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Study of Hydrazine Carboxamide, Characterization Method and Biological Activities with Transition Metal Using Cu (II) & Mn (II) as Central Metal

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ABSTRACT

The co-ordination chemistry of transition metals and their derivatives has received much attention in the recent years, primarily because of their biological importance¹⁻³, Nitrogen, Oxygen and Sulphur donor ligands possess a range of biological applications like antitumour⁴, antiviral⁵, antimicrobial⁷ and antifungal activities. The legends of Hydrazine with their metal complexes with Cu (II) & Mn (II). Fungicidal activity of the ligand and their metal complexes were also done to establish any relation with the metal and ligands.

Keywords: Hydrazine; Metal complexes; Cu (II) & Mn (II); Fungicidal activity.

1.0 Experimental

The entire reagent used were of AR grade otherwise purified before used.

1.1 Preparation of the ligand

Ligands were prepared in following steps:

(i) Materials & 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.

(ii) Synthesis of 5/6 nitro indol - 2,3 dione

First, (0.05 mol) Isonitrosoacetanilide was added to conc. Sulphuric acid (50 ml) in a beaker & start constant stirring for about 30 minutes. The reaction mixture was heated at 70°C for 10 min and cooled down with crushed ice. After cooled down the

resultant precipitate it was filtered & keep it dried in the presence of air. It was purified followed by recrystallization with glacial acetic acid. The compound so obtained is the desired product.

Yield (calculated)	=	8.23 gm.
(Found)	=	6.73 gm.
Percentage	=	75%
Melting Point	=	237°C
Elemental analysis data are given in table.		

2.0 Preparation of the Complexes

A equimolar & bimolar reaction of Mn(II), Cu(II) metal salt with ligands were carried out in dry methanol. This reaction mixture was refluxed for 14-15 hours and then cooled at room temperature. After the removal of solvent the residue was dried. The resulted complexes were recrystallized in methanol. The important properties and physical data of the complexes are reported in table.

3.0 Result & Discussion

Molecular weights were determined by the Rast camphor method. I.R. spectra were recorded on a Perkin Elmer 577 grating spectrophotometer. Electronic spectra of the complexes were recorded in DMF on a UV-160A Shimadzu spectro- photometer

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in the range 200-600nm. ESR spectra were get recorded from IIT Roorkee. Nitrogen was estimated by Kjeldahl's method Sulphur estimations were done by usual oxidation to sulphate and precipitation as BaSO₄ method.

Different Schemes for the preparation of ligand as well as metal complexes are as follow:

4.0 Conductivity Measurement

Molar conductivity of the complexes was measured in 0.001 M Nitrobenzene solutions at room temperature.

Low molar conductivity data for all the complexes indicate the absence of free anions, which shows that the anions have entered into the co-ordination sphere during the complex formation reaction.

The same has been confirmed by the analytical tests for the Cl⁻, NO₃⁻ and acetate ions.

5.0 Infra Red Spectra

In the IR spectra of the ligand show medium intensity bands at 3300-3100 cm⁻¹ due to νNH vibrations. Strong bands at 1682 Cm⁻¹ are due to νC=O vibration indicating the formation of hydrazine carboxamide.

On comparing the I.R. spectra of the ligand with its metal complexes it has been observed that band due to νNH vibration disappears indicating deprotonation followed by co-ordination.

A sharp band at is 1620 cm⁻¹ due to νC=N shifts to slightly towards lower frequency (10-20 cm⁻¹) in the complexes.

Analytical Data of Complex of Hydrazine Carboxamide of 5/6 Nitro Indole 2, 3 Dione with Their Chlorides of Divalent Mn & Cu

Molecular Formulae	Colour	Elemental Analysis % Calculated/Observed					
		C	H	N	O	Cl	M
[MnCl ₂ (C ₉ H ₇ N ₅ O ₄) ₂]	Buff	34.61 (34.59)	2.24 (2.22)	22.43 (22.41)	20.51 (20.50)	11.37 (11.35)	8.81 (8.79)
[CuCl ₂ (C ₉ H ₇ N ₅ O ₄) ₂]	Green	34.15 (34.14)	2.21 (2.20)	22.13 (22.10)	20.23 (20.21)	11.22 (11.20)	10.03 (10.00)

Analytical Date of Complex of Hydrazine Carboxamide of 5/6 Nitro Indole 2, 3 Dione with Their Nitrates of Divalent Mn & Cu

Molecular Formulae	Colour	Elemental Analysis % Calculated/Observed				
		C	H	N	O	M
[Mn(NO ₃) ₂ (C ₉ H ₇ N ₅ O ₄) ₂]	Buff	31.90 (31.89)	2.06 (2.04)	24.81 (24.80)	33.08 (33.06)	8.12 (8.11)
[Cu(NO ₃) ₂ (C ₉ H ₇ N ₅ O ₄) ₂]	Green	31.50 (31.49)	2.04 (2.04)	24.50 (24.48)	32.67 (32.65)	9.26 (9.25)

Analytical Date of Complex of Hydrazine Carboxamide of 5/6 Nitro Indole 2, 3 Dione with their Acetates of Divalent Mn & Cu

Molecular Formulae	Colour	Elemental Analysis % Calculated/Observed				
		C	H	N	O	M
[Mn(CH ₃ COO) ₂ (C ₉ H ₇ N ₅ O ₄) ₂]	Buff	39.34 (39.33)	2.98 (2.96)	20.86 (20.84)	28.61 (28.60)	8.91 (8.17)
[Cu(CH ₃ COO) ₂ (C ₉ H ₇ N ₅ O ₄) ₂]	Green	38.85 (38.83)	2.94 (2.92)	20.60 (20.59)	28.25 (28.23)	9.34 (9.33)

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	ν_2 / ν_1
Mn-Complexes	5.50	17680	$4T_{1g}(G) \leftarrow 6A_{1g}(\nu_1)$	8103.33	736.66 (960.00)*	1.30
		22990	$4T_{2g}(G) \leftarrow 6A_{1g}(\nu_2)$			
		24650	$4E_g(G) \leftarrow 6A_{1g}$			
		27300	$4T_{2g}(G) \leftarrow 6A_{1g}$			
Cu- Complexes	1.18	13180	$2T_{2g} \leftarrow 2E_g$			

*Free ion B Value

Magnetic Moment, Electronic Transitions and Ligand Field Parameters of the Metal Acetate –L– Complex

Complexes	Magnetic moment $\mu_{\text{eff B.M}}$	Bands (cm^{-1})	Assignment	10Dq	B	ν_2 / ν_1
Mn-Complexes	5.50	17680	$4T_{1g}(G) \leftarrow 6A_{1g}(\nu_1)$	8103.33	736.66 (960.00)*	1.30
		22990	$4T_{2g}(G) \leftarrow 6A_{1g}(\nu_2)$			
		24650	$4E_g(G) \leftarrow 6A_{1g}$			
		27300	$4T_{2g}(G) \leftarrow 6A_{1g}$			
Cu- Complexes	1.18	13180	$2T_{2g} \leftarrow 2E_g$			

Indicating the co-ordination of azomethine nitrogen to the metal ion. Strong bands at 1682 cm^{-1} is due to $\nu\text{C=O}$ in the case of the aforesaid ligand. These bands disappear in the case of the complexes suggesting enolization of the ligands and their chelation through the enolic oxygen.

The bands observed in the region $3430\text{--}3350 \text{ cm}^{-1}$ attribute to asymmetric & symmetric mode of the NH_2 group remain at nearly the same position in the spectra of the complexes. The aforesaid co-ordination pattern of the metal derivatives is further strengthened by the appearance of non-ligand bands in the spectra of metal complexes in the region $490\text{--}450 \text{ cm}^{-1}$, $420\text{--}370 \text{ cm}^{-1}$ and $340\text{--}285 \text{ cm}^{-1}$ are due to $\nu\text{Mn-O}$, $\nu\text{Mn-N}$ and Mn-Cl vibrations respectively.

In fact, shift in the position of an absorption band, upon coordination depends on its conjugation with the adjacent heterocyclic group and on the capacity of the metal ion to transfer the electron density from its "d orbitals" to the ligand π orbital. In high transfers of the electron density either the band disappears on shifts to a considerably low frequency.

Considerable shift has been observed in the oxygen and azomethine $\nu(\text{C=N})$ stretching frequencies indicate the transfer of electron density to a significant extent. This fact also gets support by the considerable metal-ligands overlapping as calculated by the ν_2/ν_1 value from the ν_2 and ν_1 electronic spectral frequency. The vibration related to Nitro group does not show any appreciable change indicating that Nitro group is not taking part in coordination. In chloro complexes, medium intensity absorption bands corresponding to the metal-to-ligand co-ordination have been observed in the far IR region at $540\text{--}580$, $350\text{--}430$ and $270\text{--}330 \text{ cm}^{-1}$ which are assignable to M-N , M-O and M-Cl stretching vibrations respectively. In the IR of nitrate-complexes three additional sharp bands at $1010\text{--}15$, $1270\text{--}85$ and $1430\text{--}35 \text{ cm}^{-1}$ have been observed in all the metal nitrate ligand complexes. These are assigned to ν_2 , ν_1 and ν_4 band respectively. The difference between ν_4 and ν_1 band is $160\text{--}165 \text{ cm}^{-1}$ confirms coordination of nitrate ions in a Unidentate manner also.

In complexes, the co-ordination of the anion with the metal has been confirmed by comparing spectra of metal-acetate with the spectra of respective complexes. Frequencies at 1580-90 and 1390-1410 cm^{-1} which are assignable, respectively to the ν_{as} and ν_{s} carboxylic modes of the acetate ions (in the metal salts), have been found to be shifted on the opposite sides upon complex formation i.e. ν_{as} frequencies were shifted invariably, towards higher side by 20-30 cm^{-1} while the ν_{s} band were found to be shifted by 14-30 cm^{-1} towards the lower side.

This larger separation between the asymmetric and symmetric frequencies, in comparison to the uncoordinated acetate ions, thus confirms the coordination of these ions as unidentate anion through the CO moiety of their respective carboxylic group. The band obtained near about 1636 cm^{-1} which is due to ν (C=N) frequencies in the free ligand is completely unchanged after complex formation. This shows that nitrogen of carboxamide is not taking part in co-ordination. The ν_{NH} asymmetric and symmetric stretching frequencies appeared in the region 3424 and 3265 cm^{-1} respectively also decrease due to interaction of lone pair of electrons of nitrogen with π electron system of the conjugated system which reduces the ν_{NH} band strength. Thus, giving an idea about the point of attachment with metal ion. Thus, the nitrogen of $\nu_{\text{C=N}}$ oxygen of carboxamide are taking part in co-ordination.

The (M-N) stretching is of particular interest, since it provides direct information about the co-ordinate bond. Because of the relatively heavy mass of the metal and the low bond order of the co-ordinate bond the ν (M-N) stretching vibration may appear in the lower frequency. A number of strong weak bands are obtained in the region 330-290, 320-305, 320-295 cm^{-1} which are assigned to ν (Ni-N), ν (Co-N), ν (Cu-N) vibrations respectively. In the spectra complexes, bands appear in the region 270-250, 264-255, 256-230 cm^{-1} which may be assigned to ν (Ni-S) ν (Co-S), ν (Cu-S) vibrations.

6.0 Magnetic Moment & Electronic Spectral Studies

6.1 Manganese (ii) complexes

Manganese having $3d^5$ 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 (d^5) configuration. Magnetic moment values in the acetate complexes were found to be in the range 5.65 B.M. Suggesting the formation of high spin octahedral complexes with d^5 configuration. However, in chloro and nitrate complexes, the value of magnetic moment was found to be on lower side, (i.e. between 4.00-4.15 B.M.) which may be due to the magnetic interaction between the metal ions indicating the formation of binuclear complexes. This type of lowering in the magnetic moment values have not been observed in acetate complexes, reason is that the large anions might have hindered the magnetic interaction between the metal ions.

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 ${}^4T_{1g}(G) \leftarrow {}^6A_{1g}(G)$, ${}^4T_{2g}(G) \leftarrow {}^6A_{1g}$ & ${}^4A_{1g}(G) \leftarrow {}^6A_{1g}$ 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.

6.2 Copper (ii) complexes

In copper complexes one broad asymmetric band at 413200 cm^{-1} is observed in the case of all three Cu(II) complexes which is assignable to ${}^3T_2(F) \leftarrow {}^2E_g$ transition only. This suggests a tetragonally distorted structure for these complexes.⁸² 10Dq values are taken directly from ${}^2T_{2g} \leftarrow {}^2E_g$ transition. B values suggest sufficient metal-ligand overlap in the complexes.

As regards to the magnetic studies for Cu(II) complexes with d^9 configuration, B.N. Figgis^{83,84} particularly predicts an approximate demarcations as

- (i) μ_{eff} values greater than 1.90 B.M. for tetrahedral complexes.
- (ii) μ_{eff} values less than 1.90 B.M. for square planer and octahedral complexes.

The magnetic moments values are usually found in the range lying between 1.5 to 2.5 B.M.⁸⁵⁻⁸⁶ In the present complexes, the μ_{eff} values were found to be in the range 1.15-1.30 B.M. only.

These sub-normal values for the presently reported complexes may be attributed as due to the appreciable magnetic interaction between the two

copper ions present in the reported binuclear complexes.

This has been further supported by the E.S.R. studies of the Cu(II) complexes.

7.0 Fungicidal Activity

The presence study has revealed that the metal legends have more antifungal activity compare to metal complexes which has been proved by using the growth method against different fungi viz.

Fusarium Oxysporum & Altrnariet Alternata and antibacterial activity against Escherichia Coli and Pseudomonas Cepaciocola at 50, 100 and 200 concentration.

It is reported in the literature that the fungitoxicity or the fungicidal activity of an organic molecule increases with the addition of chlorine in the organic compounds.

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