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SYNTHESIS AND CHARACTERIZATION OF MANGANESE (II), COBALT (II), NICKEL (II) AND COPPER (II) N, N′ – BIS(BENZOIN)ETHYLENEDIIMINATO COMPLEXES

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ABSTRACT
The manganese (II), cobalt (II), nickel (II) and copper (II) complexes of N, N′ – bis(benzoin)ethylenediiminato have been prepared and characterized by infrared, elemental analysis, conductivity measurements and solubility. The potentiometric, and elemental analyses studies of the complexes revealed 1:1 metal to ligand ratio.

Key words: Spectrophotometry, potentiometry, N, N′ – bis(benzoin)ethylenediimine, complexes.

INTRODUCTION

The condensation reaction of primary amines and the compounds containing a carbonyl group gives Schiff bases (Holm *et al*., 1966; Hobday and Smith, 1972; Pierre, 1987). It has been known that large number of metal ions on interaction with Schiff bases yield chelates. Holm *et al* (1966) reported the synthesis and characterization of some Schiff bases of copper (II) complexes. In another report, Gupta *et al* (2002) explained the formation of cobalt (II) N, N′ - bis(acetylacetone)ethylenediiminato complex from the interaction of cobalt (II) salt and N, N′- bis(acetylacetone)ethylenediimine Schiff base ligand. Recently, Xishi *et al*. (2003) reported the synthesis and spectroscopic properties of Mn (II), Co (II) and Cu (II) complexes with novel Schiff base ligand derived from 2, 2′ bis(p-methoxylphenylamine) and salicylic aldehyde. Schiff base complexes of transition metals are of great importance in medicine, biochemistry and industries among others. For example, the field of medicine has witnessed an increase in the number of complexes with therapeutic value. Cobalt (II) Schiff base complexes are potential antiviral agents, cis-dichlorodiamineplatinum (II) complex is an anti cancer agent while copper (II) Schiff base is an anti-tubercular agent (Lippard, 1994; Bleomink and Reedi, 1996). The use of atom radical cyclisation mediated by copper (II) Schiff base complexes to furnish nitrogen heterocyles most of which are biologically active molecules and also the use of copper Schiff base catalyst in carbon based radical cyclisation reactions were recently investigated (Clerk and Jones, 1989; Clerk *et al*., 1998; Clerk *et al*., 1999). This paper reports the Synthesis and Characterization of Manganese (II), Cobalt (II), Nickel (II) and Copper (II) N, N′ – Bis(Benzoin)ethylenediiminato Complexes due to paucity of information.

MATERIALS AND METHODS

The chemicals and solvents used in this work were of Analar grade. All the glass wares used were washed thoroughly with distilled water and dried in an oven. Weighing was carried out on an electric metler balance, model AB 54. Melting point, decomposition temperature and coordinated water were determined on Gallenkamp melting point apparatus. Infrared spectral analyses were recorded using Fourier Transform IR, Genesis series model in Nujol within 400-4000 cm^{-1}. Electrical conductivity measurements were carried out using conductivity meter model 4010, while UV – visible spectral measurements were done on a Pye Unicam UV – visible spectrophotometer.

Preparation of Benzoin

To a 500 cm^3 round bottom flask were added 65 cm^3 of rectified spirit, 47.5 cm^3 of benzaldehyde and a solution of 5g of sodium cyanide in 50 cm^3 of water. Few anti-bumping granules were introduced into the flask. A condenser was then attached and mixture was refluxed on a steam bath for 30 minutes. The round bottomed flask and its contents were cooled in an ice-bath and pale yellow crystals were observed. These were filtered, washed with cold water, dried and then recrystallized from 40 cm^3 of hot ethanol. The crystals were dried at 50^0C and weighed (Vogel, 1966).

Preparation of N, N′ – Bis(benzoin)ethylenediimine Ligand

To a methanolic solution of benzoin (2.12g) and ethylenediamine (0.60 cm^3) was added anhydrous sodium acetate (4g) and the mixture refluxed for an hour. The hot solution was poured into ice-cold water where upon yellow precipitate of the schiff's base separated: it was filtered. Washed with water, dried and recystallised from ethanol (Mohapatra *et al.,* 1978).

Preparation of N, N′ – Bis(benzoin)ethylenediiminato Metal Complexes

0.01 mol ethanolic solutions of metal chlorides were treated separately with ethanolic solution of N, N′ – Bis(benzoin)ethylenediimine the schiff base in the ratio 1:1, followed by dropwise addition of ammonia.

The metal chelates separated out, were filtered, washed with ethanol followed by ether and dried in an oven at 50^0 C (Mohapatra, *et al.,* 1978).

Determination of Coordinate Water in the Complex Compounds

Specific weight of a complex compound (02.g) was placed in an oven at 110°C until constant. The lost in weight was recorded and the percentage composition of water in the complex determined as below (Vogel, 1966);

$$\frac{lost\ in\ weight}{Weight\ of\ taken(0.2g)} X100\%$$

RESULTS AND DISCUSSION

The interaction between N, N′ – bis(benzoin)ethylenediimine and manganese (II), cobalt (II), nickel (II) and copper ions, respectively produced high yield of the desired complex compounds (Table 1). The metal complexes are crystalline and coloured as is usual with complexes of such metals ions (Table 1). The complexes are found to decompose in the temperature range 132 – 164°C, indicating fairly stable complex compounds (Table 1). The complex compounds are insoluble [Table 2] in water and common organic solvents, but are readily soluble in acetone. The molar conductance measurement [Table 3] of the complex compounds in 1 x 10^{-3}M acetone were within the range 7.8 – 8.5ohm^{-1} cm^2 mol^{-1}, suggesting their non-electrolytic nature (Geary (1971). The free Schiff base and the complexes IR spectra [Table 5] show bands at 1550-1610cm^{-1} which are assigned to ν(C==N) stretching vibrational mode, a fundamental feature of azomethine group (Boutcher and Day, 1977). The complex compounds show bands in the regions 2830 - 2870cm^{-1}, 3500 – 3660cm^{-1} and 1140 - 1200cm^{-1}, which were assigned to ν(C—H) asymmetric and symmetric stretching vibration modes, ν(O—H) stretching vibrations for coordinated water and ν(C—C) stretching vibration, respectively. The bands within 550 - 580cm^{-1} and 430 - 460cm^{-1} were assigned to ν(M—O) and ν(M—N) stretching vibrations, respectively (Nakomato, 1963; Patel and Agwara, 1990). The bands due to M—O and M—N established the coordination of the Schiff base to the respective metal ions in each complex compound. The elemental analysis of the complex compounds revealed 1:1 metal to ligand ratio and two water molecules coordinated to each metal ion, resulting in octahedral complexes, which are common in Mn (II), Co (II), Ni (II) and Cu (II) complex compounds. From the analytical results, the following general molecular structure is proposed.

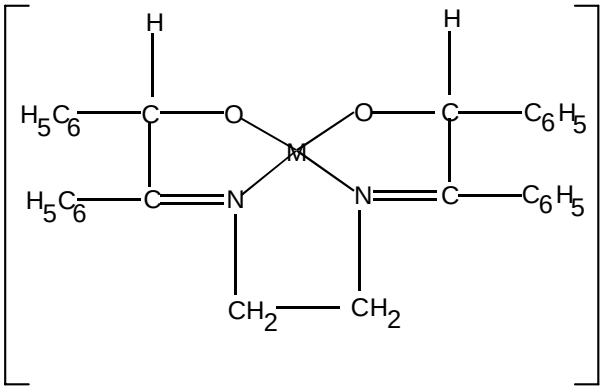

Fig 1: Shows the general molecular structure of bis(benzoin)ethylenediiminatometal (II) compmlexes, where M represents Mn (II), Co (II), Ni (II) and Cu (II) ions

Table 1: Colour, %yield and decomposition temperature of the complexes

Compound	Colour	%yield	Decomposition temperature
$[CoL(H_2O)_2]$	Pink crystals	56.54	147
$[CuL(H_2O)_2]$	Brown crystals	57.00	132
$[NiL(H_2O)_2]$	Green crystals	59.20	164
$[MnL(H_2O)_2]$	Brown crystals	66.70	142

Where, L = bis(benzoin)ethylenediiminato

Table 2: Solubility data of the Schiff base and the complexes

Compound	Water	Methanol	Ethanol	Acetone	Nitromethane	Chloroform
Bis(benzoin)ethylenediimine	NS	SS	SS	S	SS	SS
$[MnL(H_2O)_2]$	NS	SS	SS	S	SS	SS
$[CoL(H_2O)_2]$	NS	SS	SS	S	SS	SS
$[NiL(H_2O)_2]$	NS	SS	SS	S	SS	SS
$[CuL(H_2O)_2]$	NS	SS	SS	S	SS	SS

Where, NS = Not soluble, SS = Slightly soluble, S = Soluble

Table 3: Molar conductivity data of $1x10^{-3}$M complexes in acetone

Compound	Specific conductance (k)	Molar conductance ($ohm^{-1}cm^2mol^{-1}$)	Remark
$[MnL(H_2O)_2]$	8.2×10^{-6}	8.2	Non electrolyte
$[CoL(H_2O)_2]$	8.5×10^{-6}	8.5	Non electrolyte
$[NiL(H_2O)_2]$	7.8×10^{-6}	7.8	Non electrolyte
$[CuL(H_2O)_2]$	8.5×10^{-6}	8.5	Non electrolyte

Table 4: IR spectral data of the complex compounds

Compound	ν(C-H)	ν(C-C)	ν(C=N)	ν(O-H)		ν(M-O)	ν(M-N)	ν(M-O)	ν(M-N)
Bis(benzoin)ethylenediimine	2870	1140	1550	3520 3630	-	-	-	-	-
$[MnL(H_2O)_2]$	2860	1200	1590	3540 3660	–	570	430	570	450
$[CoL(H_2O)_2]$	2830	1180	1570	3520 3610	–	560	460	560	440
$[NiL(H_2O)_2]$	2850	1160	1610	3500 3630	–	550	420	550	460
$[CuL(H_2O)_2]$	2840	1150	1590	3530 3580	–	580	450	580	430

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