

SYNTHESIS AND CHARACTERIZATION OF A TRINUCLEAR Ni(II) COMPLEXES WITH TRICOMPARTMENTAL MACROCYCLIC LIGAND

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ABSTRACT : Kinetic template reaction between nickel bromide, glyoxal and hydrazine develops blue crystals of $[\text{Ni}(\text{GDFI})_2\text{Br}_2]$ on one hand and green crystals of 13, 14- exocyclicdioxo-1, 5, 8, 12-tetraaza-2, 3 : 10,11-dibenzocyclotetradeca-2, 4, 8, 10-tetraenato [2-] nickel (II) by kinetic template condensation of nickel acetate, salicylaldehyde and 1:2- diaminoethane on the other. Finally the blue and green crystals are allowed to undergo self assembly process in the molar ratio 1:2 in DMF medium under nitrogen at 100°C to produce orange red crystals of a trinuclear nickel (II) clathrochelate. The compound has been characterized with elemental analysis, conductivity and magnetic susceptibility measurements, infrared and visible spectral studies. The nickel(II) ions are found to be in different stereochemical environments.

Keywords: Clathrochelate, spectral studies, tricompartamental ligand.

I. INTRODUCTION

The unique properties of metal ions encapsulated in the cage of a macropolycyclic ligand and isolated from the influence of external factors have allowed the use of clathrochelates as models of important biological systems, electron carriers and catalysts of photochemical redox processes. In continuation of our earlier interest in the field⁵⁻¹⁰ we in the present communication, report a pair of mononuclear precursors and a trinuclear nickel (II) clathrochelate.

II. EXPERIMENTAL

Salicylaldehyde, glyoxal, hydrazine hydrate hydrochloride and nickel(II) salts were all Aldrich reagents. The synthesis follow the path as proposed earlier.¹¹

Preparation of dibromobis (glyoxaldihydrazone) nickel (II)

It was prepared as per literature procedures. Glyoxal (1.16 g, 0.02 mol) in ethanol was treated dropwise, with constant stirring, with an ethanolic solution of nickel(II) bromidehexahydrate (3.2 g, 0.01 mol). The resulting mixture was warmed to boiling and hydrazine hydrate (2.0g, 0.04 mol) was added dropwise with constant stirring when a bluish violet crystals were readily obtained. It was refluxed on a hot water bath for nearly two hours. The compound was filtered after cooling, washed with alcohol, followed by ether and analysed after drying.

The complex 13, 14-exocyclicdioxo-1, 5, 8, 12-tetraza-2, 3 : 10, 11-dibenzocyclotetradeca-2, 4, 8, 10-tetraenato (2-) nickel (II) has been prepared by the method reputed in literature.¹² Finally the two precursors were allowed to undergo condensation in 1 : 2 molar ratio in DMF solution at 100°C in atmosphere of nitrogen. The resulting solution was cooled and slow evaporation under vacuum produced beautiful red crystals which were dried in vacuo and analyzed. Analytical results are in good agreement with proposed formula within one percent. [Found (Calc)] for $[\text{Ni}_3 (\text{C}_{40}\text{H}_{32}\text{N}_{16})\text{Br}_2] : \text{Ni}$ 16.32 (16.50), C44.38 (44.73), H 2.96 (2.98), N 20.58 (20.88), Br 14.83 (14.91).

III. RESULTS AND DISCUSSION

In order to elucidate, the structure, i.r. and electronic spectra of the precursors and tricyclomacrocyclic complex were recorded respectively on Shimadzu-160 and Beckman-20 spectrophotometers. Conductivity and magnetic susceptibility have also been measured on Systronics conductometer model 303 and Guoy balance respectively. Low value of molar conductivity in the range 10-15 Ohm cm² mol⁻¹ indicate the precursors and macrocyclic complex to be non-electrolytic in nature. The magnetic moment of macrocyclic precursors, [Ni C₁₈ H₁₄ N₄ O₂] indicates it to be diamagnetic. Electronic spectrum with a broad band with low intensity at 21000 cm⁻¹ suggests the stereochemistry to be square planar. Non-macrocyclic precursors [Ni (C₄ H₁₂ N₈) Br₂] has $\mu_{\text{eff}} = 3.16$ B.M. indicating it to be octahedral in nature. The electronic spectrum with three bands at 16000, 19000 and 25000 cm⁻¹ respectively also supports octahedral environment around Ni(II) ion.

The μ_{eff} of tricyclomacrocyclic complex has been found to be 3.85 B.M. and is presumed to be due to central octahedral and terminal square planar environment of Ni(II) ions, the excess value is most probably due to TIP contribution.

IV. IR SPECTRA

The intense and strong bands in the region 3250-3450 cm⁻¹ in the spectrum of non-macrocyclic precursor is absent in the spectrum of trinuclear clathrochelate due to Schiff base condensation of suitably oriented uncoordinated NH₂ group of the non-macrocyclic precursor, [Ni (C₄ H₁₂ N₈) Br₂] with the exocyclic- oxo group of the cyclic precursor, [Ni (C₁₈H₁₄N₄O₂)] during macrocyclization. This is supported by disappearance of strong band at 1700 cm⁻¹ due to $\nu_{\text{C=N}}$ from the spectrum of clathrochelate.

A strong sharp band of medium intensity is present in the spectra of all the complexes, precursors as well as tricyclomacrocyclic in the range 1630-1640 cm⁻¹ and can be assigned to $\nu_{\text{C=N}}$. The presence of a strong band in the region 470-450 cm⁻¹ can be assigned to $\nu_{\text{N=N}}$. The bands at 1050-1060 cm⁻¹ are assigned to $\nu_{\text{N-N}}$ of the hydrazide moieties.

On the basis of above information, the structure of the ligand 10, 11 : 18, 19 : 30,31 : 38,39 - tetrabenzo-2, 3, 6, 7, 9, 13, 16, 20, 22, 23, 26, 27, 29, 33, 36, 40-hexadecaazatricyclo-[26, 12, 0, 08'21 tetraaconta- , 3, 5, 7, 10, 12, 16, 18, 21, 23, 25, 27, 30, 32, 36, 38-hexadecaene, C₄₀H₃₂N₁₆ and tricyclo clathrochelate can be proposed to be shown in fig. I and 2 respectively ¹H NMR, mass spectral and XRD studies are in progress.

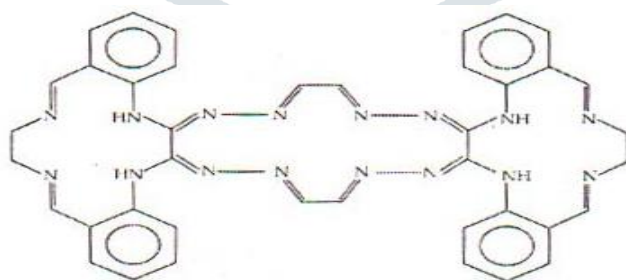


Fig. I

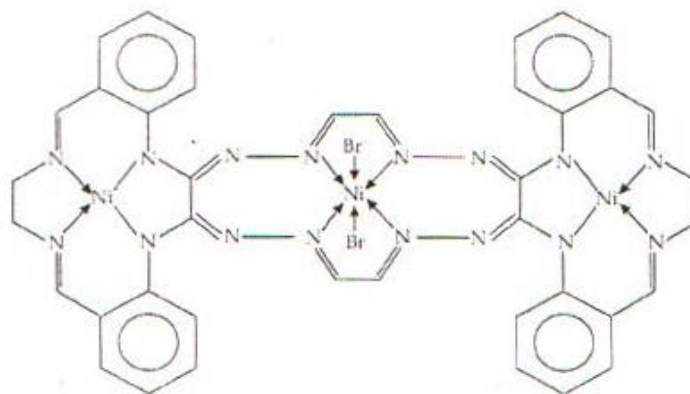


Fig. 2

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