



Thermal Analysis of Metal Complexes with 2-[(1H-Indol-3-yl methylene) amino]-4-methyl-phenol (AMPIA)

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Abstract

2-[(1H-Indol-3-yl methylene) amino]-4-methyl-phenol with used to synthesize Ti(IV), Zr(IV), Cd(II) and Hg(II) chelates. Metal complexes were characterized by Carbon, Hydrogen and Nitrogen elemental analysis, UV-Visible, Infra-red, ^1H NMR, X-ray diffraction and TGA/DSC. The thermal stabilities of these metal complexes were investigated by simultaneous Thermo gravimetric and differential scanning methods. The thermal behaviours of all the metal complexes were studied in the range of room temperature to 1000°C and for Hg (II) metal complex up to 500°C .

Keywords: TGA/DSC, AMPIA, Ti (IV), Zr (IV), Cd (II) and Hg (II) complexes

1. Introduction

Indole derivatives and their metal complexes have received much attention due to their wide application in physiology¹ and pharmacology². They constitute an important class of compounds possessing antibacterial³, anticonvulsant⁴ and antihypertensive activity. These observation led to the conception that Schiff bases of indole 3-aldehyde would possess potential antimicrobial properties. Indole and its derivatives are widely used in making perfumes, dyes, agrochemicals and medicines. Schiff bases are usually synthesized from the condensation of primary amines and active carbonyl group⁵. Schiff bases are characterized by the $-\text{N}=\text{CH}$ - (imines) group which is important for elucidating the mechanism of transamination and racemisation reactions in biological systems and are also known to have biological activities such as antimicrobial⁶, antifungal⁷, antitumor⁸ and herbicidal⁹ activity.

Review of literature did not reveal synthesis and characterization to explore the coordination chemistry of transition metal complexes with 2-[(1H-Indol-3-yl methylene) amino]-4-methyl-phenol (Schiff base) ligand. This has prompted us to synthesize and structural studies of metal complexes involving this newly synthesized ligand. This compound 2-[(1H-Indol-3-yl methylene) amino]-4-methyl-phenol here after referred to as AMPIA is a hetero cyclic ligand having phenolic-OH, azomethine and Metal chelates of 2-[(1H-Indol-3-ylmethylene)-amino]-4-methyl-phenol secondary amine donor atoms. After observing the structure of ligand it indicates, it have coordination tendency.

2. Experimental Section

All the chemicals used for the synthesis of metal complexes are of Merck and Sigma-Aldrich. 0.01M solution of 2-[(1H-Indol-3-ylmethylene)-amino]-4-methyl-phenol were prepared in warm ethyl alcohol. The Merck make 0.01M Metal chloride solution was also

prepared in ethyl alcohol. Metal ion solution was added drop wise with constant stirring. The P^H of reaction mixture was maintained about 6.5 to 6.9 by adding alcoholic ammonia solution drop by drop. The reaction mixture was refluxed for about four hours on water bath. Appearance of dark reddish brown precipitate was allowed to digest for half an hour. It is filtered through whatmann filter paper. The complex was purified by washing with distilled water and little hot ethanol to apparent dryness. The complex is dried and yield was recorded. Synthesis method was given in details in published papers.

3. Result And Discussion

Thermal study of prepared complexes:

Results of TG analysis are used to determine the nature of water molecules present and decomposition pattern of the complexes. Lattice water molecules were lost in the 70-110⁰C temperature range while coordinated water molecules were eliminated at relatively high temperature range of 150-317⁰C. Complete decomposition of ligand occurs at about 725⁰C and observed residue corresponds to respective metal oxide. The TGA/DSC scanning of Hg (II) complexes were in the range of room temp-500⁰C¹⁰. TGA/DSC of Ti (IV), Zr (IV) and Cd (II) scans are in the range of room temp-1000⁰C. The range of temperature and the experimental and calculated mass losses of the decomposition reaction are given in the table and figures 1, 2, 3 and 4.

Thermal study of [Ti (AMPIA) ₂] Cl₂

TGA of bis2-[(1H-indol-3-ylmethylene)-amino]-4-methyl-phenolTi (IV) dichloride complex indicates decomposition in three steps. There is a loss in mass 40.51% in the range 130-273⁰C indicating decomposition of methyl benzene with chloride part. As the temperature increases to 415⁰C there is loss of 37.54% indicating loss of indole moiety of the metal complex. Further at 415-616⁰C, 8.61% loss observed indicating loss of remaining azomethine part of organic molecule. At 616⁰C, 12.78% of the complex remains in the form of oxide as TiO₂¹¹.

Thermal study of [Zr (AMPIA)₂]Cl₂.H₂O

Bis 2-[(1H-indol-3-ylmethylene)-amino]-4-methyl-phenolZr(IV) dichloride complex shows a loss in mass 2.47% at 120⁰C indicates the presence of lattice water¹². Weight loss at 258⁰C is found to be 26.39% which is close to calculated value 26.54 indicating loss of methyl benzene part of complex which shows by exothermic peak.

In the temperature range 258-368⁰C, 34.04% loss occur indicating decomposition of indole moiety. Further at 368-619⁰C loss of 18.24 percent was occur indicating loss of azomethine with chloride part of the metal complex. At 619⁰C weight of residual metal oxide was found to be 17.98 percent which is close to theoretical value 18.16.

Thermal study of [Cd (AMPIA) H₂O] Cl₂.H₂O

The TGA study of 2-[(1H-indol-3-ylmethylene)-amino]-4-methyl-phenol aquo Cd (II) chloride complex shows the loss of lattice water by exothermic peak. The percentage loss of lattice water molecule at 115⁰C was found¹³ to be 4.09% which is very close to theoretical value 4.15. Further decomposition at 115-268⁰C shows the loss of coordinated water¹⁴ with methyl benzene part of the complex which indicated by endothermic peak. The decomposition of indole moiety of the complex occurs in the temperature range 268-410⁰C, weight loss is found to be 26.65 percent which is close to calculated value 26.79.

Similarly at 410-640⁰C loss of 14.33% was occurs indicating loss of azomethine with chloride moiety. At 640⁰C horizontal nature of the curve indicates the presence of thermally stable residual metal oxide¹⁵. The percentage of residual metal oxide was found to be 26.49 which it very close to theoretical value 29.66.

Thermal study of [Hg(AMPIA)Cl]H₂O

Mono chloro 2-[(1H-indol-3-ylmethylene)-amino]-4-methyl-phenol Hg(II) complex shows the loss of lattice water¹⁶ at 135⁰C, which is 3.25% and close to calculated value 3.57%. This water molecule is present outside the coordination sphere.

Second stage of thermal decomposition of [Hg (AMPIA)Cl]H₂O complex is in the range 135-

286^oC . In this temperature range 53.31% loss is obtained which indicates of ligand moiety shown by endothermic peak. Above 286^oC

straight line graph is obtained indicate the formation HgO¹⁷.

Thermal analysis data of metal complexes

Complexes	Mass loss(%) obs (cal)	Temperature in °C	Expected nature of decomposition
[TiC ₃₂ H ₂₆ N ₄ O ₂]Cl ₂	40.51 (40.68)	130-273	Methyl benzene with chloride part
	37.54 (37.60)	273-415	Indole moiety
	8.61 (8.75)	415-616	Azomethine part
	12.78 (12.95)	616-1000	Residue
[ZrC ₁₄ H ₁₁ N ₂ O ₄ (H ₂ O)Cl ₂] Cl.2H ₂ O	6.66 (6.88)	Room Temp- 123	Lattice water
	43.93 (44.00)	123-263	Coordinated water with methyl benzene and nitrobenzene
	11.65 (11.95)	263-420	Azomethine with chloride part
	13.45 (13.58)	420-590	Chloride part
	23.27 (23.57)	590-1000	Residue
[CdC ₁₄ H ₁₁ N ₂ O ₄ (H ₂ O)]Cl	56.16 (56.30)	175-290	Coordinated water with methyl benzene and nitrobenzene
	14.06 (14.30)	290-585	Azomethine with chloride part
	29.29 (29.38)	585-1000	Residue
[HgC ₁₄ H ₁₁ N ₂ O ₄ Cl]H ₂ O	3.30 (3.42)	Room Temp- 126	Lattice water
	55.14 (55.40)	126-259	Ligand moiety
	41.09 (41.24)	259-500	Residue

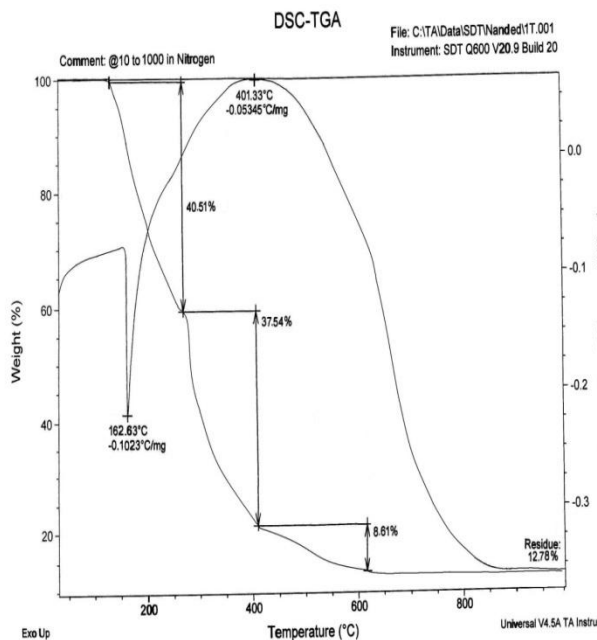


Figure 1: TG/DSC pattern of Complex[Ti(AMPIA)₂]Cl₂

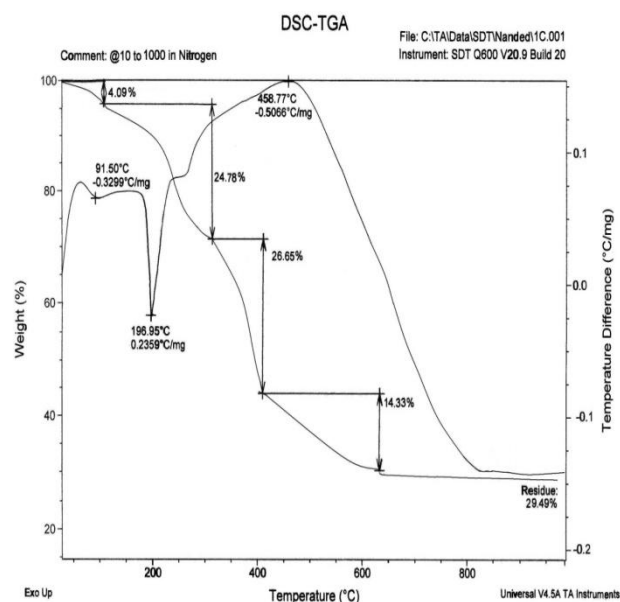


Figure 3: TG/DSC pattern of Complex[Cd(AMPIA)H₂O]Cl.H₂O

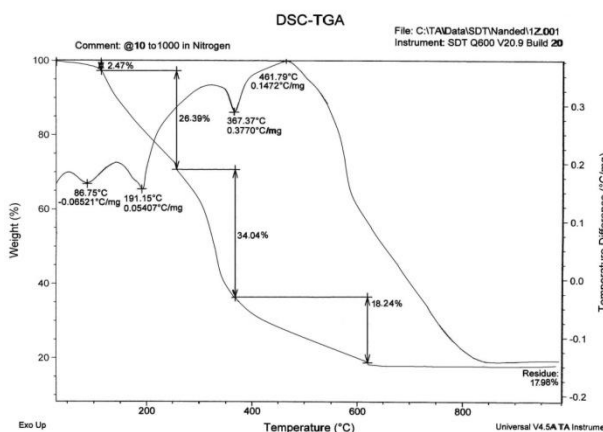


Figure 2: TG/DSC pattern of Complex[Zr(AMPIA)₂]Cl₂.H₂O

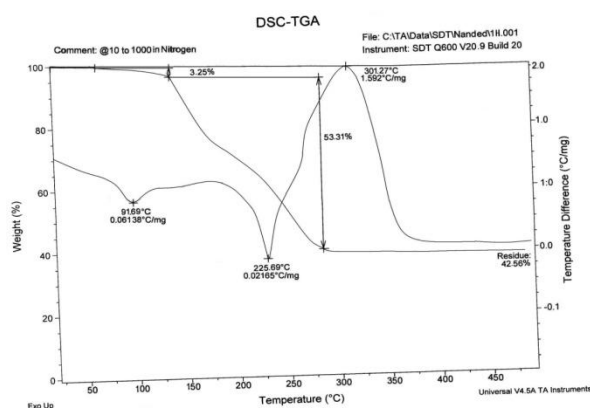
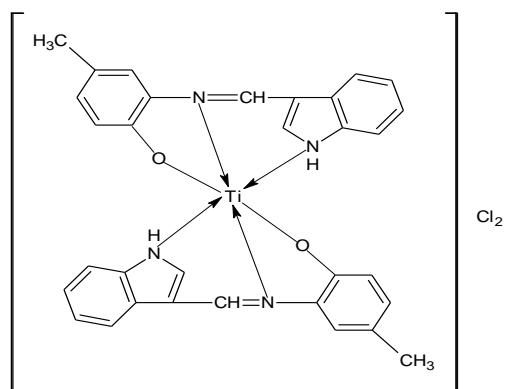
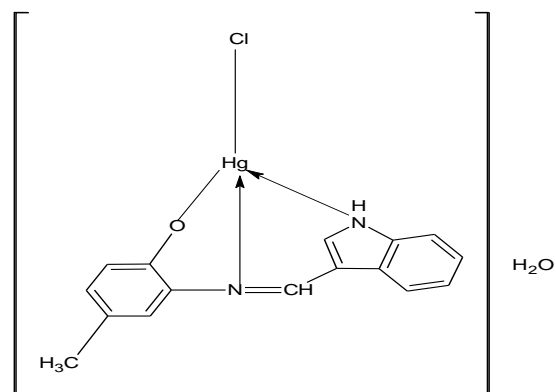


Figure 4: TG/DSC pattern of Complex[Hg(AMPIA)Cl]H₂O

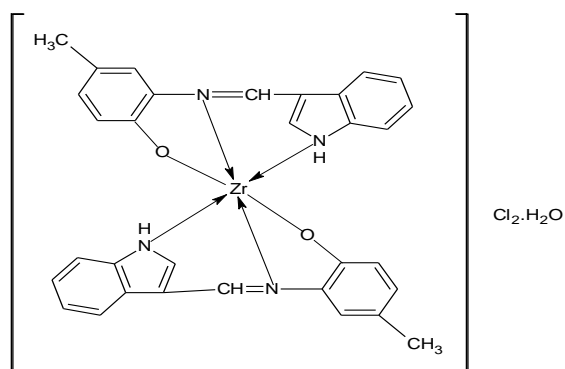
Proposed structures of metal chelates



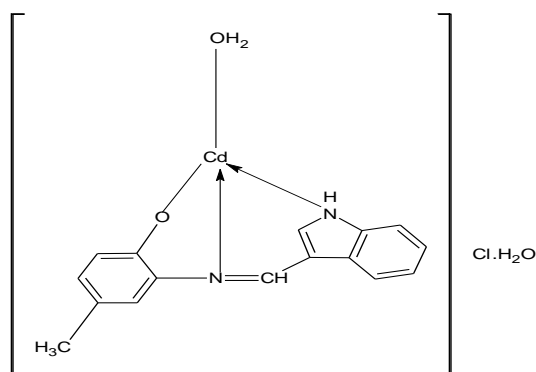
[Ti (AMPIA) ₂] Cl₂



[Hg(AMPIA)Cl]H₂O



[Zr (AMPIA)₂]Cl₂.H₂O



Cd (AMPIA) H₂O] Cl.H₂O

4. Conclusion

The heterocyclic ligand AMPIA can form metal chelates with transition metal ion viz. Ti(IV), Zr(IV), Cd(II) and Hg(II), coordination number for Ti(IV) and Zr(IV) is found to be six and for Cd(II) and Hg(II) is four. Ligand behaves as uni-negative tridentate in nature. High decomposition points of the complexes suggest good thermal stability at normal conditions.

Thermal studies also support presence of coordinated water molecule in cadmium complex. Lattice water molecules present in Zr(IV), Cd(II) and Hg(II) complexes.

5. Acknowledgement

The author would like to thanks the Principal and Head Department of Chemistry, Shri Shivaji College, Parbhani for providing all necessary facilities.



6. References

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