



NOTE

Synthesis and Characterization of [2+2] Cu(II) Macrocyclic Schiff Base Complexes

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[2+2]Cyclocondensation of $L_{22py} = N-(2\text{-pyridylmethyl})\text{-}N-(2\text{-aminoethyl})\text{-}1,2\text{-diaminoethane}$, $L_{23py} = N-(2\text{-pyridylmethyl})\text{-}N-(2\text{-aminoethyl})\text{-}1,3\text{-diaminopropane}$, $L_{33py} = N-(2\text{-pyridylmethyl})\text{-}N-(3\text{-aminopropyl})\text{-}1,3\text{-diaminopropane}$ and 2,6-diformyl-4-methylphenol (dfp), in the presence of $\text{Cu}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ in equimolar ratios gave three new binuclear Cu(II) macrocyclic complexes. Resulting compounds, $[\{\text{Cu}(\text{H}_2\text{L}^1)(\text{H}_2\text{O})\}_2](\text{ClO}_4)_4$ (**1**), $[\{\text{Cu}(\text{H}_2\text{L}^2)(\text{H}_2\text{O})\}_2](\text{ClO}_4)_4$ (**2**) and $[\{\text{Cu}(\text{H}_2\text{L}^3)(\text{H}_2\text{O})\}_2](\text{ClO}_4)_4$ (**3**), were characterized by IR spectroscopy, elemental analysis and mass diffraction method. The Cu(II) ions in latter binuclear complex from penta-coordinated complexes.

Key Words: Cyclocondensation, Tripodal, Macrocyclic complex.

Macrocyclic compounds have attracted increasing interest owing to their role in the understanding of molecular processes occurring in biochemistry, material science, catalysis, encapsulation, activation, transport and separation phenomena, hydrometallurgy, etc.¹⁻⁸. Many ligands have been designed to mimic the function of natural carriers in recognizing and transporting specific metal ions, anions or neutral molecules and in understanding and reproducing the catalytic activity of metallo-enzymes and proteins¹⁻⁸. Among this, a large variety [2+2] macrocyclic complexes Schiff base ligands have been synthesized to ascertain correctly the role of the different donor atoms, their relative position, the number and size of the chelating rings formed, the flexibility and the shape of the coordinating moiety on the selective binding of charged or neutral species and on the properties arising from these aggregations^{9,10}. Herein we report the synthesis and characterization of a number of binuclear macrocyclic Cu(II) of three asymmetric tripodal amino ligand with 2,6-diformyl-4-methylphenol (dfp). The resulting complexes were characterized by elemental analysis, IR and mass spectrophotometer.

Hydrated metal salts were obtained from Aldrich and were used without further purification. Two tripodal ligands L_{22py} , L_{23py} and L_{33py} were prepared as their hydrochloride salts *via* literature methods¹¹. IR spectra were measured on a Perkin-Elmer FT-IRGX spectrophotometer. Mass spectra were measured on a Bruker micro TOFQ.

Preparation of $[\{\text{Cu}(\text{H}_2\text{L}^1)(\text{H}_2\text{O})\}_2](\text{ClO}_4)_4$ (1**):** $L_{22py} \cdot 3\text{HCl}$ (0.1 g, 0.33 mmol) and NaOH (0.039 g, 0.93 mmol) were

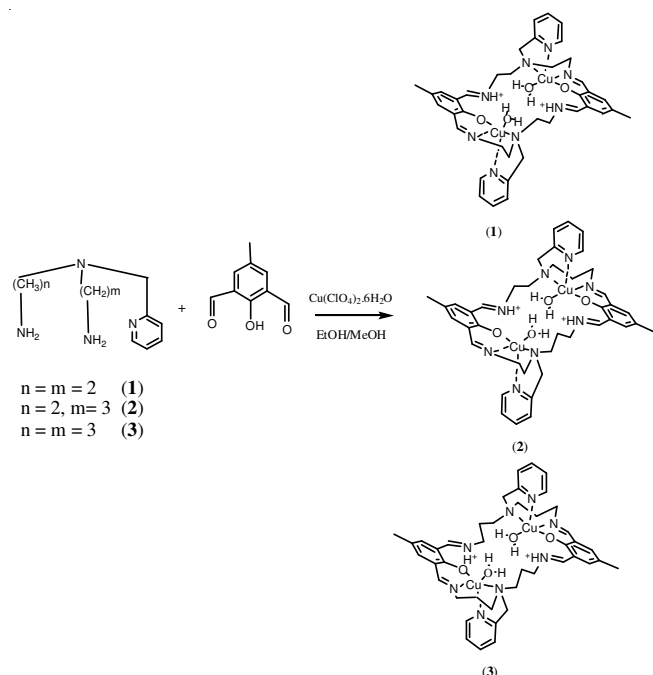
mixed and heated under reflux for 0.5 h in EtOH (15 mL). The NaCl which formed upon cooling was filtered off. The filtrate was added to a mixed of 2,6-diformyl-4-methylphenol (0.05 g, 0.31 mmol) and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.08 g, 0.31 mmol) in dry MeOH (40 mL) with continues stirring. The mixture was stirred in room temperature for 72 h, NaClO_4 (0.09 g, 0.62 mmol) was added. The solution was filtered and the filtrate was reduced to ca 10 cm³. Crystalline compound was obtained by slow diffusion of Et₂O vapour into this solution. Yield: (40 %). % Anal. calcd. (found) for $\text{C}_{38}\text{H}_{46}\text{N}_8\text{O}_{20}\text{Cl}_4\text{Cu}_2$: C, 38.01 (37.42); H, 3.82 (3.64); N, 9.33 (9.72). IR (Nujol, cm⁻¹): 1622 $\nu(\text{C}=\text{N})$ Schiff base, 3340 and 3290 $\nu(\text{N}-\text{H})$ stretching, 1603 and 1572 $\nu(\text{C}=\text{N})$ and/or $\nu(\text{N}-\text{H})$ bending, 1087 $\nu(\text{Cl}-\text{O})$ stretching. Accurate mass spectrometry (ESI-MS): $m/z = 1101.0689$ $[\text{M}_2\text{L}](\text{ClO}_4)_3^+ \text{C}_{38}\text{H}_{46}\text{N}_8\text{O}_{16}\text{Cl}_3\text{Cu}_2$ requires 1101.2506.

Synthesis of $[\{\text{Cu}(\text{H}_2\text{L}^2)(\text{H}_2\text{O})\}_2](\text{ClO}_4)_4$ (2**):** Complex **2** was prepared in an analogous manner. Yield: (38 %). % Anal. calcd (found) for $\text{Cu}_2\text{C}_{40}\text{H}_{50}\text{N}_8\text{O}_{20}\text{Cl}_4$: C, 39.21 (38.91); H, 3.72 (3.56); N, 9.11 (9.43). IR (Nujol, cm⁻¹): 1624 and 1631 $\nu(\text{C}=\text{N})$ Schiff base, 3346 and 3285 $\nu(\text{N}-\text{H})$ stretching, 1603 and 1573 $\nu(\text{C}=\text{N})$ and/or $\nu(\text{N}-\text{H})$ bending, 1087 $\nu(\text{Cl}-\text{O})$ stretching. Accurate mass spectrometry (ESI-MS): $m/z = 1129.9435$ $[\text{M}_2\text{L}](\text{ClO}_4)_3^+ \text{C}_{40}\text{H}_{50}\text{N}_8\text{O}_{16}\text{Cl}_3\text{Cu}_2$ requires 1129.1002.

Synthesis of $[\{\text{Cu}(\text{H}_2\text{L}^3)(\text{H}_2\text{O})\}_2](\text{ClO}_4)_4$ (3**):** Complex **3** was prepared in an analogous manner. Yield: (51 %). % Anal. calcd (found) for $\text{Cu}_2\text{C}_{42}\text{H}_{54}\text{N}_8\text{O}_{20}\text{Cl}_4$: C, 40.14 (39.87); H, 4.43 (4.36); N, 8.91 (8.63). IR (Nujol, cm⁻¹): 1626 $\nu(\text{C}=\text{N})$ Schiff base) 1335 and 3285 $\nu(\text{N}-\text{H})$ stretching, 1605 and 1573 $\nu(\text{C}=\text{N})$

and/or $\nu(\text{N-H})$ bending, $1092 \nu(\text{Cl-O})$ stretching. Accurate mass spectrometry (ESI-MS): $m/z = 1157.1224$ $[\text{M}_2\text{L}](\text{ClO}_4)_3^+$ $\text{C}_{42}\text{H}_{54}\text{N}_8\text{O}_{16}\text{Cl}_3\text{Cu}_2$ requires 1157.1315.

All complexes **1-3** were synthesized by the template condensation of the neutralized tripodal ligands $\text{L}_{22\text{py}}$, $\text{L}_{23\text{py}}$ and $\text{L}_{33\text{py}}$ with 2,6-diformyl-4-methylphenol (dfp) in the presence of Cu(II) metal ion (Scheme I). The resulting compounds were characterized by IR, elemental analysis and mass spectrometry. Condensation of all the primary amino groups are confirmed by the lack of N-H stretching bands in the IR region ($3450\text{--}3150 \text{ cm}^{-1}$) and the presence of strong C=N (Schiff-base) stretching bands at $1670\text{--}1620 \text{ cm}^{-1}$, respectively. A broad intense band at *ca.* 1100 cm^{-1} for all complexes due to ClO_4^- shows no splitting, indicating the absence of coordination of ClO_4^- for all compounds.



Scheme-I: Outcome of template condensation of tripodal tetraamins ($\text{L}_{22\text{py}}$, $\text{L}_{23\text{py}}$ and $\text{L}_{33\text{py}}$) and dfp in the presence of Cu(II) ion.

The mass spectra of all complexes are also consistent with their structure and formulation. The clear intense peaks associated to $[\text{ML}]^+$ species are observable in all spectra. In all cases the isotopic patterns are similar to calculated isotopic patterns for latter species.

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