

## Study of Mono- and Bi-nuclear Copper(II) Complexes of Tridentate Reduced Schiff Bases

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Spectral, electrochemical and magnetic studies of mononuclear complexes  $\text{CuL} \cdot n\text{H}_2\text{O}$ ,  $\text{Cu}(\text{L})\text{A}$  and binuclear complexes  $\text{Cu}_2\text{L}_2 \cdot n\text{H}_2\text{O}$  and  $\text{Li}(\text{Cu}_2\text{L}_2^2\text{A}_{-\text{H}})$  where L is a tridentate reduced Schiff base ligand and A is imidazole, reveal strong antiferromagnetic interactions in the binuclear complexes.

Binuclear copper(II) complexes of tridentate Schiff base ligands have been studied and their antiferromagnetic properties have been explained.<sup>5</sup> Recently the study of binuclear copper(II) complexes of a few reduced Schiff bases has also been reported.<sup>6</sup> The present paper reports the synthesis of some mono- and bi-nuclear copper(II) complexes of reduced Schiff base ligands obtained by the reaction of amino acids with salicylaldehyde. These complexes have been characterized by spectral, variable temperature magnetic, mass spectral, electrochemical and EPR studies.

Mononuclear complexes of the type  $\text{CuL} \cdot n\text{H}_2\text{O}$  were obtained by the reaction of 5 mmol of reduced Schiff base ligand with 5 mmol of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in water–ethanol (2:1) in the presence of NaOH.

Binuclear complexes of the type  $\text{Cu}_2\text{L}_2 \cdot n\text{H}_2\text{O}$  were obtained by the reaction of 2 mmol of reduced Schiff base ligand with 2 mmol  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in methanol in the presence of lithium methoxide.

The binuclear complex  $\text{Li}(\text{Cu}_2\text{L}_2^2\text{A}_{-\text{H}})$  was obtained by reaction of  $\text{Cu}_2\text{L}_2^2$  with imidazole in methanol. The pH of the reaction mixture was raised to *ca.* 12 by the addition of lithium methoxide.

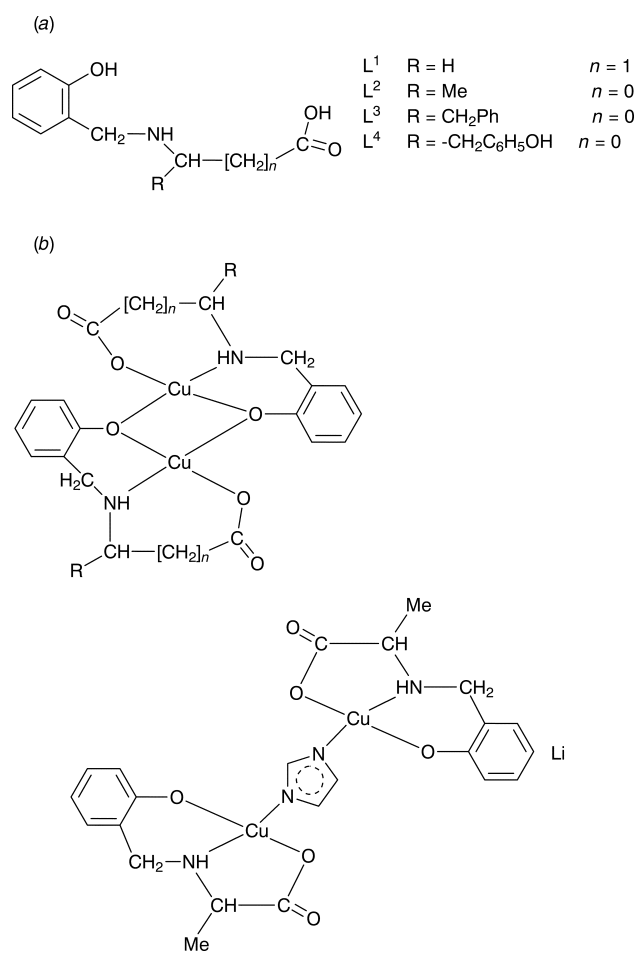
Elemental analysis of the mono- and bi-nuclear complexes correspond to expected formulae. The expected structure of the binuclear complexes is shown in Fig. 1. Thermogravimetric analysis of the binuclear complexes shows a weight loss at 100–130 °C indicating the loss of lattice water molecules. For mononuclear complexes the weight loss occurred in two steps. Weight loss at 100–130 °C indicated the loss of lattice water molecules while a weight loss at 200 °C indicated the removal of coordinated water.

The electronic spectra of mono- and bi-nuclear complexes show broad bands in the region 630–690 and 620–660 nm, respectively. For  $\text{Li}(\text{Cu}_2\text{L}_2^2\text{A}_{-\text{H}})$  where  $\text{A}_{-\text{H}}$  is the bridging imidazolate anion there is a shift in the d–d transition band to shorter wavelength by 40 nm relative to  $\text{Cu}_2\text{L}_2^2$ .

IR spectra of  $\text{CuL} \cdot n\text{H}_2\text{O}$  and  $\text{Cu}_2\text{L}_2 \cdot n\text{H}_2\text{O}$  complexes show a broad band in the region 3300–3500  $\text{cm}^{-1}$ , indicating the presence of water. A band at 1600  $\text{cm}^{-1}$  is due to secondary amine N–H bending vibration. Strong absorptions at 1580  $\text{cm}^{-1}$  are attributed to  $\nu_{\text{COO}^-}$  stretching. Comparison of the ligand bands in the mono- and bi-nuclear complexes shows that there is no significant shift in the band position of  $\nu_{\text{COO}^-}$  upon coordination to the metal. It has been suggested earlier<sup>6</sup> that in the binuclear complexes bridging is through the phenolate  $\text{O}^-$  group.

FAB mass spectra of two binuclear complexes  $\text{Cu}_2\text{L}_2^2$  and  $\text{Li}(\text{Cu}_2\text{L}_2^2\text{A}_{-\text{H}})$  were recorded. For  $\text{Cu}_2\text{L}_2^2$  a peak at  $m/z = 513$  corresponds to the parent ion  $\text{Cu}_2\text{L}_2^2+$  and a fragment at  $m/z = 257$  corresponds to  $\text{CuL}^2$ .

For  $\text{Li}(\text{Cu}_2\text{L}_2^2\text{A}_{-\text{H}})$   $m/z = 581$  corresponds to the parent ion while peaks at  $m/z = 325$  and 257 correspond to  $\text{CuL}^2\text{A}_{-\text{H}}$  and  $\text{CuL}^2$  respectively.



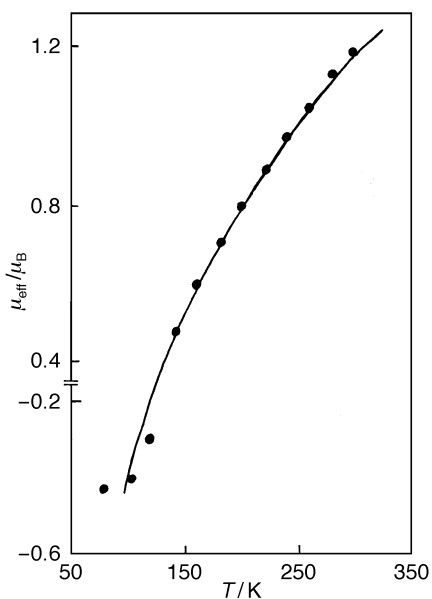
**Fig. 1** (a) Structure of ligands and (b) structures of the binuclear complexes

All binuclear complexes show a subnormal magnetic moment at room temperature. For the complex  $\text{Cu}_2\text{L}_2^2$ , magnetic measurements were carried out over the range 77–296 K. Magnetic analysis for the compound was carried out using the Bleaney–Bowers equation. Good magnetic simulation was obtained with  $J = -211 \text{ cm}^{-1}$ ,  $g = 2.14$  and  $p = 0.0004$ . For this complex the susceptibility decreases with decreasing temperature. A plot of  $\mu_{\text{eff}}$  vs. temperature is shown in Fig. 2.

EPR spectra of the binuclear complexes show a seven-line spectrum in the  $g_{\parallel}$  region. This is in accordance with electron spin coupling with two  $\text{Cu}^{\text{II}}$  nuclei ( $I = 3/2$ ). This shows that electrons are delocalized over both  $\text{Cu}^{\text{II}}$  centers.<sup>8</sup>

The mononuclear complex  $\text{Cu}(\text{L}^2)\text{A}$  shows quasireversible behaviour in its cyclic voltammogram. In the cathodic scan,  $\text{Cu}^{\text{II}} \rightarrow \text{Cu}^{\text{I}}$  reduction was observed at  $-1.1 \text{ V}$ , while in the reverse cycle  $\text{Cu}^{\text{I}} \rightarrow \text{Cu}^{\text{II}}$  oxidation occurs at  $-0.81 \text{ V}$ .

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**Fig. 2** Plot of  $\mu_{\text{eff}}$  vs.  $T$  for  $\text{Cu}_2\text{L}_2^{2-}$ . The solid line represents the best fit of the data to the Bleaney–Bowers equation

In an electrochemical study of the binuclear complexes, no reduction peak was obtained in the first cathodic scan up to  $-2.0$  V. However, in the anodic scan two peaks were obtained during the first reverse cycle. This can be assigned to stepwise oxidation process  $\text{Cu}^{\text{II}}\text{Cu}^{\text{II}} \rightarrow \text{Cu}^{\text{II}}\text{Cu}^{\text{III}} \rightarrow \text{Cu}^{\text{III}}\text{Cu}^{\text{III}}$ .

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Techniques used: C, H, N, metal analysis, UV–VIS, variable-temperature magnetic measurements, thermogravimetry, EPR, cyclic voltammetry, FAB mass spectroscopy

Table 1: Elemental analysis

Fig. 3: EPR Spectra of  $\text{Cu}_2\text{L}_2^{2-}$

Fig. 4: Cyclic voltammogram of  $\text{Cu}_2\text{L}_2^{2-}$

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