Synthesis, Characterization and Electro-Spectroelectrochemical Studies of Four Macroyclic Schiff-Base Co(II) Complexes having N₂O₂ Set of Donor Atoms

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Four macrocyclic Schiff-base cobalt complexes, [CoL₁][NO₃]₂.3H₂O, [CoL₂][NO₃]₂.4H₂O, [CoL₃][NO₃]₂.4H₂O and [CoL₄][NO₃]₂.2H₂O, were synthesized by reaction of salicylaldehyde derivatives with 1,4-bis(3-aminopropoxy)butane or (+)-trans-1,2-diaminocyclohexane and Co(NO₃)₂.6H₂O by template effect in methanol. The metals to ligand ratio of the complexes were found to be 1:1. The Co(II) complexes are proposed to be tetrahedral geometry. The macrocyclic Co(II) complexes are 1:2 electrolytes as shown by their molar conductivities (λ_m) in DMF (dimethyl formamide) at 10⁻³ M. The structure of Co(II) complexes is proposed from elemental analysis, FTR, UV-Visible spectra, magnetic susceptibility, molar conductivity measurements and mass spectra. Electrochemical and thin-layer spectroelectrochemical studies of the complexes were comparatively studied in the same experimental conditions. The electrochemical results revealed that all complexes displayed irreversible one reduction processes and their cathodic peak potential values (E_pc) were observed in around of -1.14-0.95 V. It was also seen that [CoL₁][NO₃]₂.3H₂O and [CoL₃][NO₃]₂.4H₂O exhibited one cathodic wave without corresponding anodic wave but, [CoL₃][NO₃]₂.4H₂O and [CoL₄][NO₃]₂.2H₂O showed one cathodic wave with corresponding anodic wave, probably due to the presence of different ligand nature even if the complexes have the same N₂O₂ donor set. In view of spectroelectrochemical studies [CoL₁][NO₃]₂.4H₂O showed distinctive spectral changes in which the intensity of the band (λ = at 316 nm, assigned to n→π⁺ transitions) decreased and a new broad band in a low intensity about 391 nm appeared as a result of the reduction process based on the cobalt center in the complex.

![Figure 1. Suggested structure of the complexes](image-url)

References:
