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Synthesis of a macrocyclic Ligand, Me_4-[16]-Tetraene-N_4 and its Metal Complexes with Chromium, Iron, Cobalt and Nickel

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A series of metal complexes of chromium, iron, cobalt and nickel with a macrocyclic ligand 6,8,14,16-Me_4-[16]-6,8,14,16-tetraene-1,5,9,13-N_4 has been prepared and characterized on the basis of infrared, electronic, PMR spectral studies as well as conductivity and magnetic moment studies. The ligand reacts with metal(II) acetates under conditions of non-aqueous chelation to give the nautral macrocyclic complex M(Me_4-[16]-tetraenato-(2-)N_4). (M=Cr, Fe, Co or Ni).

INTRODUCTION

There has been a spectacular growth in interest in metal complexes with tetra-aza macrocyclic lingands followed by extensive work on the metal-controlled template and metal-free non-template synthesis of macrocylic species[1–6]. Recent electrochemical studies have shown 16-membered macrocyclic rings to be most stable towards reduction among 14-, 16-, 18- and 20- membered macrocycles[7]. Substituents on the ligand frame and degree of unsaturation/conjugation also have significant effect on stability. In continuation with our work in the field[8–10], we report here a series of metal complexes with the macrocyclic title ligand Me_4-[16]-tetraene-N_4.

EXPERIMENTAL

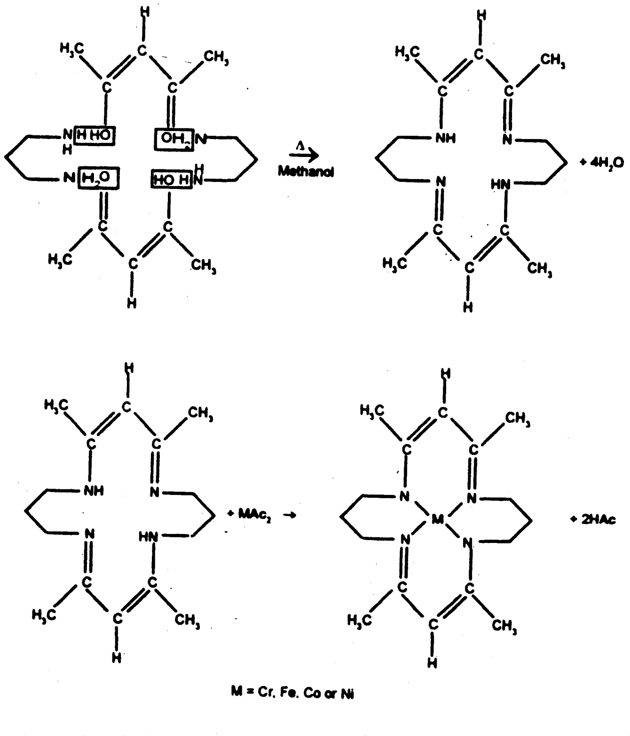
The metal acetates used were of BDH make. 1,3-Diaminopropane and acetylacetone (E. Merck) were used as such. For the preparation of the ligand procedure as reported in literature was followed[11]. 1,3-Diaminopropane was dissolved in dry and cold methanol and allowed to react with methanolic solution of acetylacetone in equimolar proportion under reflux on a water bath for several hours at room temperature. The solution thus obtained on crystallisation gave a cream-coloured solid which was filtered, washed and dried. The complexes were prepared by refluxing together metal acetates and ligand in equimolar proportion in methanolic medium. On chemical analysis, the stoichiometry of the complexes was found to be of the type M(Me_4-[16]-tetraenato (2-)-N_4). Metal ion catalysed *in situ* method, in which 1,3-diaminopropane and acetylacetone were allowed to organise themselves around central metal cation, gave similar results. Yield was found to be in the range of 55–60%.

The infrared spectra of the ligand as well as its complexes were recorded on a Beckmann conductometer model 303 using dimethylsulfoxide as a solvent. Magnetic moments were measured by the Gouy method using $Hg[Co(NCS)_4]$ as a calibrant. The absorption spectra of dimethylsulfoxide solution of these complexes were recorded on a Cary-2390 spectrophotometer using a pair of 1 cm quartz cuvettes. ^1H NMR spectra were recorded on a Varian F-16 spectrometer. Analytical, infrared and electronic spectra alongwith magnetic moment and conductivity data of the complexes have been recorded in Table-1. Chromium(II) complex is green whereas the remaining three complexes are brown.

RESULTS AND DISCUSSION

Synthesis:

The reaction taking place in the preparation of the ligand and of its metal complexes involving 1,3-diaminopropane, acetylacetone (enolic form) and metal(II) salts can be represented as follows:



M = Cr, Fe, Co or Ni

All the coloured solid complexes are stable at room temperature. The molar conductance values for the complexes using 10^{-3} molar solution in DMSO (Table-1) indicate their non-electrolytic as well as covalent nature. The analytical data show that these macrocyclic complexes can be represented as

$[M(C_{16}H_{26}N_4)]$ where M=Cr, Fe, Co and Ni. Molecular weights of these complexes indicate the monomeric nature of the complexes.

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF THE COMPLEXES

Compd. (Colour)	μ_{eff} (B.M.)	Λ_m $\Omega^{-1}cm^2$ mol^{-1}	IR spectral data (cm^{-1})		Electronic spectral data (cm^{-1})	Analysis %, found (calcd)	
			$\nu_{C=N}$	$\nu_{M=N}$		M	N
$Cr(C_{16}H_{26}N_4)$ (Green)	4.60	40	1620	455	15400–14700	15.92 (15.52)	16.98 (16.96)
$Fe(C_{16}H_{26}N_4)$ (Brown)	5.00	35	1622	450	11900–11200	16.93 (16.96)	16.99 (16.86)
$Co(C_{16}H_{26}N_4)$ (Brown)	1.82	35	1615	445	14500–13000	17.76 (17.71)	16.85 (16.71)
$Ni(C_{16}H_{26}N_4)$ (Brown)	diamag	30	1618	450	16900–15000 20000–19500	17.71 (17.81)	16.82 (16.71)

Infrared spectra

The IR spectrum of the macrocyclic ligand shows a weak band at 3250 cm^{-1} and a strong band at 2915 cm^{-1} which are associated with ν(N—H) and ν(C—H) respectively. The $C—CH_3$ and $—CH_2—$ groups present in the ligand are indicated by bands at 1375 and 1435–1425 cm^{-1} respectively.

The characteristic bands due to chelated acetylacetone ligand appear at 1570–1500 cm^{-1}. All the complexes show a band around 1620 cm^{-1} due to νC=N. At the same time, no band is observed around 1800–1700 cm^{-1} which indicate the condensation of the amine and ketone. The bands appeaning around 450 cm^{-1} in all the complexes indicate ν(M—N) vibration which further confirms the coordination of these groups with the metal ion.

Electronic spectra and magnetic moment studies

All the complexes show bands at 34000–31500 cm^{-1} which may be due to charge transfer transitions. The observed magnetic meoment values of 5.0 B.M. for the Fe(II) macrocyclic complex and a weak intensity band at 11900–11200 cm^{-1} region may be assigned to ${}^5T_{2g} \rightarrow {}^5E_g$ transition which are consistent with the octahedral geometry around Fe(II) ion. In case of Cr(II) complex, the observed magnetic moment of 4.60 B.M. and electronic spectra showing a weak band at 15400–14700 cm^{-1} assignable to ${}^5E_g \rightarrow {}^5T_{2g}$ transition are consistent with the octahedral geometry artound Cr(II) ion. The Co(II) complex shsows a band at 14500–13000 cm^{-1} and has magnetic moment of 1.82 B.M. The band may be assigned to the transition ${}^2E_g \rightarrow {}^2T_{1g}$ and is suggestive of octahedral stereochemistry. In contrast to octahedral geometry for Cr(II), Fe(II) and Co(II) complexes, a square-planar geometry, showing two bands at 16900–15000 cm^{-1} assignable to transitions ${}^1A_{1g} \rightarrow {}^1B_1g$ and ${}^1A_{1g} \rightarrow {}^1B_{2g}$ respectively for Ni(II) complex, is proposed. Ni(II) complex is found to be diamagnetic.

Magnetic moment and electronic spectral data are in close agreement with earlier reports[12]

The ^{-1}H NMR spectrum of the ligand shows five kinds of protons, namely $—CH_3$ $>$CH, $—CH_2—$ (two kinds) and $>\ddot{N}—H$ protons. The signal due to $>\ddot{N}—H$ proton disappears in the spectra of complexes and signal due to $—CH_2—$ shifted downfield indicating coordination of the adjacent N-atoms to the metal ion. The results are in good agreement with the literature[12]

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