

SYNTHESIS OF BINUCLEAR COPPER (II) COMPLEXES WITH EXPANDED PORPHYRINS

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ABSTRACT : *The synthesis and characterization of some new binuclear copper(II) complexes, based on the use of large, pyrrole- containing macrocycles, the so called "expanded porphyrins", $[Cu_2(\text{macrocycle})]^{+4}$ is described. Electron Spin Resonance (ESR) studies indicate a weak "half-field line", which is characteristic of the Cu(II)-Cu(II) dimer, is observed at about 1600G. The observation of this band strongly suggests that the hyperfine structure arises from a spin triplet species.*

KEY WORDS : *Copper(II), Expanded Porphyrins, Complexes.*

INTRODUCTION :

Metal-metal interactions in compounds which contain metal ions have been the subject of a large number of papers and reviews [1-5]. A variety of subclasses of compounds have been used to describe more conveniently the nature of the metal-metal interactions. In some cases, one may be justified in speaking of a "direct" metal-metal bond; in others, the interaction occurs only because of the involvement of other atoms, such as bridging ligands.

For three decades it has been known that copper(II) will form the following complexes: $[(L)Cu(B)_2Cu(L)]X_2, nH_2O$, where L is a bidentate ligand, X is counter anion, n is the

number of water molecule, and B is an anion [6-10]. The molar magnetic susceptibility and structural data for a number of di- μ -chloro-bridged copper(II) [11-25], di- μ -bromo-bridged copper(II) [26-28], and sulfo-bridged copper(II) [29-44] complexes have been investigated previously.

Magnetic and structural data also exist for a number of mono-chloro-bridged [45-50], mono-cyano-bridged [51-55], and mono-hydroxo-bridged copper(II) [45-57] complexes. Report on binuclear copper(II) complexes with expanded porphyrin are rare. Here, we present the result of synthesis and the ESR studies of copper(II)

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complexes with three expanded porphyrins.

EXPERIMENTAL :

Materials

All chemicals were of reagent grade quality, and purchased commercially. CH_2Cl_2 was dried over CaH_2 . Merck type 60(230-400 mesh) silica gel was used for column chromatography.

Physical measurements

Electronic spectra were recorded on a Beckman Du-7 spectrophotometer. Fast atom bombardment (FAB) spectra obtained using a Finnigan-Mat TSQ-70 instrument. 3-Nitrobenzil alcohol or glycerol was used at the matrix for FAB mass spectra. X-band electron spin resonance spectra ($\nu = 9.4\text{GHz}$) were obtained in CHCl_3 at room and liquid nitrogen temperatures with an IBM ER 300 spectrometer. DPPH was used as a reference material.

Preparation of Amines and Dialdehydes

Dialdehydes (1) and (2) were synthesized by the method of Bullock et al. [58] and Sessler et al. [59]. Tetraamine (3) was purchased from Aldrich Chemical Company (Milwaukee, WI, USA). Diamine (4) was synthesized by the method of Cheesman [60].

Preparation of Macrocyclus

A 250mL two-necked round bottom flask fitted with a thermometer, a stirrer, and a reflux condenser was attached to a nitrogen line. To it was added 50mL CH_3OH , 50mL CHCl_3 , 1mmol amine, 1mmol dialdehyde, and 5 drops of concentrated HCl. After the addition, the content of the flask was allowed to reflux by means of a heating mantle for one hour.

The resulting solution was concentrated to dryness on a rotary evaporator. The residue was taken up in CHCl_3 and eluted through a silica gel column with 5% $\text{CH}_3\text{OH}/\text{CHCl}_3$ as eluent.

Preparation of Copper(II) Complexes

To 250mL round bottom flask fitted with a magnetic stirring bar, a thermometer, a reflux

condenser, and a heating mantle, was added 100mL of pyridine, 1mmol of macrocycle, and 2mmol of copper(II) acetate. The flask was allowed to reflux for 24 hours. The solvent was removed by a rotary evaporator and purified by a silica gel column with 10% $\text{CH}_3\text{OH}/\text{CHCl}_3$ as eluent.

RESULTS AND DISCUSSION :

Up to date, no well-characterised binuclear copper(II) complex with expanded porphyrin have been obtained. The new complexes were prepared in low yield.

All metaloporphyrins show the following characteristic spectra:

- (1) Q-bands: Two visible bands between 500 and 600nm. The lower-energy band (sometimes called α) is the electronic origin $Q(0,0)$ of the lowest-energy excited singlet state. The higher-energy band (sometimes called β) includes one mode of vibrational excitation and is denoted $Q(1,0)$.
- (2) B-bands: An exceedingly intense band (sometimes called the Soret band) appears between 380 and 420nm. It is origin $B(0,0)$ of the second excited singlet state. All these bands are interpreted as (π, π^*) in origin [61].

The absorption spectra of the free ligand and its complex with copper(II) acetate shows Cu_2L_5 complex has a Soret-like band at 398nm and two weak Q-bands at 610, and 637.5 nm. The free ligand exhibits a band at 379 nm. The spectrum of Cu_2L_6 shows an intense Soret-like band at 395 nm. The Q-type bands occur at 560.5 nm and 523 nm. The free ligand shows an absorption maximum at 417 nm. The absorption spectra of Cu_2L_7 complex exhibits an intense Soret-like band at 398 nm and two Q-type bands are seen at 456 nm and 528nm. The free ligand has two bands which appear at 430 nm and 658.5 nm (Table 1).

Observation of ESR spectra of chloroform solutions of the various binuclear copper(II) complexes at 294K and 135K are shown in Figs. (1-3). The ESR spectra of all complexes are similar. They exhibit typical superhyperfine

Table 1: UV- Visible, ESR, and Mass data for the complexes.

Complex	g_{av}	g^*_{av}	Soret-band nm	Q-band nm	m^+/e
Cu_2L_5	2.08	4.15	398	637.5,610	1152
Cu_2L_6	2.08	4.07	395	560.5,523	1028
Cu_2L_7	2.07	4.11	398	564,528	1013

* At half-field

splitting due to the ^{14}N bound to copper. The observed ESR parameters for the complexes are virtually independent of the nature of the solvent. As seen in Figs. 1(A)-3(A) the main hyperfine line is split into nine lines. The spacings between these lines are nearly the same, and about 16 gauss, which can be attributed to an interaction with the four ^{14}N nuclei.

In Figs. 1(B)-3(B) a weak half-field line which is characteristic of the Cu(II)-Cu(II) dimer, is observed at about 1600 gauss at 135K. The observation of this band strongly suggests that the hyperfine structure arises from spin-spin interaction through the π system.

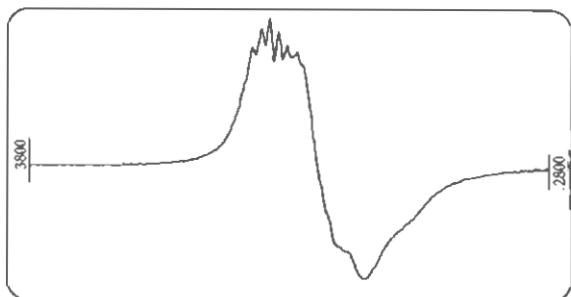


Fig. 1A: ESR spectra of the complex $Cu_2(L_5)$ in $CHCl_3$ at 294K.

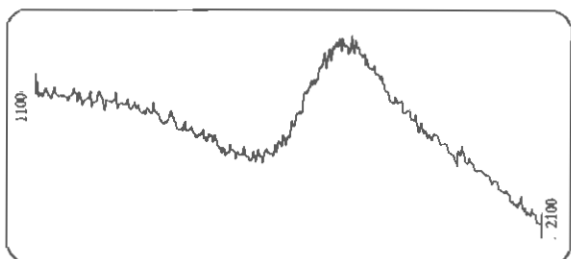


Fig. 1B: ESR spectra of the complex $Cu_2(L_5)$ in $CHCl_3$ at 135K.

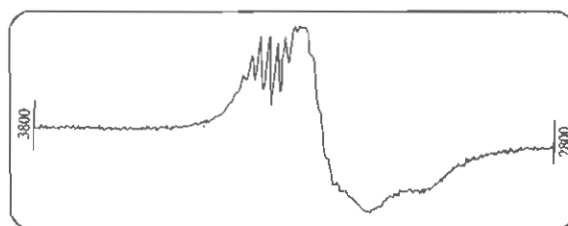


Fig. 2A: ESR spectra of the complex $Cu_2(L_6)$ in $CHCl_3$ at 294K.

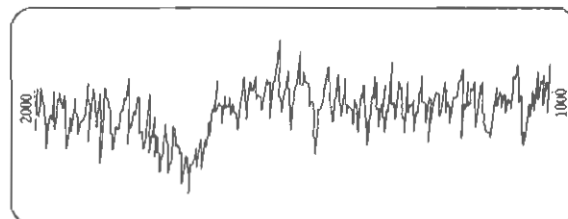


Fig. 2B: ESR spectra of the complex $Cu_2(L_6)$ in $CHCl_3$ at 135K.

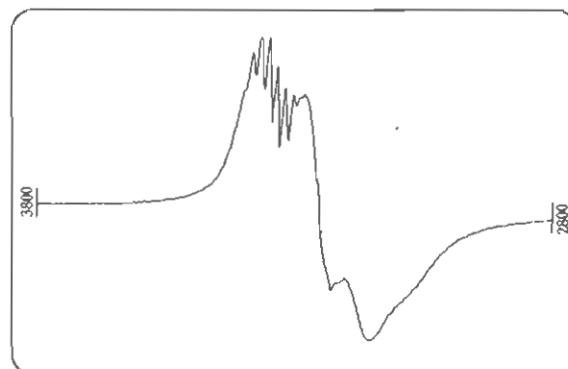


Fig. 3A: ESR spectra of the complex $Cu_2(L_7)$ in $CHCl_3$ at 294K.

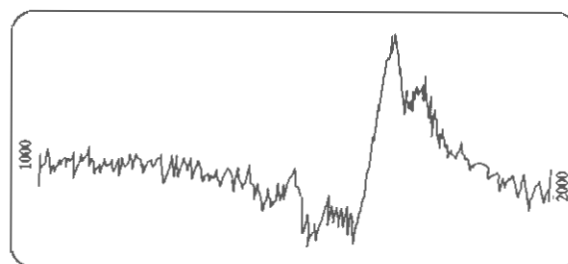
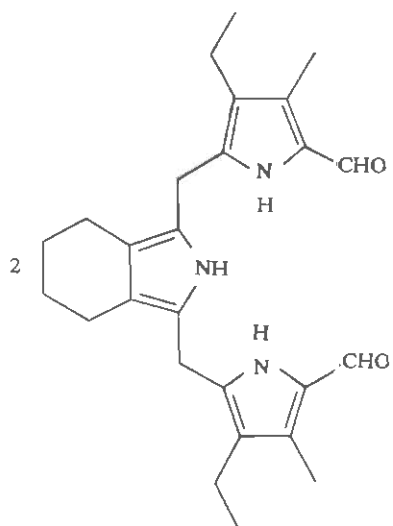
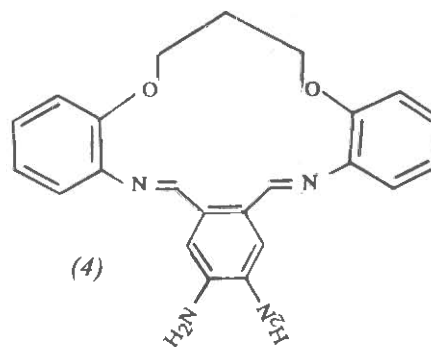
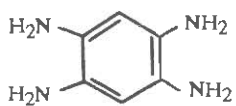
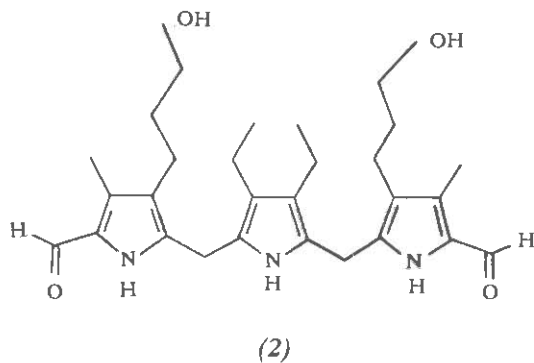
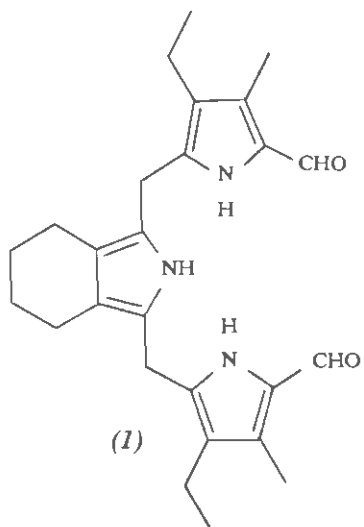


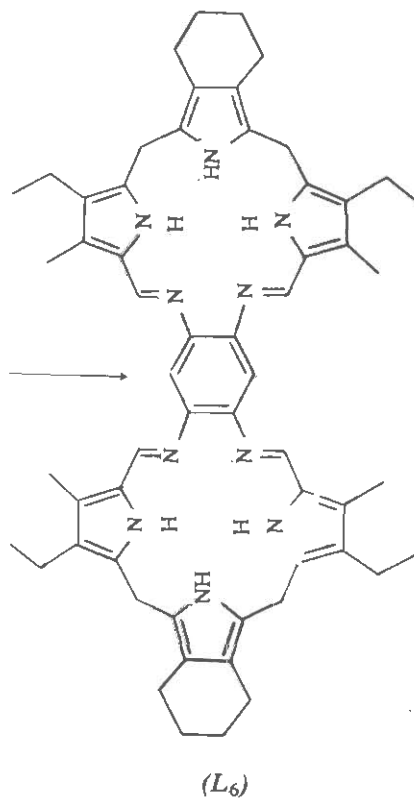
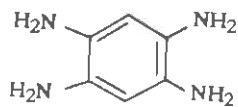
Fig. 3B: ESR spectra of the complex $Cu_2(L_7)$ in $CHCl_3$ at 135K.

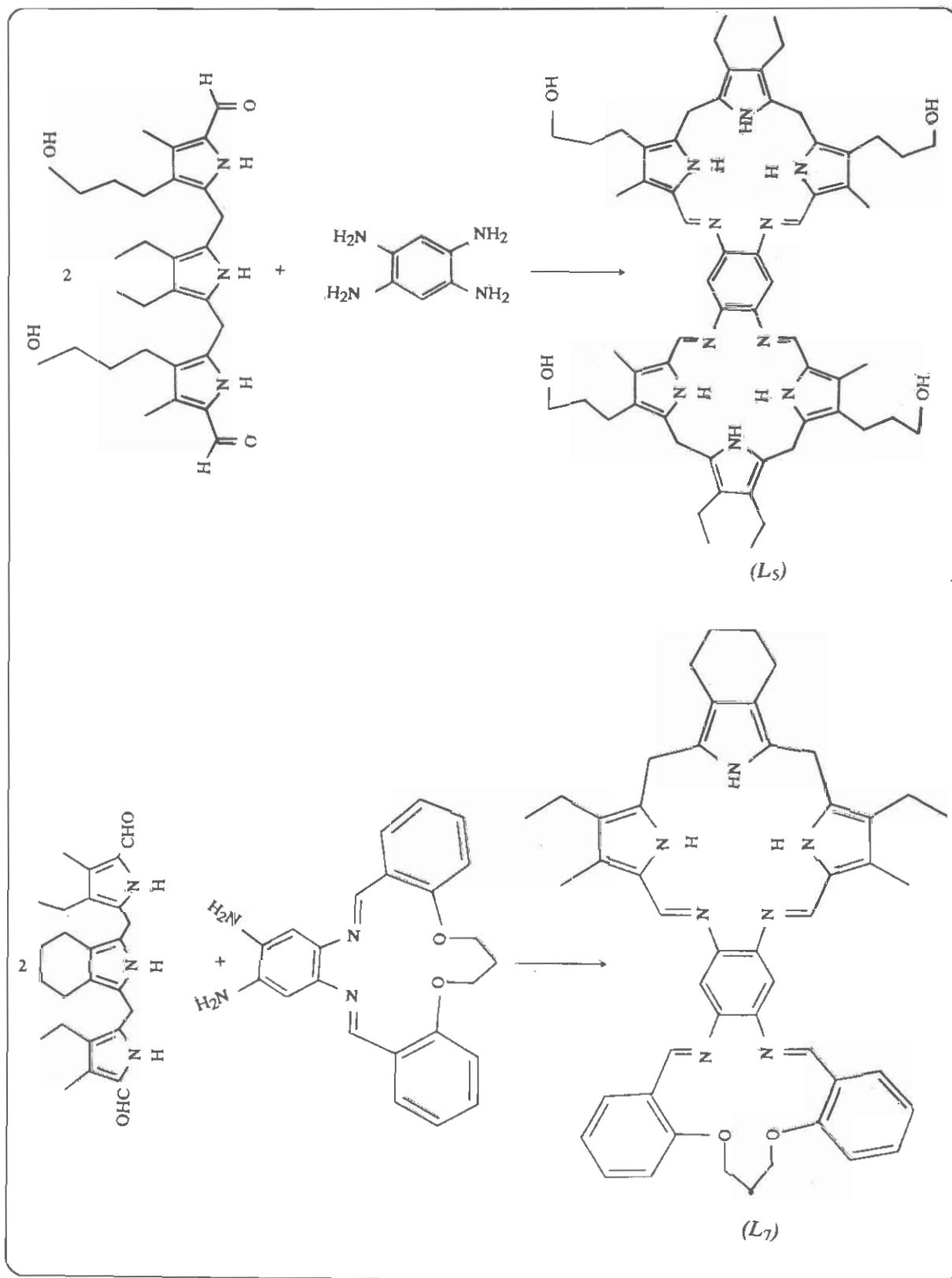
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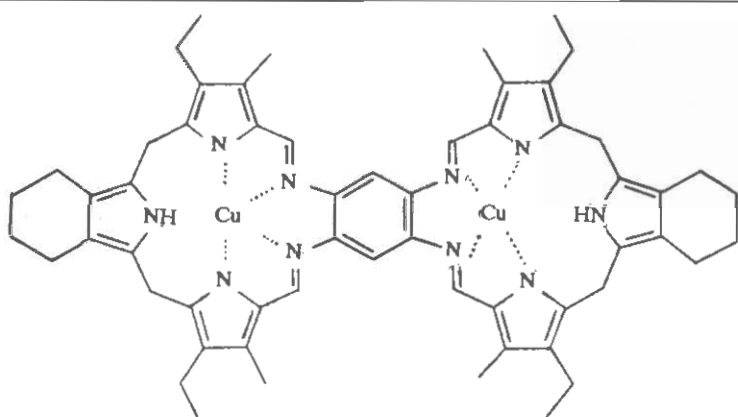
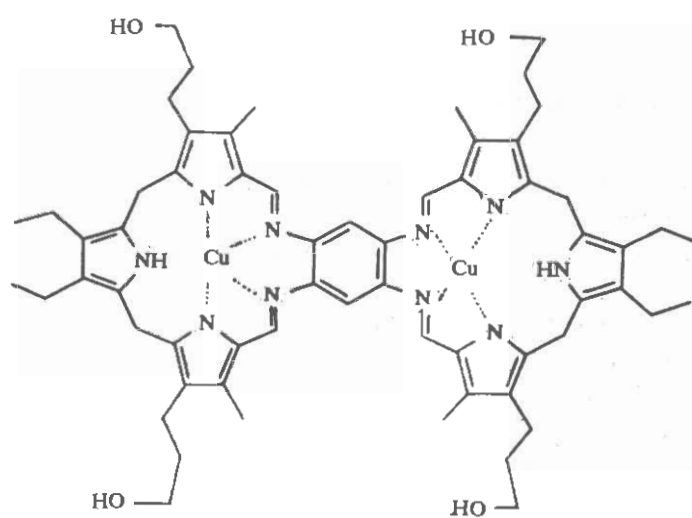
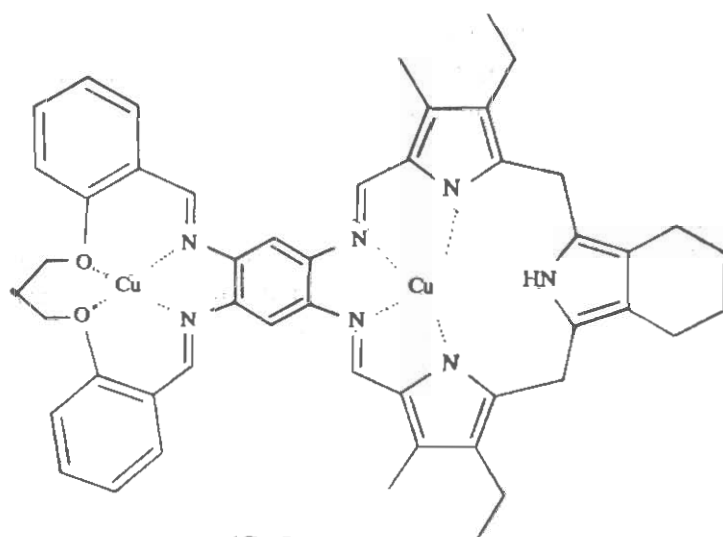
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 (Cu_2L_6)  (Cu_2L_5)  (Cu_2L_1)

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