

## Synthesis, Spectral Studies and DFT Calculation of Copper(II) Complexes with Mixed Ligands

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The reaction of copper(II) chloride with Schiff bases and alkanolamines in 1:1:1 molar ratio(s) resulted a series of mixed ligand copper(II) complexes of general formula  $[Cu(sb)(aa)]$  (**1-6**), [where sb = Schiff base; salicylidene-1-aminobenzene (sabH) (**1,4**), salicylidene-4-chloro-1-aminobenzene (scabH) (**2,5**), salicylidene-4-methyl-1-aminobenzene (smabH) (**3,6**) and aa = alkanolamine; ea = ethanolamine **1-3**, pa = propanolamine **4-6**]. These complexes were found to be coloured solid and are soluble in DMF and DMSO. All the complexes were characterized by elemental analysis (C, H, N and Cu), IR, ESI-MS, ESR, PXRD, TG-DTG and SEM-EDAX spectroscopic studies. In order to provides a theoretical support to experimental observation, energy calculation of synthesized complexes has been done through the DFT calculations by using Gaussian 09 program with basis set B3LYP. On the basis of these observations distorted square planar geometry around the copper(II) is tentatively proposed.

**Keywords:** Copper(II) complex, Schiff base, ESR, DFT, Square planar geometry.

### INTRODUCTION

Mixed ligand metal complexes of Schiff base derived from salicylaldehyde with aromatic amines have received significant attention in the recent years [1] because of their interesting physico-chemical properties [2], varied structural features [3] and biologically activities [4]. The high affinity for the chelation of the Schiff bases toward the copper metal ions is employed in synthesis of their important biologically potent coordination complexes. Therefore, significant work has been devoted to the synthesis and characterization of mixed ligand copper(II) complexes with several Schiff base ligands [5]. Electrochemical studies of some copper (II) complexes show that the complexes with lower reduction potential are more biologically active [6]. Copper complexes show significant antibacterial and antifungal activities [7]. Due to the presence of nitrogen and oxygen donor sites in the ligands in their backbones they form stable and intensely coloured coordination complexes of copper [8,9]. The occurrence of an amine group in the alkanolamine offers further possibilities of inter molecular hydrogen bond [10] formation with Schiff bases, which may lead to metal complexes with three-dimensional network structures.

Survey of literature reveals that there is no report of synthesis and structural studies of complexes of copper with mixed ligand such as salicylidene-1-aminobenzene (sabH), salicylidene-4-chloro-1-aminobenzene (scabH), salicylidene-4-methyl-1-

aminobenzene (smabH) and alkanolamine *e.g.*, ethanolamine (ea) or propanolamine (pa) with molecular modeling. In this present course of investigation, we reported synthesis, spectral, structural characterization and DFT study of a new mono-nuclear series of copper(II) complexes having the molecular formula  $[Cu(sb)aa]$  [sb = Schiff base, aa = alkanolamine]. This study provides insights about the chelation and coordination mode of two entirely different ligands with copper. A SEM analysis of the complex was also carried out to see the surface morphology of these mixed ligand complexes. Powder X-ray diffraction and quantum chemical calculations are used in order to confirm the structure of complexes. The spectral study using FT-IR, ESI-MS and ESR analyses are also investigated in order to find a correlation between molecular structure and vibrational frequencies of complexes.

### EXPERIMENTAL

The chemicals and solvents of analytical grade were purchased directly from Sigma-Aldrich and CDH and used without further purification. Copper was estimated by iodometric titration [11]. The FT-IR spectra were recorded on spectrometer ( $4000-450\text{ cm}^{-1}$ ) in KBr pellets on a Perkin-Elmer 1000 FT-IR spectrophotometer. The elemental analysis was performed on CHN-932 on Perkin- Elmer 7300 DV elemental analyzers. Powder X-ray diffraction (PXRD) was recorded on X' Pert Pro XRD. HRMS were recorded in ESI mode. X band

ESR spectra were done on JES-FA200 Spectrometer. SEM-EDAX was recorded on JEOL, Japan (JFC 1600, Auto Fine Coater).

The electron density and molecular orbital energy of ligand and complexes were analyzed by computational method using density functional theory (DFT). The Gaussian 09 programs were used for optimization of geometry by employing a widely used hybrid exchange-correlation functional B3LYP and LANL2DZ basis set.

**Synthesis of Schiff-base ligands:** The Schiff bases (sabH, scabH and smabH) [12,13] were synthesized by refluxing about 5 h a mixture of an equimolar amount of salicylaldehyde with corresponding amines (such as aminobenzene, 4-methyl-1-aminobenzene and 4-chloro-1-aminobenzene) in methanol on a water bath. The resulting products were recrystallized by using methanol. The resulting crystals of Schiff base were filtered off and washed.

**Synthesis of complexes:** An appropriate amount of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.5 g, 2.93 mmol) is dissolved in hot methanol (20 mL), which was further mixed with a boiling methanolic solution (30 mL) of salicylidene-1-aminobenzene (sabH) (0.578 g, 2.93 mmol) followed by addition of ethanolamine (0.179 g, 2.93 mmol). The mixture was heated on a water bath for about 3 h and filtered. The filtrate was left to stand overnight, yielding shining dark green crystals of the complex, which were filtered off. The crystals thus formed were washed with ethanol and dried in a desiccator over anhydrous silica gel.

All the complexes **1-6** were synthesized through similar procedure.

**[Cu(sab)ea] (1):** Yield, 50 %; Anal. calcd.  $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_2\text{Cu}$ : C, 56.33; H, 5.04; N, 8.76; Cu, 19.87; Found: C, 56.27; H, 5.00; N, 8.80; Cu, 19.81 %. IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3414 (-NH<sub>2</sub>), 1644 (-C=N), 689, 613 (Cu-N), 549, 468 (Cu-O).

**[Cu(scab)ea] (2):** Yield, 60 %; Anal. calcd.  $\text{C}_{15}\text{H}_{15}\text{N}_2\text{O}_2\text{ClCu}$ : C, 50.85; H, 4.27; N, 7.91; Cu, 17.94. Found: C, 50.80; H, 4.20; N, 7.86; Cu, 17.87 %. IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3423 (-NH<sub>2</sub>), 1634 (-C=N), 652, 627, (Cu-N), 512, 465 (Cu-O).

**[Cu(smab)ea] (3):** Yield, 50 %; Anal. calcd.  $\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}_2\text{Cu}$ : C, 57.56; H, 5.43; N, 8.39; Cu, 19.03; Found: C, 57.59; H, 5.40; N, 8.45; Cu 18.94 %. IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3437 (-NH<sub>2</sub>), 1636 (-C=N), 667, 603 (Cu-N), 522, 461 (Cu-O).

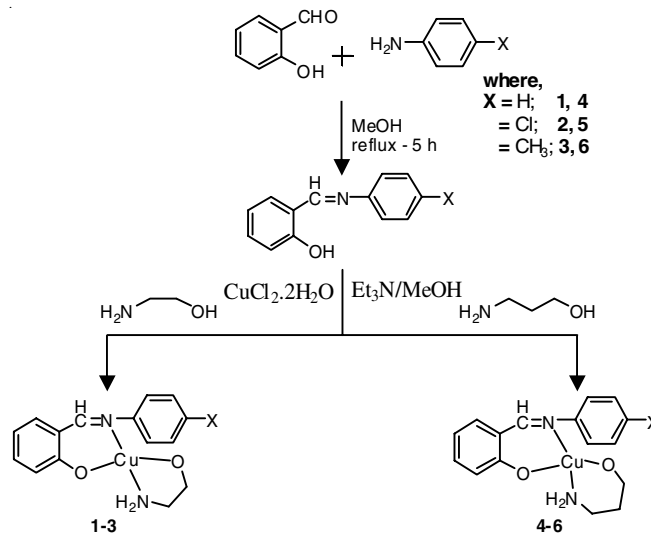
**[Cu(sab)pa] (4):** Yield, 58 %. Anal. calcd.  $\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}_2\text{Cu}$ : C, 57.56; H, 5.43; N, 8.39; Cu, 19.03. Found: C, 56.49; H, 5.38; N, 8.30; Cu, 18.97 %. IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3423 (-NH<sub>2</sub>), 1606 (-C=N), 689, 617 (Cu-N), 525, 468 (Cu-O).

**[Cu(scab)pa] (5):** Yield, 67 %; Anal. calcd.  $\text{C}_{16}\text{H}_{17}\text{N}_2\text{O}_2\text{ClCu}$ : C, 52.18; H, 4.65; N, 7.61; Cu, 17.25. Found: C, 52.10; H, 4.58; N, 7.57; Cu, 17.18; IR ( $\text{cm}^{-1}$ ): 3423 (-NH<sub>2</sub>), 1603 (-C=N), 622, 590 (Cu-N), 510, 468 (Cu-O).

**[Cu(smab)pa] (6):** Yield, 61 %. Anal. calcd.  $\text{C}_{17}\text{H}_{20}\text{N}_2\text{O}_2\text{Cu}$ : C, 58.69; H, 5.79; N, 8.05; Cu, 18.27. Found: C, 58.60; H, 5.70; N, 8.00 %; IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3428 (-NH<sub>2</sub>), 1623 (-C=N), 617, 649 (Cu-N), 519, 459 (Cu-O).

## RESULTS AND DISCUSSION

Mixed ligand complexes of Cu(II) are coloured solids, non-hygroscopic and stable at room temperature have been synthesized according to **Scheme-I**. These Cu(II) complexes



**Scheme-I:** Synthetic route for copper(II) mixed ligand complex **1-6**

are soluble in common organic solvent (chloroform, dichloromethane) and also in pyridine, DMSO and THF on slight heating.

**Infrared spectra:** The characteristic band due to phenolic O-H of Schiff bases present in the region 3485-3450  $\text{cm}^{-1}$  were found to be absent in the copper complexes [12,13]. The disappearance of this band indicates deprotonation of phenolic O-H and appearance of new band in the region 525-510  $\text{cm}^{-1}$  indicates coordination of phenolic oxygen to copper. This coordination mode (Cu-O) was further supported by the lowering in the frequency of phenolic C-O [14]. The azomethine band  $\nu(-\text{C}=\text{N})$  of the free Schiff bases appear in the region 1648-1660  $\text{cm}^{-1}$  shows a lower shift and appear in the region 1644-1606  $\text{cm}^{-1}$  for the metal complexes is indicative of coordination of the azomethine nitrogen to copper.

The alkanolamines shows infrared absorption in the region 3550-3500  $\text{cm}^{-1}$  due to  $\nu(\text{O}-\text{H})$  and in the region 3460-3448  $\text{cm}^{-1}$  due to  $\nu(\text{N}-\text{H})$  vibrations [15,16]. The disappearance of band in the region 3550-3500  $\text{cm}^{-1}$  and shifting of N-H stretching frequencies in the lower frequency region in complexes clearly indicates coordination of oxygen and nitrogen atom of alkanolamines to the copper atom. The above assigned coordination mode of copper with nitrogen and oxygen of Schiff base and alkanolamine was further supported by appearance of bands in the region 689-590  $\text{cm}^{-1}$  due to Cu-N while in the region 459-549  $\text{cm}^{-1}$  due to Cu-O [15]. The IR frequency in the range 846-806  $\text{cm}^{-1}$  is observed in the Schiff base (scabH) and in complexes **2** and **4** due to  $\nu(\text{C}-\text{Cl})$  stretching [13,17].

**ESI-Mass spectral studies:** The mass spectra [18] of complexes **3** and **5** (Fig. 1) were recorded in positive mode exhibiting peaks at  $m/z$  319.0287, 333.4534, 333.0149 and 368.9817 due to complex  $[\text{Cu}(\text{sab})(\text{ea}) + \text{H}]^+$  (calcd.  $m/z$  319.8457),  $[\text{Cu}(\text{smab})(\text{ea}) + \text{H}]^+$  (calcd.  $m/z$  333.8723),  $[\text{Cu}(\text{sab})(\text{pa}) + \text{H}]^+$  (calcd.  $m/z$  333.8723) and  $[\text{Cu}(\text{scab})(\text{pa}) + \text{H}]^+$  (calcd.  $m/z$  368.3174), respectively. The result shows there is good 1:1:1 binding mode between Schiff base, ethanolamine (**1**, **3**)/propanolamine (**4**, **5**) with copper(II).

**ESR spectra:** The ESR spectrum of Cu(II) complex (**1**, **2**, **4** and **6**) offers information about the geometry and environment of the ligating sites of the Schiff base and metal ions [19]. The X-band ESR spectrum of Cu(II) complex has been

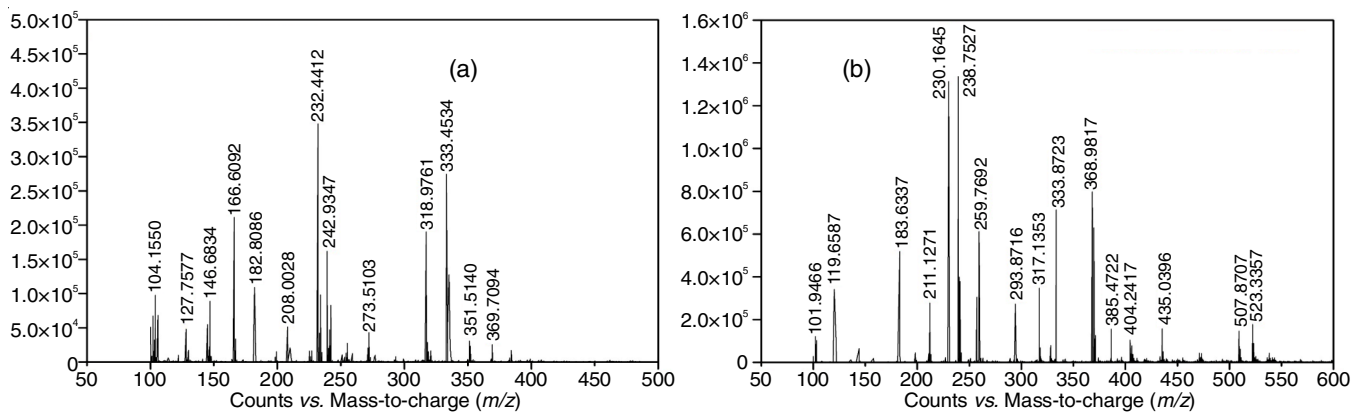


Fig. 1. ESI-MS spectra of complex (a) [Cu(smab)ea] (3) and (b) [Cu(scab)pa] (5)

recorded in solid state at room temperature at a frequency of 9.1 GHz. The spectrum is shown in Fig. 2. The parameters  $g_{\parallel}$ ,  $g_{\perp}$ ,  $g_{av}$  and  $G$  values have been calculated and given in Table-1. The  $g_{\parallel}$  value is an important function for indicating the metal-ligand bond character, for covalent character  $g_{\parallel} < 2.3$  and for ionic character  $g_{\parallel} > 2.3$  respectively [20]. In these complexes the  $g_{\parallel}$  value of Cu(II) complex is less than 2.3, indicating an appreciable covalent character of the metal-ligand bond. The order of  $g$  value is found to be  $g_{\parallel} > g_{\perp} > g_e$  (2.0023) indicating the unpaired electron is localized in  $d_{x^2-y^2}$  orbital with  $^2B_{1g}$  which is the ground state of Cu(II) square planar complex [21]. In the present case the observed measurements of Cu(II) complex is  $g_{\parallel}$  (2.228)  $>$   $g_{\perp}$  (2.064)  $>$  2.0023 indicate that the complex is axially symmetric and copper site has a  $d_{x^2-y^2}$  ground state. The geometric parameter ( $G$ ) is the measure of extent of exchange interactions and is calculated by using  $g$ -tensor values of the expression  $G = g_{\parallel} - 2.0023/g_{\perp} - 2.0023$ .

TABLE-1 ESR SPECTRAL DATA FOR COMPLEXES (1, 2, 4 AND 6)					
S. No.	Complex	$g_{\parallel}$	$g_{\perp}$	$g_{av}$	$G$
1	Cu(sab)ea (1)	2.228	2.064	2.916	3.570
2	Cu(scab)ea (2)	2.210	2.050	2.893	4.200
3	Cu(sab)pa (4)	2.190	2.053	2.874	3.580
4	Cu(smab)pa (6)	2.215	2.075	2.906	2.344

**Powder XRD analysis:** Powder XRD is widely used to characterize a crystalline solid as it was challenging to isolate suitable single crystal for X-ray crystallography. XRD spectrum

[22] of complexes 1, 3, 4 and 6 clearly showed crystalline material. The powder diffraction analysis of metal complexes, 1, 3, 4 and 6 show well defined crystalline peaks (Fig. 3). The indexing and calculations of unit cell parameters were performed using Powder-X software and scattering angles ( $2\theta$ ) corresponding to each reflection, inter-planar spacing ( $d$ ) along with Miller's indices and lattice constants were evaluated which corresponds to cubic crystal system for complexes 1, 3, 4 and 6. For calculation of the crystallite size, we use Debye Scherrer formula as given below,

$$D = 0.91 \lambda / \beta \cos \theta$$

where constant 0.91 is the shape factor,  $k$  is the X-ray wavelength of  $\text{CuK}\alpha$  radiation (1.5406 Å),  $\theta$  is the Bragg diffraction angle and  $\beta$  is the full width at half maximum (FWHM). The experimental average grain sizes of 1, 3, 4 and 6 complexes were found to be 16, 32, 24 and 41 nm respectively. Summary of XRD data and refinement parameters of metal complexes are given in Table-2. All the peaks were matched with the JCPDF.

**Thermal analysis:** The thermal analysis [21,22] of all complexes (Fig. 4) were performed between 30 to 800 °C in dynamic nitrogen atmosphere at heating rate 20 °C/min. All the complexes show two steps of weight loss in the TG curve accompanied by two endothermic peaks in the DTG curve. The molecular mass of complex [Cu(sab)ea] (1) is 319.8457 exhibits weight loss between 170 °C and 551 °C constantly due to loss of 59.68 (18.66 %) which is equal to the approximate weight of one coordinated ligands ethanolamine (eaH) [C<sub>2</sub>H<sub>6</sub>NO,

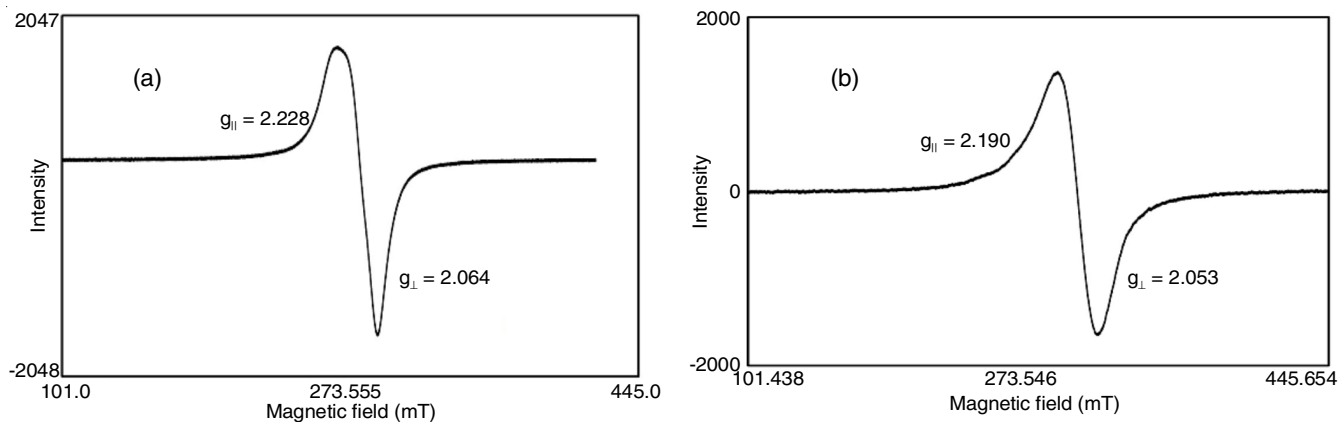


Fig. 2. ESR spectra of (a) [Cu(sab)ea] (1) and (b) [Cu(sab)pa] (4)

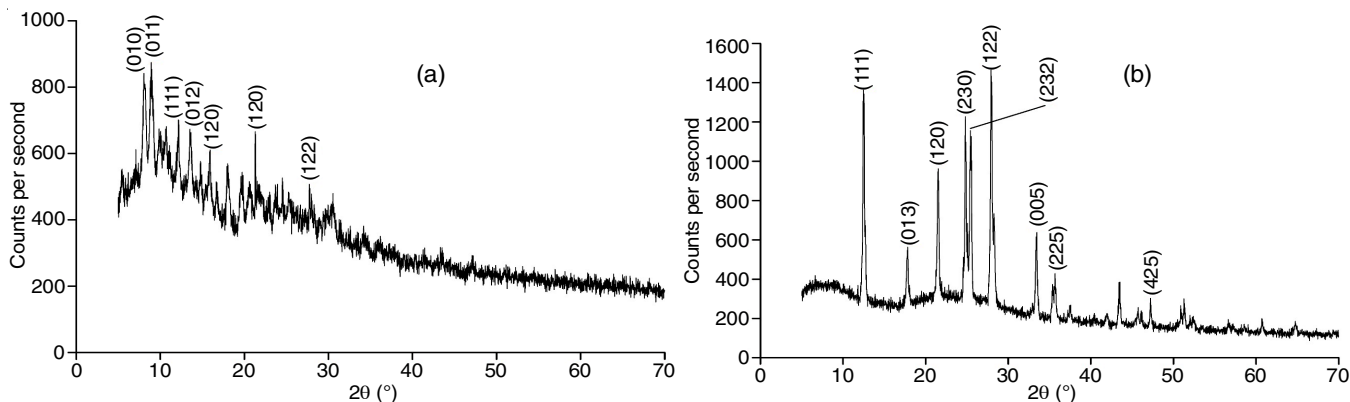


Fig. 3. Powder XRD spectra of complex (a) [Cu(sab)ea] (1) and (b) [Cu(sab)pa] (4)

TABLE-2  
REFINEMENT PARAMETERS FOR XRD DATA OF METAL COMPLEXES

Parameter	Complex 1	Complex 3	Complex 4	Complex 5
Formula	C <sub>15</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> Cu	C <sub>16</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub> Cu	C <sub>16</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub> Cu	C <sub>17</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub> Cu
F.W.	319.8457	333.07	333.87	347.08
Temperature (K)	298	298	298	298
Wavelength	1.540598	1.540598	1.540598	1.540598
Radiation	CuK <sub>α</sub>	CuK <sub>α</sub>	CuK <sub>α</sub>	CuK <sub>α</sub>
Crystal system	Triclinic	Orthorhombic	Triclinic	Triclinic
Unit cell dimension				
a (Å)	10.175	16.491	10.175	10.175
b (Å)	12.064	14.663	12.064	12.064
c (Å)	14.483	16.750	14.483	14.483
α (°)	104.65	–	104.65	104.65
β (°)	90.44	–	90.44	90.44
γ (°)	110.85	–	110.85	110.85
2θ (°)	10-70	10-70	10-70	10-70

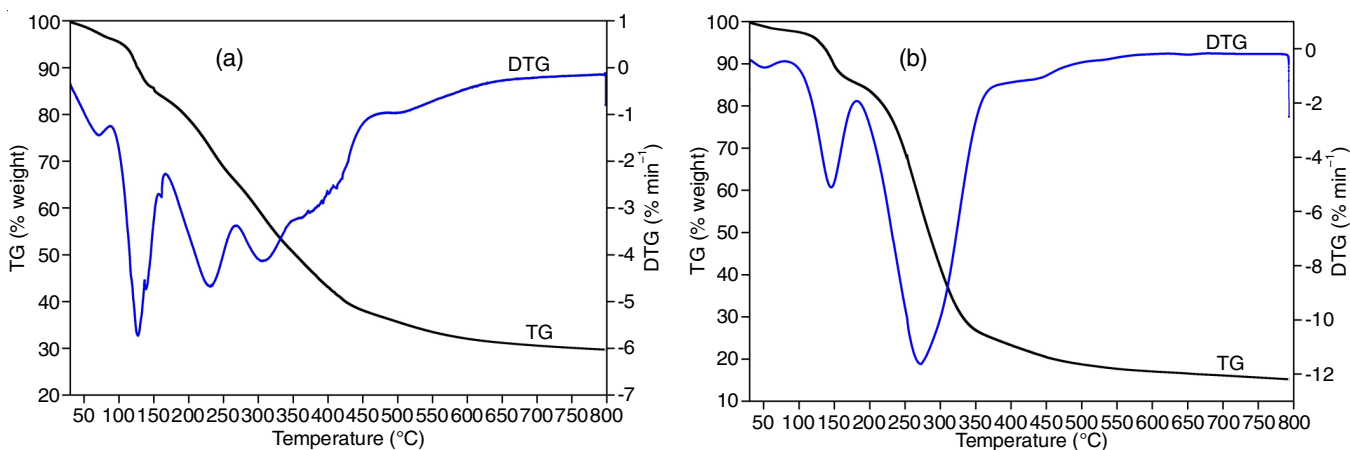


Fig. 4. TG-DTG spectrum of (a) [Cu(sab)ea] (1) and (b) [Cu(sab)pa] (4)

calcd. weight 60.07 (18.78 %) and 177.00 (55.34 %) which corresponds to the weight loss of organic segment of another ligand sabH [C<sub>13</sub>H<sub>10</sub>N, calcd. weight 180.22 (56.35 %)]. The residual weight of 26.00 % (calcd. 24.87 %) corresponds to copper oxide, CuO, which is stable after 551 °C.

The molecular mass of the complex [Cu(sab)pa] (4) is 333.8723 exhibit weight loss of 73.26 (22.00 %), indicating the loss of one coordinated ligands propanolamine (paH) [C<sub>3</sub>H<sub>7</sub>NO, calcd. weight 74.10 (22.25 %)] at 225 and at 590 °C a weight loss of 54.26 % due to organic segment of another coordinated ligand sabH [C<sub>13</sub>H<sub>10</sub>N, calcd. weight 180.22 (54.12

%)]. Thermogram of complex 4 from ambient to 800 °C shows that total 76.26 % weight loss of the complex. After 590 °C a stable residue 23.74 % is obtained which is due to CuO (calcd. weight 23.88 %) is obtained.

**SEM and EDX:** The SEM images of complex 1, 2 and 4 were recorded [23,24] to study the surface morphology of the material. SEM image gives information about the surface morphology of complexes. It was seen from SEM image (Fig. 5) that the morphology of the all three complexes are quite similar in appearance with well disseminated stone like structure. The EDX spectrum of the complexes was recorded

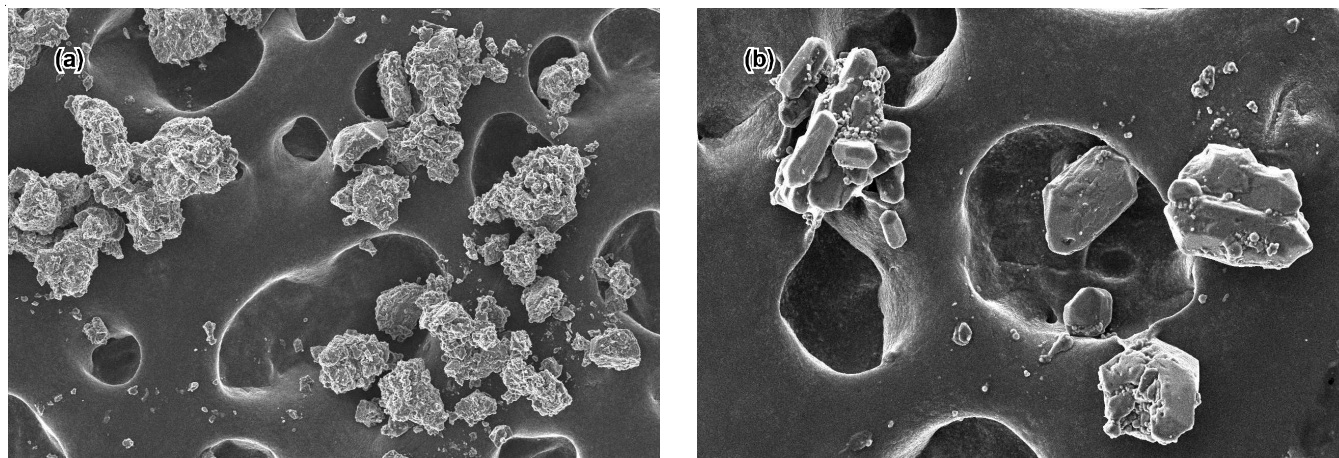


Fig. 5. SEM image of (a) [Cu(sab)(ea)] (1) and (b) [Cu(sab)(pa)] (4)

in order to get the evidence about the presence of metals. The EDX spectrum (Fig. 6) of complexes shows that the presence of copper metal.

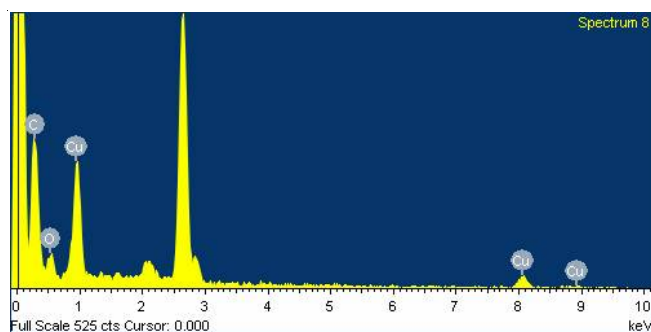


Fig. 6. EDX of [Cu(sab)(ea)] (1)

**Computational detail:** The most stable, optimized geometry of ligands and their Cu(II) complexes were calculated by density functional theory (DFT) using Gaussian 09W Software [25]. The LUMO-HOMO energy gaps were successfully calculated for ligand, smabH and scabH, and their corresponding complexes **3** and **5** and its frontier molecular orbital diagram were shown in Fig. 7. The HOMO energy characterizes the electron

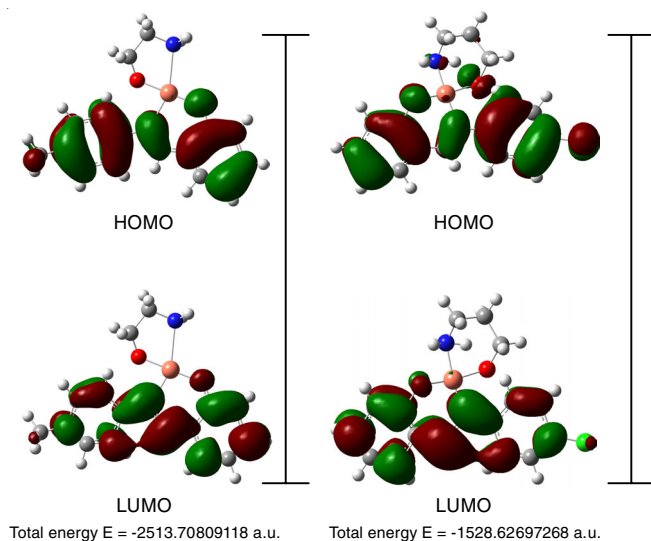


Fig. 7. HOMO and LUMO gap for [Cu(sab)(ea)] (3) and [Cu(sab)(pa)] (5)

donating ability, while LUMO energy characterizes the electron withdrawing ability of the complex. Energy gap of HOMO and LUMO shows the molecular chemical stability, which is a critical parameter in determining molecular electrical transport properties because it is a measure of electron conductivity. The optimized structure of the complexes suggests slightly distorted square planar geometry around the metal center and calculated bond length and bond angles are in accordance with the other reported square-planar copper(II) complexes of N,O donor ligands [26,27].

## Conclusion

The present paper includes the synthesis, structural and spectroscopic studies of six copper(II) mixed ligands complexes with a bidentate NO donor Schiff base and alkanolamines (ethanolamine, **1-3**/propanolamine, **4-6**). All these complexes have been synthesized by similar method. The spectroscopic observation reveals four coordination around copper. The ESR spectral studies indicate about the square planar geometry of all complexes. Powder XRD data reveals that the crystalline nature of complexes. Theoretical calculations on ligands and their copper(II) complexes suggest a good agreement between theoretical studies of electronic structure with the experimental one. SEM analysis shows a stone like shape of all complexes and EDAX represent a good signature of copper in all complexes.

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