

**SYNTHESIS, CHARACTERIZATION AND  
ELECTROCHEMISTRY OF A BINUCLEAR COPPER(II)  
COMPLEX OF SCHIFF BASE DERIVED FROM  
2-AMINOMETHYL-BENZIMIDAZOLE AND  
SALICYLALDEHYDE**

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**Abstract**—A dinuclear Cu<sup>II</sup> compound (Cu<sub>2</sub>L<sub>2</sub><sup>2+</sup>) with the phenoxide form of N-salicylidine 2-aminomethylbenzimidazole has been synthesized and characterized on the basis of elemental analysis, UV-visible, IR and variable temperature ESR spectra, magnetic moment and electrochemical studies. Thermal studies indicate that the decomposition takes place in two stages. Lowering of ESR peak intensity with lowering in temperature indicates the dimeric nature of the compound. A stopped flow kinetic study indicated that the acid catalysed decomposition of the compound occurred *via* two consecutive steps, thus providing further evidence for the dimeric nature of the compound. Evidence of equilibrium NH deprotonation of the benzimidazole moiety of Cu<sub>2</sub>L<sub>2</sub><sup>2+</sup> at 0.005 ≤ [OH<sup>-</sup>], mol dm<sup>-3</sup> ≤ 0.02 is presented.

The kinetics and equilibria of ternary complexes of nickel(II)- and copper(II)-2-aminomethylbenzimidazole(I), [M(AMBZ)]<sup>2+</sup> with salicylaldehyde have been studied in solution<sup>1,2</sup> and showed that in the presence of salicylaldehyde, a mixed ligand complex, [M(AMBZ)Sal]<sup>+</sup> was formed as intermediate which further condensed to a Schiff base complex, [M(SB)]<sup>+</sup>. Furthermore, Schiff bases constitute an interesting class of chelating agents, capable of coordination with one or more metal ions and thus forming mononuclear as well as polynuclear metal complexes, which could find applications in analytical chemistry and serve as biochemical models.<sup>3,4</sup> As such, it was thought worthwhile to isolate the title Schiff base complex of Cu<sup>II</sup> in the solid state and study its physico-chemical properties. In this

context, the isolation of a dinuclear complex of Cu<sup>II</sup> with N-salicylidine-2-aminomethylbenzimidazole (phenoxide form) and its characterization by several physical methods are reported here.

## EXPERIMENTAL

### *Preparation of the complex*

2 - Aminomethylbenzimidazoldihydrochloride was prepared by the method of Cescon and co-workers<sup>5</sup> and recrystallized from 95% ethanol as a white crystalline solid with m.p. 263°C (literature<sup>5</sup> m.p. 263°C). The Cu<sup>II</sup> complex was prepared as follows.

2-Aminomethylbenzimidazole (6.8 mmol) dissolved in minimum volume of water was added to a solution (ethanol/water, 80/20 vol%) of copper(II)

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acetate (6.82 mmol). The mixture was refluxed over a sand bath at  $\sim 70^\circ\text{C}$  for 1 h. A precipitate formed immediately but dissolved slowly on heating. The solution deposited shining green needle-shaped crystals which were filtered while hot, washed thoroughly with alcohol and air dried. Found: C, 51.1; H, 3.4; N, 11.7; Cu, 18.1; Cl, 9.8. Calc. for  $\text{C}_{30}\text{H}_{24}\text{N}_6\text{Cu}_2\text{Cl}_2\text{O}_2$ : C, 51.6; H, 3.4; N, 12.0; Cu, 18.2; Cl, 10.2%.

### Physical measurements

Microanalysis was carried out on a C, H, N analyser at CDRI, Lucknow. Copper(II) and chloride were estimated iodometrically<sup>6</sup> and gravimetrically as AgCl, respectively. UV-visible spectra were recorded on a JASCO 7800 recording spectrophotometer using 10 mm matched quartz cells. Infra-red spectra in the range  $4000\text{--}400\text{ cm}^{-1}$  in KBr pellets were recorded on a Perkin-Elmer model 597 recording spectrophotometer. Magnetic measurements at room temperature were made by using a Gouy balance. A vibrating sample magnetometer available at RSIC, Madras, was used for magnetic measurements at variable field strength. Diamagnetic corrections for ligands and counter ions were made using Pascal's constant.<sup>7</sup> The X-band ESR spectrum of the solid sample was recorded on a Varian EPR-E-112 Spectrophotometer operated at field strength 3000 G and modulation frequency 100 kHz using DPPH as reference. Electrochemical measurements were performed on a cyclic voltameter, PAR model 370-4, using a Pt working electrode, DMF as solvent and TEAP as supporting electrolyte. The potentials reported are against a saturated calomel electrode (SCE). TG-DTA was recorded using a Shimadzu DT-30 automatic Thermal Analyser with a heating rate of  $10^\circ\text{C min}^{-1}$  in static air.

### Kinetic measurements

The kinetic measurements at  $25^\circ\text{C}$  were made using a fully automated HI-TECH stopped-flow spectrophotometer with Apple-II GS computer interface. All kinetic measurements were made in the mixed solvent medium (DMF: water = 50:50 vol%) at 420 nm. The relatively slower second stage reaction was also followed by conventional spectrophotometry.

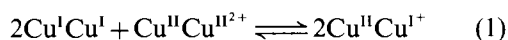
## RESULTS AND DISCUSSION

The analytical data agreed with the molecular formula  $\text{C}_{30}\text{H}_{24}\text{N}_6\text{Cu}_2\text{Cl}_2\text{O}_2$ . The molar conductance of the specimen in DMF solution

( $\Lambda_m = 140\text{ ohm}^{-1}\text{ cm}^2$ ) is slightly lower than the expected value for uni-bivalent electrolyte ( $\Lambda_m = 240\text{ ohm}^{-1}\text{ cm}^2$ ).<sup>8</sup> The IR spectrum shows the presence of secondary NH ( $\nu_{\text{obs}} = 3040\text{ cm}^{-1}$ ) of the benzimidazole moiety. The bands at 1635 and  $1600\text{ cm}^{-1}$  are attributed to the aldimine ( $\text{—C=N—}$ ) linkage and the secondary -NH group.

The TG-DTA showed that the complex is stable up to  $170^\circ\text{C}$  in the solid state (Fig. 1). The first stage decomposition starts at  $175^\circ\text{C}$ . An exothermic peak at  $210^\circ\text{C}$  corresponds to the loss of two chloride ions in the form of HCl while the second stage decomposition is also accompanied by a broad exothermic peak in the range  $465\text{--}725^\circ\text{C}$ . No further weight loss is observed after  $750^\circ\text{C}$ . The final product corresponds to CuO.

The cyclic voltammogram (Fig. 2) shows two stepwise one electron transfer reactions ( $\text{Cu}^{\text{II}}\text{Cu}^{\text{II}} \longleftrightarrow \text{Cu}^{\text{II}}\text{Cu}^{\text{I}}$  and  $\text{Cu}^{\text{II}}\text{Cu}^{\text{I}} \longleftrightarrow \text{Cu}^{\text{I}}\text{Cu}^{\text{I}}$ ) in the potential range  $-0.6$  to  $-0.95\text{ V}$  during the cathodic sweep. Since the  $E^\circ$  for the reduction of  $\text{Cu}^{\text{II}}$  to  $\text{Cu}^{\text{I}}$  in water is  $+0.153^9$  it appears that the binucleating ligand stabilizes  $\text{Cu}^{\text{II}}$  much more than it stabilizes  $\text{Cu}^{\text{I}}$ . Oxidation of the complex occurs in a quasi-reversible manner at potential of *ca*  $-0.44\text{ V}$ . The potential of the two redox couples are  $-0.67$  ( $E^1 = \text{Cu}^{\text{II}}\text{Cu}^{\text{II}} \longrightarrow \text{Cu}^{\text{II}}\text{Cu}^{\text{I}}$ ) and  $-0.91\text{ V}$  ( $E^2 = \text{Cu}^{\text{II}}\text{Cu}^{\text{I}} \longrightarrow \text{Cu}^{\text{I}}\text{Cu}^{\text{I}}$ ) vs SCE. The difference between  $E^1$  and  $E^2$  can be used<sup>9</sup> to evaluate the conproportionation constant,  $K_{\text{con}}$ , for reaction (1).



$$(E^1 - E^2 = 0.0591 \log K_{\text{con}})$$

The  $K_{\text{con}}$  value obtained ( $1.15 \times 10^4$ ) is similar to that for several binuclear  $\text{Cu}^{\text{II}}$  complexes of Schiff bases.<sup>3</sup> For a stable mixed valence species a higher value of  $K_{\text{con}}$  ( $\geq 10^8$ ) is expected. Thus, the result shows that the mixed valence species from the title complex upon reduction is not significantly stable.

Room temperature magnetic susceptibility measurement of the title complex shows the value of  $\mu_{\text{eff}} = 1.12\text{ B.M.}$  per Cu atom which is less than that expected for one unpaired electron on each  $\text{Cu}^{\text{II}}$  ion. The field strength was also varied from 2 to 10 kG. The field independent magnetic susceptibility per  $\text{Cu}^{\text{II}}$  atom also turned out to be  $1.22 \pm 0.045\text{ B.M.}$ , in satisfactory agreement with the above result. The lower value of magnetic susceptibility may be due to the antiferromagnetic interaction between  $\text{Cu}^{\text{II}}$  centres. Similar observations have been reported in the case of binuclear oxo-bridged complexes of  $\text{Cu}^{\text{II}}$ .<sup>3</sup>

Room temperature X-band ESR spectrum (Fig. 3a) of the powdered sample shows only one broad

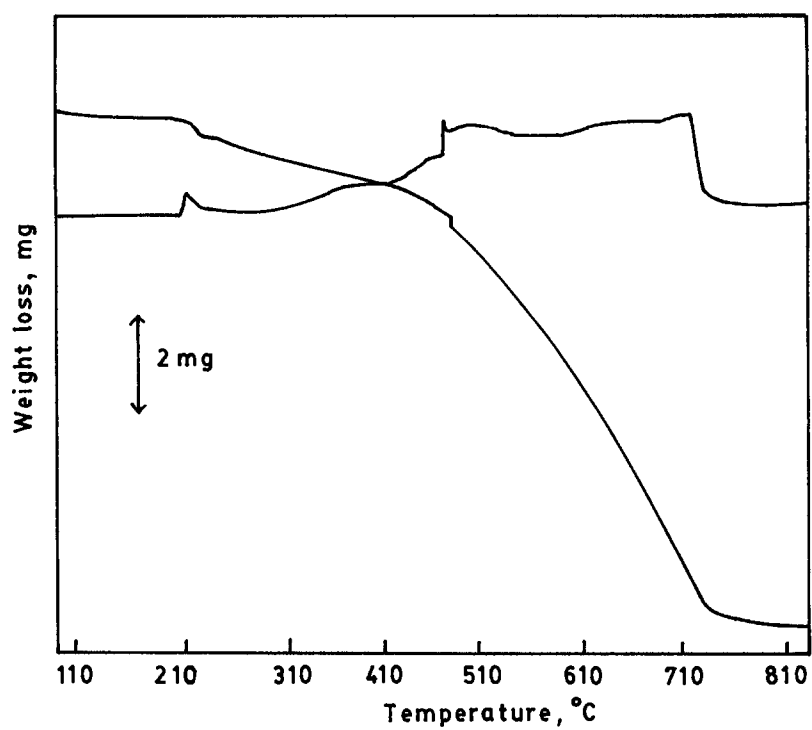


Fig. 1. TG-DTA of the  $[\text{Cu}_2\text{L}_2]\text{Cl}_2$ . Sample = 15 mg.

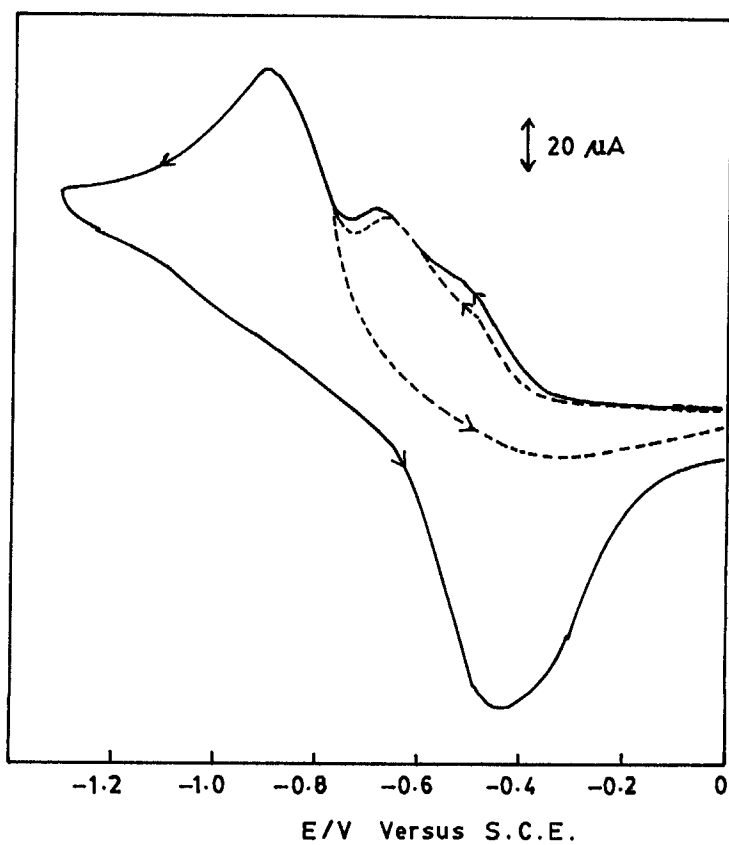


Fig. 2. Cyclic voltammogram of  $[\text{Cu}_2\text{L}_2]\text{Cl}_2$  in DMF at a scan rate  $50 \text{ mV s}^{-1}$ .

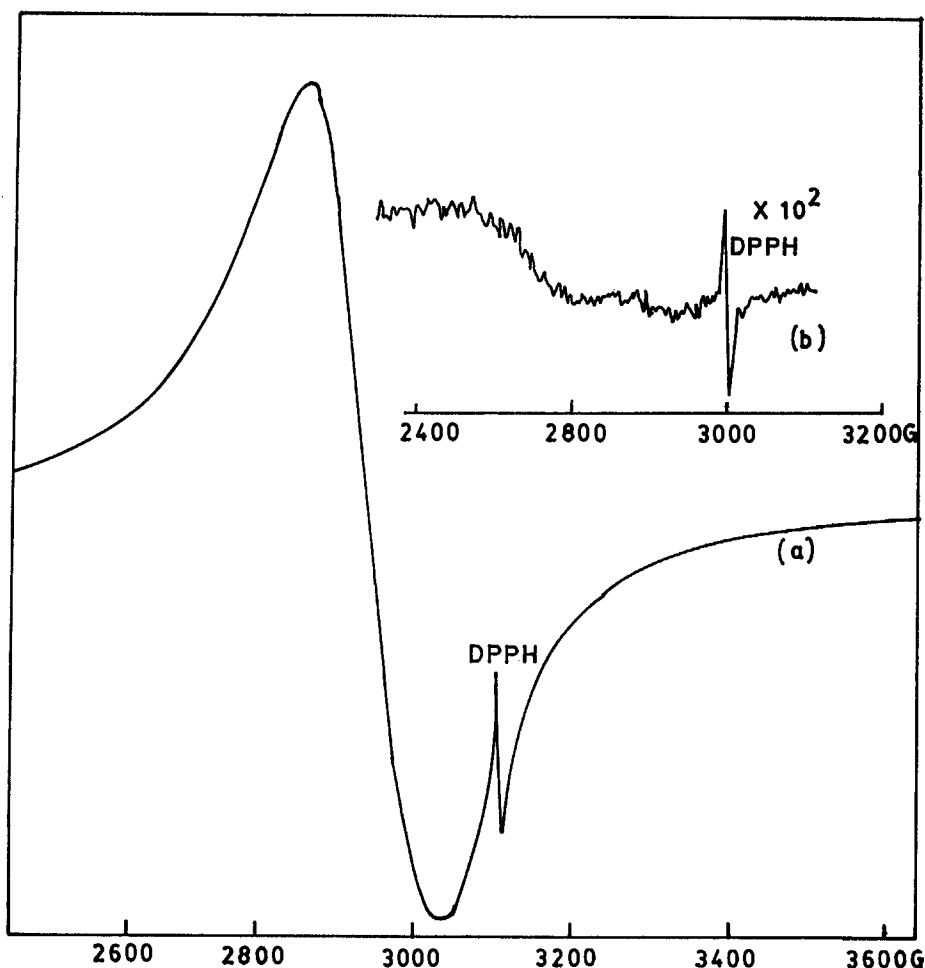
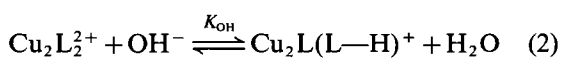


Fig. 3. X-band ESR spectra at (a) RT and (b) 77 K.

peak (peak separation  $\sim 200$  G;  $g = 2.11$ ). Lowering of temperature of the sample to 77 K decreased the intensity of the signal significantly ( $g_{av} = 2.17$ ) (Fig. 3b). The decrease in intensity suggests that the antiferromagnetic spin coupling between the two  $\text{Cu}^{\text{II}}$  centres increases with lowering of temperature.

#### Kinetics and acid-base equilibria

The UV-visible spectrum in DMF displays a maximum at 635 nm (Fig. 4). The spectrum remained virtually unchanged with time in absence of acid or alkali indicating the stability of the complex. Addition of acid decomposed the complex. However, addition of alkali strongly modified the spectrum of the complex (see Fig. 4) which is ascribed to be deprotonation of NH group of benzimidazole moiety (eq. (2)).



Similar observations have been reported from our laboratory on the N—H deprotonation of cobalt(III) bound benzimidazole.<sup>10</sup> The alkali dependence of the absorbance data at 660 nm (see Fig. 5A) for a given  $[\text{Complex}]_{\text{T}} = 1.0 \times 10^{-3}$  mol  $\text{dm}^{-3}$  (cell path length = 1 cm) and at 25°C ( $I = 0.2$  mol  $\text{dm}^{-3}$ ) are related to  $K_{\text{OH}}$  (eq. (2)) and  $[\text{OH}^-]$  as given in eq. (3)

$$\frac{1}{A_{\text{obs}} - A_0} = \frac{1}{(\varepsilon_2 - \varepsilon_1)a} + \frac{1}{K_{\text{OH}}a(\varepsilon_2 - \varepsilon_1)[\text{OH}^-]} \quad (3)$$

where  $A_0$  is the absorbance of the species  $\text{Cu}_2\text{L}_2^{2+}$  at  $[\text{OH}^-]_{\text{T}} = 0$  and  $A_{\text{obs}}$  is its absorbance at a given  $[\text{OH}^-]_{\text{T}}$ ;  $\varepsilon_1$  and  $\varepsilon_2$  are the molar extinction coefficients of  $\text{Cu}_2\text{L}_2^{2+}$  and  $\text{Cu}_2\text{L}(\text{L}-\text{H})^+$ , respectively and  $a$  is the complex concentration. Using the value of  $10^{-3} K_{\text{OH}} = 7.93 \pm 0.86$  (obtained from the slope and intercept of the plots of  $1/(A_{\text{obs}} - A_0)$  vs  $1/[\text{OH}^-]$ ) and  $K_w (= 13.72$  at  $I = 0.2$  mol  $\text{dm}^{-3}$ ),

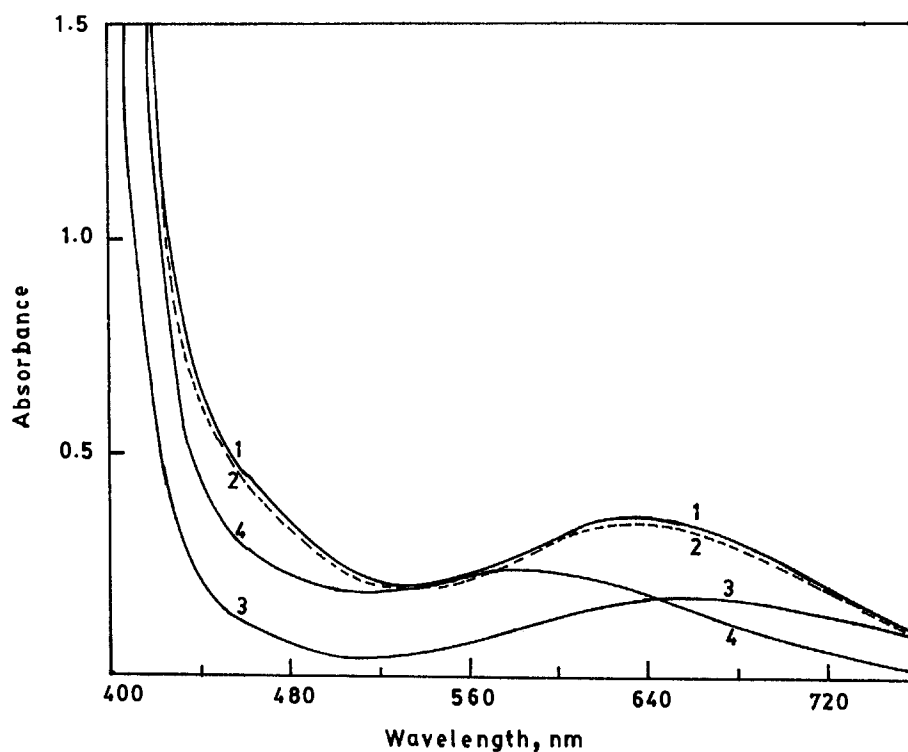


Fig. 4. UV-visible spectrum in DMF, (1) and (2) are recorded respectively after 1 and 60 min,  $[\text{complex}] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ; (3)  $[\text{complex}] = 1.0 \times 10^{-3}$ ,  $[\text{HClO}_4] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ; (4)  $[\text{complex}] = 1.0 \times 10^{-3}$ ,  $[\text{NaOH}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ .

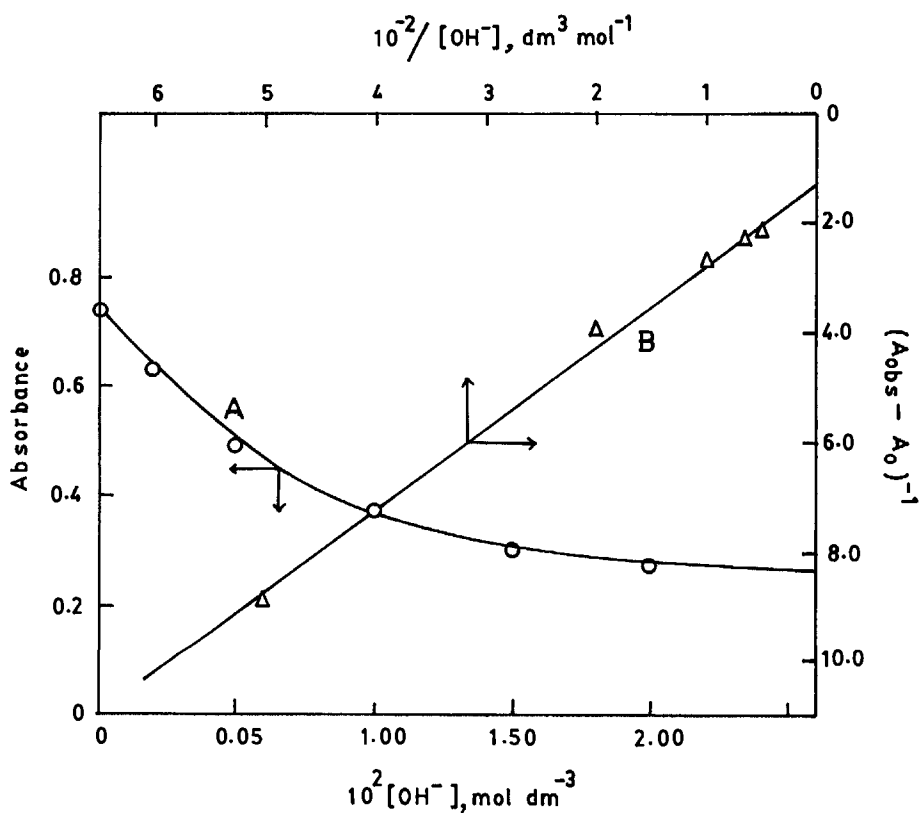


Fig. 5. (A) Alkali dependence of absorption at 660 nm. (B) Plot of  $(A_{\text{obs}} - A_0)^{-1}$  vs  $[\text{OH}^-]_{\text{T}}^{-1}$ .

we obtained  $pK_{NH} (= pK_w + pK_{OH})$  as 11.62. The  $pK_{NH}$  of benzimidazole has been reported to be 12.3<sup>11</sup> and 12.57<sup>12</sup> at  $I = 0.0385$  and  $0.5 \text{ mol dm}^{-3}$  ( $25^\circ\text{C}$ ), respectively. The decrease in  $pK_{NH}$  indicated the effect of coordination of benzimidazole to the  $\text{Cu}^{II}$  centre.

In the presence of acid the title complex decomposes as indicated by the UV-visible spectra (Fig. 4). The decomposition, i.e. the hydrolysis of the coordinated imine, followed by dissociation occurs via two steps as shown in Scheme 1, for which

$$k_{\text{obs}}^{\text{fast}} = k_1[\text{H}^+] \quad (4)$$

and

$$k_{\text{obs}}^{\text{slow}} = k_2 K[\text{H}^+]/(1 + K[\text{H}^+]). \quad (5)$$

The acid dependence of the  $k_{\text{obs}}$  terms are shown in Fig. 6(A–C). The values of  $k_1$ ,  $k_2$  and the equilibrium constant ( $K$ ) calculated using eqs (4) and (5) are  $8.8 \pm 1.6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $(2.4 \pm 0.3) \times 10^{-2} \text{ s}^{-1}$  and  $17 \pm 3 \text{ dm}^3 \text{ mol}^{-1}$  respectively ( $25^\circ\text{C}$ ,  $I = 0.1 \text{ mol dm}^{-3}$ , DMF: water = 50:50 vol%). The protonation constant of  $\text{CuL}^+$  compares satisfactorily with the protonation constant of coordinated salicylate in  $(\text{en})_2\text{CoSal}^+$   $\{pK = 1.0 \pm 0.2, 30\text{--}40^\circ\text{C}, I = 0.3 \text{ mol dm}^{-3}\}$ <sup>13</sup> and  $1.0 \pm 0.3$  at  $25^\circ\text{C}$ <sup>14</sup> indicating protonation of coordinated phenoxide. The relatively greater hydrolytic stability of the imine linkage in  $\text{CuL}^+$  is due to the bicyclic chelate ring.<sup>1</sup> This provides further evidence for the nature and stability of the binuclear species.

On the basis of the above physico-chemical studies, a tentative structure of the complex can be assigned, as given in Fig. 7.

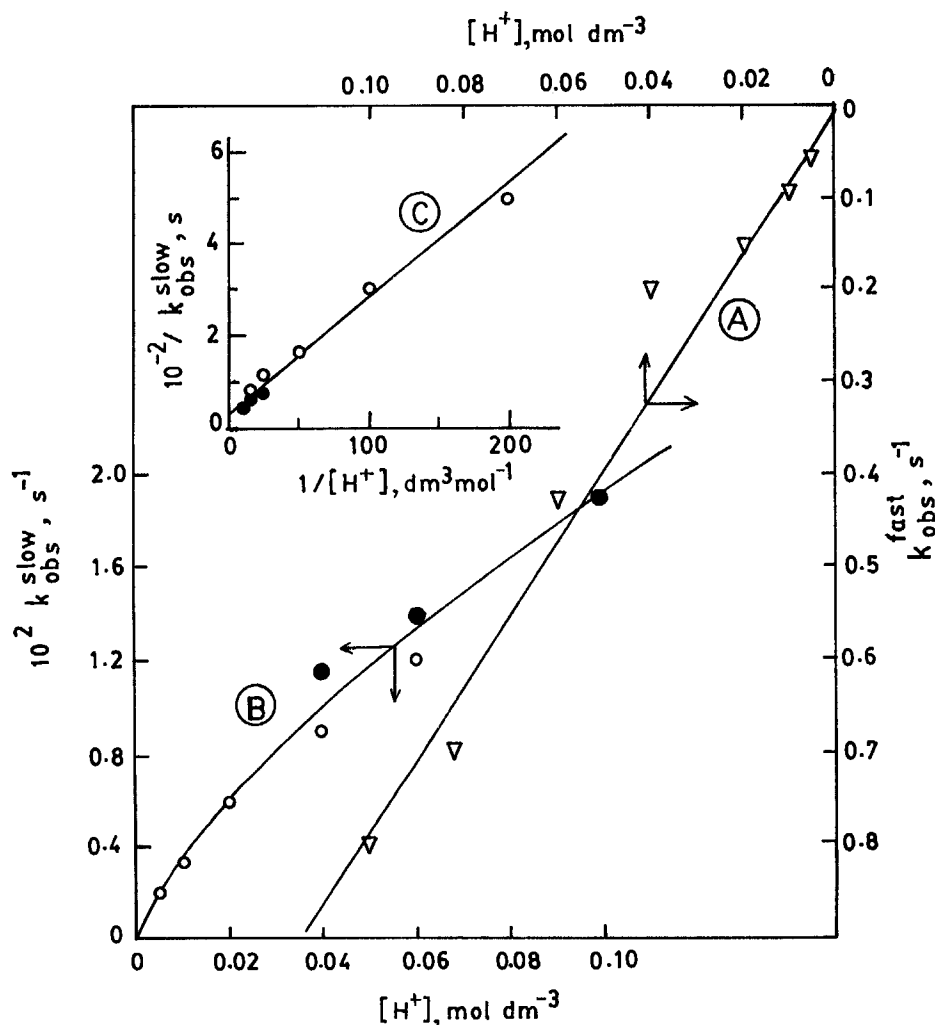
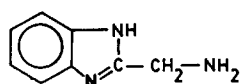
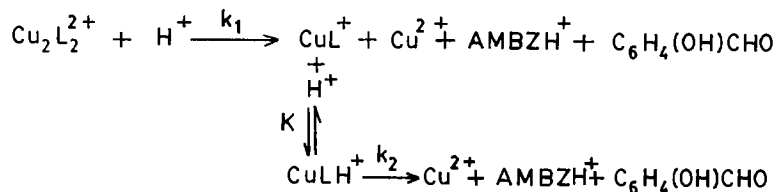


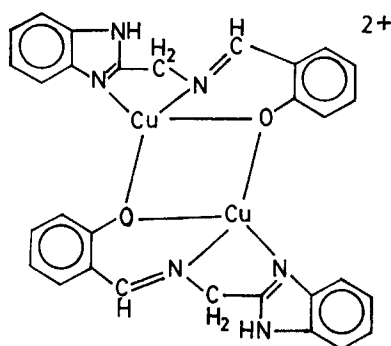
Fig. 6. (A)  $k_{\text{obs}}^{\text{fast}}$  vs  $[\text{H}^+]$  for first step; (B)  $k_{\text{obs}}^{\text{slow}}$  vs  $[\text{H}^+]$  for second step; (○) values obtained from spectrophotometer; (●) value obtained from stopped flow spectrophotometer; (C)  $1/k_{\text{obs}}^{\text{slow}}$  vs  $1/[\text{H}^+]$ .



(T) 2-Aminomethylbenzimidazole



Scheme 1.

Fig. 7. Proposed structure for  $[\text{Cu}_2\text{L}_2]^{2+}$ .

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