



**PREPARATION, CHARACTERIZATION AND THEORETICAL  
STUDIES OF SOME TRANSITION METAL ION COMPLEXES**

By

**Manal Ahmed Mahmoud Afifi**

A thesis Submitted in Partial Fulfillment

Of

The Requirements for the degree of

**Master of Science**

In

**Inorganic Chemistry**

Department of Chemistry

Faculty of Science, Fayoum

**Fayoum University**

**2014**

**PREPARATION, CHARACTERIZATION AND THEORETICAL  
STUDIES OF SOME TRANSITION METAL ION COMPLEXES**

By

**Manal Ahmed Mahmoud Afifi**

B. Sc. in Chemistry (special Chemistry), Fayoum University. 2010

**Under the Supervision of:**

**Prof.Dr. Samir Moustafa El-Medani**

Professor of Inorganic Chemistry, Faculty of Science – Fayoum University

Signature .....

**Prof.Dr. Hussein Mohamed Moustafa**

Professor of Physical Chemistry, Faculty of Science – Cairo University

Signature .....

**Dr. Amr Abd El-Nabi Esawy**

Lecturer of Inorganic Chemistry, Faculty of Science – Fayoum University

Signature .....

## **Title Sheet**

**Name of Researcher:** Manal Ahmed Mahmoud Afifi

**Date of Birth:** 1/7/1989

**Place of Birth:** Fayoum

**First University Degree:** B.Sc. & Ed., May 2010 (Excellent with Honor).

**Name of University:** Fayoum.

## **Summary**

This thesis includes the study of complexes resulted from the reaction of Tb(III) and Sm(III) metal ion with anthranilic acid (AA) and 5-chloroanthranilic acid (AACl) as ligands. The carboxylic and amine groups are the possible bonding sites in AA and AACl. The importance of the two ligands and their metal complexes refers to the variety of their applications including; biological, clinical, and analytical fields in addition to their important roles in polymer industry. In this work, the two ligands and their metal complexes were characterised by elemental analysis, spectroscopic studies such as IR, UV–Vis, and mass to elucidate the structures and the coordination sites that may be involved in chelation with the metal in the reported complexes. These studies were confirmed by theoretical studies which include the geometry and the ground state properties. The results were found to be in good agreement with those calculated for the suggested complex structures. Thermal and biological activity studies were also considered.

The present work includes; (1) the Spectroscopic characterization of the reported ligands (AA and AACl) and their complexes and (2) the theoretical studies.

### **1. Spectroscopic Characterization**

This part include the infrared (IR), mass spectroscopic analyses and the elemental analysis of the ligands and complexes. The reaction of anthranilic acid (AA) with  $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$  gave the two complexes  $[\text{Sm}(\text{AA})_3]$  and  $[\text{Tb}(\text{AA})_3]$ , respectively. In addition, the reaction of chloroanthranilic acid (AACl) with these two salts gave the two complexes  $[\text{Sm}(\text{AACl})_3]$  and  $[\text{Tb}(\text{AACl})_3]$ , respectively. The elemental

analysis and mass spectroscopy proved that the complexes are structurally formulated in 1:3 [Metal]:[Ligand] ratio. The IR spectra of the complexes are compared with those of the free ligands in order to determine the coordination sites that may be involved in chelation. The IR spectra of the AA ligand and its complexes showed that the  $\nu_{as}(\text{NH}_2)$  and  $\nu_s(\text{NH}_2)$  stretching frequencies of the free AA ligand were shifted to the range 155-166  $\text{cm}^{-1}$  and 123-184 $\text{cm}^{-1}$ , respectively. Also, the stretching frequency  $\nu(\text{C}=\text{O})$  for the free AA ligand (at 1664  $\text{cm}^{-1}$ ) disappeared on complexation. In the same time, the stretching frequencies  $\nu_{as}\text{COO}^-$  and  $\nu_s\text{COO}^-$  for AA complexes were shifted to 63-68  $\text{cm}^{-1}$  and 18-20  $\text{cm}^{-1}$ , respectively. These results indicated that the metals were coordinated oxidatively to the bidentate anthranilic acid via the ionised oxygen of the carboxylate group and to the nitrogen of amino group.

In 5-chloroanthranilic acid (AACl), the metals were coordinated oxidatively to the bidentate carboxylate group without bonding to amino group where no significant IR shifts were observed in the  $\nu_{as}(\text{NH}_2)$  and  $\nu_s(\text{NH}_2)$  vibrations on complexation. Furthermore, the stretching frequency  $\nu(\text{C}=\text{O})$  for the free AACl ligand (at 1671  $\text{cm}^{-1}$ ) disappeared on complexation. Also, the stretching frequencies  $\nu_{as}\text{COO}^-$  and  $\nu_s\text{COO}^-$  for AACl complexes were shifted to 78  $\text{cm}^{-1}$  and 56  $\text{cm}^{-1}$ , respectively. These results indicated the coordination of the metals oxidatively to the bidentate chloroanthranilic acid via the two oxygen of the carboxylate group.

The Uv-vis absorptionspectra of the ligands and their complexes were studied. The spectra revealed broad absorption band at  $\lambda_{\text{max}} = 331 \text{ nm}$  that estimate  $\epsilon$  value around 21780  $\text{mol}^{-1} \text{ L cm}^{-1}$ . This band could be assigned to  $n-\pi^*$  transition in AA. On complexation, Sm(III) and Tb(III) complexes showed a slight blue shift by 2 nm and enhancement of the absorbance value due to complex formation. The estimated  $\epsilon$  values for the

Sm(AA)<sub>3</sub> and Tb(AA)<sub>3</sub> complexes amount, respectively, to 31600 and 34000 mol.<sup>-1</sup> L cm<sup>-1</sup> with a noticeable increase compared to free ligand.

The AACl ligand and its Tb(III) and Sm(III) complexes monitored UV-vis absorption spectra at  $\lambda_{\text{max}}=348$  nm ( $\epsilon = 30760$  mol.<sup>-1</sup> L cm<sup>-1</sup>) indicating blue shift by 4 nm and estimated  $\epsilon$  values 38200 and 42000 mol.<sup>-1</sup> L cm<sup>-1</sup>, respectively. These results may reflect the role of Cl atom in reinforcing lanthanoid-AACl coordination through two oxygen of carboxylate group rather than the preferential O- and N coordination sites elucidated in lanthanoid-AA complexation.

Thermal properties of the complexes were investigated and confirmed the proposed structures of the reported complexes. Thermal analysis confirmed that all reported complexes don't include any coordinated water molecules.

Biological studies showed that the two ligands and their complexes showed significant biological activity towards *Escherichia coli* (G-) and *Staphylococcus aureus* (G+) bacteria. The study resulted that no biological activity was observed for the complexes towards *Aspergillus flavus* (fungus). The results indicated, also, that the two ligands and their complexes showed biological activity towards *Candida albicans* (fungus) except the Tb(AA)<sub>3</sub> complex where no biological activity was observed.

## **II: Theoretical characterization**

The second part of the thesis deals with the electronic structure and ground state properties of ligands and their complexes. Density Functional Theory (DFT) calculations at the B3LYP/6-311++G (d,p)\_ level of theory have been carried out to investigate the equilibrium geometry of the ligand.

The optimized geometry parameters of the complexes were evaluated using SDDALL basis set. From the results of the geometries and ground state properties, one can reveal the following:

- 1- In our calculation, the anion used because the energy difference  $E_g$  between LUMO (lowest unoccupied molecular orbital) and HOMO (highest occupied molecular orbital) is smaller in case of  $\text{AACl}^{-1}$  and  $\text{AA}^{-1}$  ligands than that of the HAACl and HAA ligands itself. The lower  $E_g$  the higher the reactivity, this indicates that  $\text{AACl}^{-1}$  and  $\text{AA}^{-1}$  ligand is more reactive than the HAACl and HAA ligand; respectively.
- 2- The dipole moment for  $\text{AACl}^{-1}$  and  $\text{AA}^{-1}$  is higher than the dipole moment of HAACl and HAA ligands. The higher the dipole moment usually indicates higher polarity and higher tendency to react with other charged compounds.
- 3- From the computed net charge, it was found that the most negative centers in  $\text{AA}^{-1}$  are N10 and O8. Whereas in  $\text{AACl}^{-1}$ , the most negative centers are O8 and O9. The reason why  $\text{AA}^{-1}$  ligand bonded through N10 and O8 while  $\text{AACl}^{-1}$  ligand bonded through O8 and O9 –atoms.
- 4- In case of  $\text{AA}^{-1}$ , the charge density of the HOMO is localized in the phenyl ring, N10 of the amino group and O8 of the hydroxyl in carboxylate. In case of  $\text{AACl}^{-1}$ , the charge density localized on the two oxygen atoms of the carboxylate (O8 and O9). Therefore, ligand  $\text{AA}^{-1}$  coordinated with the metal to form complex through O8 and N10 and ligand  $\text{AACl}^{-1}$  coordinated with the metal through O8 and O9.
- 5- The bonds between M and the ligand sites in  $\text{M}(\text{AA})_3$  complexes i.e. M-N and M-O are too long, 2.730 Å for M-N10, 2.758 Å for M-N27,

2.728 Å for M-N42, 2.160 Å for M-O12, 2.182 Å for M-O26 and 2.171 Å for M-O39 compared to the typical M-N and M-O bonds. The too long M-N bonds for  $M(AA)_3$  complexes mean that the ionic character of these bonds is small. In case of  $M(AACl)_3$  the M-O bonds is of the same range of the typical M-O bonds this mean that the ionic character in case of  $M(AACl)_3$  complexes is greater than the  $M(AA)_3$  complexes.

- 6- The longest bond length for  $M(AA)_3$  is M-N27 and for  $M(AACl)_3$  is M-O27. The calculated values of the bond angles (between metal ion and binding sites)  $\angle MNC$  and  $\angle OMN$ , in case of  $M(AA)_3$  vary between  $61^\circ$  and  $124^\circ$  which compare nicely with the experimental data obtained from x-ray data for  $O_h$  complexes indicates octahedral geometry. In case of  $M(AACl)_3$  complexes, the  $\angle OMO$ ,  $\angle MOC$  and  $\angle OCO$  angles vary between  $55^\circ$  and  $95^\circ$  which compare with the experimental data reported in literature.
- 7- The values of the dihedral angles around metal ion in  $M(AA)_3$  complexes, are far from  $0.0^\circ$  or  $180^\circ$  which indicate that the metal ion is not in the same plane of the donating sites. On the other hand, the dihedral angles of the  $M(AACl)_3$  complexes are  $0.0^\circ$  and  $180^\circ$  indicating that the metal ion is in the same molecular plane of the donating sites.
- 8- As the energy gap of the studied complexes decreases, the reactivity of the complexes increases. In our complexes, the reactivity follows the order:  $Tb(AACl)_3 > Sm(AACl)_3 > Tb(AA)_3 > Sm(AA)_3$ .
- 9- The complexes of  $Sm(AACl)_3$  and  $Tb(AACl)_3$  are more reactive than  $Sm(AA)_3$  and  $Tb(AA)_3$  complexes. This can be explained in terms of the energy gap which measures the reactivity, as the



energy gap decreases the reactivity increases, and the amount of electronic charge transfer from the ligand to the central metal ion.

10 -Theoretically, the reactivity of the prepared complexes follows the order:  $\text{Tb}(\text{AACl})_3 > \text{Sm}(\text{AACl})_3 > \text{Tb}(\text{AA})_3 > \text{Sm}(\text{AA})_3$  which is of the same order of the reactivity towards  $\text{G}^-$  and  $\text{G}^+$  .

11- The Mullikan electronic charge from the ligand to the central metal ion of the studied complexes follows the order:  $\text{Sm}(\text{AACl})_3 > \text{Tb}(\text{AACl})_3 > \text{Tb}(\text{AA})_3 > \text{Sm}(\text{AA})_3$  which is of the same order of the reactivity towards  $\text{G}^-$  and  $\text{G}^+$ .