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Mono- and Homobinuclear Copper(II) Complexes of Pyrrole-containing Schiff Base Macrocycles

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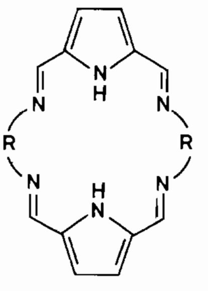
The generation of tetraimine Schiff base macrocycles derived from heterocyclic dialdehydes, *e.g.*, pyridine-2,6-; furan-2,5-; and thiophen-2,5-dicarboxaldehyde, has claimed much recent attention [1–4]. We report here the synthesis of mono- and homobinuclear copper(II) complexes of macrocycles derived from pyrrole-2,5-dicarboxaldehyde (Hpdc) and α,ω-alkanediamines.

The addition of excess KOH to a methanolic solution of Hpdc gave, on addition of ether, a precipitate of the potassium salt of Hpdc, Kpdc. The appropriate diamine, in methanol, was then added to a methanolic solution containing Kpdc and copper(II) ethanoate. The molar ratio used was 2:2:1 and the green solution produced a precipitate either immediately or after refluxing for 0.5 hours. The solid was then separated by filtration and dried *in vacuo* over silica gel.

The macrocyclic complexes prepared from 1,2-diaminoethane, 1,2-diaminopropane, and 1,3-diaminopropane were dark green and mononuclear having the formulation (Cu(m/c)) (m/c = L_1, L_2, L_3). Those prepared from 1,4-diaminobutane, 1,5-diaminopentane and 1,6-diaminohexane were light green and homobinuclear having the formulation (Cu_2(m/c)$(OMe)_2$) (m/c = L_4, L_5, L_6) [5].



H_2L_1, R–$(CH_2)_2$)–
H_2L_2, R –$CH_2CH(CH_3)$–
H_2L_3, R –$(CH_2)_3$–
H_2L_4, R –$(CH_2)_4$–
H_2L_5, R –$(CH_2)_5$–
H_2L_6, R –$(CH_2)_6$–

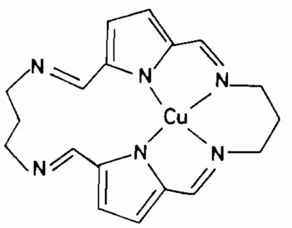


Fig. 1. Schematic representation of the molecular structure of (CuL_3).

The infra-red spectra of the complexes exhibit one, or two, bands in the region 1600–1630 cm^{-1} due to the imine $\nu_{C=N}$, but show no bands in the regions 1640–1670 cm^{-1} ($\nu_{C=O}$ for the unreacted dialdehyde) and 3330–3350 cm^{-1} (ν_{NH_2} for the primary diamines). The m.s. of (CuL_3) shows the presence of a peak at m/e = 322 corresponding to H_2L_3 and indicative of macrocycle formation.

The solid state electronic spectrum of (CuL_3) shows a shoulder at 17.500 cm^{-1} which suggests a distorted tetrahedral geometry for the metal site and similar diffuse reflectance bands are noted for (CuL_2) and (CuL_1) indicative of a common structure.

The macrocyclic nature of the complexes is verified by an X-ray crystallographic structure of (CuL_3) [6], which shows the molecule to have the features illustrated in Fig. 1. The pdc units are in *cis–trans* configurations and the metal sits in a distorted tetrahedral site composed of chelating units from each terminal unit.

The infra-red spectra of the complexes ($Cu_2L(OMe)_2$) show, in addition to the imine bands, further bands at *ca.* 2800 cm^{-1} which can be ascribed to the alkoxide ν_{CH} [7]. The d.r.s exhibit bands in the region 12.000–14.000 cm^{-1} which suggests a square-planar (or slightly distorted planar) geometry for the copper(II) atom.

The structure (I) is assigned to these complexes and the use of molecular models indicates that it is sterically favorable to include the –$Cu(OMe)_2Cu$– unit within macrocycles where $n \geqslant 4$ (n = the number of bridging CH_2 units), provided that the uncoordinated imine N atom is directed away from the cavity of the macrocycle. The presence of two distinct imine bands in the i.r. (*ca.* 1610 and 1640 cm^{-1}) also reflects this requirement. For $n < 4$ the diamine

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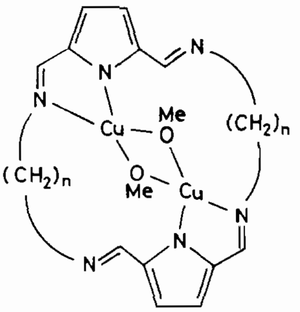
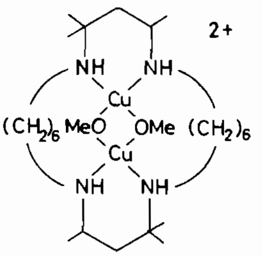


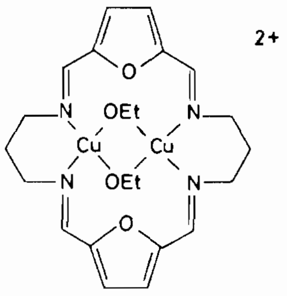
(I)

chain is of insufficient length to generate a cavity of diameter sufficient to enclose the binuclear unit [8].

A recent publication has described the synthesis and structure of a related di-μ-alkoxo-bridged copper(II) complex in which the macrocyclic ligand is 2,2,4,4,13,13,15-hexamethyl-1,5,12,16-tetraazacyclodocosane. The bridging alkane unit is $-(CH_2)-$ and the $-Cu(OMe)_2Cu-$ unit is similarly terminally coordinated by the head units of the macrocycle, (II) [9]. The $-Cu(OEt)_2Cu-$ unit present in the macrocyclic complex ($Cu_2(m/c)(OEt)_2(NCS)_2$) where the ligand is derived from furan-2,5-dicarboxaldehyde and 1,3-diaminopropane is, in contrast, laterally coordinated by adjacent imine units (III) and there is no coordination by the furan oxygen atoms [10].



(II)



(III)

Binuclear complexes, and particularly those containing copper, are of current interest with regard to studies of magnetic exchange mechanisms and electron-transfer properties. These studies lead to the consideration of such binuclear species as potential synthetic models for bimetallobiomolecules such as oxyhaemocyanin, tyrosinase, and the Type 3 centres in copper oxidases [11].

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