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Synthesis, Characterization and Biological Activity of Some Cobalt Metal Complexes Obtained from Novel Hydrazones

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Abstract: The novel complexing reagents are obtained by condensation of semicarbazide with different hydrazone derivatives. The cobalt metal complexes have been prepared by treating cobalt sulphate with different newly prepared hydrazone ligands. The present ligands and metal complexes have been characterised by elemental analysis and various physicochemical techniques such as Electronic absorption, Molar conductance, Magnetic susceptibility, Infrared spectral studies and Thermal analysis. The results of various physicochemical techniques discussed in detail and the possible structures are proposed to the reagents and complexes. These complexes showed biological activity.

Keywords: Aldehyde; hydrazone; synthetic; structural; biological activity.

I. INTRODUCTION

In recent years, the study of transition metal complexes has attracted the interest of most of the chemists because of their applications in various fields. It is well known that transition metal complexes are biologically active against pathogenic¹⁻⁵ microorganisms. As well as transition metal complexes with hydrazone derivatives have been amongst the widely studied coordination compounds in the past few years, since they are found to be widely applicable in many fields such as biochemicals, analytical⁶ and antimicrobial fields. The Co(II) complexes of novel hydrazone derivatives are known for their versatile coordination. The ligand containing oxygen and nitrogen donor atoms acts as excellent coordination property. First, they can show various coordination modes⁷ and hence the resulting metal complexes possess large structural diversities. Second, nitrogen and oxygen containing ligands as well as their metal complexes show biological activity. The presence of functional group, near the site of coordination in the hydrazone ligands, gives a five or six membered chelate⁸ ring on reaction with metal ion, which shows structural variations⁹ depending upon the type of substituent present on aromatic ring. Thus, the purpose of this study is to synthesis and structural elucidation of Co(II) metal complexes with novel hydrazone derivatives.

II. EXPERIMENTAL

A. Step-I

B. Step-II

C. Step-III

D. Step-IV

Fig. 1 Cobalt metal complex

III. RESULTS AND DISCUSSION

All cobalt metal complexes are brown solids (Table-I), insoluble in water and shows varying solubility in common organic solvents. The complexes are non-hygroscopic and thermally stable having decomposition temperature more than 320°C indicating a strong metal-ligand bonding. The value observed for molar conductance of all complexes fall between 0.0005 to 0.0011 mhos.cm²mol⁻¹ in 10⁻³ M DMSO solution indicate^{10,11} the complexes are non-electrolytic in nature.

Table I: Physical and analytical data of complexes

Comp	Molecular formula (Formula wt.)	Yield %	Decomposition Temperature in °C	μ_{eff} (B.M.)	Color	% Elemental analysis found (calculated)			
						Co	C	H	N
C ₁	[C ₃₂ H ₃₂ N ₁₀ O ₆ Co.2H ₂ O] (747.63)	78	>320	5.18	Brown	7.88 (7.86)	51.40 (51.41)	4.86 (4.88)	18.73 (18.72)
C ₂	[C ₃₀ H ₂₈ N ₁₀ O ₄ Co.2H ₂ O] (687.58)	81	>320	4.95	Brown	8.57 (8.58)	52.41 (52.42)	4.69 (4.68)	20.37 (20.39)
C ₃	[C ₃₀ H ₂₆ N ₁₂ O ₈ Co.2H ₂ O] (772.57)	83	>320	5.32	Brown	7.61 (7.60)	46.62 (46.61)	3.38 (3.39)	21.74 (21.76)
C ₄	[C ₃₈ H ₃₄ N ₁₀ O ₄ Co.2H ₂ O] (787.70)	80	>320	4.98	Brown	7.46 (7.47)	57.79 (57.80)	4.85 (4.86)	17.74 (17.72)
C ₅	[C ₃₂ H ₃₄ N ₁₀ O ₄ Co.2H ₂ O] (715.63)	81	>320	5.08	Brown	8.25 (8.26)	53.46 (53.47)	5.26 (5.24)	19.62 (19.61)

A. Infrared Spectra

The FTIR spectra of the metal complexes (Table-II) were recorded in KBr over the range 4000-400 cm^{-1} . The FTIR spectrum of the free ligands show four characteristics bands at around 3250-3300, 3404, 1633 and 1600 cm^{-1} assignable to (-N-H), free (-O-H) stretching phenolic moiety, amide carbonyl (-C=O) and azomethine (-C=N), stretching mode respectively. The absence of a weak broad band in 3250-3300 cm^{-1} region, noted in the spectra of the metal complexes indicates^{12,13} deprotonation of bonded (-NH) group during complex formation and subsequent coordination of the oxygen of amide carbonyl to metal ion.

The ν (C=N) band is shifted to lower wavenumber with respect to free ligand, indicating that the nitrogen of azomethine group is coordinated to the metal ion. The spectra of metal complexes showed a new band at around 515 cm^{-1} and 430 cm^{-1} for ν (Co-O) and ν (Co-N) vibrations respectively. Hence, coordination takes place via oxygen of amide and nitrogen of azomethine group of ligand molecule.

Table II: IR Spectral Bands (cm^{-1}) of the Cobalt Complexes

Inference	C ₁ [C ₃₂ H ₃₂ N ₁₀ O ₆ Co.2H ₂ O]	C ₂ [C ₃₀ H ₂₈ N ₁₀ O ₄ Co.2H ₂ O]	C ₃ [C ₃₀ H ₂₆ N ₁₂ O ₈ C o.2H ₂ O]	C ₄ [C ₃₈ H ₃₄ N ₁₀ O ₄ Co. 2H ₂ O]	C ₅ [C ₃₂ H ₃₄ N ₁₀ O ₄ C o.2H ₂ O]
ν (C=N) azomethine	1607	1602	1590	1592	1591
ν (N=C-O)	1135	1099	1107	1116	1107
ν (Co-O)	514	515	525	527	520
ν (Co-N)	448	438	430	429	433

Fig. 2: IR Spectrum of C₁ [C₃₂H₃₂N₁₀O₆Co.2H₂O]

B. Magnetic Susceptibility Measurement

The effective magnetic moments were calculated after applying diamagnetic corrections for the ligand components using¹⁴ Pascal's constants. The room temperature μ_{eff} value for the cobalt(II) complexes were found in the range 4.95-5.32 B.M., these magnetic susceptibilities of the complexes are consistent with octahedral geometry around the central Co(II) metal ion. The magnetic moments of the compounds investigated are in agreement with the findings of electronic absorption spectra.

C. Electronic Spectra

The electronic spectra of cobalt(II) metal complexes exhibit low intensities d-d bands in the ranges 12330-12406 cm^{-1} , 16087-17035 cm^{-1} and 27778-28653 cm^{-1} due to $d_{xy}(b_2) \rightarrow d_{xz}$, $d_{yz}(e\pi^*)$, $d_{xy}(b_2) \rightarrow (dx^2 - y^2)(b_1^*)$ and $d_{xy}(b_2) \rightarrow (dz^2)(a_1^*)$ transitions¹⁵ respectively. The electronic spectra also exhibit a fourth high energy band around 40650-41841 cm^{-1} , which can be assigned as a ligand to metal charge transfer transition.

D. Thermal Measurements

All the Cobalt complexes investigated shows similar behavior in their thermogram. In the first step the complex losses two water¹⁶⁻¹⁹ molecule in the temperature range between 100°C to 180°C indicates that the complex is thermally stable up to nearly 100°C above which it loses the water molecule. The thermogram of all the complexes consists of three steps. The complex is stable upto 180°C after which in the second step the complex losses some moiety like $\text{C}_{15}\text{H}_{15}\text{CHN}_5$ in the temperature range between 180°C to 360°C. The complex losses another moiety in the third step in the temperature ranges between 360°C to 560°C which could be attributed due to loss of $\text{C}_{15}\text{H}_{15}\text{CHO}_5\text{N}_5$. Further decomposition occurs in the temperature range of 560°C to 680°C corresponds to the final residue estimated as free cobalt oxide.

Figure 3: TG/DTA Thermogram of $\text{C}_1 [\text{C}_{32}\text{H}_{32}\text{N}_{10}\text{O}_6\text{Co}.2\text{H}_2\text{O}]$

IV. BIOLOGICAL ACTIVITY

Antibacterial activity done by agar well diffusion method. Muller Hinton agar and Escherichia coli, Staphylococcus aureus bacteria used for well diffusion method. The antifungal activity of the complexes against Candida albicans and Aspergillus niger pathogenic fungi was determined by Tube Dilution Method and Sabouraud broth used for antifungal activity.

Table III: Antimicrobial Activity of the Co(II) complexes

Complex	Antibacterial activity at 450 ppm (zone of inhibition in mm)		Antifungal activity at 350 ppm (% Inhibition)	
	<i>E. coli</i>	<i>S. aureus</i>	<i>C. albicans</i>	<i>A. niger</i>
C1	6	5	44	53
C2	5	4	47	55
C3	7	6	39	57
C4	4	5	51	62
C5	6	7	40	52
Na-MINAP	3	2	15	14
$\text{CoSO}_4.7\text{H}_2\text{O}$	3	2	31	33
Tetracycline	13	15	-	-
Amphotericin	-	-	97	98

V. CONCLUSION

Based on the above results the following conclusion may be drawn. The higher decomposition temperature and electrical conductance studies show the presence of strong metal-ligand bonding and non-electrolytic nature of the complexes, respectively. Room temperature magnetic studies are indicative of paramagnetic nature and an octahedral geometry of the Co(II) complexes which is supported by the electronic spectra. The IR spectra show bonding of the metal through N- and O- donor atoms of the two ligands. Thermal analysis confirms the presence of coordinated water molecules. The MIC complexes at which the culture does not show bacterial and fungal growth were found to be 450ppm and 350ppm respectively.

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