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# Synthesis and spectroscopic characterization of copper (II) metal complexes of a 16 membered pentaaza (N<sub>5</sub>) bis (macrocyclic) complexes

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#### Abstract

Copper (II) complexes were synthesized with 1,1'-diphenyl, and 1,1'-diphenyl methanebis(8,10-dimethyl-1,3,7,11,15-pentaazacyclohexadeca-7,11-diene) a tetradentate ligand (L) and characterized by elemental analysis, molar conductance measurements, IR, electronic and EPR spectral studies. The molar conductance measurements of all the complexes in DMF solution correspond to non-electrolytic nature for  $(ML)_2RX_4$  complexes,1:4 electrolytes for  $(ML)_2RY_4$ . Thus the complexes may be formulated by  $[(ML)_2RX_4]$  and  $[(ML)_2R]Y_4$  respectively [where M = Cu (II), R =  $(C_6H_4NH_2)_2$ ,  $(C_6H_4NH_2)_2CH_2$ , X= Cl<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and Y = ClO<sub>4</sub><sup>-</sup>. All the complexes are of the high-spin type and found to have six-coordinated octahedral geometry except the complexes of perchlorate which were four coordinate and square planar in geometry.

Keywords: Macrocyclic; Pentadentate; Spectroscopic studies; Transition metals.

#### Introduction

The preparation of bis(macrocyclic) nitrogen donor ligands with binucleating properties towards transition metals has recently attracted much attention, and a variety of systems of this type have been reported [1,2] bis(cyclams) appear to be better electrocatalysts than are the corresponding mononuclear species [3,4]. The thermodynamic and kinetic inertness of transition metal complexes of poly azamacrocyclic ligands are significant industrial application [5-8].

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In this paper we report the synthesis and characterization of new bis(macrocyclic) binuclear copper(II) complexes of 1,1'-diphenyl and 1,1'-diphenylemethane- bis(8,10- dimethyl-1, 3, 7, 11, 15-penta-aza-cyclohexa-deca-7,11-diene),  $[(Cu(me_2(16)aneN_5)_2RCl_4], [(Cu(me_2(16)aneN_5)_2R(NO_3)_4], [(Cu(me_2(16)aneN_5)_2(CH_3COO)_4], [(Cu(me_2(16)aneN_5)_2R] (ClO_4)_4].$  These binuclear complexes were prepared from the template condensation of the appropriate nitrogen-nitrogen linker formeldehyde, 1, 3 diaminopropane copper (II), and 2, 4 pentanedione in 1:4:4:2:2 molar ratios (Figure 1).

#### **Experimental**

All the chemicals used were of AnalaR grade, and procured from sigma-Aldrich. Metal salts were purchased from E. Merck and were used as received. All the solvents used were of standard/spectroscopic grade.

#### **Synthesis of Complexes**

To a solution of bridging diamine (.0025mol) ( benzidine; 4,4'-diaminophenylmethane) as appropriate in methanol (20ml), a solution of 36% formaldehyde (0.01mol, 0.27ml) in methanol (20ml) was added. After 20 min a methanol solution of 1,3- diaminopropane( 0.01 mol,0.83ml ) in methanol (20ml) was added.



Fig.1 Preparation of Metal Complexes by Template Method

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Finally a solution of metal salt of cupper (.005mol) and 2,4-pentanedione (.005mol, 0.52gm) in methanol (20ml) was added and the resulting mixture was stirred for ca.16h at room temperature. The brown solid product was filtered off, washed with methanol and dried over fused CaCl, in desiccators.

#### **Physical Measurements**

The C, H, and N content were determined on a carlo-Erba 1106 elemental analyzer. Molar conductance was measure on the ELICO (CM82T) conductivity bridge. Megnetic susceptibility was measured at room temprature on a Gouy balance using  $CuSO_4.5H_2O$  as a calibrant. IR spectra (KBr) were recorded on FTIR spectrum BX-II spectrophoto- meter. The electronic spectra were recorded in DMF on Shimadzu UV mini-1240 spectrophotometer. EPR spectra of the complexes were recorded as polycrystalline sample and in the solution of DMF, at liquid nitrogen temperature for Cu(II) and at room temperature for Cu (II) complexes on  $E_4$ -EPR spectrometer using the DPPH as a g-marker.

#### **Results and Discussion**

The IR spectrum of the ligand does not exhibit any bond corresponding to a free primary diamine and keto group [9]. The vibration due to v (C=N) skeletal is present at 1407cm<sup>-1</sup>. The strong band at 1529 cm<sup>-1</sup> usually due to v(C-N) group. A bond appearing at 1597cm<sup>-1</sup> may be assigned to symmetric or asymmetric v(C=N) vibration. On complexation, The shifting of the position of (C=N) bonds towards the lower side indicates coordination through the nitrogen atoms of the C=N groups. All compounds gave satisfactory elemental analysis (Table.1). The higher melting point of the complexes suggests the thermal stability of complex.

#### Complexes

On the basis of elemental analysis, the complexes were found to have the composition shown in Table1. The molar conductance measurements of the complexes in DMF solution correspond to their non electrolytes nature for  $(ML)_2RX_4$  [where X= Cl<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, NO<sub>3</sub><sup>-</sup>,] and 1:4 electrolytes for  $(ML)_2RY_4$  [whereY=  $ClO_4^{-}$ ]. Thus the complexes may be formulated as [( ML)<sub>2</sub>RX<sub>4</sub>], [( ML)<sub>2</sub>R]Y<sub>4</sub> (where M= Cu(II)) and L= Ligand.[Table.1].

#### **Copper(II) complexes** (where X=Cl<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, NO<sub>3</sub><sup>-</sup>)

The magnetic moment values for Cu(II) lie in the 1.92-2.02 BM range corresponding to two unpaired electron (Table2). Electronic spectrum of the copper complexes displays band in range 9975-10992, 145074-18621, 20856-28571 cm<sup>-1</sup>. First two bonds may be assigned to the transitions:  ${}^{2}B_{1g}$   ${}^{2}A_{1g}(d_{x2-y2}-d_{z2})(v_{1})$ ,  ${}^{2}B_{1g}$   ${}^{2}B_{2g}(d_{x2-y2}-d_{zy})(v_{2})$  and third band may be due to charge transfer shown in [Fig.2].

The EPR spectra of Cu(II) complexes were recorded on X band at frequency  $9.1\text{GH}_{z}$  under the magnetic strength 3400G scene rate 2000, recorded at room temperature, and in DMF solution at liquid nitrogen temperature, (LNT) polycrystalline spectra shown [Fig.3] a well resolved anisotropic broad signal [10]. The analysis of spectra give  $g_{\parallel}=2.4628-2.5201$  and  $g_{\perp}=1.9785$ -

2.0255 (Table.3a, 3b). The trend  $g_{\parallel}>g_{\perp}>2.0023$  observed for the complexes indicates that the unpaired electron is localized in the  $d_{x^2-y^2}$  orbital of the Cu(II) ion and spectral features are characteristic for the axial symmetry. Tetragonally elongated geometry are thus confirmed for the Cu(II) complexes[11]. The presence of the absorption bands at 18652-19811, 14134-15620 and 9617-11213 cm<sup>-1</sup>, in the i.r. spectra of the Cu(II) nitrate complexes suggest the both nitrate groups are coordinated to central ion in a unidentate fashion [12-14].

#### **Copper(II) complexes** (where Y=ClO<sub>4</sub>-,)

The magnetic moment value of Cupper (II) perchlorate complexes were found to be 1.93 and 2.00 repectively. (Table.2) [15-16]. The electronic spectra of these complexes display band in range 15873-16949, 21276-22727. These bands corresponds to the transition  ${}^{2}B_{1g} - {}^{2}A_{1g}(d_{x2-y2} - d_{z2})(v_{1})$ ,  ${}^{2}B_{1g} - {}^{2}B_{2g}(d_{x2-y2} - d_{zy})(v_{2})$  and  ${}^{2}B_{1g} - {}^{2}E_{g}(d_{x2-y2} - d_{zy}d_{yz})(v_{3})$  respectively [17].



Fig.2 Elecronic spectra of the Complexes

These transitions suggest  $D_{4h}$  symmetry. The energy level sequence will depend on the amount of the tetragonal distortion due to ligand field and John Tellor distortion effect.

Another parameter G is calculated by using the expression  $G = (g_{\parallel} - 2 \setminus g_{\perp} - 2)$ . According to Chandra et.al if G<4 indicates considerable exchange intraction in the solid complexes. The calculated G values are larger than 4, suggesting that there is no intraction between the copper contents (Table. 3b).





 $[(M(Me_2[16]aneN_5))_2RX_4]$ 

Where,  $X = Cl^{-}$ ,  $NO_{3}^{-}$  and  $CH_{3}COO^{-}$ ,  $Y = ClO_{4}^{-}$ ; R =







# Fig.4 Suggested structure of the complexes

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