



## RESEARCH ARTICLE

### STUDY OF LIGANDS COMPETITION TOWARD SOME TRANSITION METAL IONS

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#### ABSTRACT

The competition of both dimethylglyoxime (DMG) and L tryptophan (L tryp.) as ligands against three transition metals ions, Zn<sup>+2</sup>, Cd<sup>+2</sup> and Co<sup>+3</sup> were studied. FTIR, <sup>1</sup>H NMR, atomic absorption chlorine contents were used to support the final view of complexes formation. Both Zn<sup>+2</sup> and Cd<sup>+2</sup> were complexed with L tryp. While Co<sup>+3</sup> binds only with DMG. Hard soft acid base (HSAB) idea is suggested to explain the difference in binding mode of metal ions.

## INTRODUCTION

Complexes stability depend on several factors such as chelate effects, the number of chelate rings, ring size, Steric effects (Housecroft and Sharpe, 2005; Bothara, 2007; Cowan, 1997) and Hard Soft Acid Base (HSAB) principle. (HSAB) is widely published for all the metals and nonmetals as acids and bases but the classification of ligands as bases is not known (Smith and Williams, 2006; Sastri, 2011). Tri- and tetra dentate chelates increases the stability of the metal complex as a function of the number of chelate rings (Dwyer, 1964; Burger, 1973; Timothy, 2003). Complexes contain five and six membered ring are more stable than others (four, seven, eighth..etc.) (Geoffery, 2010). Ligands have bulk group substituents decrease the stability due to the repulsions between these group. Competition between ligands toward metal ions using HSAB principle is the main factor that governing the explanation of binding sites in this work.

### Experimental Section

#### 1-Reagents and Materials

ZnCl<sub>2</sub>, C<sub>2</sub>H<sub>5</sub>OH, CdCl<sub>2</sub>.2H<sub>2</sub>O and Na<sub>3</sub>Co(NO<sub>2</sub>)<sub>6</sub> are of analar grade.

#### 2- Instruments

-pH meter TWT 7110

-Sensitive balance  
-Atomic Absorption spectrophotometer- aurora –canada  
- FTIR – perkinelmer  
-<sup>1</sup>H NMR

## RESULTS AND DISCUSSION

The main observed vibrational frequencies of both ligands (DMG and L tryp.) and their corresponding assignments are given in Table 1. For DMG ligand several bands are observed, especially 3207cm<sup>-1</sup>, 1444cm<sup>-1</sup>, 2928cm<sup>-1</sup>, 1143cm<sup>-1</sup>, 758cm<sup>-1</sup> corresponding to O-H, C=N, C-H, N-O, C=N-O stretching respectively (Wagner and Baran, 2004; Rao *et al.*, 2013; Jadhav *et al.*, 2013; Osunlaja *et al.*, 2009; Shaker, 2010) while the following bands: N-Hindol (3209cm<sup>-1</sup>), NH<sub>2</sub>as(3356 cm<sup>-1</sup>), NH<sub>2</sub>s(3315cm<sup>-1</sup>, C-H(2978cm<sup>-1</sup>), C-N (1049 cm<sup>-1</sup>), C=O(1695cm<sup>-1</sup>) are assigned to L-trypt. Groups (Corbeil and Beauchamp, 1988; Patil *et al.*, 2011; Quyoom, 2014; Kasarc *et al.*, 2013). The important bands of the all studied complexes are shown in table (2). It is clearly shown that Cd<sup>+2</sup> and Zn<sup>+2</sup> are coordinated to L tryp. only due to the shifted observed of amine groups to the higher frequency and the appearance of COO<sup>-</sup>as and COO<sup>-</sup>s which confirm the deprotonation of carboxylic group and coordinated with metal ion through negative oxygen. Cobalt is the only one ion that coordinated with the two nitrogen atoms of DMG. Also, the obtained data confirm the presences of water molecules in the cobalt and cadmium ions complexes.

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**Table 1. Vibrational frequencies of DMG and L-tryp**

DMG	O-H	C=N	C-H	N-O	C=N-O	.....
	3207	1444	2928	1143	758	.....
L-tryp.	N-Hindol	NH <sub>2</sub> <sub>as</sub>	NH <sub>2</sub> <sub>s</sub>	C-H	C-N	C=O
	3209	3356	3315	2978	1049	1695

**Table 2. Vibrational frequencies of DMG and Tryp. and their corresponding metal complexes**

Ligand and their complexes	NH <sub>2</sub> <sub>as</sub>	NH <sub>2</sub> <sub>s</sub>	COO <sub>as</sub>	COO <sub>s</sub>	C=N	N-O	H <sub>2</sub> O <sub>wag</sub>	M-O	M-N
Try.	3356, 3315	-----	-----	-----	-----	-----	-----	-----	-----
DMG	-----	-----	-----	-----	1444	1144	-----	-----	-----
Zn <sup>+2</sup>	3474, 3368	-----	1621	1474	-----	-----	-----	621	509
Co <sup>+3</sup>	-----	-----	-----	-----	1564	1093	838	-----	520
Cd <sup>+2</sup>	3537, broad*	-----	1580, 1411	-----	-----	-----	845	617	465

**Table 3. <sup>1</sup>H NMR signal of DMG and Try**

ligand	N-H	Ar- proton	N-H amine	CH <sub>3</sub>	C-H alpha	CH <sub>2</sub> beta	C-H gama	C-H sigma	
Try.	-----	11,09	6,52- 7,72	6,05	-----	4,53	3,22-3,38	-----	----
DMG	11,28	-----	-----	-----	1,9	-----	-----	-----	----

**Table 4. <sup>1</sup>H NMR signal of DMG and Try and their corresponding metal complexes**

	NH <sub>2</sub>	C-H alpha	Ar- proton	CH <sub>3</sub>
Tryp.	6,05	4,53	6,52-- 7,72	-----
DMG	-----	-----	-----	1,90
Zn <sup>+2</sup>	6,03	4,46	6,50--7,72	-----
Co <sup>+3</sup>	-----	-----	-----	2,23
Cd <sup>+2</sup>	5,98	4,40	6,48-6,62	-----

**Table 5. Metal and chlorine contents in the complexes**

Chemical formula	Chlorine%		Metal%		M:L ratio
	Calc. %	found%	Calc.	found	
[Zn(tryptophan)Cl <sub>2</sub> ]	20,2	18,8	19,2	20,3	1:1
[Co(DMG) .2H <sub>2</sub> O]	0	0	27,92	29,1	1:1
[Cd(tryptophan)H <sub>2</sub> O.Cl]	9,604	8,9	30,4	30,9	1:1

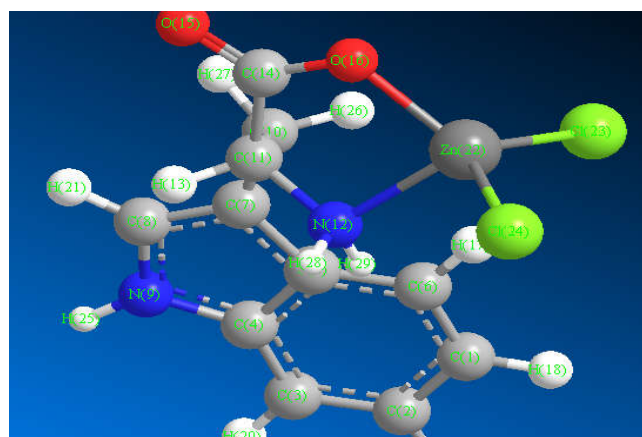
**Table 6. HSAB classification of ions and ligands**

Zn <sup>+2</sup> + Tryptophan + DMG	Zn <sup>+2</sup> + Tryptophan	Softer- Softer
Co <sup>+3</sup> + Tryptophan + DMG	Co <sup>+3</sup> + DMG	Harder - harder
Cd <sup>+2</sup> + Tryptophan + DMG	Cd <sup>+2</sup> + Tryptophan	Softer- Softer

### <sup>1</sup>H NMR study

Table (3) and (4) record the chemical shifts of the all signals referring to the ligands and their corresponding metal ions complexes formed. It is clearly confirmed from the data obtained that both Zn<sup>+2</sup> and Cd<sup>+2</sup> are coordinated to L tryp. Only due to the appearance of aromatic protons in their <sup>1</sup>H-NMR spectrum of tryptophan complexes which are absent in Co<sup>+3</sup> complex. Another evidence is the signal of methyl group which is observed upfield shift from 1.9 ppm to 2.23 ppm. Despite the importance of O-H proton belonged to DMG but their interaction by hydrogen bonding leads to disappearance of this signal. As seen in table-5 the obtained results refer to the 1:1 metal ratio of the all complexes in the addition of metal and chlorine contents in each one. Figures (2-4) show the geometries of each studied complex. The competition between ligands toward metal ions is governed by the hard soft acid base (HSAB) principles. It can be classified the studied metal ion as follows: Co<sup>+3</sup> (hard acid), Zn<sup>+2</sup> (border line acid), Cd<sup>+2</sup> (soft acid). It is not easy to classify the studied ligands due to HSAB theory but it can be concluded that DMG

is a harder base than L tryp. And this suggestion can be confirmed by its coordination with hard acid Co<sup>+3</sup>, while the other two ions Zn<sup>+2</sup> and Cd<sup>+2</sup> coordinate with L tryp. Which can be suggested as the softer ligand.

**Fig. 1. Geometry of zinc complex**

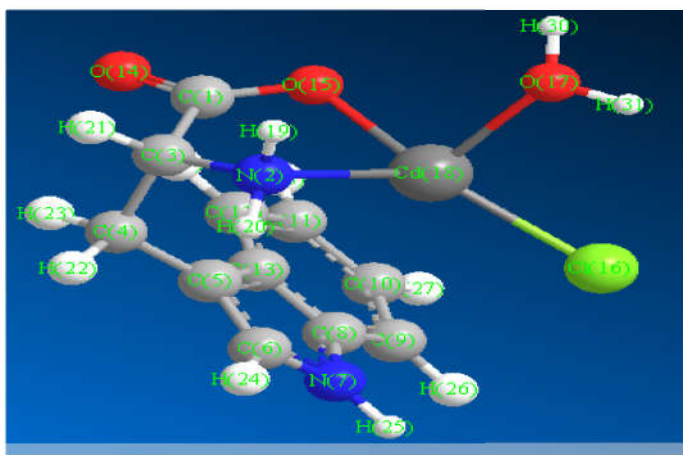


Fig. 2. Geometry of cadmium complex

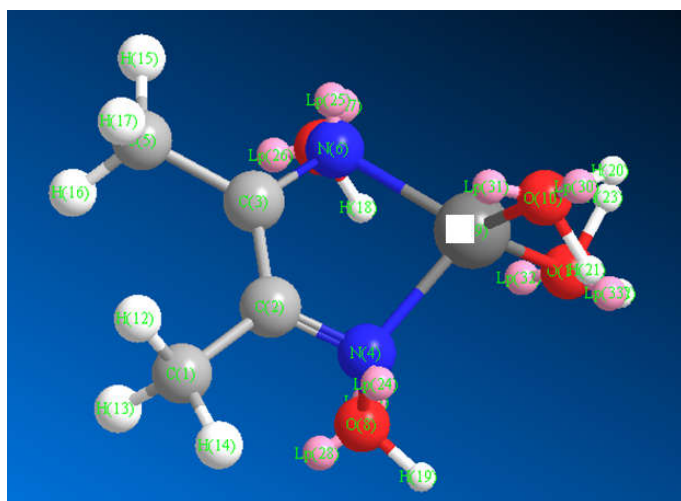


Fig. 3. Geometry of cobalt complex

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