



NOTE

Synthesis and Characterization of Ni(II) Schiff Base Macrocyclic Complexes

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[2+2]Cyclocondensation of L_{22py} = N-(2-pyridylmethyl)-N-(2-aminoethyl)-1,2-diaminoethane, L_{23py} = N-(2-pyridylmethyl)-N-(2-aminoethyl)-1,3-diaminopropane and 2-[3-(2-formyl phenoxy)propoxy]benzaldehyde and 2-[4-(2-formyl phenoxy)butoxy]benzaldehyde in the presence of $Ni(ClO_4)_2 \cdot 4H_2O$ in equimolar ratios gave three new binuclear Ni(II) macrocyclic complexes. Resulting compounds, $[Ni(H_2L^1)](ClO_4)_2$ (**1**), $[Ni(H_2L^2)](ClO_4)_2$ (**2**) and $[Ni(H_2L^3)](ClO_4)_2$ (**3**), were characterized by IR spectroscopy and elemental analysis. The Ni(II) ions in latter complexes are six coordinated.

Key Words: Cyclocondensation, Tripodal, Macrocyclic complex.

Schiff bases have been extensively employed^{1,2} in the understanding of molecular processes occurring in biochemistry, material science, catalysis, encapsulation, activation, transport and separation phenomena, hydrometallurgy, *etc.* A variety of [1+1] and [2+2] macrocyclic 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^{3,4}. The evolution of these Schiff bases has produced macrobicyclic ligands obtained in one-step multiple condensation reactions^{4,5}. Their acyclic or cyclic nature has been proposed especially by IR and NMR spectroscopy and mass spectrometry and often confirmed by single crystal X-ray structural determinations.

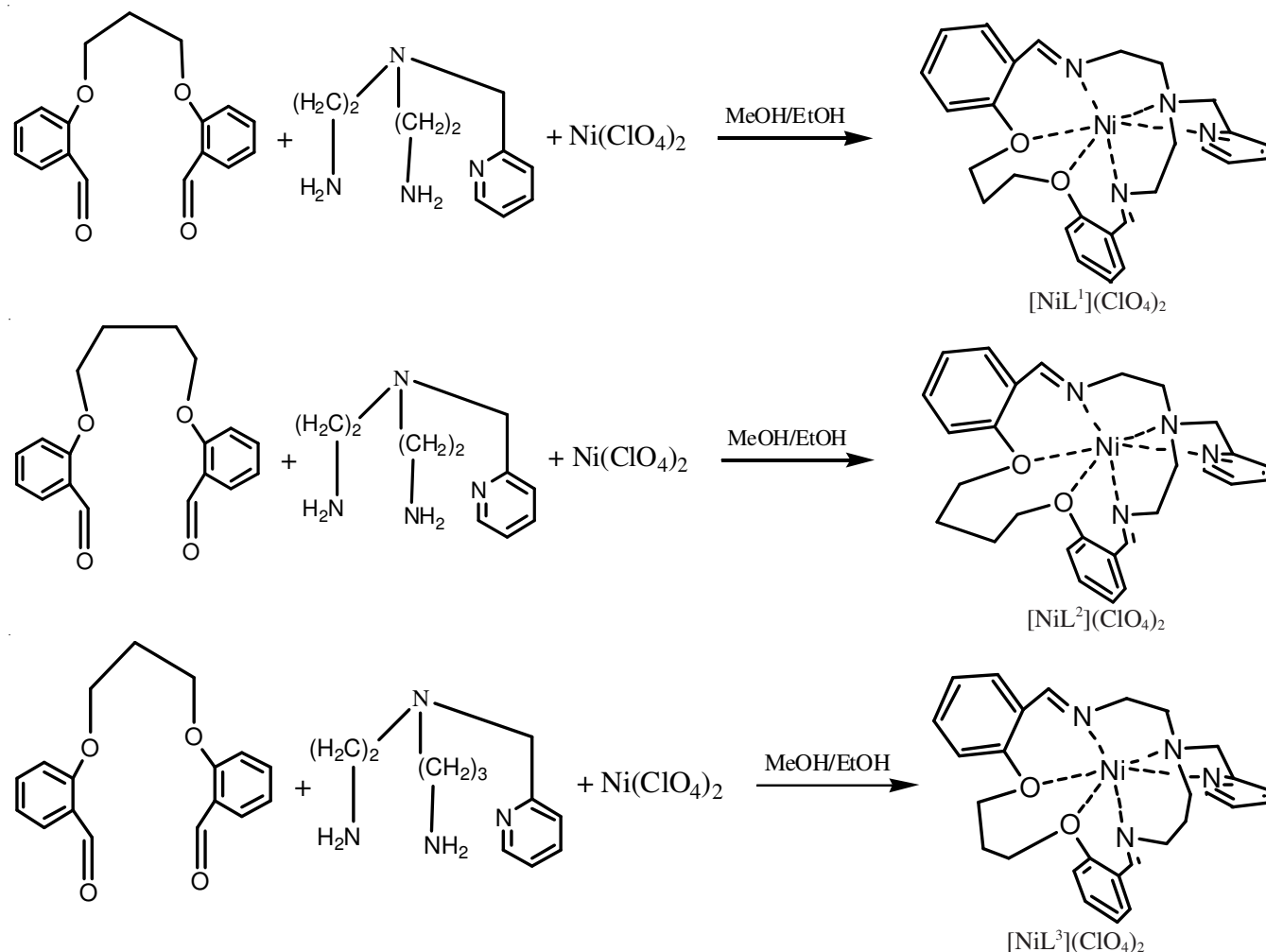
The cyclic [3+2] Schiff base condensation represents the extension of the [2+2] macrocyclic coordination systems into the third dimension. The introduction of specific functionalities at the periphery of the coordinating moiety gives rise to quite sophisticated systems capable of contemporary multi-recognition processes, specific separation and transport processes across membranes or activation and catalysis in eco-compatible solvents. For macrocyclic receptors the hole size represents an additional parameter which may influence greatly the ability to discriminate among the different charged or neutral species to be recognized. The progressive enlargement of the coordinating moiety allowed studies aimed at a deep understanding of physico-chemical properties arising from the simultaneous

presence of two or more metal ions in close proximity within the same coordinating moiety. Herein we report the synthesis and characterization of a number of binuclear macrocyclic Ni(II) of three asymmetric tripodal amino ligand with appropriate aldehydes. The resulting complexes were characterized by elemental analysis and IR spectrophotometer.

Hydrated nickel(II) salts were obtained from Aldrich and were used without further purification. Two tripodal ligands L_{22py} and L_{23py} were prepared as their hydrochloride salts *via* literature methods⁶. IR spectra were measured on a Perkin-Elmer FT-IRGX spectrophotometer.

Preparation of $[NiL^1](ClO_4)_2$ (1**):** $L_{22py} \cdot 3HCl$ (0.1 g, 0.33 mmol) and NaOH (0.039 g, 0.93 mmol) were mixed and heated under reflux for 30 min in EtOH (15 ml). The NaCl which formed upon cooling was filtered off. The filtrate was added to a mixed of 2-[3-(2-formylphenoxy)-propoxy]benzaldehyde (0.04 g, 0.99 mmol) and $Ni(ClO_4)_2 \cdot 6H_2O$ (0.1 g, 0.33 mmol) in dry MeOH (40 mL) with continues stirring. The mixture was stirred in room temperature for 72 h. The solution was filtered and the filtrate was reduced to *ca.* 10 mL. Crystalline compound was obtained by slow diffusion of Et₂O vapor into this solution. Yield: (30 %). % Anal Calcd. (Found) for $C_{27}H_{30}N_4O_{10}Cl_2Ni$: C, 46.43 (46.11); H, 4.12 (4.15); N, 8.58 (8.86). IR (Nujol, cm^{-1}): 1627 $\nu(C=N)$ Schiff base, 3341 and 3293 $\nu(N-H)$ stretching, 1605 and 1574 $\nu(C=N)$ and/or $\nu(N-H)$ bending, 1089 $\nu(Cl-O)$ stretching.

Synthesis of $[NiL^2](ClO_4)_2$ (2**):** Complex **2** was prepared in an analogous manner. Yield: (22%). % Anal. calcd (found) for $C_{28}H_{32}N_4O_{10}Cl_2Ni$: C, 46.43 (46.11); H, 3.72 (3.56); N, 8.58



Scheme-I: The outcome of template condensation of tripodal tetraamins (L_{22py} and L_{23py}) and appropriate aldehydes in the presence of Ni(II) ion

(8.86). IR (Nujol, cm^{-1}): 1621 and 1630 $\nu(\text{C}=\text{N})$ Schiff base, 3342 and 3283 $\nu(\text{N}-\text{H})$ stretching, 1601 and 1571 $\nu(\text{C}=\text{N})$ and/or $\nu(\text{N}-\text{H})$ bending, 1089 $\nu(\text{Cl}-\text{O})$ stretching.

Synthesis of $[\text{NiL}^3](\text{ClO}_4)_2$ (3): Complex 3 was prepared in an analogous manner. Yield: (32 %). % Anal. calcd (found) for $\text{C}_{28}\text{H}_{32}\text{N}_4\text{O}_{10}\text{Cl}_2\text{Ni}$: C, 46.43 (46.08); H, 3.61 (3.12); N, 8.46 (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 $\nu(\text{N}-\text{H})$ bending, 1092 $\nu(\text{Cl}-\text{O})$ stretching.

Synthesis and characterization: All complexes **1-3** were synthesized by the template condensation of the neutralized tripodal ligands L_{22py} and L_{23py} with 2-[3-(2-formyl phenoxy) propoxy] benzaldehyde and 2-[4-(2-formyl phenoxy) butoxy] benzaldehyde in the presence of Ni(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 $1620\text{-}1670\text{ cm}^{-1}$, 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.

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