

Cobalt (II) complexes with a 18-member macrocyclic Schiff base ligand

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Abstract: A number of cobalt (II) complexes of the type $[\text{Co}(\text{SB})\text{X}_2]$ where X=chloride, acetate or nitrate and SB=a 18-member macrocyclic Schiff base ligand obtained by metal ion catalysed template macrocyclization between orthophenylenediamine and 2, 5-diformyl furan. The complexes possess characteristic colors, are non hygroscopic, sparingly soluble in water and can be stored for a long period without decomposition. Low value of molar conductivity in the range $7\text{--}10\text{Sm}^2\text{mol}^{-1}$ indicated complexes to be non electrolytic in nature. Absence of N-H stretch of orthophenylenediamine, C=O stretch of 2, 5-diformyl furan and appearance of C=N stretch in the infrared spectra of complexes corroborates Schiff base condensation during macrocyclization. Low molar conductivity alongwith presence of vibrational bands characteristics of M-Cl, M-N and M-O stretch in the far infrared range indicated involvement of anions in coordination.

(Key words : cobalt complexes, Schiff base, macrocyclic, spectral study)

Introduction

Extensive studies on metal complexes belonging to first transition series with macrocyclic Schiff base ligands have been done due to their biological activities and pharmaceutical importance¹⁻⁶. Consequently, synthesis and characterization of a series of three complexes of Co (II) of the type, $\text{M}(\text{SB})\text{X}_2$ with X as acetate, chloride and nitrate is being communicated in the present paper.

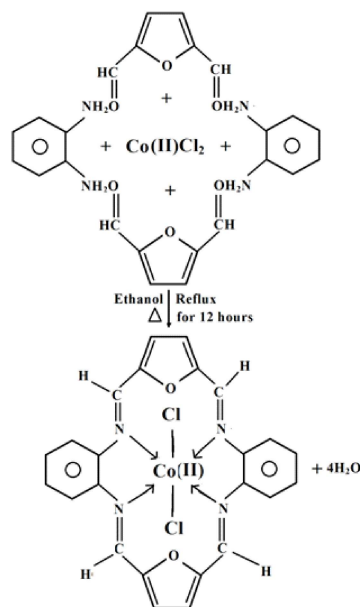
Experimental

Chemicals such as cobalt chloride,

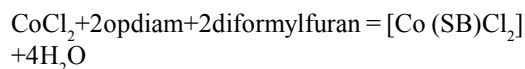
cobalt acetate, cobalt nitrate, orthophenylenediamine, 2, 5-diformyl furan were obtained from Sigma Aldrich as analytical grade reagents and used as such without further purification. Solvents were from BDH.

Preparation of complexes

1. Preparation of $[\text{Co}(\text{SB})\text{Cl}_2]$, $[\text{CoC}_{24}\text{H}_{16}\text{N}_4\text{O}_2\text{Cl}_2]$, 5, 8, 14, 17-tetra aza-1, 3: 10, 12-di furano-6, 7: 15, 16-di benzo cyclo octa deca-4, 8, 13, 17-tetra ene di chlorido cobalt (II).



Synthetic reaction taking place during the synthesis of the complex has been presented below:-



Procedure:

10 millimoles of each of opdiam and diformyl furan were dissolved in 20 ml of ethanol separately. 5 millimoles of cobalt II chloride were dissolved in 10 ml of ethanol. Three solutions were mixed together and refluxed for 12 hours, cooled and solids separated were filtered, washed, dried and analysed as $[\text{CoC}_{24}\text{H}_{16}\text{N}_4\text{O}_2\text{Cl}_2]$

Analytical results are shown below		
	Found %	Calculated %
Cobalt	11.02	10.29
Carbon	54.96	55.18
Hydrogen	3.05	3.06
Nitrogen	10.49	10.73
Chlorine	13.28	13.60

$[\text{Co}(\text{SB})\text{X}_2]$ where X = acetate or nitrate can be prepared by the procedure for chloro complexes replacing cobalt chloride with cobalt acetate or cobalt nitrate. Analytical results were found to be within 1% of deviations as compared to the proposed formulations.

Infrared spectra

Significant spectral bands have been presented in Table-1.

Table-1 Selected Infrared Spectral Bands (cm^{-1})

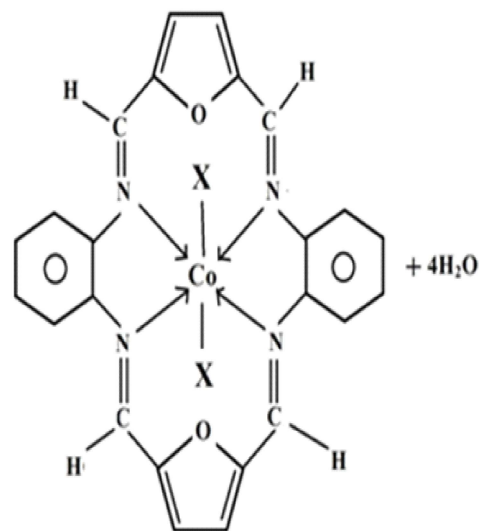
Complex	$\nu_{\text{C-N}}$	$\nu_{\text{Co-N}}$	$\nu_{\text{Co-O-Cl}}$
$[\text{Co}(\text{SB})\text{Cl}_2]$	1610, 1588	630	428
$[\text{Co}(\text{SB})\text{Ac}_2]$	1605, 1585	635	516
$[\text{Co}(\text{SB})(\text{NO}_3)_2]$	1608, 1578	640	550

The absence of bands corresponding to free amino group and carbonyl (aldehydic) group on one hand and appearance of bands characteristic of coordinated imines as well as cobalt-nitrogen, cobalt-oxygen and cobalt-chlorine on the other indicate the formation of the macrocyclic cavity in which metal ion is embedded. Infrared spectra also corroborate the behaviour of anions to act in an unidentate manner.

Magnetic moment and electronic spectra

Magnetic moment in the range 4.75-4.90 B M and three electronic spectral bands in the range, 8000-9000; 18000-19000 and 22000-23000 cm^{-1} assignable to the transitions, ${}^4\text{T}_{1g}(\text{F})$ ${}^4\text{T}_{2g}(\text{F})$; ${}^4\text{T}_{1g}(\text{F})$ ${}^4\text{A}_{2g}(\text{F})$ and ${}^4\text{T}_{1g}(\text{F})$ ${}^4\text{T}_{1g}(\text{P})$ suggest octahedral stereochemistry with some tetragonal distortions for the complexes.

On the basis of above mentioned observations, structure as shown below has been proposed for the complexes.



References

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