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Studies on the formation of metal complexes with trifluoroacetylacetone in presence of other bioligands in solution - pHmetry

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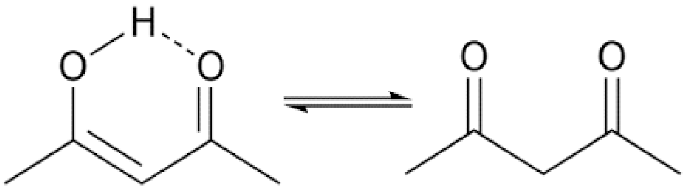
ABSTRACT

Stabilities associated with complexation between trifluoroacetylacetone and bivalent metal ions in presence of other biologically important ligands such as N,N donors(1,10-phenanthroline or 2,2-bipyridyl) N,O donors(amino acids) at $T=30^0C$ and $\mu = 0.1$ M (KNO_3) in aqueous media are measured potentiometrically. The effect of trifuoro groups are discussed by comparing the ternary stability data of acetylacetone with trifluoroacetylacetone in similar experimental conditions.

Key words: Stability constant , pH metry ,Trifluoroacetylacetone.

INTRODUCTION

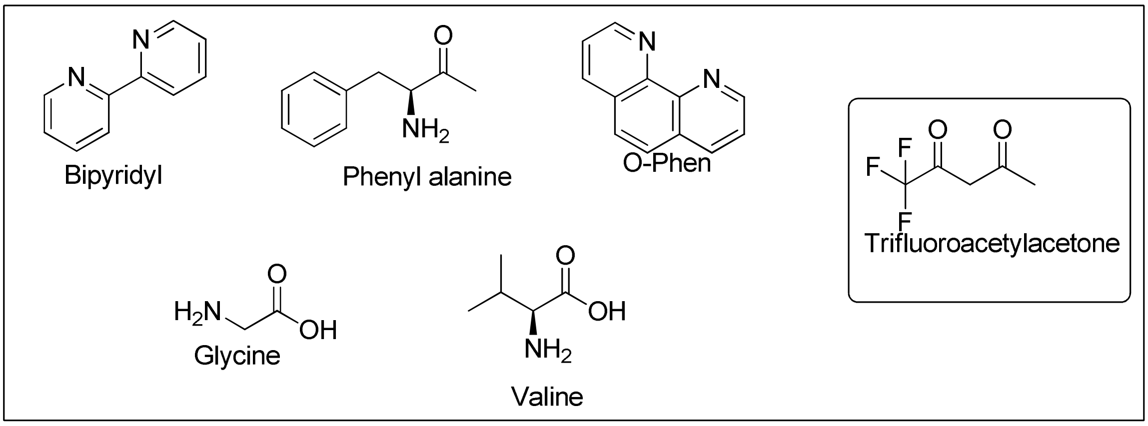
Hydrogen bonding is one of the most prominent of all inter and intramolecular interactions. It is an important phenomenon in many chemical and biological systems and plays a key role in the chemistry of living systems. A particular situation could be created by intramolecular hydrogen bonds (IHBs), when two functional groups of the same molecule interact, resulting in a ring like structure. β-Dicarbonyl compounds, as interesting examples, display a tautomeric equilibrium between the keto and the enol forms. The chelated *cis* enol form is stabilized by a strong intramolecular hydrogen bond (1-4)and is predominant in the gas phase and in solution with low dielectric constant (5-6). The simplest members of this class of compounds are malonaldehyde(MA) and acetylacetone (AA), well known both by experimental and theoretical studies to adopt an asymmetrical in their most stable conformation(7-13).



Enolic form and General structure of Acetylacetone

In view of its catalytic activity with different metal ions, the present pH metric work is undertaken. The trifluoroacetylacetone was allowed to react with different metal ions in presence of other ligands viz., bipy,o-phen,glycine,phenylalanine and valine. The stabilities of the thus formed ternary complexes are evaluated andcompared to check the factors by which they are governed.

Ligandsstructures



MATERIALS AND METHODS

The ligands,glycine,valineL-phenylalanine were obtained from Fluka (Switzerland). Trifluoro acetyl acetone and Bipyridyl,1-10 Phenanthroline obtained from Sigma-Aldrich. The metal salts of Co^{2+}, Ni^{2+}Cu+^{2}and Zn^{2+} are of AnalaR grade and their solution are standardized volumetrically by titration with the sodium salt of EDTA (14). Potentiometric measurements are carried out at 30^{o}C in aqueous medium (with 0.1 moldm^{-3} (KNO_3) as background electrolyte) using control dynamics pH meter. The pH meter readings are plotted against a (moles of base added per mole of ligand) or m (moles of base added per mole of metal ion). Calculations are carried out with the help of computer program – BEST (15).

RESULTS AND DISCUSSION

Acid Dissociation Constants(a) Trifluoroacetyl acetone: the free ligand titration curve (HL^{+}) of this ligand show inflection at a=1, followed by a buffer region in higher pH. The pKais calculated in the region a = 0 to a = 1 respectively.

(b)bipyridyl/1-10phenanthroline/glycine/valine/l-phenylalanine:Free ligand titration curves of all these lignads show a single inflection at a = 1.The constants calculated in the buffer region a = 0 to a = 1 are presented in Table 1. The values are good agreement with values found in literature (16-19).The titration curves of ternary complexes of TFAA (Trifluoroacetyle acetone),bipy,and Cu^{+2}are given in Fig.1 along with other curves.

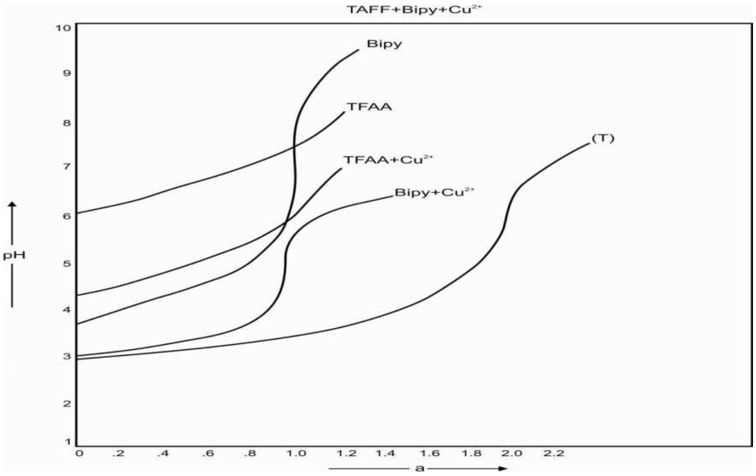


Table 1: Logorithms of the stability constants of different systems

Temp: 30°; μ = 0.1 M (KNO_3), aqueous medium

Ligands	pKa	pK_{2a}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
Trifluoroacetyl acetone	6.53 ± 0.03	-	3.60 ± 0.02	3.73 ± 0.02	4.93 ± 0.01	2.86 ± 0.04
Bipy	4.35 ± 0.01	-	6.86 ± 0.09	7.55 ± 0.09	7.19 ± 0.09	6.00 ± 0.1
O-phen	4.95 ± 0.01	-	7.02 ± 0.03	7.29 ± 0.07	7.30 ± 0.09	7.25 ± 0.08
Glycine	9.53 ± 0.04	-	5.10 ± 0.03	5.89 ± 0.08	8.10 ± 0.02	5.46 ± 0.06
Valine	9.23 ± 0.07		4.66 ± 0.09	7.70 ± 0.04	5.26 ± 0.09	5.60 ± 0.08
L-Phenyl alanine	9.06 ±0. 02		4.13 ± 0.08	4.99 ± 0.06	6.73 ± 0.09	4.43 ± 0.09

Binary Complexes

(a) M^{2+}-trifluoroacetylacetone: Potentiometric titration curves of M^{2+}-trifluoroacetylacetone in 1:1 ratio shows a inflection at m=1 followed by a buffer region. The separate of (M-L) curve from the free ligand curve is small, suggesting complex formation with low stability constants. The stability constants obtained and presented in Table I are in good agreement with literature values (16-17).

(b)M^{2+}bipy/o-phen/gly/valin/l-phenylalanine: Potentiometric titration curves of M^{2+}-bipy,o-phen, glycine, valine(vln),l-phenylalanine(l-pa) in 1:1 ratio show a single inflection at m = 1. The stability constants calculated in the buffer region m=0 to m=1 are presented in Table-1.

Ternary Complexes

M^{2+} -tfaa and bipyridyl/o-phen/glycine/valine/l-phenylalanine: The potentiometric titration curves of the ternary complexes in 1:1:1 ratio show a inflection at m = 2 indicating the step-wise coordination. The constants are calculated in the buffer region m=1 to m=2, using the pKa of trifluoroacetylacetone and pKa of BIPY(or)O-PHEN(or)GLYor)VLN(or)L-PA and tfaa in simultation.. The values then obtained are presented in Table 2.

Table 2: Logorithms of the stability constants of ternary complexes of bivalent metal ions
Temp: 30°; μ = 0.1 M (KNO_3), aqueous medium

Ligand combinations	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
TFAA+Bipy	4.27 ± 0.05	5.05 ± 0.09	6.17 ± 0.07	3.85 ± 0.08
TFAA+O-Phen	4.35 ± 0.04	4.89 ± 0.09	6.23 ± 0.08	4.22 ± 0.03
TFAA+Gly	4.91 ± 0.04	5.34 ± 0.07	6.39 ± 0.06	5.23 ± 0.05
TFAA+Valine	4.14 ± 0.07	4.50 ± 0.05	5.55 ± 0.04	4.89 ± 0.09
TFAA+L-phenyl alanine	4.61 ± 0.07	4.88 ± 0.05	5.94 ± 0.02	4.98 ± 0.01

The Concept of Δlog K

The relative stability of the ternary metal complexes (MLA) as compared that of the corresponding binary complexes have been quantitatively expressed in terms of the parameter Δ log K, given by the Eq.1.

$$\Delta \log K = \left|\log K^{MA}_{MLA} - \left(\log K^{M}_{MLA} + \log K^{M}_{MLA}\right)\right| \qquad \ldots 1$$

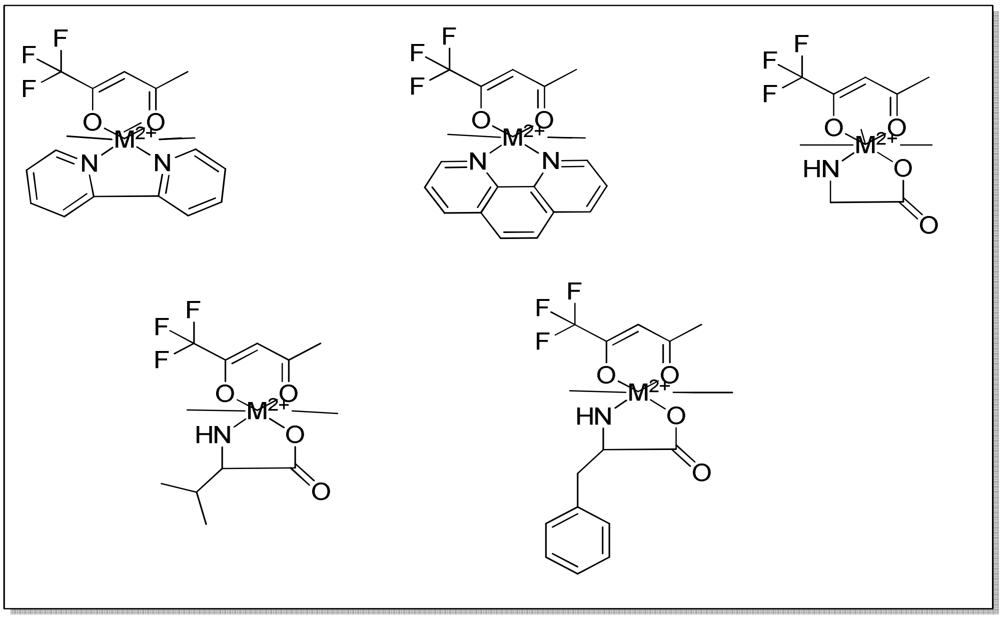
In case of trifluoroacetylacetone (TFAA) complexes, TFAA binds to the metal through oxygen . The statistically expected Δ log K value for the interaction of two different bidentate ligands with square planar (or) distorted octahedral metal ion are -0.6 or 0.9 respectively.

The Δ log Kvalues for ternary complexes containing bipy,o-phen, and gly,valine,l-phenylalanine are more negative (Table 3) when compared to either(a), Δ log K value of AA values expected on the stasticalgrounds reflecting the extensive destabilization of these complexes. This destabilization is due to electrostatic repulsion between the negatively charged oxygenatoms of tfaa and glycine/valine/l-phenylalanine. The more destabilization of fluorine atoms which makes tfaa and consequently less stable metal complex.

Table 3: µ log K values of ternary complexes of bivalent metal ions

Ligand combinations	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
TFAA + Bipy	+0.97	+1.68	+1.15	+1.49
TFAA+O-Phen	+1.05	+1.52	+1.21	+1.86
TFAA+Glycine	-0.19	-0.55	-1.71	-0.37
TFAA+Valine	-0.52	-1.5	-2.15	-0.37

The sequence of stability of ternary complexes with respect to their ligands decrease in the order :bipy>o-phen>phenylalanine>gycine>valine. The tentative structures of ternary complex is shown in Fig.2.



The stability constants of ternary complexes of bivalent metal ions is in the order Cu^{2+}> Ni^{2+}> Co^{2+}> Zn^{2+}. This order is comparing with Irving-William's natural order of stabilities.

Distribution Diagrams

From a knowledge of proton-ligand and metal-ligand formation constants, the distribution of the total metal among the various metal-ligand species as a function of pH has been calculated by a computer programme BEST **(15).** As a representative case, the distribution diagram for (trifluoroacetylacetone + Cu^{+2} + bipy) system along with relevant data is given in Fig.2.

The maximum percentage of the Cu-bipy(or) ML is 16.2 at pH5 as the pH increase the percentage of ML reaches minimum. The other binary species (Cu-tfaa) has attained maximum percentage of 72.5 at pH 5.6. After pH 4 the formation of ternary complex has started (appearance of curve MLA) and percentage goes on increasing with increase in pH with simultaneous decrease in percentage of both binary species (i.e., MA and ML).Thespecies is the only predominant species in higher pH.

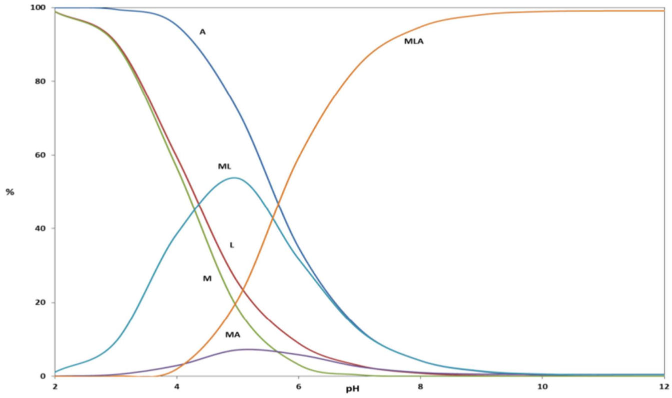


Fig.3: BEST (SPE) computed distribution of complex species with pH for [TFAA-Cu2+-bipy] complex

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