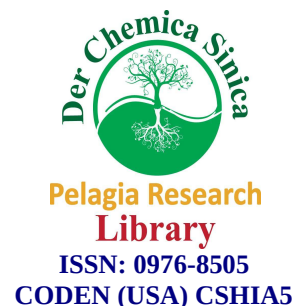




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Der Chemica Sinica, 2013, 4(3):10-13



Physico-chemical studies of the complexes of 2-carboxyphenylhydrazo-acetoacetanilide (2-CPHAAA) with Cu(II), Ni(II), Mn(II), and Co(II) ions in ethanol-water mixed solvent system

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ABSTRACT

Potentiometric titrations have been used to calculate the dissociation constants of 2-Carboxyphenylhydrazoacetoacetanilide (2-CPHAAA) and its stability constants with Cu(II), Ni(II), Mn(II), and Co(II) ions in ethanol-water mixed solvent system at different temperatures, and constant ionic strength of 0.1M solution sodium nitrite.

Key words: β -diketones, metal complexes, stability constant.

INTRODUCTION

Classical diketones and related ligands have been studied for more than a century and their ability to give rise to rich and interesting coordination chemistry is well documented [1-3].

In the last decades, β -diketones and their metal complexes have been used as chelating ligands for lanthanides and transition metals.[4] β -diketones are bidentate ligands with the possibility of complexation with almost all the metal ions. The nature of bonding and chelation was elucidated by Werner and Morgan.[5] A wide variety of β -diketones with different substituents and their complexes have been synthesized and their properties such as volatility, Lewis acidity or aggregation state, standard molar enthalpies of formation, standard molar enthalpies of sublimation, vapour pressures, and enantioselective catalytic property have been studied.[6,7]

β -diketone and their metal complexes are among the most widely studied coordination compounds since they have wide application in the industry.[8]

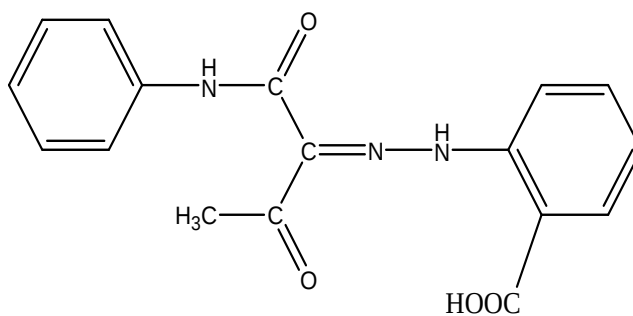
MATERIALS AND METHODS

Materials

Most of the chemicals used were of Analar grade, materials which are not generally provided into Analar grade were of the highest available purity.

Preparation of 2-CPHAAA

The ligand under investigation was prepared by coupling the diazonium salt of 2-aminobenzoic acid with acetoacetanilide in sodium acetate medium to give 2-Carboxyphenylhydrazoacetoacetanilide (2-CPHAAA). The crude product was recrystallized several times from dioxane. Yellow crystals have been collected filtered and dried the melting point was 145°C. The results of elemental analysis were as follows: %cal./(found), %C 62.8/(63.02), %H 4.62/(4.85), and %N12.92/(12.78).[9]



Structure of 2-Carboxyphenylhydrazoacetanilide (2-CPHAAA)

Procedure

A 7.50ml of 0.2M ligand solution in ethanol was placed in a dry titration vessel, to which was added 15ml of pure ethanol, 0.75ml of 0.1M metal salt solution and 3ml of 1.0M KNO₃. The volume is made to 30ml by addition of doubly distilled water. The solution gives a ligand concentration 5×10^{-3} M and metal ion 2.5×10^{-3} M at ionic strength 0.1M KNO₃ in 75% ethanol-water. The pH of the solution was read after each addition of base (KOH 0.091M in 75% ethanol-water) using a digital Philips-PW 9409 pH-meter. In case of free ligand titration no metal ion was added.

RESULTS AND DISCUSSION

The pH-metric titration curves of 2-CPHAAA ligand in absence and presence of metal ions are shown in figure (1).

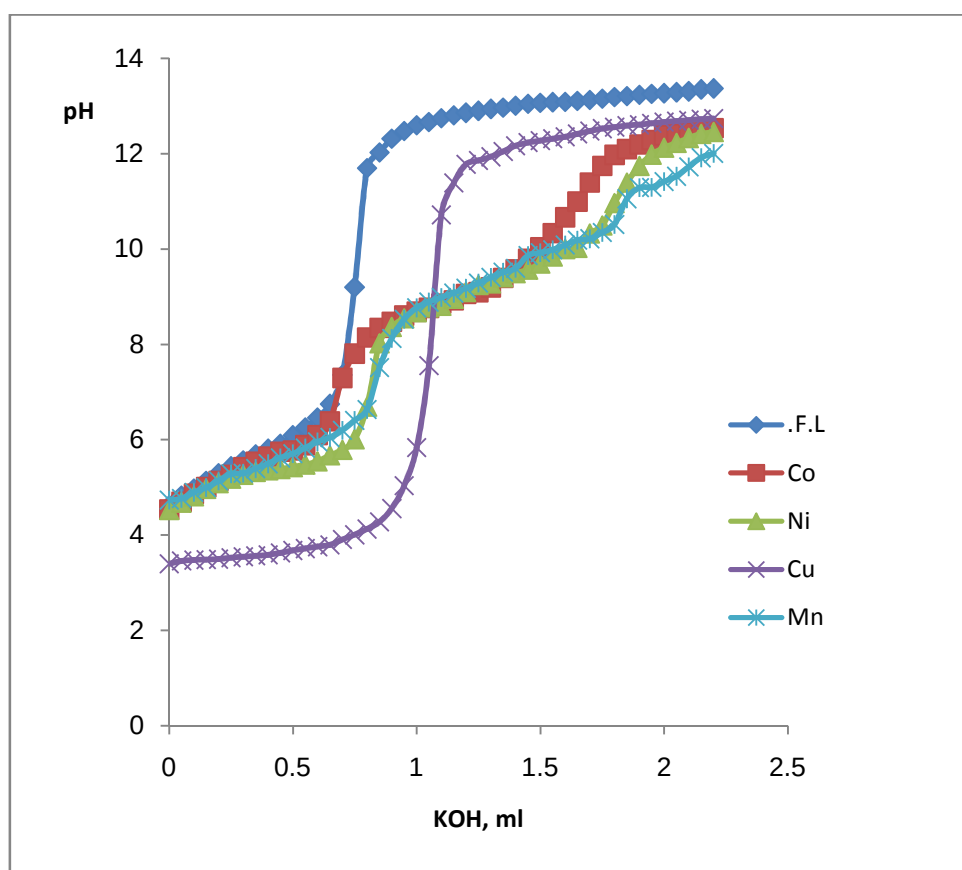


Figure (1): Potentiometric titration curves of 2-CPHAAA ligand in absence and presence of metal ions at 25°C.

The proton dissociates from ortho substituted carboxyl group between $a=0$ and $a=1$ (where a is the number of moles of KOH added/ moles of ligand). At higher pH values, second additional proton dissociates from hydrazo group at $a=2$. The first and second ionization constants were calculated at different temperatures and in 75% ethanol-water. Table 1 shows a set of values for first and second dissociation constants of the ligand at different temperatures.

The dissociation of ortho carboxy substituent group is acidic compared to the corresponding value for benzoic acid under similar conditions. This is may be due to the withdrawing effect of the Azo group in ortho position which facilitates the separation of the proton.

The higher basicity of hydrazo group is due to the presence of carboxylate anion in ortho position as repelling group which increase of the electron density on hydrazo nitrogen leading to the retardation of deprotonation. The formation of strong hydrogen bond and the anion also retards the deprotonation.

Table.1 Dissociation constants for 2-CPHAAA ligand at different temperatures

15°C		25°C		35°C		45°C	
pK _{a1}	pK _{a2}	pK _{a1}	pK _{a2}	pK _{a1}	pK _{a2}	pK _{a1}	pK _{a2}
7.2	12.88	6.07	12.81	5.96	12.77	5.88	12.59

The calculation of overall stability constants of the formed complexes were carried out using standard procedure given by Irving and Rossotti.[10] This method is based on the calculation of the average number of ligand molecules bound per metal ion, n^- , and the free ligand concentration, $[A^-]$, and then the data plotted graphically for some metal ion chelates at certain temperatures. The calculated values are listed in table (2).

Table.2. Overall stability constants values at 25°C

Metal Ion ²⁺	Cu	Ni	Mn	Co
Overall stability constants	13.95	11.58	10.70	9.76

The order of stability for the studied complexes was as following: Cu > Ni > Mn > Co. This finding is in agreement with that of Williams and Irving [11], except the position cobalt. Copper complex is more stable due to the tetragonal distortion of the octahedral symmetry in the coordination sphere.[12-17]

The values of ΔG at 25°C of the formed complexes have been calculated using the following formula

$$\Delta G = -2.303RT \log K$$

Were T=298 k and R=8.314J/k.mol. The values are presented in table (3).

Table.3. ΔG values of the complexes at 25°C

Metal Ion ²⁺	Cu	Ni	Mn	Co
ΔG (KJ/mol)	- 79.596	- 66.073	- 61.052	- 55.689

The negative indicate the spontaneity of the complex formation process.

CONCLUSION

The results of the potentiometric studies on 2-CPHAAA and its complexes with Cu(II), Ni(II), Mn(II), and Co(II) in 75% v/v ethanol-water medium using pH titration technique indicates that the order of stability is Cu > Ni > Mn > Co. The negative free energy change indicates the spontaneity of the complex formation process.

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