Asian Journal of Chemistry Vol. 20, No. 7 (2008), 5497-5502

Study of Stability Constants of Some of the Transition Metal Complexes with β-Diketones by Spectrophotometery

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In this study, the complexes of acetyl acetone(acac) with Cu(II), Cr(III) and Fe(III) cations were synthesized and their visible spectrum were recorded. The maximum wavelength of absorption was derived from the recorded spectrum. Using from procedure of continues variations (Job method) in maximum wavelength, optimized pH was formed; the complex and stoichiometry were defined. The stability constants of these complexes were determined by UV-Vis spectrometry. The other derivatives of acetylacetone such as benzoylacetone (Bac) and benzoyltrifluoroacetone (Btfac) were also determined. On the other hand, further study about the systems of water and water-ethanol 50 % and water-dioxane 75 % solution were also performed. The results show that benzoylacetone complexes are more stable than the benzoyltrifluoroacetone complexes. For the mentioned complexes, the arrangement of the solvent systems were as follow: water < water-dioxane 75 % < water-ethanol 50 %.

Key Words: Spectrophotometery, Stability constants, Transition metal complexes, β-Diketones.

INTRODUCTION

A number of β-diketones and their complexes have been studied because of their interesting and important properties[1,2]. By determining the stability constant, a clear prediction about the coordinating ability in the stability of metal complexes may be provided. Each parameter which is altered due to the complex formation, provides the possibility of studying the structure of complex. Legrand and his collogues[3] studied the chelates of β-diketone with the bivalent intermediate elements in the binary system of water and dioxane.

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Investigation about thermal stability of β-diketones including acetyl acetone (acac) and benzoyltrifluoroacetone (Btfac) with vanadium in benzene and nitrobenzene was carried out by Carlin and Walker[4]. Izzat *et al.*[5] studied the stability constant of bivalent and trivalent intermediate ions and Th(IV) with acetylacetone in water and dioxane. Stanely and Manoranjan[6] studied about the substitution effect of phenyl group on dipolar momentum for some metal complexes of β-diketones with Rh^{2+}, Co^{2+}, Zn^{2+}, Cu^{2+}, Pt^{2+}, Pa^{2+}, Ni^{2+}. Richard *et al.*[7], investigated about the presence of various substitutions in the structure of β-diketones by NMR. They studied the correlation of chemical shift with the acidity dissociation constant of ligand and stability constant of complex.

In this study, the stability of complexes including acetylacetone, benzoylacetone and benzoyltrifluoroacetone with the cations involving Fe(III), Cr(III), Cu(II) in water-ethanol 50 % and water-dioxane 75 % were examined by using the UV-Vis spectrophotometric method[8].

EXPERIMENTAL

All chemicals are AnalaR grade. $CuCl_2·2H_2O$ (Carlo Erba), $CrCl_3·6H_2O$, benzoylacetone, benzoyltrifluoroacetone (Fluka), $FeCl_3·6H_2O$, acetylacetone, 1,4-dioxane (99 %, v/v), hydrochloric acid (37 %, v/v), buffer solutions of 4,9-titrizole (Merck).

Shimadzu spectrophotometer, Model 2550; spectrophotometer, Spectronic 20 (Germany) Balance with 0/0001 precision-Metrohm pH-meter .

After synthesizing the complexes of acetylacetone (acac) with Cu(II), Cr(III), Fe(III)[9], UV spectrum of complexes was recorded by spectrophotometer instrument of UV-Vis Shimadzu, Model 2550. Maximum wavelength of absorption is shown in Table-1.

TABLE-1
MAXIMUM WAVELENGTHS OF ACETYLACETONE COMPLEXES

Complex	$Fe(acac)_3$	$Cr(acac)_3$	$Cu(acac)_2$
λ_{max} (nm)	433	555	634

In order to determine stoichiometry of complexes and optimized pH, the continuous variations method was used. In this stage, the concentration of cation and ligand for complex Fe(III) is 2.5×10^{-3} M and for complexes of Cr(III) and Cu(II) is 6×10^{-3} M. Proper pH for formation of complexes including $Fe(acac)_3$, $Cr(acac)_3$, $Cu(acac)_3$ are 3.6, 3.7 and 3.4, respectively.

It should be mentioned that the chromium complex solutions were heated in the bath of warm water and the absorption of solutions, after reaching room temperature with wavelength of 555 nm against blank was recorded.

In order to determine the stability spectrum by using spectrometry of UV-Vis[8], the solutions including cation and ligand were prepared so that the cation concentration in solution was considered as ten fold of ligand concentration in solution. For various solutions the cation concentration was variable. For complexes of Fe(III), whole concentration of ligand is 6×10^{-5} M. At pH = 3.4, the absorption of solution for the wavelength of 433 nm against blank was recorded. For complexes of Cu(II), at pH = 3.6, the absorption of solutions in room temperature for the wavelength of 634 nm, against blank was extracted. For chromium complex at pH = 3.7, were heated in warm water bath for 2 h and the absorption of solutions after reaching room temperature for wavelength of 555 nm against blank was taken (blank is including metal cations with the same volumetric ratio as in the solution involving cation and ligand).

K_f and ε for stoichiometry 1:2 and for stoichiometry 1:3 are calculated by the correlation of eqns. 1 and 2, respectively:

$$\frac{[M][L]}{A} = \frac{1}{K_f \varepsilon [L]} + \frac{4[M]}{\varepsilon} \qquad (1)$$

$$\frac{[M][L]}{A} = \frac{1}{K_f \varepsilon [L^2]} + \frac{9[M]}{\varepsilon} \qquad (2)$$

λ_{max} and calculated values of K_f and ε are listed in the Tables 1-3.

TABLE-2
VALUES OF STABILITY CONSTANTS FOR METAL COMPLEXES OF IN VARIOUS SOLVENT SYSTEMS

Solvent system	Metal cation	Acac log K_f	Bac log K_f	Btfac log K_f
Water	Fe(III)	10.8 ± 0.3	10.3 ± 0.4	–
	Cr(III)	5.1 ± 0.6	5.5 ± 0.3	–
	Cu(II)	3.3 ± 1.1	–	–
Water-ethanol 50 %	Fe(III)	10.0 ± 0.5	9.5	10.1 ± 0.6
	Cr(III)	6.7 ± 0.3	5.9 ± 0.2	6.4 ± 0.3
	Cu(II)	4.1 ± 1.7	4.3 ± 0.4	4.0 ± 1.4
Water-dioxane 75 %	Fe(III)	9.8 ± 3.9	10.9 ± 0.6	9.2 ± 1.1
	Cr(III)	6.0 ± 1.3	5.7 ± 1.1	5.7 ± 0.8
	Cu(II)	3.7 ± 0.3	3.9 ± 0.6	3.5 ± 0.6

RESULTS AND DISCUSSION

It is noted that the λ_{max} of the main absorption band is a sensitive function of a number of parameters, the most important being probably due to cationic charge, cationic size and its distortion effect on the ring π-system and the

TABLE-3
VALUES OF MOLAR ABSORPTION COEFFICIENT FOR METAL COMPLEXES IN VARIOUS SOLVENT SYSTEMS

Solvent system	Metal cation	Acac ε	Bac ε	Btfac ε
Water	Fe(III)	9045.5 ± 8.2	7875.0 ± 9.3	–
	Cr(III)	3675.0 ± 2.4	2592.5 ± 3.7	–
	Cu(II)	162.6 ± 6.2	–	–
Water-ethanol 50 %	Fe(III)	129910.7 ± 11.8	450000	202500.0 ± 12.8
	Cr(III)	881.4 ± 4.2	1783.1 ± 2.6	824.8 ± 3.9
	Cu(II)	170.4 ± 1.4	165.7 ± 4.0	149.7 ± 13.8
Water-dioxane 75 %	Fe(III)	133928.6 ± 8.0	90000	1633928.6 ± 25.9
	Cr(III)	442.0 ± 5.3	378.2 ± 22.9	435.2 ± 15.1
	Cu(II)	1046.3 ± 2.5	725.6 ± 5.4	995.8 ± 5.2

π-bonding ability of the metal ion. In a conjugated system it has been shown that as the number of atomic centers over which electrons are delocalized increases, λ_{max} shifts to longer wavelengths. With the complexes of the transition metals, $d\pi$-$p\pi$ bonding increases the length of the π-electron system. It is interesting description of the shoulder on the long wavelength side of the principal band in the UV spectra of these compounds. Two possibilities may arise here: 1) n-π^* transition 2) singlet-triplet ($^1\pi$-$^3\pi^*$) transition. The n-π^* transition would involve n-electrons (non-bonding) on the ring oxygens moving to anti-bonding MO's of the π-system. As has been pointed out, such bands have been observed in some cyclic conjugated systems such as in pyridine. Bands of this type are expected to be solvent dependent; solvent effects on the spectra of pyridine and diazines have been found[9]. The shoulders observed here were most evident in the diamagnetic acetylacetonates and Cu(acac)$_2$. These shoulders show little or no solvent dependence either in intensity or position. However, the shoulder in the Cu(acac)$_2$ spectrum completely disappears when the compound is measured in a solution. In any event, solvent effects may be diminished in the acetylacetonates by partial shielding of the ring oxygens by neighboring-CH$_3$ groups so that failure to observe them does not constitute firm evidence against the n-π^* assignments. No direct evidence concerning the possibility of singlet-triplet transitions of the π-electrons in the chelate ring system is found. Evans[10] has identified singlet-triplet absorption bands in benzene and other aromatic hydrocarbons by perturbing the triplet state with the homogenous field of the paramagnetic oxygen molecule. In the acetylacetonates, the paramagnetic metal ion, intimately associated with the π-system, might have been expected to accomplish a similar enhancement of the intensity. However, we have been unable to distinguish these bands as either n-p*, singlet-triplet or in some cases, ligand field absorptions.

The present results indicate that the stability for studied cations are as follow:

$$Fe(III) > Cr(III) > Cu(II)$$

According to the Pearson's classification[11], Cr(III) and Fe(III) as well as oxygen are among hard elements. In this classification, Cu(II) is among medium elements. Therefore, the complexes of Cr(III) and Fe(III) are more stable than Cu(II) complexes.

β-Diketones are always in a equilibrium form of *keto-enol* tautommer. More density of negative charge on oxygen result in more stronger hydrogen bond and more stronger bond of metal-oxygen. Electrophilic of substitutions cause decrease of charge density on carbonyl oxygen atom. Bulky substitutions cause C=O groups to approach each other[12]. Therefore, a more stronger hydrogen bond will be provided. Complexes of benzoylacetone due to the bulky phenyl group with the spatial effect, provide more stability than the benzoyltrifluoroacetone complexes.

For complexes of benzoyltrifluoroacetone, substitution of CF_3, because of the electron withdrawing of flour groups, causes decrease of charge density on oxygen and decrease of complex stability[13].

The percentage of enolic form for acetylacetone derivatives is different so that the per cent of enolic form for acac and Bac are 81 and 100 %, respectively[14]. However, as seen in results, the per cent of enolic form is affected by solvent system and so the stability may be changed. Also the amount of acidity dissociation of ligand is under the direct influence of solvent system. With respect to the Table-4, the per cent of enolic form in ethanol and dioxane are equal but despite this fact that the volume ratio of ethanol (50 %) is less than dioxane (75 %) solution, as pointed above, stability in ethanol 50 % is more than in dioxane 75 % solution. So it may be concluded that the acidity dissociation of present ligands may be more in the water-ethanol 50 % systems.

TABLE-4
SPECIFICATIONS OF USED SOLVENTS [Ref. 13]

Solvent	Donation number	Dielectric constant	Enol (%)
Water	18.0	78.5	16
Ethanol	19.0	24.3	82
Dioxane	14.8	2.2	82

Enol (%) = The per cent of enolic form of β-diketones in solvents.

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(*Received*: 17 September 2007; *Accepted*: 2 May 2008) AJC-6568