

Synthesis and characterisation of Schiff base complexes with Ti (III), Cr (III) and Ni (II)

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(Received: March 29, 2008; Accepted: April 30, 2008)

ABSTRACT

New complexes of Ti (III) Cr (III) and Ni(II) with Schiff bases synthesised by condensation of Anthracene-9-carboxaldehyde with L-histidine, L-tryptophan, L-valine, L-methionine & L-glycine have been synthesised and characterised by elemental analyses, molar conductance, magnetic susceptibility measurement, thermogravimetric analysis, I.R. & electronic spectral studies. These complexes have been found to possess 1:2 (M.L.) Stoichiometry. The ligands and their corresponding complexes were screened for their antimicrobial activities.

Key words: Complexes, Schiff bases, synthesis.

INTRODUCTION

Schiff bases are important class of ligands and had got wide applications in various fields¹. Cyclic imides have wide applications in pharmacological² and industrial³ fields. Amino acids are the building units of all proteins and enzymes and are intimately associated with metal ions in biological system. Metal complexes of amino acids possess biological activities⁴. Mixed ligands metal complexes with cyclic imides and different amine bases have been prepared⁵⁻⁷ and encouraged by these reports, we have synthesised the metal schiff base complexes of Cr (III), Ni (II) and Ti(III).

EXPERIMENTAL

All the chemicals used were of A.R. & equivalent grade. Amino acids were obtained from Loba-Chem, while aldehyde was purchased from sisco chem industries.

Preparation of Metal Complexes

The complexes were prepared by stirring aqueous solution of sod. salt of amino acids with hot ethanolic solution of aldehyde in 1:1 molar ratio

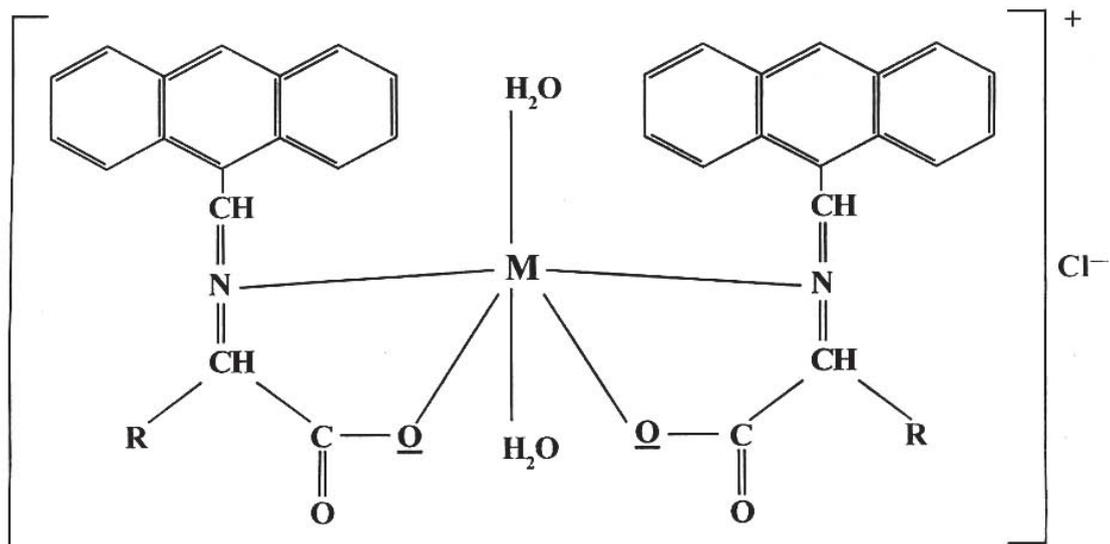
and then aqueous ethanolic solution of metal salt was added in equimolar ratio with constant stirring.

The products so formed were filtered, washed with ethanol & ether. The samples were dried in vacuum desiccator over anhydrous calcium chloride. In case of Titanium (III) complexes the whole operation was carried out in a glove bag under the atmosphere of nitrogen in order to avoid oxidation of Ti (III) into Ti (IV).

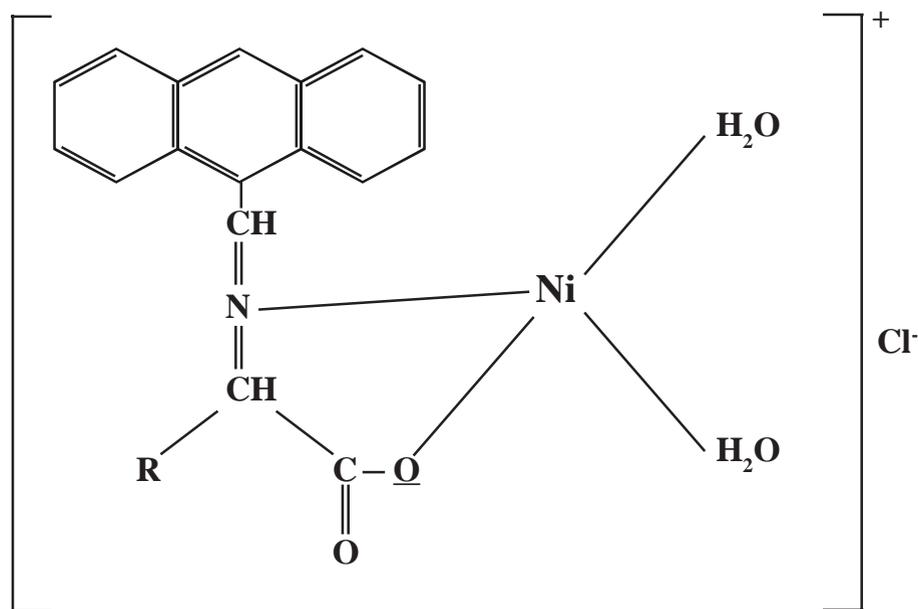
The elemental analyses for C, H & N were carried out at C.D.R.I., Lucknow. Metals were estimated gravimetrically, IR spectra were recorded on Perkin-Elmer spectrophotometer. The molar conductance at 10⁻³ molar dilution were measured by Elico conductometer bridge. The magnetic susceptibility was determined by Gouy balance using copper sulphate as standard material. Electronic spectra were recorded on Beckman DU spectrophotometer.

RESULTS AND DISCUSSION

The metal complexes were solid and non-hygroscopic. The empirical composition of the



Complexes of Ti(III) & Cr (III)



Complexes of Ni(II)

Where

M

= Ti(III) & Cr (III)

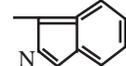
R

=

-CH₂ 

(In complexes of L-histidine)

=

-CH₂ 

(In complexes of L-tryptophan)

=

-CH₂ - CH₂S CH₃

(In complexes of L-methionine)

=

-CH - CH₃

(In complexes of L-valine)

=

-CH₃

(In complexes of L-glycine)

=

H

Scheme 1

Table 1: Molecular formulas, analytical data and other characteristics of complexes

S. No. of complexes	Name & Molecular formula	Molecular weight	Colour	m.p. °C	Elemental analyses				Magnetic moment in B.M.	
					% C	% H	% N	% S		% M
1.	Anthracene-9-carboxaldehyde-L-histidine Ti (III) Chloride (C ₂₁ H ₁₆ N ₃ O ₂) ₂ 2H ₂ O. TiCl	803.38	Yellow	270	62.734 (63.371)	3.983 (4.342)	10.455 (11.488)		5.959 (6.137)	1.73
2.	Anthracene-9-carboxaldehyde-L-typtophan Ti (III) Chloride (C ₂₆ H ₁₉ O ₂ N ₂) ₂ 2H ₂ O. TiCl	865.40	Dark Brown	290	71.98 (72.105)	4.020 (4.391)	6.320 (6.489)		5.050 (5.535)	1.70
3.	Anthracene-9-carboxaldehyde-L-methionine Ti (III) Chloride (C ₂₁ H ₁₈ O ₂ NS) ₂ 2H ₂ O. TiCl	8.15.40	Pale Yellow	300	61.79 (61.810)	3.895 (4.415)	3.055 (3.433)	7.222 (7.848)	5.050 (5.874)	1.74
4.	Anthracene-9-carboxaldehyde-L-valine Ti (III) Chloride (C ₂₀ H ₁₈ O ₂ N) ₂ 2H ₂ O. TiCl	727.40	Light Green	310	64.955 (65.988)	3.890 (4.849)	3.213 (3.849)		6.401 (6.585)	1.72
5.	Anthracene-9-carboxaldehyde-L-Glycine Ti (III) Chloride (C ₁₇ H ₁₀ O ₂ N) ₂ 2H ₂ O. TiCl	643.49	Yellowish Orange	305	62.815 (63.404)	3.022 (3.729)	4.000 (4.351)		7.443 (6.980)	1.71
6.	Anthracene-9-carboxaldehyde-L-Histidine Ni (II) Chloride (C ₂₁ H ₁₆ N ₃ O ₂ 2H ₂ O. NiCl)	472.21	Light Pink	280	53.000 (53.366)	3.121 (3.388)	7.990 (8.89)		11.850 (12.264)	2.90
7.	Anthracene-9-carboxaldehyde-L-Tryptophan Ni (II) Chloride (C ₂₆ H ₁₉ O ₂ N ₂ H ₂ O. NiCl)	521.21	Light Green	301	59.235 (59.860)	3.020 (3.645)	4.975 (5.372)		10.831 (11.264)	2.90
8.	Anthracene-9-carboxaldehyde-L-Methionine Ni (II) Chloride (C ₂₁ H ₁₈ O ₂ NS.H ₂ O. NiCl)	478.21	Orange	285	51.880 (52.696)	3.060 (3.764)	2.020 (2.927)	6.000 (6.691)	11.790 (12.277)	2.81

Table 1. Cont

9.	Anthracene-9-carboxaldehyde-L-valine Ti (III)Chloride (C ₂₀ H ₁₈ O ₂ NS. 2H ₂ O. NiCl)	434.21	Yellow	297°C	55.170 (55.272)	3.805 (4.145)	2.985 (3.224)	12.995 (13.521)	2.86
10.	Anthracene-9-carboxaldehyde-L-Glycine Ti (II) Chloride (C ₁₇ H ₁₀ O ₃ N.2H ₂ O. NiCl)	392.21	Light Green	305°C	51.859 (52.012)	2.090 (3.059)	3.040 (3.569)	14.441 (14.969)	2.85
11.	Anthracene-9-carboxaldehyde-L-Histidine Ni (II)Chloride (C ₂₁ H ₁₆ N ₃ O ₂ 2H ₂ O. CrCl)	879.50	Green	284°C	57.305	3.638	9.550	5.912	2.85
12.	Anthracene-9-carboxaldehyde-L-Tryptophan Cr (III) Chloride (C ₂₆ H ₁₉ O ₂ N ₂ 2H ₂ O. CrCl)	905.50	Yellow	299°C	68.912	4.196	6.184	5.742	3.84
13.	Anthracene-9-carboxaldehyde-L-Methionine Cr (III)Chloride (C ₂₁ H ₁₈ O ₂ NS) ₂ .2H ₂ O. CrCl	819.50	Light Blue	280°C	61.500	4.392	3.416	7.809	3.85
14.	Anthracene-9-carboxaldehyde-L-valine Cr (III)Chloride (C ₂₀ H ₁₈ O ₂ N) ₂ .2H ₂ O. CrCl	731.50	Dark Brown	295°C	65.618	4.921	3.827	7.108	3.88
15.	Anthracene-9-carboxaldehyde-L-Glycine Cr (II) Chloride (C ₁₇ H ₁₂ O ₂ N) ₂ .2H ₂ O. CrCl	647.50	Pale Yellow	306°C	63.011	3.706	4.324	8.030	3.89

complexes has been confirmed on the basis of analytical data (Table 1). The molar conductance values at room temperature and 10-3M dilution in DMF & DMSO showed that all complexes are electrolytic in nature.

The broad band in the 2900-3300 cm^{-1} region in all complexes attributed to the presence of water molecules, which is confirmed by thermal analysis. The IR spectrum of these complexes exhibited a new band in the range of 3500-3550 cm^{-1} which may be attributed to νOH vibrations of coordinated water. The appearance of band around 860 cm^{-1} due to wagging and rocking modes of coordinated water molecules(8, 9) also supports the above assumption of the presence of coordinated water molecules.

The 15-25 cm^{-1} shift in intense band appearing in the range 1640-1620 cm^{-1} for all the complexes has indicated the involvement of nitrogen atom of azomethine group in coordination and suggests imine structure¹⁰. As for as the coordination of the carboxylate ion is concerned the information is drawn from the position of asymmetric and symmetric COO^- frequencies occurring at about 1515 and 1530 cm^{-1} respectively in the spectrum of the complexes. This is clear indication of the involvement of the carboxylate ion in the coordination. In this way ligands are behaving in bidentate manner coordinating through carboxylate ion and N atom of azomethine group.

The electronic spectra of all the metal complexes were recorded in DMF solutions. These bands undergo a bathochromic shift and broadening in all the complexes and are located in the range 26041-20202 cm^{-1} . The broad bands in this range may have d-d transition components in admixture. This is further confirmed by the fact that all complexes are coloured and paramagnetic in nature¹¹.

Ni (II) Complexes

The electronic spectra of Ni(II) complexes the bands appeared in the range of 20500-20703 cm^{-1} may be assigned to $3t_1 - 3t_1(\text{P})$ transition, which support tetrahedral geometry¹² of the complexes.

For Ni (II) complexes, the weight loss corresponding to two molecules of water took place at about 180°C. This is further in the support of the presence of coordinated water molecules.

The magnetic moment of the complexes have the value in the range 2.80-2.90 BM which is very close to the value expected for two unpaired electrons.

Cr (III) Complexes

The electronic spectrum of the complexes exhibits bands in the range 18500-23400 cm^{-1} , these can be assigned to ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$ and ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}$ transitions which are typical of octahedral coordination¹³.

The complexes showed weight loss corresponding to two molecules of water at about 185°C. This further indicates that water molecules are coordinated with the metal.

The magnetic moment of the complexes have the value in the range 3.84-3.89 BM which is very close to the value expected for 3 unpaired electrons.

Ti (III) complexes

The titanium (III) complexes gave only one band at 19607-20408 cm^{-1} , which is obviously derived from the transition ${}^2\text{T}_{2g} \rightarrow {}^2\text{E}_g$ for an Oh symmetrically¹⁶.

The thermogram showed weight loss corresponding to two molecules of water at about 180°C. This further indicates that water molecules are coordinated with the metals.

The effective magnetic moment of the Ti (III) complexes was found to be in the range of 1.70 - 1.74 BM which indicates that the metal remain in +3 oxidation state ($3d^1$) even on complexation as the value is very close to 1.73 BM, expected for d^1 system.¹⁴ This is characteristic of octahedral geometry and paramagnetic nature of the complexes.

Preliminary testing of the ligand and metal complexes for anti-microbial activity on the gram +ve *S. aureus* and gram -ve *E. coli* shows that the

ligand is active only against *S. aureus* and activity is enhanced by complexation. The metal complexes exhibit more bacteriostatic activity against *E. Coli*. The appearance of activity may be due to synergistic mechanism¹⁵.

ACKNOWLEDGMENTS

The authors are thankful to Dr. R.P. Singh Principal, Bareilly College, Bareilly for providing laboratories facilities to carry out this research work.

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