, **3** and **4**.

Bond angles (°)					
[Cu(bdmpe)( $\mu_{1,1}$ -N <sub>3</sub> )] <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ( <b>1</b> )		[Cu <sub>2</sub> (dmpe) <sub>2</sub> ( $\mu_{1,1}$ -N <sub>3</sub> ) <sub>2</sub> ( $\mu$ -CH <sub>3</sub> COO)]PF <sub>6</sub> ( <b>3</b> )		[Cu <sub>2</sub> (dmpe) <sub>2</sub> ( $\mu_{1,1}$ -N <sub>3</sub> ) <sub>2</sub> ( $\mu$ -HCOO)]PF <sub>6</sub> ( <b>4</b> )	
N(6)-Cu(1)-N(5)	98.62(9)	O(1)-Cu(1)-N(4)	93.93(12)	O(1)-Cu(1)-N(4)	94.00(10)
N(6)-Cu(1)-N(1)	98.05(9)	O(1)-Cu(1)-N(1)	94.74(11)	O(1)-Cu(1)-N(1)	95.76(10)
N(5)-Cu(1)-N(1)	162.95(8)	N(4)-Cu(1)-N(1)	170.45(12)	N(4)-Cu(1)-N(1)	168.60(10)
N(6)-Cu(1)-N(3)	171.85(8)	O(1)-Cu(1)-N(3)	172.46(11)	O(1)-Cu(1)-N(3)	173.07(9)
N(5)-Cu(1)-N(3)	82.00(8)	N(4)-Cu(1)-N(3)	89.89(12)	N(4)-Cu(1)-N(3)	89.34(10)
N(1)-Cu(1)-N(3)	80.99(8)	N(1)-Cu(1)-N(3)	81.96(12)	N(1)-Cu(1)-N(3)	81.61(10)
N(6)-Cu(1)-S(1)	105.68(6)	O(1)-Cu(1)-N(4i)	90.87	O(1)-Cu(1)-N(4i)	90.99
N(5)-Cu(1)-S(1)	88.86(6)	O(1)-Cu(1)-S(1)	91.77	O(1)-Cu(1)-S(1)	92.51
N(1)-Cu(1)-S(1)	90.06(6)	N(1)-Cu(1)-S(1)	92.37	N(1)-Cu(1)-S(1)	92.50
N(3)-Cu(1)-S(1)	82.45(5)	N(1)-Cu(1)-N(4i)	88.55	N(1)-Cu(1)-N(4i)	88.80
N(1)-Cu(1)-N(6i)	90.39	N(3)-Cu(1)-S(1)	81.64	N(3)-Cu(1)-S(1)	81.24
N(3)-Cu(1)-N(6i)	91.64	N(3)-Cu(1)-N(4i)	95.80	N(3)-Cu(1)-N(4i)	95.34
N(5)-Cu(1)-N(6i)	88.94	N(4)-Cu(1)-S(1)	91.35	N(4)-Cu(1)-S(1)	92.95
S(1)-Cu(1)-N(6i)	173.93	N(4)-Cu(1)-N(4i)	87.32	N(4)-Cu(1)-N(4i)	85.14
N(6)-Cu(1)-N(6i)	80.26	N(4i)-Cu(1)-S(1)	177.12	N(4i)-Cu(1)-S(1)	176.12
Cu(1)-N(6)-Cu(1i)	99.74	Cu(1)-N(4)-Cu(1i)	87.68	Cu(1)-N(4)-Cu(1i)	89.33

The chelate bite angles in the five membered rings formed by the thiophenol-S and two pyrazole-N are 82.45, 82.00 and 80.99°, respectively. So the coordination polyhedron around the copper atom consists of four short equatorial bonds (<2.2 Å) and two much longer axial bonds (>2.5 Å). Analysis of crystal structure of complex **1** revealed that two azide ions bridge with two copper(II) centers in end-on ( $\mu$ -1,1) mode and produce a planar  $\text{Cu}_2\text{N}_2$  ring. Two azide ligands are nearly linear with N-N-N angle is 176.06°. The intradimer Cu....Cu distance is 3.494 Å and this is consistent with structural data obtained with other reported binuclear end-on azide bridging complexes [47-48].

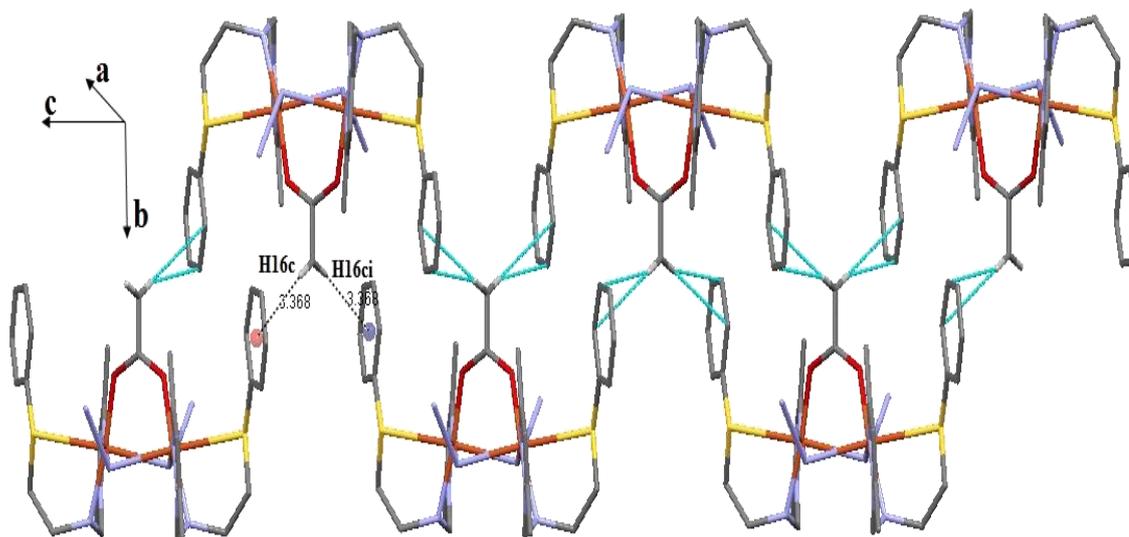
In addition, the adjacent discrete binuclear  $[\text{Cu}_2(\text{bdmpe})_2(\mu_{1,1}\text{-N}_3)_2]^{2+}$  molecules are arranged into a 1D chain along b-axis by intermolecular C/H... $\pi$  interaction between hydrogen atom of pyrazole methyl group (C10-H10c) and phenyl ring and corresponding distance is 2.543 Å [Fig.2.8(b)] [49-50].



**Fig.2.8(b).** Polymeric 1D structure of **1** along b-axis formed by the interdimer C-H/ $\pi$  interactions, shown as dotted lines. (H atoms omitted for clarity).

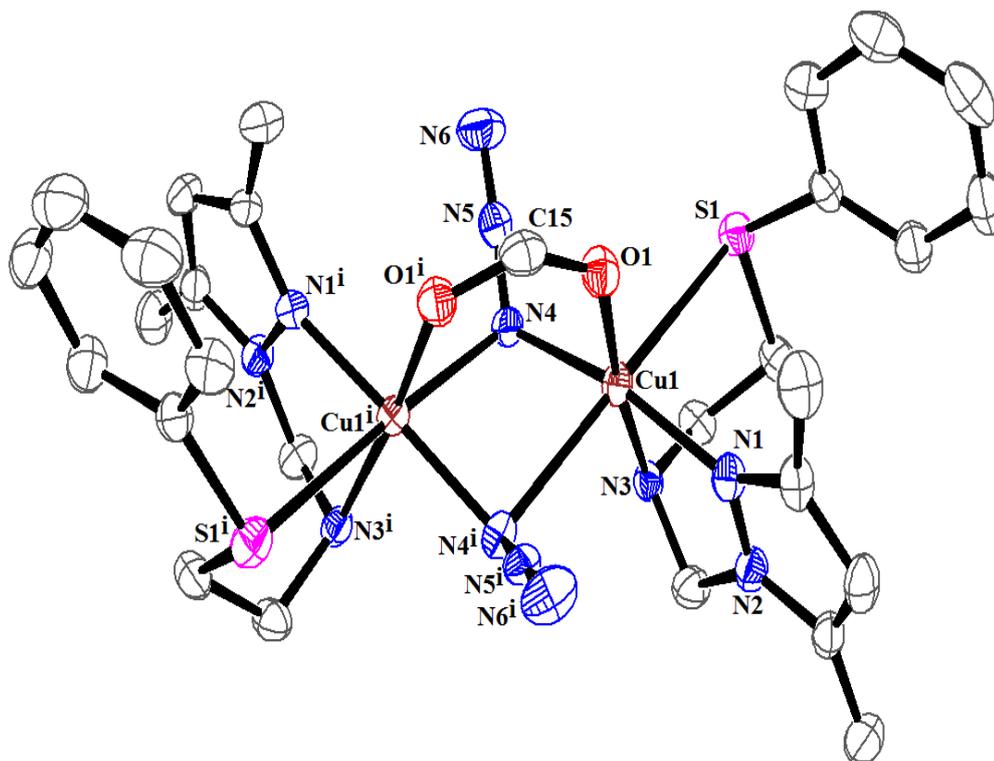


In complex **3**, the equatorial bond distances Cu(1)-N(1) [1.997 Å], Cu(1)-N(3) [2.047 Å], Cu(1)-N(4) [1.993 Å], Cu(1)-O(1) [1.945 Å] are nearly equal, whereas the axial bond distances Cu(1)-S(1) [2.818 Å] and Cu(1)-N(4i) [2.523 Å] are very long and not equal. The coordination geometry around the copper atom is distorted octahedral with four short bonds (< 2.047 Å) and two much longer bond (>2.523 Å). The Cu...Cu distance is 3.151 Å and this is consistent with other binuclear end-on azide and *syn-syn* acetate bridged complex reported in literature [51].



**Fig.2.9(b).** Polymeric 1D structure of **3** along c-axis formed by the interdimer C-H/ $\pi$  interactions, shown as dotted lines. (H atoms omitted for clarity).

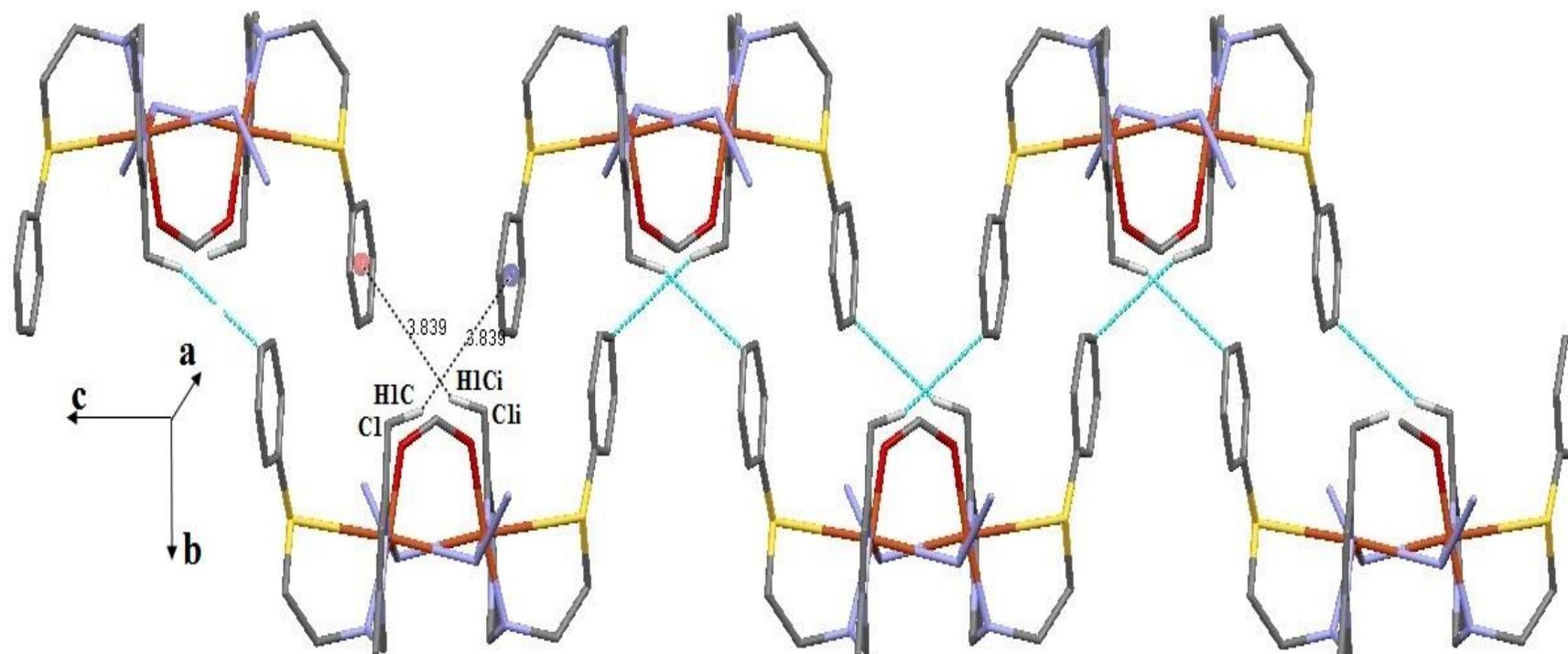
In addition, the adjacent discrete binuclear  $[\text{Cu}_2(\text{dmpe})_2(\mu_{1,1}\text{-N}_3)_2(\mu\text{-CH}_3\text{COO-k-O}^1, \text{O}^{1i})]^+$  molecules are arranged into a 1D chain along c-axis by intermolecular C/H... $\pi$  interaction between two hydrogen atoms (C16-H16c, C16-H16ci) of acetate group and two phenyl rings and the corresponding distances are 3.368 Å [Fig.2.9(b) [49-50]].



**Fig.2.10(a).** ORTEP diagram depicting the cationic part of the complex  $[\text{Cu}_2(\text{dmpe})_2(\mu_{1,1}\text{-N}_3)_2(\mu\text{-HCOO-k-}O^1, O^{1i})]\text{PF}_6$  (**4**) with atom numbering scheme (40% probability factor for the thermal ellipsoids).

In complex **4**, the equatorial bond distances of Cu(1)-N(1) [2.001Å], Cu(1)-N(3)[2.047Å], Cu(1)-N(4) [1.983Å] and Cu(1)-O(1Å)[1.959Å] are shorter than the axial bond distances of Cu(1)-N(4i) [2.543Å] and Cu(1)-S(1) [2.821Å]. So, the geometry around the copper atom consists of a distorted octahedral with four short bonds(< 2.047Å) and two much longer bond (>2.543Å). The Cu...Cu distance is 3.199 Å and this is consistent with structural data obtained with other binuclear end-on azide and formate bridged complex [52].

In addition, the adjacent discrete binuclear  $[\text{Cu}_2(\text{dmpe})_2(\mu_{1,1}\text{-N}_3)_2(\mu\text{-HCOO-k-}O^1, O^{1i})]^+$  molecules are arranged into a 1D chain along c-axis by intermolecular C/H... $\pi$  interaction between hydrogen atoms of pyrazolyl methyl group (C1-H1c) and phenyl ring and the corresponding distance is 3.839 Å [Fig.2.10(b)] [49-50].



**Fig.2.10(b).** Polymeric 1D structure of **4** along c-axis formed by the interdimer C-H/ $\pi$  interactions, shown as dotted lines. (H atoms omitted for clarity).

### 2.4.3. Magnetic study

The temperature dependence of the magnetic properties of the complexes **1**, **3** and **4** as plot of  $\chi_M T$  versus  $T$  ( $\chi_M$  is the molar magnetic susceptibility for two copper(II) ions) can be shown in Fig.2.11. The values of  $\chi_M T$  are 0.91, 0.82 and 0.78  $\text{cm}^3 \cdot \text{mol}^{-1} \text{K}$  at 300 K for complexes **1**, **3** and **4**, respectively and these value are slightly higher than the theoretical value of 0.75  $\text{cm}^3 \cdot \text{mol}^{-1} \text{K}$  expected for two non-interacting  $S = \frac{1}{2}$   $\text{Cu}^{\text{II}}$  ions with  $g = 2.00$ . Starting from room temperature, the  $\chi_M T$  values decreases smoothly upon cooling and indicating dominant anti-ferromagnetic exchange interactions between the two  $\text{Cu}^{\text{II}}$  ions for the complexes **3** and **4**. The  $\chi_M T$  values decreases very fast with decreasing temperature after 50 K and at 1.8 K, the  $\chi_M T$  values are 0.007  $\text{cm}^3 \cdot \text{mol}^{-1} \text{K}$  for complex **3** and 0.24  $\text{cm}^3 \cdot \text{mol}^{-1} \text{K}$  for complex **4**, indicating an anti-ferromagnetically coupled ground state with  $S = 0$ . The shape of the magnetic plot is typical for anti-ferromagnetically coupled systems. The magnetic data have been thus approximately modeled using isotropic spin Heisenberg Hamiltonian  $H = -2J\{S_{\text{Cu1}} \cdot S_{\text{Cu2}}\}$ , where  $J$  is the exchange interactions within the binuclear Cu(II) unit Cu(I)-Cu(2) and  $S_i$  is the spin operators for each centers [53-55]. The best fit parameters are  $J = -15.3(1) \text{ cm}^{-1}$ ,  $g = 2.130(1)$  for complex **3** and  $J = -18.6(1) \text{ cm}^{-1}$ ,  $g = 2.350(1)$  for complex **4**.

For complex **1**,  $\chi_M T$  value is 0.75 at 300 K and the value does not change till temperature reaches 20 K and finally the value is 0.3 at 1.8 K. The best fit parameter is  $J = -2.33(3) \text{ cm}^{-1}$  and  $g = 2.220$  and the value is much higher than the complexes **3** and **4**. This suggests the exchange interaction is very weak for complex **1** and this can be explained by the bridging geometry, as two Cu-N (of bridging azides) are very long ( $\sim 2.580 \text{ \AA}$ ) and the exchange interaction is bound to be weak. The overall anti-ferromagnetic exchange interactions found in **3** and **4** are stronger probably due to good overlap of the orbital through the carboxylato bridge linked to the two  $\text{Cu}^{\text{II}}$  ions with oxygen atoms through equatorial bond lengths 1.932  $\text{ \AA}$  for complex **3** and 1.952  $\text{ \AA}$  for complex **4** and weak overlap of two double end-on azide bridges due to long Cu-N(bridging azide) bond length ( $>2.50 \text{ \AA}$ )

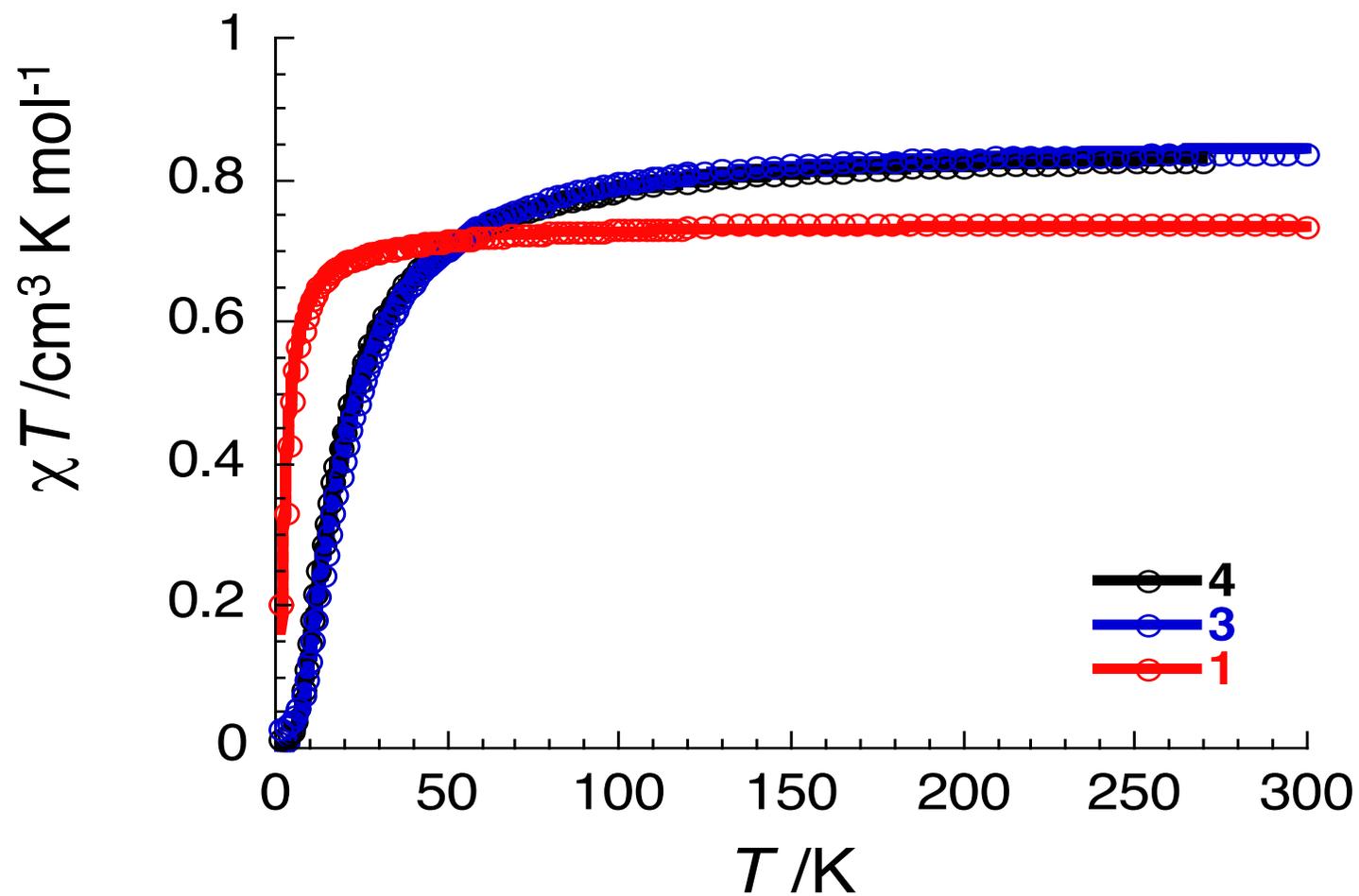


Fig.2.11. Magnetic properties of the three compounds 1, 3 and 4 (colour dots) and fits (lines) using the model explained in the text.

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## 2.5. Conclusion

One new N<sub>3</sub>S coordinate tripodal ligand *N,N*-bis((3,5-dimethyl-1*H*-pyrazol-1-yl)methyl)-2-(phenylthio)ethan-1-amine (bdmpe) has been synthesized and characterized. Two new binuclear double end-on azide bridged complexes [Cu(bdmpe)(μ<sub>1,1</sub>-N<sub>3</sub>)<sub>2</sub>(X)<sub>2</sub>] [X = ClO<sub>4</sub><sup>-</sup> (**1**), PF<sub>6</sub><sup>-</sup> (**2**)] and two new binuclear triple bridged copper(II) complexes with double end-on azide and *syn-syn* acetate / formate bridge complexes [Cu<sub>2</sub>(dmpe)<sub>2</sub>(μ<sub>1,1</sub>-N<sub>3</sub>)<sub>2</sub>(Y)]PF<sub>6</sub> [where dmpe = *N*-((3,5-dimethyl-1*H*-pyrazol-1-yl)methyl)-2-(phenylthio)ethan-1-amine, Y = CH<sub>3</sub>COO<sup>-</sup> (**3**) or HCOO<sup>-</sup> (**4**)] have been synthesized and characterized with X-ray structures. Crystal structures of the complexes **1**, **3** and **4** show that ligand (bdmpe) behave as a tetradentate N<sub>3</sub>S-donor for complex **1** and for complexes **3** and **4** it transformed into tridentate N<sub>2</sub>S-coordinate ligand (dmpe) during in situ complexation reaction. Variable temperature magnetic studies of the complexes showed that azide bridge has almost no role in the magnetic properties of the complexes because of long Cu-N(bridging azide) (~2.580Å) but *syn-syn* (O, O) acetate or formate bridge complexes produce weak anti-ferromagnetic interaction.

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