

Study of Hydrazine Carboxamide of 5 nitro indol 2,3 dione & their metal complexes with CO(II), Ni(II) and Mn(II)

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Abstract

Among the organic chelating ligands hydrazine are gaining importance day by day because a large no. of such compounds and their metal chelates are known which possess, appreciable antibacterial¹, fungicidal², antituberculous³ and anticancerous activities⁴. Various such compounds have been proved of great importance in the field of medicine, industry, biochemistry and research.

Hydrazine carboxamide derived from different indol have been prepared and used as chelating agent, bactericidal and fungicidal agents. Biologically active coordination compounds, the present paper include the preparation of Hydrazine carboxamide of 5 nitro indol 2, 3-Dione & 6-nitro indol 2,3-dione and their metal complexes with Co(II) and Zn(II).

1. Introduction

1.1 Preparation of the Ligand

Ligands were prepared in following steps

1.2 Materials and methods

All the reagents were dried and distilled before use. The hydrazine carboxamide 5-nitro-indol-2,3 dione and 6 nitro indol-2,3 dione was prepared by the condensation of ethanolic solution of 5-nitro indol 2,3 dione & 6, nitro indol 2,3 dione with aqueous solution of semicarbazide hydrochloride (in the presence of sodium acetate) in 1:1 molar ratio. The resulting mixture was boiled under reflux for 30-40 min. On cooling, the crystals separated out which were recrystallized using the same solvent and finally dried in vacuo. These were characterized and analyzed before use.

1.3 Synthesis of 5/6 nitro indol - 2, 3 dione

Isonitro acetanilide (0.05 mol) was added to conc. Sulphuric acid (50 ml) in about 30 min. with constant stirring. After the addition of H₂ SO₄ the reaction mixture was heated at 70 °C for 10 min and poured into 10 times the in crushed ice. The resultant precipitate was filtered and dried in air. It was purified by recrystallization from glacial acetic acid. The compound so obtained is the desired product.

Yield (calculated)	=	9.06 gm
(Found)	=	7.86 gm.
Percentage	=	86%
Melting Point	=	237°C
Elemental analysis data are given in table.		

2. Preparation of the Complexes

A common method was used for the synthesis of all the complexes with the ligand as follows.

For the preparation of Mn(II), Co(II) and Ni(II) complexes equi. molar of & bimolar reaction of respective metal salt with ligands were carried out in dry methanol. The reaction mixture was refluxed for 10-15 hours and then cooled at room temperature. The solvent was removed and residue was dried in vacuum after being repeatedly washed with dry cyclohexane. Finally the complexes were recrystallized in methanol. The important properties and physical data of the complexes are reported in table.

3. Results and Discussions

3.1 Magnetic moment & electronic spectral studies

3.2 Manganese (II) Complexes

Magnetic moment and electronic transitions of metal complexes has been given in Table 2.

Mn(II) having 3d⁵ configuration forms either spin free or spin paired complexes depending upon the strengths of the ligand field. However, the spin free complexes are more predominant due to a comparatively more stable half filled d shell (d⁵) configuration.

In Mn-ligand complexes, the bands were observed in the region 17430- 18200, 22400-23260 and 25350-25600 cm⁻¹ which are tentatively assignable to 4T_{1g} (G) ← 6A_{1g} (G), 4T_{2g} (G) ← 6A_{1g} and 4A_{1g} (G) ← 6A_{1g} transition respectively. The observed magnetic moment values and the above assignments suggest the formation of high spin octahedral complexes of Manganese (II) with the ligands. 10Dq and β values as calculated by using the Figgis equation, indicate a considerable metal-ligand overlap resulting into the development of a sufficient co-valent character on the metal-ligand bonds v₂/v₁ ratio as calculated from 4T_{1g} (G) ← 6A_{1g} (v₁) and 4T_{2g} (G) ← 6A_{1g} (v₂) transition suggest a considerable distortion from the ideal geometry.

3.3 Cobalt (II) Complexes

In the electronic spectra of all the Co (II) complexes three bands were observed in the region 8450-8700, 17580-18100 and 19200-19650 Cm⁻¹ which are tentatively assigned to 4T_{2g}(F) ← 4T_{1g}(F), 4A_{2g}(G) ← 6T_{1g} (F) and 4T_{1g} (P) ← 4T_{1g} (F) transition respectively, suggesting for an octahedral environment. 10 Dq, B of v₂/v₁ values as calculated by using figgis equation shows a considerable metal-ligand overlap and distortion from the ideal Oh geometry [14-15]

3.4 Nickel (II) Complexes

In all Ni(II) complexes three bands were observed in the region 8400-8680, 14900-15350 and 25000-25600 Cm⁻¹, these bands may be assigned to 3T_{2g} (F) ← 3A_{2g} (F), 3T_{1g} (F) ← 3A_{2g} and 3T_{1g}(P) ← 3A_{2g} transitions respectively corresponding to the octahedral geometry for spin-free Ni(II) complexes [16-18].

3.5 Magnetic moment & electronic spectral studies Manganese (II) Complexes

Magnetic moment and electronic transitions of metal complexes has been given in Table 2.

Mn(II) having 3d⁵ configuration forms either spin free or spin paired complexes depending upon the strengths of the ligand field. However, the spin free complexes are more predominant due to a comparatively more stable half filled d shell (d⁵) configuration.

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Table 1: Magnetic moment, electronic transitions and ligand field parameters of the metal Chlorides complexes

Complexes	Magnetic Moment $\mu_{\text{eff B.M}}$	Bands (cm^{-1})	Assignment	10Dq	B	v_2 / v_1
Mn-Complexes	3.80	17460	4T1g (G) \leftarrow 6A1g (v1)	8002.50	727.50 (960.00)*	1.30
		22780	4T2g (G) \leftarrow 6A1g (v2)			
		24520	4Eg (G) \leftarrow 6A1g			
		26950	4T2g (G) \leftarrow 4A1g			
Co-Complexes	2.98	8620	4T2g(F) \leftarrow 4T1g(F)(v1)	10091.17	1051.20 (1120.00)*	2.06
		17770	4A2g \leftarrow 4T1g(F)(v2)			
		19360	4T1g(T) \leftarrow 4T1g(F)			
Ni- Complexes	2.52	8750	3T1g(P) \leftarrow 3A2g(v1)	8750.00	982.85 (1040.00)*	2.19

Table 2: Magnetic moment, electronic transitions and ligand field parameters of the metal Nitrate -L- complexes

Complexes	Magnetic Moment $\mu_{\text{eff B.M}}$	Bands (cm^{-1})	Assignment	10Dq	B	v_2 / v_1
Mn-Complexes	5.50	17680	4T1g (G) \leftarrow 6A1g (v1)	8103.33	736.66 (960.00)*	1.30
		22990	4T2g (G) \leftarrow 6A1g (v2)			
		24650	4Eg (G) \leftarrow 6A1g			
		27300	4T2g (G) \leftarrow 6A1g			
Co-Complexes	3.10	8480	4T2g (F) \leftarrow 4T1g (F) (v1)	99271.80	1034.14 (1120.00)*	2.13
		18100	4A2g \leftarrow 4T1g (F) (v2)			
		19620	4T1g (T) \leftarrow 4T1g (F)			
Ni- Complexes	2.62	8850	3T2g (F) \leftarrow 3A2g (v1)	8850	903.05 (1040.00)*	2.18
		13510	Spin Forbidden			
		19300	3T1g (p) \leftarrow 3A2g (v2)			

* Free ion B Volume

In Mn-ligand complexes, the bands were observed in the region 17430- 18200, 22400-23260 and 25350-25600 cm^{-1} which are tentatively assignable to 4T1g (G) \leftarrow 6A1g(G), 4T2g (G) \leftarrow 6A1g and 4A1g (G) \leftarrow 6A1g transition respectively. The observed magnetic moment values and the above assignments suggest the formation of high spin octahedral complexes of Manganese (II) with the ligands. 10Dq and β values as calculated by using the Figgis equation, indicate a considerable metal-ligand overlap resulting into the development of a sufficient co-valent character on the metal-ligand bonds v_2/v_1 ratio as calculated from 4T1g (G) \leftarrow 6A1g (v1) and 4T2g (G) \leftarrow 6A1 (v2) transition suggest a considerable distortion from the ideal geometry.

3.6 Cobalt (II) Complexes

In the electronic spectra of all the Co (II) complexes three bands were observed in the region 8450-8700, 17580-18100 and 19200-19650 cm^{-1} which are tentatively assigned to 4T2g(F) \leftarrow 4T1g(F), 4A2g(G) \leftarrow 6T1g (F) and 4T1g (P) \leftarrow 4T1g (F) transition respectively, suggesting for an octahedral environment. 10 Dq, B of v_2/v_1 values as calculated by using figgis equation shows a considerable metal-ligand overlap and distortion from the ideal Oh geometry [14-15]

3.7 Nickel (II) Complexes

In all Ni(II) complexes three bands were observed in the region 8400-8680, 14900-15350 and 25000-25600 cm^{-1} , these bands may be assigned to 3T2g (F) \leftarrow 3A2g (F), 3T1g (F) \leftarrow 3A2g and 3T1g(P) \leftarrow 3A2g transitions respectively corresponding to the octahedral geometry for spin-free Ni(II) complexes.16-18

4. Fungicidal Activity/ Conclusions

In the present study a comparison of fungicidal activity between ligand and metal complexes were done. The fungicidal activity of ligand and the metal complexes were studied using growth method against different fungi viz. *Fusarium Oxysporum* & *Altrnariet Alternata* and antibacterial activity against *Escherichia Coli* and *Pseudomonas Cepaciocola* at 50, 100 and 200 concentrations.

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