

## Synthesis, reactivity and some physical properties of new copper(II) complexes containing {2-(*o*-hydroxyphenyl)}benzoxazole moieties

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**Abstract :** A complex  $[(\mu\text{-Cl})_2\text{Cu}_2\{\eta^2\text{-}(\text{pbox})\}_2]$  (1) has been isolated by the reaction of copper(II) chloride (hydrated) with {2-(*o*-hydroxyphenyl)}benzoxazole (pboxH) in equimolar ratio [in ethanolic medium] and was found to be insoluble in most of the organic solvents; resulting product was treated with sodium salts of various Schiff bases, isopropoxide and aluminium tetraisopropoxide in presence of THF/pyridine produced the complexes of the type  $[(\text{smab})\text{Cu}\{\eta^2\text{-}(\text{pbox})\}]$  (2),  $[(\text{sap})\text{Cu}\{\eta^2\text{-}(\text{pbox})\}]$  (3) and  $[(\text{opr}^1)_2\text{Cu}_2\{\eta^2\text{-}(\text{pbox})\}_2]$  (4),  $[\{\text{Al}(\text{opr}^1)_4\}\text{Cu}\{\eta^2\text{-}(\text{pbox})\}]$  (5). These products have been characterized by elemental analysis (C, H, N), Volhard's method (for Cl) and AAS (for Cu), melting points, spectroscopic (IR, UV-Visible, ESR, FAB-MS) and magnetic studies.

**Keywords :** Copper(II) complexes of benzoxazole, ESR, FAB-MS, magnetic studies.

### Introduction

Schiff bases and substituted benzimidazole/benzoxazole complexes of transition metals are of great importance due to its biological, pharmacological, clinical and analytical applications<sup>1,2</sup>. During last decade different group of workers involved to study the photophysics and photochemistry of Schiff bases (i) containing naphthalene or quinoline ring<sup>3</sup>, (ii) 2-(*p*-dimethylamine styryl)benzoxazole (DMASBO) and its benzothiazole analogue (DMASBT)<sup>4</sup>; whereas intramolecular proton transfer process in the photophysics of 2-(2'-hydroxyphenyl)benzoxazole and 2-(2'-hydroxyphenyl)benzothiazole was studied by Purkayastha and Chattopadhyay<sup>5</sup>. The phosphorescence of related compounds, 2-(2'-deuteriooxyphenyl)benzoxazole (DBO) and 2-(2'-hydroxy-4'-methyl phenyl)benzoxazole (*m*-MeHBo)<sub>4</sub> as well as synthesis of polyhydroxy benzoxazole<sup>6</sup> based colorimetric chemosensor for anionic species were also studied. Keeping above facts in view, we have been interested to investigate the synthesis and spectroscopic characterizations of '3d' transition metal complexes<sup>7-9</sup> containing these versatile ligands,

which were not studied in detail so far.

Therefore we report herein the synthesis, spectral (IR, UV-Visible, FAB-MS and ESR) and magnetic studies of copper(II) complexes containing {2-(*o*-hydroxyphenyl)-benzoxazole} (pboxH) moieties.

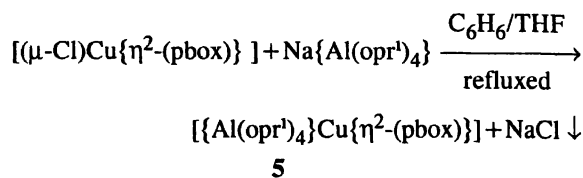
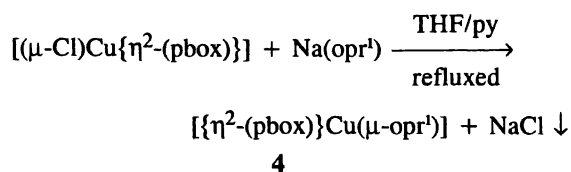
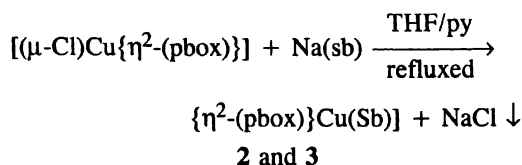
### Results and discussion

An ethanolic solution of {2-(*o*-hydroxyphenyl)}-benzoxazole (pboxH) was added to a aqueous ethanolic solution of copper(II) chloride (hydrated) in equimolar ratio, a light green coloured precipitate was obtained. Further addition of sodium acetate afforded yellowish green colour solid product  $[(\mu\text{-Cl})_2\text{Cu}_2\{\eta^2\text{-}(\text{pbox})\}_2]$  (1). The product 1 was digested, filtered, washed with aqueous ethanol and finally dried at ~ 100 °C under reduced pressure.

Attempt was made to purify the complex using a number of solvents such as benzene, isopropanol, ethanol etc. However, it has been realized that the complex is highly insoluble in most the common organic solvents as well as mixture of solvents. The complex has tendency to form

adducts, when treated with THF/pyridine. Due to insolubility in the non-polar solvents, the molecular weight determination could not be made possible either by cryoscopically or by ebullioscopically, though it is expected to be polymeric in nature.

Attempts have been made during the course of present investigation to prepare soluble complex by the interaction of sodium salt of Schiff bases; which could throw light on structure of copper(II) complexes. The reactions of chloro complex of copper(II) containing benzoxazole moiety with sodium salt of Schiff bases (sb) in the equimolar ratio, in the presence of THF/pyridine, which can be represented as follow :



(where sb = smabH (2) and sapH (3))

These mixed ligand complexes are coloured solid and found to be soluble in common organic solvents like benzene, *n*-hexane etc. and have been purified by recrystallization in the mixture of solvents such as THF and benzene

Further, the chloro complex of copper(II) was interacted with sodium isopropoxide and tetraisopropoxide aluminate salt in equimolar ratio to produces  $(\mu\text{-OPr}^1)\text{Cu}\{\eta^2\text{-}(\text{pbox})\}$  (4) and a novel bimetallic complex  $\{[\text{Al}(\text{opr}^1)_4]\text{Cu}\{\eta^2\text{-}(\text{pbox})\}\}$  (5).

*Infrared spectral studies :*

The  $[(\mu\text{-Cl})_2\text{Cu}_2\{\eta^2\text{-}(\text{pbox})_2\}]$  (1) complex exhibit characteristic IR frequencies at  $280(\text{s})\text{ cm}^{-1}$  for  $\nu_{\text{Cu-Cl}}$  bridging vibration<sup>10</sup>, suggestive for chlorine bridging between

Table 1. Synthesis and physical properties of copper(II) complexes containing benzoxazole ligand

Sl no	Reactants (g, mmol)	Product (g, % yield)	Color	Analysis (%)				M p (°C)	
				Found	Calcd	Cu	Cl		C
1	$\text{CuCl}_2 \cdot 6\text{H}_2\text{O} + \text{pboxH}$ (2.42, 14.2)	$[(\mu\text{-Cl})_2\text{Cu}_2\{\eta^2\text{-}(\text{pbox})_2\}]$ (1) (4.12, 92)	Yellowish green powdered solid	19.46 (20.50)	11.2 (11.4)	50.2 (50.43)	2.6 (2.59)	4.3 (4.53)	308-311
2	$[(\mu\text{-Cl})_2\text{Cu}_2\{\eta^2\text{-}(\text{pbox})_2\}]$ (1) + Na(smab) (0.35, 1.43)	$[(\text{smab})\text{Cu}\{\eta^2\text{-}(\text{pbox})\}]$ (2) (0.5, 91)	Dark blue solid	12.9 (13.1)		64.0 (64.32)	4.00 (4.12)	5.2 (5.77)	295-298
3	$[(\mu\text{-Cl})_2\text{Cu}_2\{\eta^2\text{-}(\text{pbox})_2\}]$ + Na(sap) (0.30, 0.97)	$[(\text{sap})\text{Cu}\{\eta^2\text{-}(\text{pbox})\}]$ (3) (0.43, 94)	Reddish brown solid	13.3 (13.4)		59.5 (61.0)	3.4 (3.60)	8.41 (8.89)	189
4	$[(\mu\text{-Cl})_2\text{Cu}_2\{\eta^2\text{-}(\text{pbox})_2\}]$ + 2Na(opr <sup>1</sup> ) (0.30, 0.98)	$[(\mu\text{-opr}^1)_2\text{Cu}_2\{\eta^2\text{-}(\text{pbox})_2\}]$ (4) (0.27, 87)	Brown crystalline solid	20.1 (20.5)		60.8 (61.66)	5.0 (5.14)	4.1 (4.23)	
5	$[(\mu\text{-Cl})_2\text{Cu}_2\{\eta^2\text{-}(\text{pbox})_2\}]$ + Na{Al(opr <sup>1</sup> ) <sub>4</sub> } (0.34, 1.11)	$\{[\text{Al}(\text{opr}^1)_4]\text{Cu}\{\eta^2\text{-}(\text{pbox})\}\}$ (5) (0.252, 1.11)	Yellowish green solid	13.29 (13.39)					

two copper(II) centers, 237(m)–234(s)  $\text{cm}^{-1}$  for  $\nu_{\text{Cu-N}}$  and 580(s)–559(m)  $\text{cm}^{-1}$  for  $\nu_{\text{Cu-O}}$ . The spectra of the ligands (smabH, sapH and pboxH) showed bands at 1647–1618  $\text{cm}^{-1}$  characteristic for  $\nu_{\text{C=N}}$  whereas bands shifted to lower frequency region at 1640–1595  $\text{cm}^{-1}$  in complexes  $[(\mu\text{-Cl})_2\text{Cu}_2\{\eta^2\text{-}(\text{pbox})_2\}]$  (1) and  $[(\text{smab})\text{Cu}\{\eta^2\text{-}(\text{pbox})\}]$  (2) suggesting coordination through the hetero nitrogen atom.

The complexes 4 and 5 exhibit characteristic peak for bridging isopropoxy group<sup>13</sup> at  $\sim 1030\text{--}1050$   $\text{cm}^{-1}$  and at 960  $\text{cm}^{-1}$  for and  $\nu_{\text{C-O}}$  respectively, whereas complex 5 exhibit one more peak at  $\sim 1150$   $\text{cm}^{-1}$  is possibly due to terminal isopropoxy groups<sup>13</sup>. Instead of these bands, band at 700  $\text{cm}^{-1}$  has been assigned for  $\nu_{\text{Al-O}}$ .

*Electronic spectral studies :*

The visible spectra (Table 2) of the complexes,  $[(\mu\text{-Cl})_2\text{Cu}_2\{\eta^2\text{-}(\text{pbox})_2\}]$  (1) and  $[(\text{smab})\text{Cu}\{\eta^2\text{-}(\text{pbox})\}]$  (2) have been recorded in pyridine/THF mixture which exhibits broad asymmetric band at  $\sim 14903$  and  $\sim 15673$   $\text{cm}^{-1}$  respectively attributed to  ${}^2E_g \rightarrow {}^2T_{2g}$  transition, due to Jahn-Teller distortion in  $d^9$  ( $\text{Cu}^{2+}$ ) systems as well as due to the presence of electronegative 'N' and 'O' donor atom causes the broadening of the absorption band, suggesting a distorted octahedral geometry (in  $D_{4h}$  symmetry) for copper(II) complexes<sup>12</sup>. Besides above bands additional intense bands have been observed at  $\sim 26882$   $\text{cm}^{-1}$  assigned as ligand to metal charge transfer band ( $L \rightarrow \text{MCT}$ ) and at  $\sim 34662$   $\text{cm}^{-1}$  assigned to intra ligand charge transfer band.

*ESR spectral studies :*

The ESR spectrum of  $\{2\text{-}(o\text{-hydroxyphenyl})\text{-benzoxazoloto}\}$ copper(II) complex 1 in polycrystalline solid state at room temperature has been measured (Table 3). ESR spectrum indicates  $g_{\parallel} > g_{\perp} > 2.02$  in  $d_{x^2-y^2}$  (or  $d_{xy}$ ) state whilst  $d_{z^2}$  ground state term usually gives a spectrum with  $g_{\perp} > g_{\parallel} = 2.00$ . Copper(II) systems studied herein, shows a pronounced peak for which  $g_{\parallel} = 2.16$ . In an axial symmetry, the expression  $G = (g_{\parallel} - 2)(g_{\perp} - 2)$ , which measures the exchange interaction between copper centers in polycrystalline solids<sup>14</sup>. The  $g_{\text{av}} = 1/3(g_{\parallel} + 2g_{\perp})$  gave values in the range  $2.17 \pm 0.03$ , which are in agreements with an orbitally non-degenerate ground state. It appears that  $g$  value obtained corresponds to molecular  $g$  value, which are characteristics of square planar geometry around copper(II), obtained as a result of coordination through nitrogen atom. These have been corroborated by IR and electronic spectral studies.

*Magnetic studies :*

The copper(II) complex of  $3d^9$  configurations exhibits paramagnetism corresponding to one unpaired spin ( $s = 1/2$ ,  $\mu_{\text{s.o.}} = 1.73$  B.M.). However, magnetic moment is usually observed to be slightly higher  $\sim 2.0$  B.M. Copper(II) complexes usually have a distorted octahedral stereochemistry, although a few are known to be square planar approaching towards a tetrahedral stereochemistry<sup>15</sup>. The observed magnetic moments at room temperature for monochloro  $\{2\text{-}(o\text{-hydroxyphenyl})\text{-benzoxazoloto}\}$ -copper(II) is 2.36 B.M. which is in agreement with reported values (1.8–2.4 B.M.) for  $\text{Cu}^{\text{II}} d^9$  system.

Table 2. UV-Visible spectral data of copper(II) complexes

Sl. no.	Complex	20920, 23256	14903	26882, 27472, 29940	31250, 33330, 35587
1.	$[(\mu\text{-Cl})_2\text{Cu}_2\{\eta^2\text{-}(\text{pbox})_2\}]^a$ (1)				
2.	$[(\text{smab})\text{Cu}\{\eta^2\text{-}(\text{pbox})\}]^b$ (2)	18692	13889		34364
3.	$[(\mu\text{-opr}^i)_2\text{Cu}_2\{\eta^2\text{-}(\text{pbox})_2\}]^b$ (4)	19608, 21276			34672

<sup>a</sup>Spectrum recorded in DMF.

<sup>b</sup>Spectrum recorded in THF solution.

Table 3. ESR spectral data of benzoxazole complex of copper(II)

Complex	$H_{11}$ (Gauss)	$H_1$ (Gauss)	$g_{\parallel}$	$g_{\perp}$	$g_{\text{av}}$	$G$
$[(\mu\text{-Cl})_2\text{Cu}_2\{\eta^2\text{-}(\text{pbox})_2\}]^b$ (1)	2740	3000	2.37	2.17	2.14	2.56
$[(\mu\text{-Cl})_2\text{Cu}_2\{\eta^2\text{-}(\text{pbox})_2\}]^c$ (1)	2800	3240	2.32	2.15	2.2	2.13
$[(\mu\text{-Cl})_2\text{Cu}_2\{\eta^2\text{-}(\text{pbox})_2\}]^b$ (1)		3000		2.16		

<sup>a</sup>Spectrum recorded in polycrystalline solid state.

<sup>b</sup>ESR spectrum recorded at room temperature.

<sup>c</sup>ESR spectrum recorded at liquid nitrogen temperature ( $\sim 77$  °C).

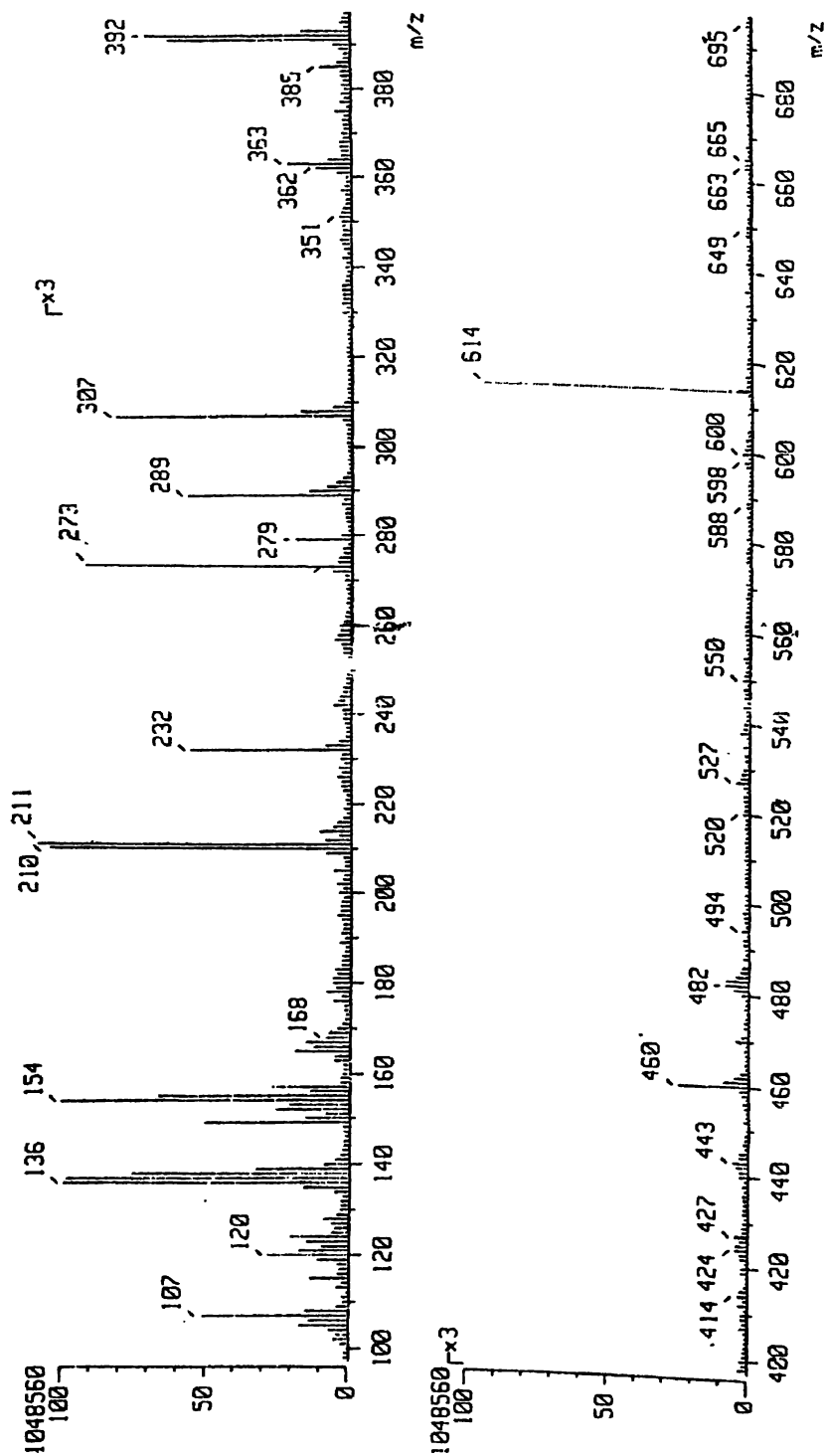
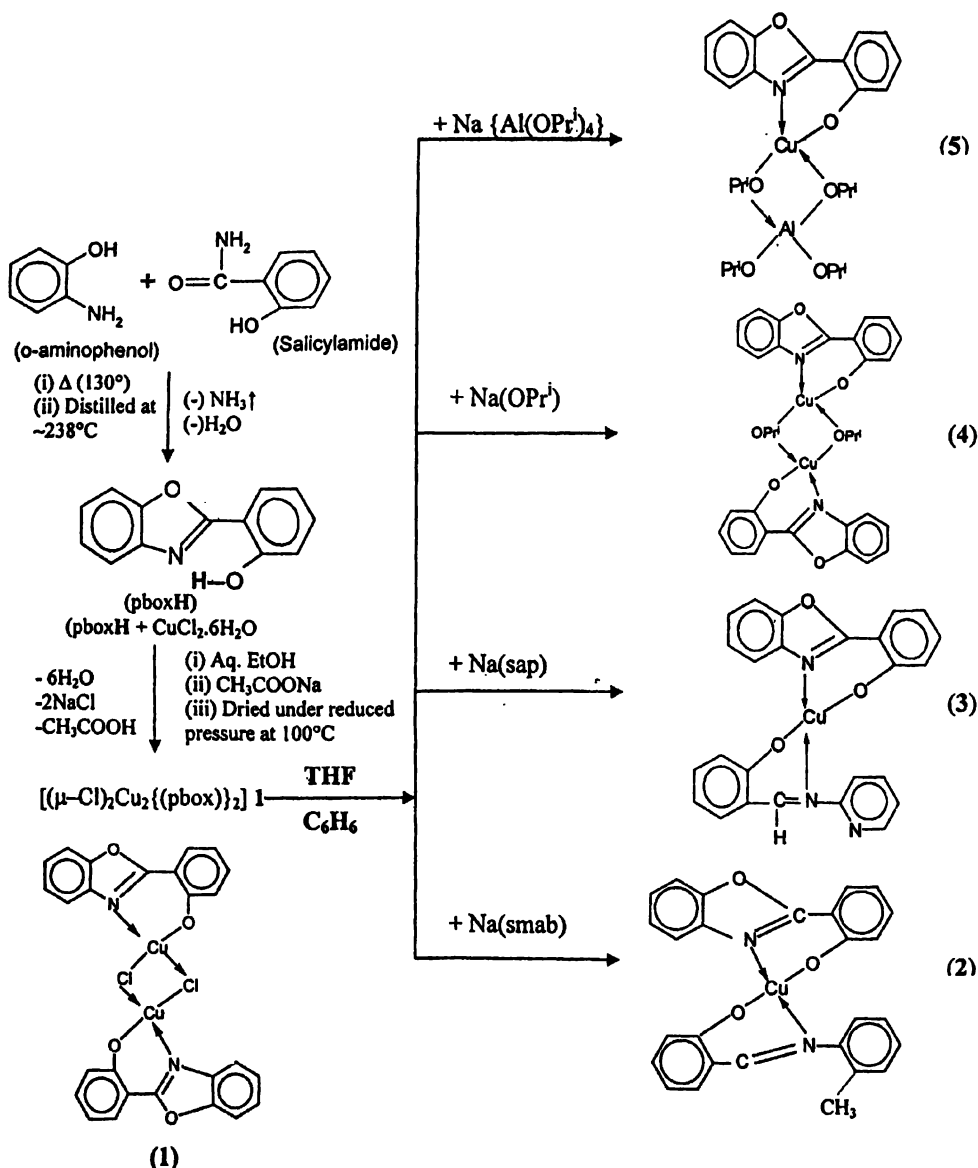


Fig. 1. FAB-MS spectrum of the  $[(\mu\text{-Cl})_2\text{Cu}_2\{\eta^2\text{-(pbox)}\}_2]$ .

Note



Scheme 1. Synthesis and reactions of monochloro-{2-(*o*-hydroxyphenyl)benzoxazolato}copper(II).

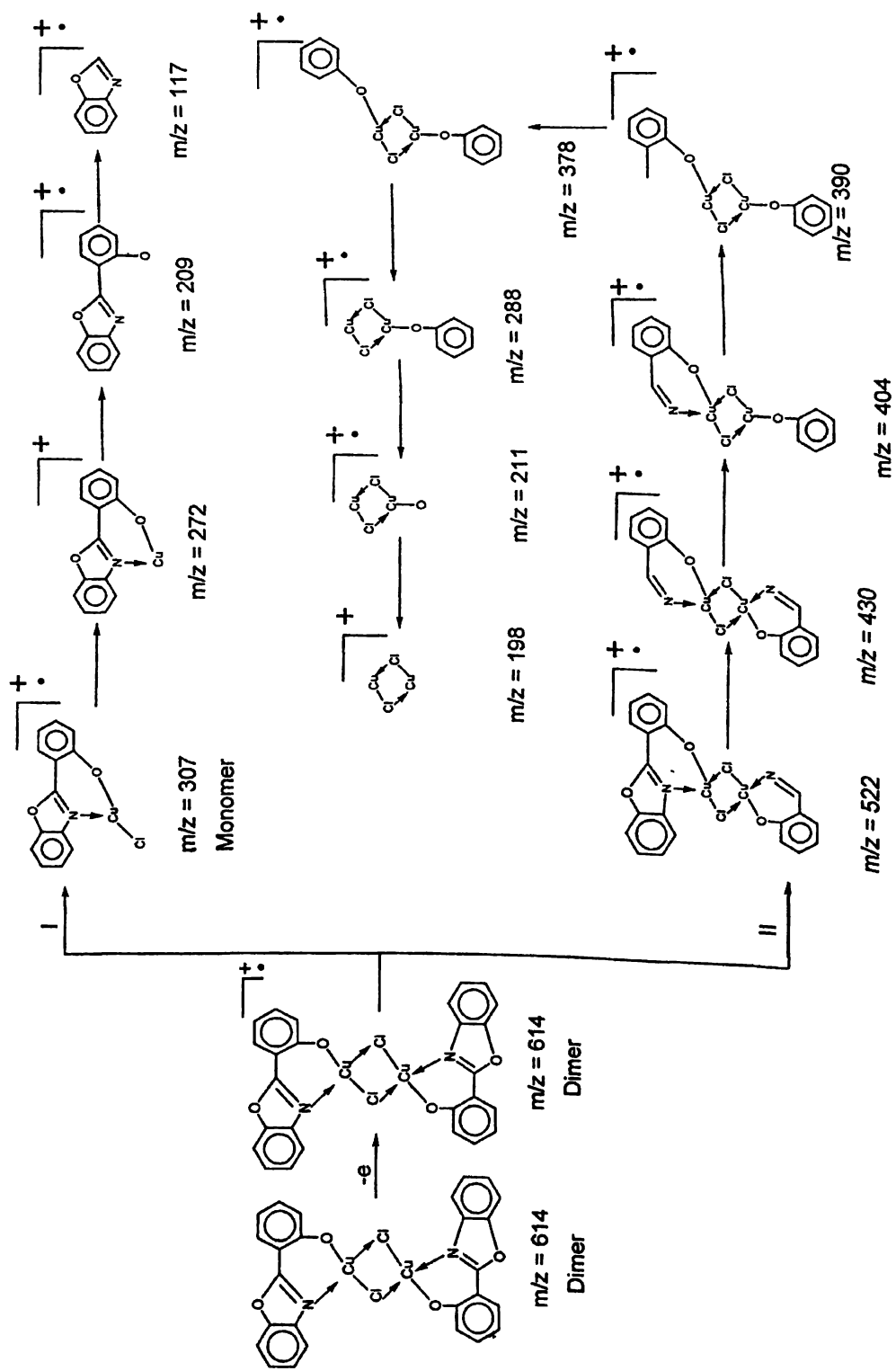
#### FAB-MS studies :

The FAB-mass spectrum<sup>7,9</sup> (Fig. 1) of the copper(II) complex  $[(\mu\text{-Cl})_2\text{Cu}_2\{\eta^2\text{-}(\text{pbox})_2\}]$  (1) showed an important peak at  $m/z$  614, which correspond to the dimeric molecular association; the dimerization takes place through bridging chlorine atom between two copper(II) centers. Which dissociate in two fragments i.e.  $m/z$  at 307 (monomer) (I) and at 522 (II) the important fragmentation peaks were observed, which are indicative for the fragmenta-

tion of parent molecule of the complex by the formation of various radical cations at different  $m/z$  for (I) 307, 272, 209, 117 and for (II) 522, 430, 404, 390, 378, 288, 211, 198. The fragmentation pattern showing structural information is represented in Scheme 2.

#### Experimental

All chemicals used throughout the course of experimental work were of G.R. or A.R. grade. Spectroscopic grade solvents were employed for recording the spectra.



Scheme 2. Fragmentation pattern of  $[(\mu\text{-Cl})_2\text{Cu}_2\{\eta^2\text{-}(\text{pbox})\}_2]$  (1) using FAB-MS spectrum.

Benzene (B.D.H.), isopropanol (B.D.H.) and tetrahydrofuran (Loba) were dried according to standard literature procedure. Aluminium isopropoxide<sup>13</sup> was prepared by dissolving aluminium foil in isopropanol, in the presence of HgCl as catalyst and refluxing it for ~6 h. Final product was purified by distillation (b.p. 95 °C). The quantitative determination of copper was carried out by Atomic Absorption Spectroscopy, GBC-92AA. Aluminium content present in the bimetallic complex was determined after precipitating aluminium as its oxinate<sup>16</sup>. Chloride content was estimated by Volhard's method<sup>16</sup>. Isopropoxide content in the corresponding isopropoxy derivative was estimated by an oxidimetric methods<sup>8</sup>. Infrared spectra (4000–400 cm<sup>-1</sup>) were recorded in Nujol; whereas 400–200 cm<sup>-1</sup> spectrum was recorded in KBr solid, using Perkin-Elmer 1000 FTIR spectrophotometer electronic spectra of the compounds were recorded in DMF and/or in C<sub>6</sub>H<sub>6</sub>/THF on a Hitachi-220 spectrophotometer. An ESR spectrum was recorded on E-112 ESR spectrometer. FAB-mass spectrum was recorded on Jeol SX 102/AD-6000 mass spectrometer/data system using argon/xenon (6 kv, 10 mA) as the FAB-gas. Magnetic susceptibility measurements were made at room temperature (23.5 °C) by Gouy method.

#### Synthesis of Schiff bases :

The ligand {2-(*o*-hydroxyphenyl)}benzoxazole (pboxH) was synthesized according to previously established literature methods<sup>17</sup>. Salicylidine-2-methyl-1-aminobenzene (smabH)<sup>18</sup> was prepared by refluxing (~6 h) equimolar amounts of toluidine (10.7 g, 100 mmol) and salicylaldehyde (12.21 g, 100 mmol) in methanol (~30 cm<sup>3</sup>). Further, sodium salt of salicylidine-2-methyl-1-aminobenzene; Na(smab)<sup>18</sup> was prepared by dissolving equimolar amounts of sodium metals and salicylidine-2-methyl-1-aminobenzene in methanol. Salicylidine-2-aminopyridine (sapH)<sup>19</sup> and its sodium salts, Na(sap) were prepared by the identical methods as given above.

2-Aminosodium phenolate was prepared by refluxing (~1–2 h) equimolar amount of 2-aminophenol and sodium metal in THF and sodium tetraalkoxyaluminate was prepared by standard literature procedure<sup>13</sup>.

*Preparation of chloro (2-(o-hydroxyphenyl)-benzoxazolato-copper(II)); [(μ-Cl)<sub>2</sub>Cu<sub>2</sub>{η<sup>2</sup>-(pbox)}<sub>2</sub>] (1) complex :*

A freshly prepared aqueous ethanolic solution (50%

ethanolic ~50 cm<sup>3</sup>) of copper(II) chloride (3.38 g, 14.2 mmol) was added dropwise to a pre-stirred hot ethanolic (~75 cm<sup>3</sup>) solution containing 2-(*o*-hydroxyphenyl)-benzoxazole (3 g, 14.2 mmol), which produced a pinkish brown coloured precipitate; further, dropwise addition of dilute sodium acetate solution with stirring afforded pink coloured precipitate; [(μ-Cl)<sub>2</sub>Cu<sub>2</sub>{η<sup>2</sup>-(pbox)}<sub>2</sub>] (1). It was then digested (~1 h), filtered, washed with aqueous ethanol and dried at ~100 °C under reduced pressure to give yellowish pink powdered solid (4.13 g, 95%). The product on analysis was found to have Cu (19.2%), Cl (11.4%) and Calcd. for Cu (19.3%), Cl (11.6%).

*Reaction of [(μ-Cl)<sub>2</sub>Cu<sub>2</sub>{η<sup>2</sup>-(pbox)}<sub>2</sub>] (1) with Na(smab) :*

To a stirred hot yellowish green suspension of chloro-{2-(*o*-hydroxyphenyl)}benzoxazole complex of copper(II) (0.3 g, 0.98 mmol) in tetrahydrofuran (~30 cm<sup>3</sup>) was added sodium salts of salicylidine-2-methyl-1-aminobenzene (0.23 g, 0.98 mmol) in equimolar ratio. The reaction mixture was allowed to reflux for ~1 h, during which time, colour of solution changed from yellowish green to red; the precipitated NaCl (0.06 g, 0.99 mmol) was removed by filtration. The solvent was removed from the filtrate under reduced pressure to afford a reddish brown solid product [(smab)Cu{η<sup>2</sup>-(pbox)}] (2) which was purified by recrystallization from benzene/THF mixture to finally give reddish brown powdered solids (0.43 g, 93%). Analysis of this derivative was found to be Cu, 12.5% and Calcd. for Cu (12.3%).

Similar procedure (Scheme 1) was adopted to isolate [(sap)Cu{η<sup>2</sup>-(pbox)}] (3), [(μ-opr<sup>i</sup>)<sub>2</sub>Cu<sub>2</sub>{η<sup>2</sup>-(pbox)}<sub>2</sub>] (4) and [{Al(opr<sup>i</sup>)<sub>4</sub>}Cu{η<sup>2</sup>-(pbox)}] (5). The analytical details are given in Table 1.

#### Acknowledgement

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