

## Computation studies on Schiff base ligands and equilibrium studies on their metal complexes

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**Abstract :** Schiff bases of furfural with L-threonine (thr) and L-glutamine (gln) were studied by quantum mechanical method using GAMESS program. Geometry of the Schiff bases was optimized by HF and MP2 methods. The Schiff bases are non-planar. Based on the Mulliken's charge density calculations, furan oxygen, imino nitrogen and carboxylato oxygen atoms were found to be the potential binding sites. Equilibrium studies of Co<sup>II</sup>, Ni<sup>II</sup>, Cu<sup>II</sup> and Zn<sup>II</sup>-furfural (A)-L-threonine (thr), L-tryptophane (trp) and L-glutamine (gln) (B) systems were done by batch wise titration method at 25 °C and ionic strength of 0.1 M (KNO<sub>3</sub>). All the systems have MAB, MAB<sub>2</sub> or M(AB)<sub>2</sub> types of Schiff base complexes. The results indicate that the Schiff base (AB) binds to the metal ions in terdentate manner through furan oxygen, imino nitrogen and carboxylato oxygen atoms.

**Keywords :** Computation, equilibrium, Schiff base, furfural, amino acid, potentiometry.

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### Introduction

Furfural is an important compound extensively used in the plastic, oil and cosmetic industries<sup>1-3</sup>. Schiff bases derived from furfural have antifungal and antitumor activities<sup>4-6</sup>. In view of the growing interest in the study of Schiff base of furfural<sup>7,8</sup>, the present paper reports the computation study of Schiff base ligands and complexes of furfural with L-threonine (thr) and L-glutamine (gln). Also, the equilibrium studies on the complexes of Co<sup>II</sup>, Ni<sup>II</sup>, Cu<sup>II</sup> and Zn<sup>II</sup> with three Schiff bases furfural-thr, furfural-trp and furfural-gln are reported.

### Results and discussion

**Theoretical studies on the binding tendency of the Schiff base ligands :** The structure of the ligands is given in Fig. 1 and their computed important parameters are given in Table 1. The furan oxygen and imino nitrogen are distorted from planarity by ~ 14°. This distortion is mainly due to repulsive force generated between furan oxygen and imino nitrogen. Mulliken charge density on the O<sub>11</sub> and N<sub>7</sub> atoms of Schiff bases is increased and decreased respectively than their corresponding amino acid. This is due to the formation of Schiff base. The HF enhanced stability due to denticity reduction and the formation of Schiff base between furfural-thr and furfural-gln is 10.92

and 16.27 kcal/mole respectively. The Schiff bases are potentially tridentate and they bind to the metal ion through carboxylato oxygen, furan oxygen and imino nitrogen. Based on the charge density, the binding ability of the hetero atoms in the Schiff base (Table 1) is of the order : carboxylato oxygen > furan oxygen > imino nitrogen.

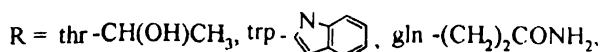
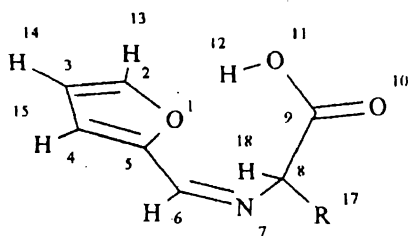
**Solution studies :** The M<sup>II</sup>-Schiff base systems (M<sup>II</sup> = Co, Ni and Zn) showed the presence of MAB, MAB<sub>2</sub> and M(AB)<sub>2</sub> Schiff base complexes, while Cu<sup>II</sup> systems showed only MAB species.

**Stability and structure of MAB species :** From the log β<sub>MAB</sub> values (Table 2) and the Scheme 1, it is clear that the ternary species are more favoured compared to binary complexes. Moreover, the presence of one ligand in the metal coordination sphere enhances considerably the addition of the other ligand to the metal ion. To be more specific, the presence of furfural in the coordination sphere of metal favours the coordination of amino acid and leads to the formation of Schiff base.

The experimental log β<sub>MAB</sub> values for Co<sup>II</sup>-furfural-thr, trp and gln systems are 10.31, 9.85 and 10.23 respectively. The CoAB complex may be a mixed ligand complex rather than a Schiff base species. If it is mixed

Table 1. Important parameters of furfural-thr and gln Schiff bases

Schiff base	RHF/6-31G*					MP2/6-31G*				
	Dihedral (°)		Charge (-)			Dihedral (°)		Charge (-)		
	C <sub>4</sub> -C <sub>5</sub> -C <sub>6</sub> -N <sub>7</sub>	N <sub>7</sub> -C <sub>8</sub> -C <sub>9</sub> -O <sub>11</sub>	O <sub>1</sub>	N <sub>7</sub>	O <sub>11</sub>	C <sub>4</sub> -C <sub>5</sub> -C <sub>6</sub> -N <sub>7</sub>	N <sub>7</sub> -C <sub>8</sub> -C <sub>9</sub> -O <sub>11</sub>	O <sub>1</sub>	N <sub>7</sub>	O <sub>11</sub>
fur-thr	167.0542	-73.7981	0.6270	0.4778	0.7264	164.9884	-71.7901	0.6460	0.4805	0.7431
fur-gln	168.3452	-77.9101	0.6289	0.4772	0.7315	166.8590	-79.8538	0.6500	0.4827	0.7506



Optimized geometry

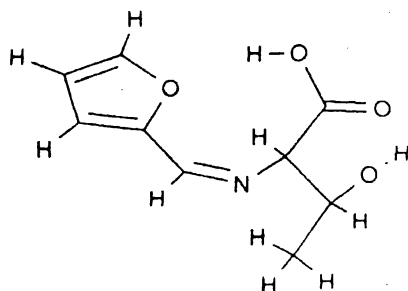
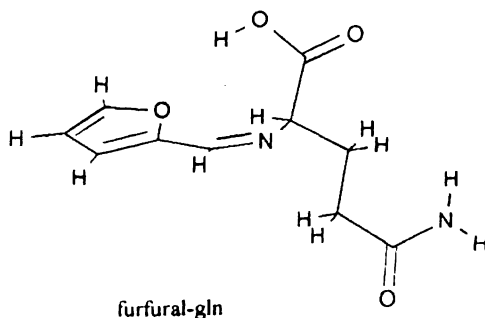


Fig. 1. Structure of Schiff base ligand furfural (A)-thr, trp and gln (B).

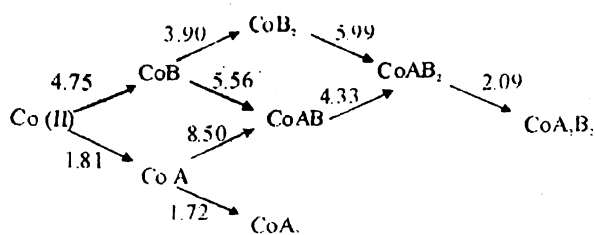
ligand complex, the calculated overall formation constants would be 6.39, 6.08 and 7.57 log units for Co<sup>II</sup>-furfural-thr, trp and gln systems respectively. This enhancement in the stability is due to the strong inter-ligand interaction between furfural and amino acid, leading to the formation of Schiff base.

When compared to Co<sup>II</sup>-furfural-valine<sup>9</sup> system the stability constant value for CoAB species of Co<sup>II</sup>-furfural-thr is greater by 0.58 log units. This enhancement is less to consider for the involvement of the additional coordination site of hydroxyl group in thr<sup>10</sup>. But this increment can be attributed to the molecular recognition caused by intermolecular hydrogen bonding formed between the free hydroxyl groups of the neighbouring complex species<sup>10</sup>. Hence, it has been concluded that the Schiff base is tridentate and binds through furan oxygen, carboxylato oxygen and imino nitrogen.

Again, the log β<sub>MAB</sub> value for furfural-trp system is slightly greater than that in furfural-valine system<sup>9</sup>. This small increment is not enough to consider for an additional bonding site in trp system. This enhancement may also be described by considering the presence of molecular recognition through intermolecular interaction through indole moiety<sup>11</sup>. Similar to furfural-thr system, the Schiff

Table 2. Stability constants M<sup>II</sup>-furfural (A)-thr, trp and gln (B) Schiff base complex systems

Parameter		Co <sup>II</sup>	Ni <sup>II</sup>	Cu <sup>II</sup>	Zn <sup>II</sup>
thr	log β <sub>MAB</sub>	10.31	11.92	17.24	10.48
	log β <sub>MAB<sub>2</sub></sub>	14.64	16.36	-	14.85
	log β <sub>MA<sub>2</sub>B<sub>2</sub></sub>	16.73	18.68	-	16.81
trp	log β <sub>MAB</sub>	9.85	11.43	16.36	9.98
	log β <sub>MAB<sub>2</sub></sub>	14.08	15.83	-	14.26
	log β <sub>MA<sub>2</sub>B<sub>2</sub></sub>	16.03	18.07	-	16.06
gln	log β <sub>MAB</sub>	10.23	11.88	17.15	10.36
	log β <sub>MAB<sub>2</sub></sub>	14.56	16.32	-	14.76
	log β <sub>MA<sub>2</sub>B<sub>2</sub></sub>	16.58	18.63	-	16.67



(A) furfural, (B) thr, (AB) Schiff base

Scheme 1. Stepwise formation of various species.

base ligand also binds to the metal ion in tridentate manner through carboxylato oxygen, furan oxygen and imino nitrogen. The stability constant value of MAB of  $\text{Co}^{\text{II}}$ -furfural-gln system is 0.50 log units greater than the corresponding  $\text{Co}^{\text{II}}$ -furfural-valine system<sup>9</sup>. This increment is due to molecular recognition through amide group<sup>12</sup>.  $\text{Ni}^{\text{II}}$ ,  $\text{Cu}^{\text{II}}$  and  $\text{Zn}^{\text{II}}$  complexes follow the similar trend.

The MAB species is predominant in 1 : 1 systems between 6.5 and 7.7 pH ranges with the maximum of ~70% of total metal ion concentration.  $\text{CuAB}$  is dominant in the lower pH range of 4.6 to 6.3 with the maximum of ~80%.

**Stability and structure of  $\text{MAB}_2$  species :** The overall formation constant of  $\text{CoAB}_2$  species is 14.64, 14.08 and 14.56 log units respectively for furfural-trp, thr and gln systems. These higher values indicate that  $\text{CoAB}_2$  is a mixed ligand complex of the type  $\text{Co}(\text{AB})\text{B}$ . Further log  $\beta_{\text{MAB}_2}$  values of  $\text{M}^{\text{II}}$ -furfural-valine systems are comparable with the above systems. Hence it can be concluded that the Schiff base AB behaves as tridentate ligand and trp, thr or gln is bidentate.  $\text{MAB}_2$  species is found to be formed above pH 7.5 and its concentration increases with the increase of pH.

**Stability and structure of  $\text{MA}_2\text{B}_2$  species :** The stability constant values of  $\text{CoA}_2\text{B}_2$  species of  $\text{Co}^{\text{II}}$ -furfural-thr, trp and gln systems are 16.73, 16.03 and 16.58 log units respectively. These higher values imply that they are Schiff base complexes. The Schiff bases AB can coordinate in tridentate mode through furan oxygen, imino nitrogen and carboxylato oxygen. The  $\text{Ni}^{\text{II}}$  and  $\text{Zn}^{\text{II}}$  complexes follow the same trend. In 1 : 2 systems  $\text{M}(\text{AB})_2$  is the dominant species formed above pH 6.5 and reaches a maximum of ~70% of the total metal ion concentration. The stability of the complexes follows Irving-Williams order as :  $\text{Co}^{\text{II}} < \text{Ni}^{\text{II}} < \text{Cu}^{\text{II}} > \text{Zn}^{\text{II}}$ .

## Experimental

*Ab initio* calculations were carried out using GAMESS program<sup>13</sup>. The 6-31G\* basis set<sup>14</sup> was used in the calculations. All the chemicals used were of A.R. grade. The ligands were obtained from Sigma. Metal ions were used in the form of their nitrate. The pH measurements were done using a digital pH meter (M/s. Systronics, Model 335) with an accuracy of  $\pm 0.01$  at 25 °C and  $I = 0.1 \text{ mol dm}^{-3}$ . Calculations were carried out with the help of computer program designed for the evaluation of Schiff base complex equilibria<sup>15</sup>. The auxiliary data for the binary complexes used under the present experimental conditions were taken from the literature<sup>16</sup>.

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