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Synthesis and physio-chemical studies on some antimicrobial Schiff bases and their transition metal complexes

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ABSTRACT

M(III) complexes of Ti,Fe and Mn with schiff bases derived from 2-amino-4-ethyl-5-hydroxy benzaldehyde N,N'-dimethyl 4-aminobenzaldehyde and thiocarbohydrazide were synthesised and characterised by elemental analyses, molar conductance measurements,magnetic susceptibility determination, electronic and IR spectral studies. Based on these studies,octahedral geometry has been proposed for all the syntesised complexes. Schiff bases as well as their corresponding M(III) complexes were screened for their antimicrobial activities.

Key words: Schiff base, antimicrobial activity, thiocarbohydrazide.

INTRODUCTION

Schiff base and their transition metal complexes have been studied extensively since these have a wide variety of applications. The finding that metal complexes of these ligands are ubiquitous is a reflection of their facile synthesis, wide application and accessibility of diverse structural modifications. Schiff base complexes are of great intrest, especially for inorganic and bioinorganic chemistry. The antimicrobial activity of schiff bases is related to their chemical structure(-R=N-)3 . The aim of the present study was to prepare, characterise and screen the schiff bases and their M(III) complexes for their antimicrobial activities. The schiff bases has been derived from 3-amino-4-ethyl-5-hydroxy benz-aldehyde, N,N,dimethyl-4-aminobenzaldehyde and thiocarbohydrazide.

EXPERIMENTAL

Materials

All chemicals used were of A.R. or equivalent grade. Fe Cl_3 and Mn Cl_3 were purchased from aldrich while $TiCl_3$ was prepared in the lab by standard method given in chemical literature. DMSO,DMF and ethanol were purchased from Sigma, 2-amino-4-ethyl-5-hydroxy benzaldehyde N,N-dimethyl benzaldehyde and thiocarbahydrazide were procured from Fluka.

Synthesis of schiff bases

These were prepared by refluxing the ethanolic solutions of thiocarbohydriazide and the respective aldehyde in the molar ratio of 1:2 for about 4h. The precipitale so obtained was filtered, washed with ethanol and dried in vacuo. The purity of the products was checked by TLC.

Syntheses of Complexes

These were prepared by mixing solution of the schiff base with that of the respective metal salt. The precipitate appeared immediately, which was filtered immediately and washed repeatedly. It was then dried in vacuo over fused $CaCl_2$. The complexes of Ti(III) were prepared in glove bag under the atmosphere of nitrogen in order to avoid oxidation of Ti(III) into Ti(IV).

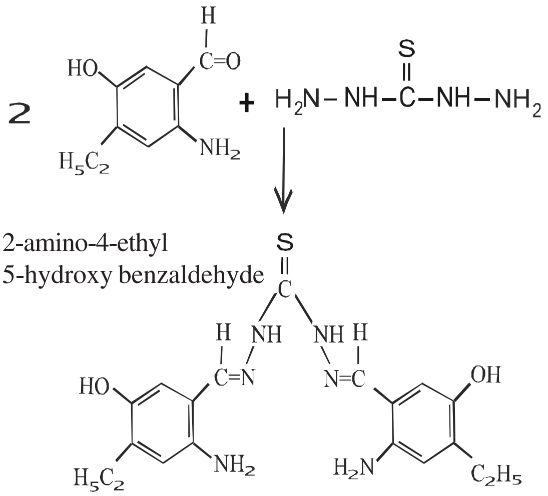
Methods

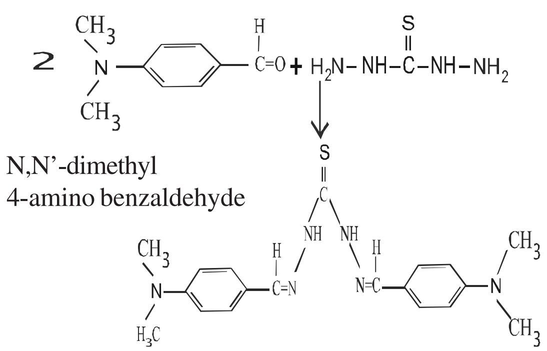
The microanalyses for C,H &N was carried out at CDRI, Lucknow. metals and sulphur were estimated gravimetrieally in the lab. The molar conductance was measured by digital conductivity meter (HPG system, G-3001) in DMSO at room temperature. Magnetic susceptibility was determined by Gouy's balance using $CuSO_4.5H_2O$ as calibrant. The electronic spectra were recorded at Beckmann DU- spectrophotometer. IR spectra were recorded in KBr phase at CDRI Lucknow.

Antimicrobial Activity

The antibacterial and antifungal activities of schiff bases and their corresponding metal chelates were evaluated by agar well. diffusion method. The antimicrobial activity of all the synthesised compounds was evaluated by measuring the zone of growth of inhibition against the test organisms with zone reader(Hi antibiotic zone scale).

The medium with DMSO as solvent was used as a negative control whereas media with ciprofloxacin (antibacterial) and griseofulvin (antifungal) were used as the positive controls.





The ligands and their M(III) complexes were tested for their antibacterial activity against bactersia E. Coli, S.Aureus,P. acruginosa and B.megaterium and for antifungal activity against the fungi K.fragilis, R. rubra, C.albicans and T.recsei.

RESULTS AND DISCUSSION

The elemental analyses suggested 1:1 stitiometry for all the synthesised complexes. The molar conductance values at 10^{-3} M dilution in DMSO suggested 1:3 electrolytic nature for all the complexes (Table-1). The value of effective magnetic moment for all the complexes of Ti(III),Fe(III) and Ru(III) suggested paramagnetic nature and octahedral geometry[5-7].

The IR spectra provided valuble information about the possible co-ordination sites. In the case of the 2-amino-4-ethyl-5-hydroxy benzaldehyde thiocarbohydrazone the IR spectrum of the ligand showed a number of important obsorption bands. The one at 3250cm^{-1} may be assigned to υNH_2. This has shifted by 20-25 cm^{-1} in the IR spectra of the complexes suggesting involvement of this group in co-ordination. The band due to υC=N has appeared at 1620 cm-1 in the IR spectrum of the ligand which has lowerd by 15-20cm^{-1} in the IR spectra of the complexes indicating co-ordination through azomethine nitrogen atom. The band at 780 cm^{-1} in the ligand spectrum assignable to υC=S group appeared unchanged in the IR spectra of the complexes excluding the possiblility of coordination through sulphur atom. Thus the ligand is behaving in tetradentate manner.

The ligand N,N'-dimethyl-4-amino bunzaldehyde thiocarbohydrazone has behaved in tri-dentate manner as indicated by IR spectra. The bands due υC=N and υC=S group have been shifted to lower positions suggesting involvement of these groups in coordination. This ligand is therfore behaving in tridentate manner.

The presence of coordinated water molecules has been suggested by the appearance of non-ligand bands in the IR spectra of the complexes in the range of 3410-3420cm^{-1}(OH), 845-855cm^{-1} (wagging) and 740-750cm^{-1} (rocking) modes of coordinated water molecules. This was

Table- 1: Elemental analyses, molar conductance and magnetic moment of the schiff bases and their M(III) complexes

S. No.	Complexes & Molecular wt.	Colour	M.P. ^0C	Elemental Analyses						Mag. Moment B.M.	Molar-conductance $Ohm^{-1}cm^2mol^{-1}$	
				%C	%H	%N	%S	%Cl	%M		DMF	DMSO
1	Ligand BTH (Fw=400)	Yellow	130	53.08 (57.00)	5.98 (6.00)	20.87 (21.00)	7.91 (8.00)	-	-	-	-	-
2	Ligand DMBTH (Fw=370)	Yellow	135	61.0 (61.62)	6.98 (7.02)	22.61 (22.70)	8.50 (8.60)	-	-	-	-	-
3	$[Ti(BTH).2H_2O]Cl_3$ (Fw=590.5)	Yellow	210	38.22 (38.61)	4.62 (4.74)	14.10 (14.22)	5.35 (5.41)	17.50 (17.78)	8.61 (8.72)	1.69	-	95
4	$[Mn(BTH).2H_2O]Cl_3$ (Fw=597.5)	Dark Brown	222	37.95 (38.15)	4.61 (4.68)	13.91 (14.00)	5.18 (5.35)	17.61 (17.82)	8.93 (9.20)	5.90	-	105
5	$[Fe(BTH).2H_2O]Cl_3$ (Fw=598.5)	Orange red	241	37.92 (38.09)	4.61 (4.67)	13.95 (14.03)	5.29 (5.34)	17.50 (17.71)	9.31 (9.35)	5.90	-	110
6	$[Ti(DMBTH).3H_2O]Cl_3$ (Fw=560.5)	Lightyellow	231	40.32 (40.67)	5.12 (5.35)	14.88 (14.98)	5.61 (5.70)	18.52 (18.90)	8.31 (8.56)	1.74	-	100
7	$[Mn(DMBTH).3H_2O]Cl_3$ (Fw=567.5)	Brown	240	39.96 (40.17)	5.10 (5.28)	14.62 (14.80)	5.54 (5.63)	17.61 (17.74)	8.97 (9.20)	5.97	-	95
8	$[Fe(DMBTH).3H_2O]Cl_3$ (Fw=568.5)	Red	248	39.92 (40.10)	5.10 (5.27)	14.61 (14.77)	5.56 (5.62)	18.51 (18.64)	9.70 (9.85)	5.98	-	115

Table 2: Antlbacteral and antifungal activity of ligand & its complexes

S. No	Compound	Inhibition Zone (mm)							
		E. coli	***S. aureus***	***P. aeruginose***	***B. megateriam***	***K. fragilis***	***R.rubra***	***C.albicans***	***J.reesi***
1	Ligand(2-amino-4-ethyl-5-hydroxy benzaldehyde thio carbohydrazone	6	7	7	7	10	5	8	12
2	Ti (III) complex	8	10	9	11	14	12	12	14
3	Mn (III) complex	10	11	12	12	16	14	14	18
4	Fe (III) complex	12	14	15	14	18	16	15	20
5	Clprofloxacln	24	22	22	20	-	-	-	-
6	Grlscofulrln	-	-	-	-	22	23	22	23
7	DMSO	0	0	0	0	0	0	0	0

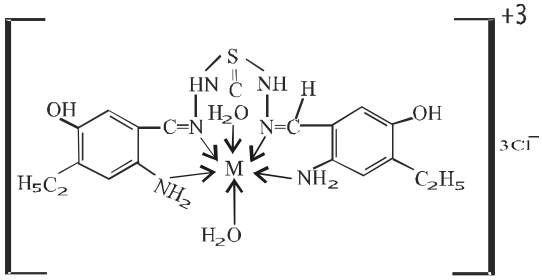
further supported by TGA. The thermiograms showed the loss of water molecules above 160°C.

The electronic spectra of the Ti(III) complexes exhibited a single band in the range 19550-20900 assignable to $^2T_{2g} \rightarrow {}^2T_{eg}$ transition, characteristic of octahedral Ti(III) complexes9. The observed value of eff of the complexes lie in the range of 1.69-1.74 B.M. at room temperature. This indicated paramagnetic nature of the complexes. The Mn(III) complexes exhibited two bands in the region of 1900-19500 and 13000-13500cm^{-1} assignable to $^5B_{1g} \rightarrow {}^5B_{1g}$ and $^5B_{1g} \rightarrow {}^5E_g$ transitions. These band are characteristic octahedral geometry[10].

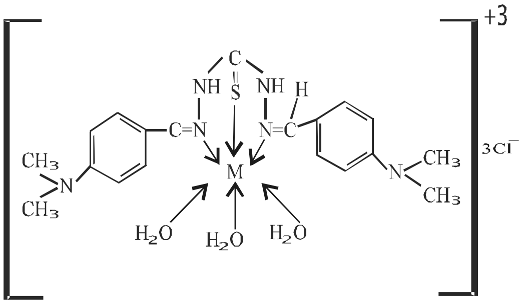
The megnetic momnet of these complexes were found to be in the range of 5.90-5.97 B.M. at room temperature. These values are similar to those reported for octahedral Mn(III) complexes11. The magnetic of Fe(III) complexes were in the range of 5.90-5.98 B.M. corresponding to high spin Fe(III) ion having five unpaired electrons.

The electronic spectrum of Fe(III) complexes showed bands in the region of 11300-11350, 2150-21750 and 27790-28000 cm^{-1} assignable to $^6A_{1g} \rightarrow {}^4T_{1g}$, $^6A_{1g} \rightarrow {}^4T_{2g}$ and $^6A_{1g} \rightarrow {}^4E_g$ transitions respectively and are characteristic of octahedral Fe(III) complexes[12].

Based on the above mentioned studies octahedral geometry may be proposed for all these synthesised complexes and may be represented as.



M(III) Complex of 2-amino-4-ethyl-5-hydroxy benzaldehyde thiocarbohydrazone(BTH) (M=Ti(III), Mn(III)or Fe(III)



M(III)Complex of N,N-dimethyl-4-aminobenzol dehyde thiocarbohydrazone (DMBTH) M=Ti(III), Mn(III)or Fe(III)

Antibacterial activities

The resultls of antimicrobial activity are tabulated in Table 2.

The ligand has shown moderate activity as compared to its metal complexes. The Ti(III) complex has shown weakest, followed by Mn(III) and Fe(III) in that order. Antibacterial and antifungl activities of the ligand and its corresponding M(III) complexes were compared with those of standard drugs ciprofloxacin and grieseofluvin.

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