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Stereochemical, Thermal and Biochemical Aspects of Transition Metal Complexes Derived from 2-hydroxy-n-phenyl-benzamide

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ABSTRACT

The ligand 2-hydroxy-N-phenyl benzamide and its metal complexes with Ti(III), V (III), Mn (III), Co (III), Ru (III), Fe (III), MoO(V) and Ru (II) were prepared and their stereochemical, thermal studies were carried out. An attempt to establish the structures of the resulting complexes on the basis of elemental analyses, magnetic measurement, IR, ^{1}H & ^{13}C NMR, electronic spectral and thermogravimetric studies. The antimicrobial screening data indicate that the metal chelates are more potent than the parent ligand.

Key words: Stereochemical, Biochemical and Antimicrobial, Complexes.

INTRODUCTION

The role of metal chelates in all aspects of biological studies has gained considerable importance, as they provide valuable approaches to the metabolic studies, oxidative phosphorylation, transmethylation and principles of chemotherapy. Azomethines, bonding through nitrogen and oxygen or sulphur atoms to the central metal ion form an important class of biologically active ligands and provide models for metal ligand binding sites in several enzymes[1-4]. Keeping those facts in view, the present ligand 2-hydroxy-N-phenylbenzamide and its transition metal complexes have been synthesized and characterized.

EXPERIMENTAL

All the chemicals and reagents used during this research work of AR grade or equivalent purity. The reagents used for the preparation of the ligand were hydrazine carboxamide of 2-hydroxy-N-phenyl benzamide, semicarbazide hydrochloride and sodium acetate. The ligand was prepared by reported method (4). Titanium (III) chloride was prepared standard method from titanouschloride (12% solution in HCl). The other metal salts like V(III), Mn(III), Co(III), Fe(III), Ru(III), Ru(III) & MoO(V) chlorides were used as procured.

Preparation of the ligand

The ligand was prepared by condensation

of hydrazine carboxamide of 2-hydroxy-N-phenyl benzamide with semicarbazide in the molar ratio of 1:1 in refluxing ethanolic medium. On cooling the crystals formed were filtered, recrystallised in the same solvent and finally dried in Vacuo.

Synthesis of complexes

The metal salt and the ligand were dissolved in dried methanol and mixed in the molar ratio of 1:2 (M:L). The reaction mixed was stirred for 2h when a solid product separated out. It was filtered, washed and dried in Vacuo. Ti (III) & V (III) complexes were prepared in a glove bag in the atmosphere of dry nitrogen gas.

The ligand and its metal complexes were subjected to elemental analyses for C, H & N while the metal and chloride were estimated gravimetrically in the lab. The melting points were determined by open capillary method and are uncorrected. The molar conductance was determined by systronics (model 305) conductivity bridge in DMF at 10^{-3} M dilution. Magnetic susceptibility was determined by Gouy's method, using $CuSO_4.5H_2O$ as calibrant. The electronic spectra were recorded by Beckmann DU spectrophotometer. The IR and NMR spectra were recorded at CDRI Lucknow.

Antimicrobial activity

Bioefficiency of ligand and its metal complexes was tested for the growth inhibiting potential against various fungal and bacterial strains using spore germination method[6-7] and paper disc technique[8] respectively.

RESULTS AND DISCUSSION

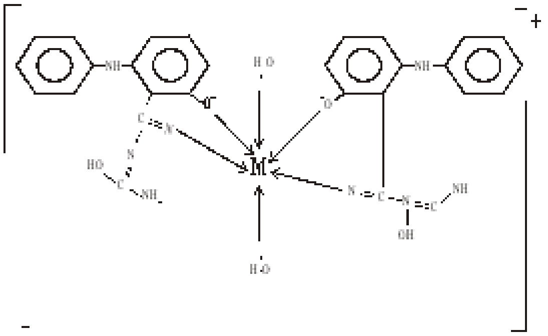
The analytical data suggested 1:2 (M:L) stiochiometry for all the synthesised complexes. The vast difference in the melting points of the ligand and its metal complexes indicated the formation of adducts. The determination of molar conductance in DMF at 25°C and 10^{-3}M dilution suggested 1:1 electrlytic nature for all the complexes except Ru (II) complex, which is non-electrolyte.

The IR spectra of the ligand and its respective metal complexes were compared in order to find out the possible coordination sites.

The IR spectrum of the ligand showed a band at 3410 cm^{-1} which may be assigned to phenolic OH group. This band disappeared in the case of metal complexes indicating the possible loss of proton on complexation and subsequent formation of M-O bond. The other important ligand band appeared at 1625 cm^{-1} assignable to azomethin group. This band has shifted downward by 20-25 cm^{-1} in the spectra of the complexes and suggested coordination through azomethine nitrogen atom. These two coordination sites were further supported by the appearance of new bands in the far i.r. region of the complexes in the range of 510-480 and 440-410 cm^{-1} assignable to nM-O and nM-N vibrations respectively[7].

The ^1H NMR spectra of the complexes show the disappearance of OH proton signal. This indicates the deprotonation and complexation through this functional group. The signal due to -NH proton attached to phenyl ring remains unaltered in the complexes. The NH_2 proton signals remain unchanged in the complexes[9]).

The ^{13}C NMR spectra of the complexes show considerable shifts in the positions of carbon



M = Ti(III), V(III), Mn(III), Co(III), Fe(III) or Ru(II)
X = Cl (In case of Ru, X = O)

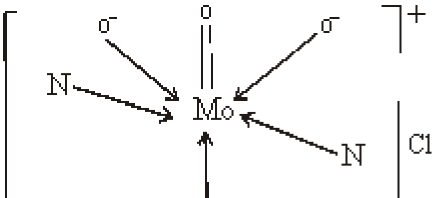


Table 1: Characterisation of the Ligand and Metal Complexes

S. No	Molecular Formula of ligand/ Complex	M.wt	Colour	M.P. ^{0}C	Elemental analyses				Magnetic Moment	Molar Conductance in (ohm^{-1} cm^2 mole^{-1})
				%C	% H	%N	%M	(B.M.)		
1.	Ligand $C_{14}H_{13}N_4O_2$	269	Brown	136	62.01 (62.45)	4.81 (4.83)	20.72 (20.81)	-	-	-
2.	$[Ti(C_{14}H_{12}N_4O_2)_2.$ $2H_2O]$ Cl Mol.	691.5	Yellow	171	48.53 (48.62)	4.00 (4.05)	16.00 (16.20)	6.79 (6.94)	1.71	60 (1:1 electrolyte)
3.	$[V(C_{14}H_{12}\ N_4O_2)_2.$ $2H_2O]$ Cl Mol.	694.5	Dark Yellow	172	48.32 (48.41)	3.97 (4.03)	16.00 (16.13)	7.18 (7.34)	2.92	62 (1:1 electrolyte)
4.	$[Mn(C_{14}H_{12}$ $N_4O_2)_2.2H_2O]$ Cl	698.5	Dark Brown	176	48.00 (48.13)	3.98 (4.01)	15.92 (16.04)	7.59 (7.87)	4.95	55 (1:1 electrolyte)
5.	$[Co(C_{14}H_{12}$ $N_4O_2)_2.2H_2O]$ Cl	702.5	Greenish brown	178	47.52 (47.86)	3.92 (3.98)	15.82 (15.95)	8.31 (8.40)	Diamagnetic	68 (1:1 electrolyte)
6.	$[Fe(C_{14}H_{12}$ $N_4O_2)_2.2H_2O]$ Cl	699.5	Dark brown	181	47.92 (48.06)	3.96 (4.00)	15.90 (16.02)	7.91 (8.01)	5.88	75 (1:1 electrolyte)
7.	$[Ru(C_{14}H_{12}$ $N_4O_2)_2.2H_2O]$ Cl	744.5	Green	203	44.96 (45.16)	3.70 (3.76)	14.91 (15.05)	13.51 (13.57)	1.96	70 (1:1 electrolyte)
8.	$[Ru(C_{14}H_{12}$ $N_4O_2)_2.2H_2O]$	709	White	199	47.10 (45.16)	3.89 (3.94)	15.68 (15.79)	13.98 (14.24)	Diamagnetic	Non- electrolyte
9.	$[Mo\ O(C_{14}H$ $_{12}N_4O_2)_2.2H_2O]$ Cl	702	Green	196	47.80 (47.86)	3.95 (3.98)	15.90 (15.95)	13.51 (13.67)	1.81	65 (1:1 electrolyte)

atoms adjacent to azomethine which further supports the proposed coordination pattern.

The IR spectra of the complexes exhibit some non-ligand bands in the range of 3500-3510 cm^{-1} assignable to nOH of coordinated water molecules and at 835-840 cm^{-1} due to wagging mode of coordinated water molecules[9]. TGA also support the coordinated nature of water molecules. The thermograms showed the loss of water molecules in the temperature range of 170-195^{0}C.

Electronic spectra

The electronic spectrum of Ti complex shows a single broad band at 19570 cm^{-1} due to $^2At_2g$ ^2Eg transition for O_h symmetry. The value of magnetic moment of this complex is 1.71 B.M. which is in the expected range for d^1 system like Ti (III) and shows paramagnetic character of the complex. It also shows that Ti (III) has not been oxidised to Ti (IV) during or after complexation, although it is very sensitive to oxidation[10].

The Mn (III) complex shows a magnetic moment of 4.95 B.M., corresponding to the presence of four unpaired electrons and high spin state of the complex. This value also suggests the absence of any kind of exchange interaction. The electronic

Table 2: Bactericidal screening data of ligands and their metal complexes

Compound	Diameter of inhibition zone, mm (Angular values)			
	Staphylococcus aureus		***Xanthomonas compestris***	
	500 ppm	**1000 ppm**	**500 ppm**	**1000 ppm**
Ligand	6.0 (14.18)	7.0 (15.32)	3.0 (9.97)	4.0 (11.54)
$[Ti(C_{14}H_{12}N_4O_2)_2.2H_2O]$ Cl	9.5 (17.95)	12.0 (20.27)	9.0 (17.46)	11.0 (19.37)
$[Mo O(C_{14}H_{12}N_4O_2)_2. 2H_2O]$ Cl	13.0 (21.13)	15.0 (22.79)	11.0 (19.37)	14.0 (21.97)

Table 3: Fungicidal screening data of ligands and their metal complexes

Compound	Conc. ppm	Helminthosporeun gramineum			Alternaria alternata		
		Total No. of spores	No. of germinated spores	No. of spores	Total No. of ungerminated spores	No. of germinated spores	No. of ungerminated spores
Ligand	500	12	2	10	10	1	9
	250	12	4	8	10	3	7
	125	12	5	7	10	6	4
	62.5	12	7	5	10	6	4
$[Ti(C_{14}H_{12}N_4O_2)_2.2H_2O]$ Cl	500	10	1	9	9	1	8
	250	10	2	8	9	2	7
	125	10	4	6	9	5	4
	62.5	10	7	3	9	7	2
$[Mo O(C_{14}H_{12}N_4O_2)_2.2H_2O]$ Cl	500	12	1	11	8	1	7
	250	12	2	10	8	2	6
	125	12	4	8	8	5	3
	62.5	12	7	5	8	6	2

spectrum of complex shows an intense and sharp charge transfer band at 22100 cm^{-1} and a spin allowed d-d transition at 18640 cm^{-1} characterstic of octahedral geometry[11].

The study of magnetic properties of the Co (III) complex indicated diamagnetic nature, as expected for a low spin d^6 ion. The electronic spectrum of the chelate displays bands at 15330. 21295 and 23510 cm^1 assignable to $^1A_{1tg} \rightarrow {}^3T_{2g}$, $^1A_{ttg} \rightarrow {}^1T_{1g}$ and $^1A_{ttg} \rightarrow {}^1T_{1g}$ transitions respectively. These are characteristic of low spin octahedral complexes of Co (III) [11].

The observed value of effective magnetic moment of the complex is 2.92 B.M., as expected for d^2 system like V (III). The electronic spectrum of the complex exhibits a band at 16210 cm^{-1} with a shoulder at 20630 cm^{-1}. The low energy band may be assigned to $^2A_{1g} \rightarrow {}^3T_{2g}$ and the high energy band to $^2A_{1g} \rightarrow {}^3T_{2g}$. These are characterized of octahedral geometry[13].

The Ru (III) complex shows a magnetic moment of 1.96 B.M. and three bands in its electronic spectrum at 13850. 17600 and 22600 cm^{-1} have been observed. These bands are assigned to $^4T_{2g} \rightarrow {}^4T_{1g}$. $^4T_{2g} \rightarrow {}^4T_{2g}$ and $^2T_{2g} \rightarrow {}^2A_{2g}, {}^2T_{1g}$ respectively, and are similar to those reported for other Ru (III) octahedral complexes[14].

The electronic spectrum of oxomolybdenum (V) complex suggested that the complex may be considered as octahedral with a strong tetragonal distortion resulting from Mo=O bond. The spectrum exhibited three distinct absorption bands in the ligand field region. The low intensity band at 13500 cm^{-1} in the long wavelength region is possibly due to first crystal field transitin $^2B_2 \rightarrow {}^2E$ (dxy, dyz, dxz). The second crystal field transition at 19100 Cm^{-1} is assignable to $^2B_2 \rightarrow {}^2B$ (dxy, $d_{x^2-y^2}$). The third peak was observed at 30100 assignable to $^2B_2 \rightarrow {}^2A_z$ (dxy, d_{z^2})[15].

The Ru (II) complex is diamagnetic in nature which shows +2 oxidation state for Ru (II) in this complex. The electronic spectrum of the complex in CH_2Cl_2 shows a band assigned to the charge transfer transition arising from the excitation of an electron from the metal t_{2g} level to the unfilled molecular orbitals derived from the p* level of the ligand in accordance with the assignments made for other similar octahedral Ru (II) complex[15]).

The magnetic moment of Fe (III) complex is 5.88 B.M. corresponding to the presence of five unpaired electrons and high spin state of Fe (III) in this complex. The electronic spectrum of this complex shows three bands at 12720, 19630 and 25100 cm^{-1} due to $^6A_{1g} \rightarrow {}^4T_{1g}$ (G), $^6A_{1g} \rightarrow {}^4T_{2g}$ (G) and $^6A_{1g} \rightarrow {}^4E_g$ (G) transition respectively in an octahedral symmetry[17].

CONCLUSION

On the basis of studies performed and discussed above octahedral geometry have been proposed for all the synthesized complexes. The Mo=O bond causes distortion in octahedral geometry of Mo O (V) complex.

Antimicrobial activity

It is evident from the antimicrobial screening data (Table) that the metal chelates are more potent than the parent ligands. The increased potency of metal complexes may be assigned to their increased lipophilic nature arising due to chelation. The representative ligands and the corresponding metal derivatives were found to be effective in controlling the leaf spot disease of brinjal plant caused by A. alternata. It was observed that the % disease control of all the compounds is quite appreciable as compared to the check, yet the superiority of the metal derivatives cannot be ruled out.

Mode of action of antimicrobials may involve various targets in microorganisms, e.g., interference with cell wall synthesis, damage to the cytoplasmic membrane as a result of which cell permeability may be altered or they may disorganize the lipoproteins leading to cell death.

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