

SYNTHESIS AND CHARACTERIZATION OF TRANSITION METAL COMPLEXES OF SCHIFF BASE DERIVED FROM ISATIN AND 2-AMINO, 4-CHLORO BENZOIC ACID

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ABSTRACT

A new Schiff base has been synthesized from 2-amino, 4-chloro benzoic acid and Isatin (ACBAI), Metal complexes of the Schiff base were prepared from chloride salt of Ti(IV), Zr(IV) and Cd(II) in alcoholic medium. Several physical tools in particular; IR, CHN, ¹H NMR, Molar conductance, Magnetic moment and Thermo gravimetric studies. On the basis of elemental and spectral studies, six and four coordinated geometry was assigned to these complexes. In the presence of these results, it is suggested that this ligand act as uninegative tridentate in nature contain tertiary nitrogen, ketonic carbonyl and carboxylic group. TGA and IR studies confirm the presence of coordinated water molecule in the complex.

Keywords: Schiff base, Metal complex, Spectral studies.

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INTRODUCTION

Isatin (1H-indol-2, 3-dione) is a synthetically versatile substrate, where it can be used for synthesis of a large variety of heterocyclic compounds, such as indoles and quinolones, and a raw material for drug synthesis. Isatin, due to its cis α -dicarbonyl moiety, is a potentially good substrate for the synthesis of metal complexes, either alone or deprotonated, Isatin has also been found in mammalian tissues¹. It stemmed from the interest in biological and pharmacological properties of isatin derivatives²⁻⁵.

Containing different donor atoms, the Schiff bases are an important class of ligands in the coordination chemistry, widely reported⁶⁻⁸. Our purpose was to synthesize metal chelates of 4-Chloro-2-(2-oxo-1, 2-dihydro-indol-3-ylidene amino)-benzoic acid with Ti(IV), Zr(IV), and Cd(II) metal ions.

EXPERIMENTAL

All the chemical and solvents used were A.R. grade. Elemental analysis was done on Perkin Elmer elemental auto analyzer. IR spectra were recorded on Perkin Elmer spectrum 100. ¹H NMR spectra were recorded on Bruker FT 300 at 300 MHz NMR spectrometer in DMSO d₆ solvent, using TMS as an internal standard. Magnetic measurement was carried out by the Gouy method at room temperature. The magnetometer was calibrated using copper sulphate and ferrous sulphate as internal standards and is uncorrected. The TGA, DTA were recorded on model TA SDT Q600 instrument at the linear heating rate of 10°C min⁻¹ under nitrogen atmosphere with in ambient temperature to 1000°C at CFC, Shivaji University, Kolhapur.

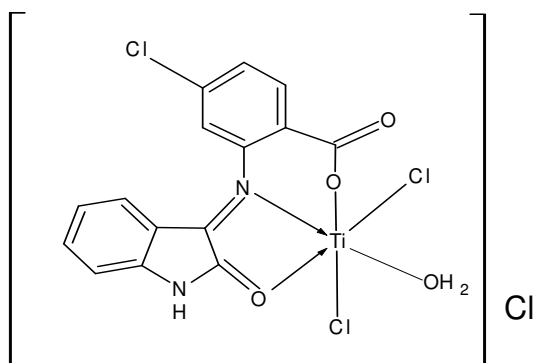
Synthesis of Schiff base

Schiff base ligand were synthesized by refluxing of 2-amino, 4-chloro benzoic acid (0.01 M) and isatin (0.01 M) in 50ml ethanol on water bath for 2-3 hours in presence of two to three drops of glacial acetic acid. The reaction mixture was poured in crushed ice, where orange colour precipitate was obtained. It was filtered by whatmann paper, washed with distilled water then alcohol, dried in vacuum desiccators'. Pure Schiff base was recrystallized from ethanol. The purity was checked by M.P and TLC

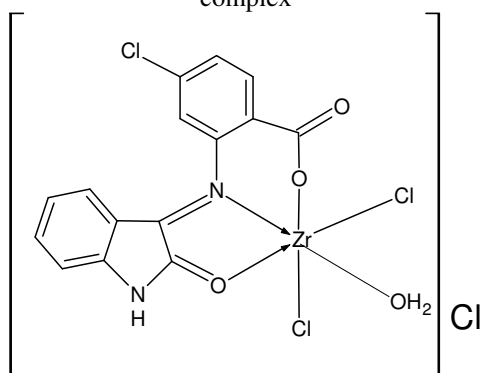
technique. Further the structures of the Schiff base were confirmed by subjecting them to CHN, IR and NMR studies.

Synthesis of Metal Complexes

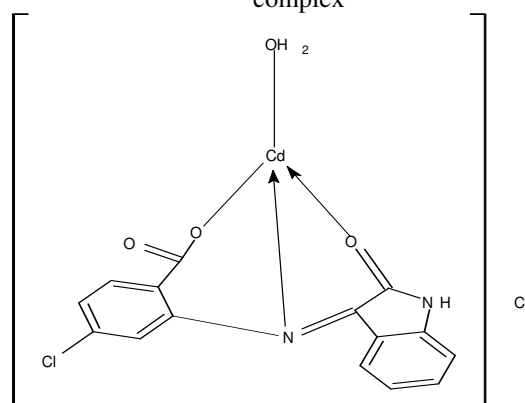
0.01 M alcoholic solutions (50ml) of metal salt were mixed with 0.01 M warm alcoholic solution (50ml) of ACBAI in round bottom flask. The P^H of reaction mixture is adjusted to 7.2 by adding alcoholic ammonia. Resulting reaction mixture refluxed for 5 to 6 hours on water bath. Pale yellow colour complex was allowed to digest and collected by filtration through whatmann filter paper. Then washed with sufficient quantity of distilled water and little hot ethanol to apparent to dryness and dried in a vacuum desiccators. Obtained product is dried and stored in a sample glass bottle.



Dichloro-[4-Chloro-2-(2-oxo-1, 2-dihydro-indol-3-ylidene amino)-benzoic acid](ACBAI) aquo Ti(IV) chloride complex



Dichloro-[4-Chloro-2-(2-oxo-1, 2-dihydro-indol-3-ylidene amino)-benzoic acid](ACBAI) aquo Zr(IV) chloride complex



Dichloro-[4-Chloro-2-(2-oxo-1, 2-dihydro-indol-3-ylidene amino)-benzoic acid](ACBAI) aquo Cd(II) chloride complex

Fig.-1

Table-1: Analytical data and other physical properties of ligand and metal chelates.

Ligand / Metal Complex	Empirical Formula	Mol. Wt.	Colour	D.P °C	% of Yield	M:L ratio	Molar Cond. (Ohm ⁻¹ cm ² Mol ⁻¹)	μ _{eff} . B.M.	Elemental analysis % Cal (Obs)				
									C	H	N	M	Cl
ACBAI	C ₁₅ H ₉ N ₂ O ₃ Cl	300.71	Orange	191	65	-	-	-	59.85 (59.45)	2.99 (3.57)	9.31 (9.21)	-	-
[Ti(ACBAI)H ₂ O.Cl ₂]Cl	C ₁₅ H ₁₀ N ₂ O ₄ Cl ₄ Ti	471.90	Yellow	240	59	1:1	71	Diamagnetic	38.15 (37.98)	2.11 (2.28)	5.93 (5.40)	10.15 (9.59)	30.09 (29.95)
[Zr(ACBAI)H ₂ O.Cl ₂]Cl	C ₁₅ H ₁₀ N ₂ O ₄ Cl ₄ Zr	515.22	Pale Brown	220	62	1:1	74	Diamagnetic	34.93 (34.73)	1.94 (1.99)	5.43 (5.13)	17.70 (17.02)	27.56 (27.47)
[Cd(ACBAI)H ₂ O]Cl	C ₁₅ H ₁₀ N ₂ O ₄ Cl ₂ C _d	465.40	Dark Yellow	242	60	1:1	76	Diamagnetic	38.67 (38.04)	2.14 (2.85)	6.01 (6.15)	24.15 (23.85)	15.25 (15.13)

Table-2: Infrared spectral data of ligand (ACBAI) and their Ti(IV), Zr(IV) and Cd(II) metal complexes.

Compound	ν(H ₂ O)	ν(OH)	ν(C=O) Carbonyl	ν(C-O)	ν(C=O) Ketonic	ν(C=N)	ν(NH)	ν(M-N)	ν(M-O)
ACBAI	-	3500	1690	1428	1740	1620	3385	-	-
[Ti(ACBAI)H ₂ O.Cl ₂]Cl	3490	-	1680	1385	1727	1610	3391	515	579
[Zr(ACBAI)H ₂ O.Cl ₂]Cl	3472	-	1678	1391	1731	1614	3395	510	585
[Cd(ACBAI)H ₂ O]Cl	3267	-	1666	1415	1733	1607	3389	505	553

RESULTS AND DISCUSSION

Characterization of the prepared complexes

After preparation of metal complexes yield physical characterization like nature, colour, decomposition point, magnetic moment (B.M.) of the prepared complexes is measured. The complexes have different colors and stable in air. The metal chelates shows decomposition point. These are insoluble in water and soluble in organic solvents such as DMF, DMSO giving respective colors to the solutions. All compounds gives satisfactory elemental analysis. Values are in close agreement with the values calculated for expected molecular formulae assigned to these complexes, suggesting 1:1 stoichiometry. The molar conductance values of all the complexes in DMF reveal their electrolytic nature⁹. For estimation of chloride by Volhard's method¹⁰ and percentage of metal ions by standard method is used¹¹.

Study of IR Spectra of Ti(IV), Zr(IV) and Cd(II) complexes

The IR spectra of the free ligands show strong ν (OH) stretching at 3500cm^{-1} corresponding to carboxylic group. This strong band has disappeared in the complexes, indicating its involvement in the bond formation process¹². The band stretching of $\nu(\text{C}=\text{O})$ vibration frequency at 1690cm^{-1} in ligand which shifted at lower wave number in complexes. This has been further indicated by $\nu(\text{C}-\text{O})$ group is lowered by $15\text{--}45\text{ cm}^{-1}$ in the spectra of complexes¹³. Besides, ligand exhibits stretching of ketonic $\nu(\text{C}=\text{O})$ at 1740cm^{-1} and $\nu(\text{C}=\text{N})$ stretching frequency at 1620cm^{-1} which on complexation shifted to lower frequency region suggesting that ketonic carbonyl and tertiary nitrogen groups are involved in coordination by an amount of $10\text{--}15\text{cm}^{-1}$ ^{14,15}. Similarly a band $\nu(\text{N}-\text{H})$ stretching frequency at 3385 cm^{-1} in ligand remains unaffected in complex providing evidence for its non-coordination. A new band at 3490cm^{-1} , 3472 cm^{-1} , 3267cm^{-1} in Ti(IV)¹⁶, Zr(IV)¹⁷ and Cd(II)¹⁸ metal complexes due to presence of coordinated water molecules. The appearance of new bands in the spectra of Ti(IV), Zr(IV) and Cd(II) metal complexes at $505\text{--}515\text{ cm}^{-1}$ due to $\nu(\text{M}-\text{N})$ ^{19,20}. Also, Metal-oxygen bonding $\nu(\text{M}-\text{O})$ at $553\text{--}585\text{ cm}^{-1}$ ^{21,22}.

Study of ¹H NMR spectral analysis

¹H NMR spectral studies of ligand ACBAI indicated signals at δ 6.47-7.67 ppm corresponding to aromatic protons (m, 7H, Ar-H) and at δ 9.0 ppm due to isatin moiety NH. A strong signals at δ 11.0 ppm assignable (s, 1H) due to carboxylic OH group.

In complexes signals corresponding to Ar-H have been shifted to lower region. Signal of NH group shifted to up field region in Ti(IV), Zr(IV) and Cd(II) metal complexes. The metal complexes signal corresponding to deshielded carboxylic group has disappeared²³. A new peak due to presence of coordinated water molecules at δ 2.0 ppm is observed in three complexes²⁴. Thus, ACBAI molecule seems to be coordinated to the metal through carboxylic oxygen, ketonic oxygen and azomethine nitrogen in Ti(IV), Zr(IV) and Cd(II) complexes.

Thermal Study of Complexes

Thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) techniques are used to determine the decomposition nature of the complex. The samples were heated in the temperature ranges room temperature- 1000°C . The range of temperature and the experimental and calculated mass losses of the decomposition reactions are given in the Table-3.

Thermal Study of Ti(IV) complex

The thermo gram of Ti(IV) complex shows weight loss corresponding to one water molecule in the range from room temperature to 176°C . The loss of water in this temperature range indicates the presence of water molecule²⁵ in the coordination sphere of Ti(IV) complex. Decomposition reaction corresponds to an experimental mass 27.01% occurs in the temperature range $176\text{--}317^{\circ}\text{C}$ attributed loss of isatin moiety²⁶ part of the complex. In the temperature range $317\text{--}512^{\circ}\text{C}$ chloro benzene with carbonyl part is lost and this loss corresponds to 28.95 percent. As the temperature increases to 715°C there is of 22.43 percent indicating loss of chloride part of metal complex. Finally $715\text{--}1000^{\circ}\text{C}$ residue²⁷ is obtained corresponding TiO_2 as stable residue 16.93 percent.

Thermal Study of Zr(IV) complex

The TGA of Zr(IV) complex indicates loss in weight in the range from room temperature to 175°C corresponding to 3.45 percent indicates the loss of coordinated water, which is shown by endothermic peak. Decomposition beyond this temperature in the range 175-405°C corresponds to mass loss of 26.53 percent in the TG curve assigned to expulsion of isatin moiety part of the complex. The decomposition occurs in the temperature 405-498°C indicates the loss of chlorobenzene with carbonyl part. Further at 498-723°C losses of 20.57 percent were occurs indicating loss of chloride part. At 723°C horizontal nature of the curve indicates the presence of thermally stable residual metal oxide²⁸. The percentage of residual metal oxide was found to be 24.21 which is very close to theoretical value 23.91.

Thermal Study of Cd(II) complex

TGA of Cd(II) complex shows weight loss corresponding to mass loss 58.63 percent. This loss corresponds to loss of coordinated water molecule with ligand part of the complex in the range from room temperature to 235°C²⁹. Further decomposition at 235-525°C loss of 13.50 percent was occurs indicating loss of carbonyl group with chloride part of the complex. The end product of decomposition is formation of CdO, weight corresponds to 27.18 percent which is equal to theoretical value 27.58.

Table-3: Thermal analysis data of Ti(IV), Zr(IV) and Cd(II) complexes.

Complexes	Mass loss(%) obs (cal)	Temperature (°C)	Expected nature of decomposition
[TiC ₁₅ H ₈ N ₂ O ₃ Cl (H ₂ O) Cl ₂] Cl	3.75 (3.81)	R.T-176	Coordinated water
	27.01 (27.33)	176-317	Isatin moiety part
	28.95 (29.24)	317-512	Chloro benzene with carbonyl part
	22.43(22.56)	512-715	Chloride part
	16.63(16.93)	715-1000	Residue
[ZrC ₁₅ H ₈ N ₂ O ₃ Cl(H ₂ O) Cl ₂] Cl	3.45(3.49)	R.T -175	Coordinated water
	26.53(26.78)	175-405	Isatin part
	24.95(25.03)	405-498	Carbonyl with chloro benzene part
	20.57(20.67)	498-723	Chloride part
	24.21(23.91)	723-1000	Residue
[CdC ₁₅ H ₈ N ₂ O ₃ Cl(H ₂ O)] Cl	58.63(58.76)	120-235	Coordinated water with ligand part
	13.50(13.64)	235-525	Carbonyl group with chloride part
	27.18(27.58)	525-1000	Residue

CONCLUSION

On the basis of analytical, spectral data analysis of Ti(IV), Zr(IV) and Cd(II) complex, the proposed structure for complexes are as shown in the following figure.

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