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Binuclear Copper(II) Complexes Containing Two Crown-Type Macrocyclic Rings

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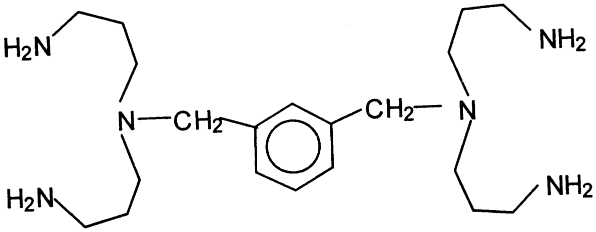
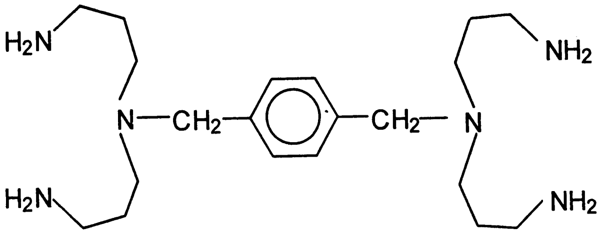
In the presence of copper(II) two hexadentate amines 1,3- and 1,4-bis[bis(3-aminopropyl)]-benzene condenses with 2,6-diacetyl-pyridine in ethanol-water solution (1 : 1), producing binuclear Schiff-base macrocycles. The effective magnetic moments of each copper atom in solution for these complexes are about 1.75 B.M., indicating that the two macrocyclic rings are probably in face-to-face fashion and some antiferromagnetic interaction is operative between the two copper(II) ions. IR and UV-VIS spectra of these complexes are also studied.

INTRODUCTION

The binuclear complexes containing metal centres in close proximity have been the subject of recent extensive investigation since these structural units are thought to be involved in a variety of important biochemical processes. A number of such a binuclear complexes have therefore been reported and studied as models of metal-metal interaction, redox catalyses and type 3 copper in enzyme systems[1]. The metal centers of these complexes are often incorporated into cavities presented by macrocyclic or macrocyclic polydentate ligands[2, 3]. Our interest in the synthesis of different polyamines and CR-type macrocycle have led us to a consideration of how these macrocycles can be connected by a rigid group, producing binuclear copper(II) complexes[1, 2] using the hexaamine PXBDP and MXBDP[4–7]



MXBDP

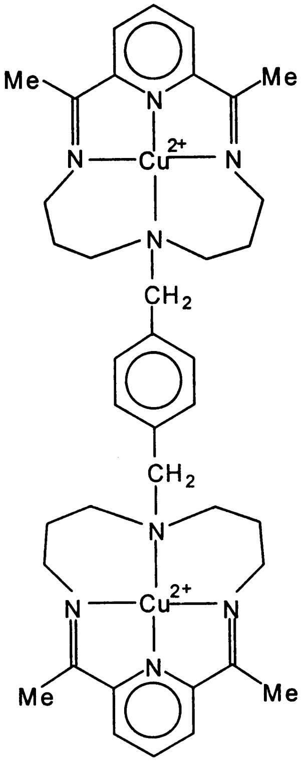


PXBDP

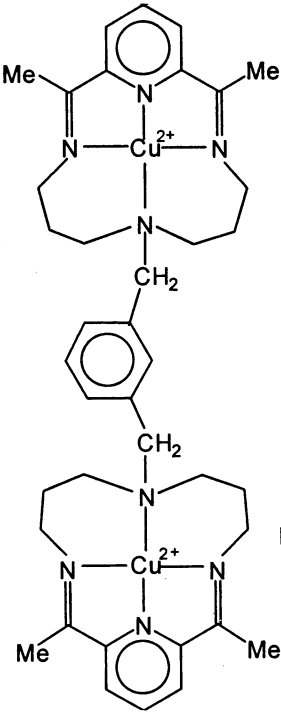
EXPERIMENTAL

2,6-Diacetylpyridine (dap) was obtained from Aldrich and used without further purification. 1,3- and 1,4-bis[bis(3-aminopropyl)]-benzene were prepared according to the methods that we have reported earlier[7]. IR, UV-VIS and NMR spectra were measured on Shimadzu IR-435, UV-265, FW and Jeol FX-90Q instruments respectively. The magnetic moments of all complexes were determined by Evan's N.M.R method[8].

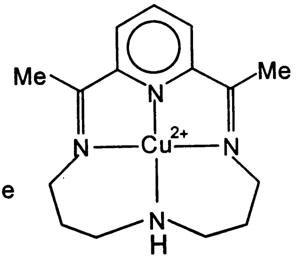
Complex (1), $(ClO_4)_2Cl_2\cdot 4H_2O$:* 2,6-Diacetylpyridine (0.5 mmol, 0.0816 g)



(1)



(2)



(3)

Caution : Perchlorate salts can be dangerously explosive. The compounds described here have never detonated in our hands, but they should be treated with care.

was added to a solution of PXBDP·6HCl (0.5 mmol, 0.3095 g), $CuCl_2 \cdot 2H_2O$ (0.5 mmol, 0.085 g) and $NaClO_4 \cdot H_2O$ (5 mmol, 0.7 g) in 350 mL methanol-water (1 :1) solution. The pH was adjusted to about 7 by addition of NaOH (1 M) and the resulting blue solution heated at about 50°C under reflux and stirred for 20 h. The solution was filtered and the filtrate reduced to ca. 40 mL. On standing at room temperature the crystalline complex was obtained as small needles; yield: 58%. (Found: C, 42.1%; H, 5.1%; N, 10.2%; $C_{38}H_{58}N_8Cl_4O_{12}Cu_2$ requires: C, 41.9%; H, 5.3%; N, 10.3%.)

Complex (2), *$(ClO_4)_2Cl_2 \cdot 4H_2O$*: 2,6-Diacetylpyridine (0.5 mmol, 0.0816 g) was added to a solution of MXBDP·6HCl (0.5 mmol, 0.3095 g), $CuCl_2 \cdot 2H_2O$ (0.5 mmol, 0.085 g) and $NaClO_4 \cdot H_2O$ (5 mmol, 0.7 g) in 350 mL methanol-water (1 : 1) solution. The pH was adjusted to about 6.7 by addition of NaOH (1 M) and the product was obtained analogously; yield: 55%; (Found: C, 41.8%; H, 5.1%; N, 10.0%. $C_{38}H_{58}N_8Cl_4O_{12}Cu_2$ requires: C, 41.9%; H, 5.3%; N, 10.3%.)

The PF_6 salt of this complex was also prepared from recrystallization of above compound in water containing four equivalents of $NaPF_6$; yield 80%. (Found: C, 33.0%; H, 3.8%; N, 7.5%. $C_{38}H_{56}N_8F_{24}O_3P_4Cu_2$ requires: C, 33.1%; H, 4.1%; N, 8.1%.)

RESULTS AND DISCUSSION

The syntheses of complexes were carried out in aqueous methanol (high dilution conditions to inhibit polymer formation during the synthesis) and best results were obtained when the pH, of the reaction mixtures were about that corresponding to the maximum concentration of the fully ligated binuclear copper(II)-hexaamine complexes. We have recently reported that the ligands PXBDP and MXBDP with a central benzene ring are not flexible enough to allow all the amine groups to bind to a single metal ion and in both metal-ligand ratios, 1 : 1 and 2 : 1, the concentrations of binuclear complexes are dominant[7]. Because of the above reasons the pHs of reaction mixtures were adjusted at about 7 and initial reactants were mixed in 1 : 1 ratio.

IR data of these complexes are compared with that of related CR complex, (3), in Table-1. The presence of ν(C═N) bands in the correct positions for Schiff-base linkages of this kind[9] and the absence of ν(C═O) and ν(N—H) absorptions indicate that the required macrocycles have indeed formed. The presence of lattice water was shown by a strong band at about 3450 cm^{-1} for both complexes. The broad intense bands at about 1100 cm^{-1} due to ClO_4^- shows no remarkable splitting, indicating particularly no coordination of ClO_4^- in both complexes.

TABLE-1

IR DATA (cm^{-1}) fOR THE COMPLEXES

Compound	ν(C═N)[a]	ν(C═N)[b]	ν(N—H)	ν(O—H)
(1)	1620 s	1583 s	–	3433 s
(2)	1621 s	1585 s	–	3427 s
(3)[c]	1623 s	1590 s	3238 s	3500 s

[a]Schiff-base; [b]Pyridine ring; [c]Ref. 10, 11

The visible absorption spectra of binuclear complexes and that of related CR complex are shown in Table-2 Both the present and the previous workers obtained CR complex (3) as a mono-hydrate. Lindoy *et al.*[10] found a structure in which one water molecule is bonded to the copper atom in the apical position of a square pyramid, and the position of visible absorption maximum (637 nm) is consistent with this. Our material absorbs at higher energy (Table-2), which is compatible with square planer structure leading us to believe that we have only lattice water present[11]. The visible absorption maxima of binuclear complexes also appear at the same positions and reveal a square-planer structure for each copper ion.

TABLE-2
ELECTRONIC SPECTROSCOPIC DATA AND MAGNETIC MOMENTS IN SOLUTION

Compound	λ_{max} (nm)	μ_{eff} B.M.
(1)	588(517)[a]	1.75
(2)	586(480)	1.76
(3)[b]	568(158)	1.89

[a]Figures in parentheses are extinction coefficients ($dm^3\ mol^{-1}\ cm^{-1}$) [b]Ref. 11

The effective magnetic moment of each copper atom in both binuclear complexes in solution at room temperature are shown in Table-2 together with that of corresponding CR in the same conditions. These results suggest that some antiferromagnetic interaction is operative between the two copper(II) ions in the bimetallic complexes. Considering the above facts and the chemical structures of (1) and (2), we can draw such a conclusion that the two coordination units face each other in the complexes.

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