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Potentiometric Studies on Chelation of Co(II), Ni(II), Cu(II) and Zn(II) with Some 6-Aryl-5-hexene-2,4-diones

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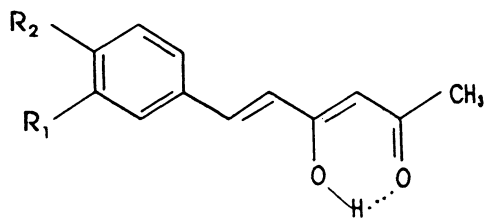
Chelate formation of Co(II), (Ni(II), Cu(II) and Zn(II) with some 6-aryl-5-hexene-2,4,-diones in 1 : 1 aqueous dioxane medium at constant ionic strength and temperature have been studied potentiometrically. The proton-ligand and metal-ligand stability constants obtained are discussed and correlated with electronic effects of aryl substituents and the results compared with corresponding values reported for simple 1,3-diketones. The order of stability constants with respect to metal ions followed the natural order.

INTRODUCTION

Exensive literature is available on the chemistry and applications of metal 1,3-diketonates in which the dicarbonyl function is directly linked with alkyl/aryl groups.[1,2] However, reports are scanty on the coordination behaviour of dicarbonyl function directly attached to olefinic carbons. Such α,β-unsatured 1,3-dicarbonyl moieties are the basic structural units present in curcuminoids, the active constituent of *Curcuma longa* L. (turmeric), a traditional Indian medicinal plant, and several other plant products of wide pharmacological interest.[3] As a part of our studies on such naturally occurring 1,3-dicarbonyls, in this communication, we report the proton-ligand and metal-ligand stability constats of a series of 6-aryl-5-hexene-2,4-diones (1a–e) with Co(II), Ni(II), Cu(II) and Zn(II) in 50% v/v aqueous dioxane medium. The method of study involved is the pH-metric titration technique as reported by Irving and Rosotti.[4]

EXPERIMENTAL

The compounds(1a–e) were obtained from the condensation of aromatic aldehydes (benzaldehyde, *para*-methoxybenzaldehyde, *para*-hydroxybenzaldehyde, vanillin and veratraldehyde) with acetylacetone by the following general



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	R_1	R_2		R_1	R_2
1a	H	H	**1b**	H	OCH_3
1c	H	OH	**1d**	OCH_3	OH
1e	OCH_3	OCH_3			

procedure. The product formed by mixing acetylacetone (0.075 mol) and boric oxide (0.055 mol) was suspended in dry ethylacetate (50 mL) containing tri(sec-butyl)borate (0.1 mol). To this mixture, kept at 0°C, a solution of the aromatic aldehyde (0.025 mol) in dry ethylacetate (15 mL) and n-butylamine (0.5 mL) were added dropwise during 90 min with constant stirring. The stirring was continued for an additional period of *ca.* 2 h and the solution was set aside overnight. The reaction mixture was then stirred for *ca.* 1 h with hot (*ca.* 50°C) hydrochloric acid (0.04 M, 20 mL) and extracted repeatedly with ethylacetate. The combined extracts were concentrated in vacuum and subjected to column chromatography (silica gel) to get pure substances. All the compounds isolated were recrystallised from hot benzene.

For pH measurements, the ligand solutions (1×10^{-3} M) were prepared in 1,4-dioxane and all other solutions in double-distilled CO_2-free water. The pH measurements were made on a Systronic-pH-meter (accuracy of ± 0.05) after calibrating with potassium hydrogen phthalate solution at 28 ± 0.1°C.

Potentiometric titrations

The following sets of pH titrations were done using a standard carbonate free 0.01 M NaOH solution at a fixed ionic strength (0.01 M KCl). The concentration of HCl used was 1×10^{-3} M.

(i) 6 mL HCl + 2 mL H_2O + 10 mL dioxane + 2 mL KCl.

(ii) 6 mL HCl + 2 mL H_2O + 1 mL ligand solution + 9 mL dioxane + 2 mL KCl.

(iii) 6 mL HCl + 1.8 mL H_2O + 0.2 mL metal(II) chloride solution (1×10^{-4} M) + 1 mL ligand solution + 9 mL dioxane + 2 mL KCl.

Duplicate titration was performed in each case under identical conditions.

RESULTS AND DISCUSSION

The proton-ligand formation number $\bar{n}_A$ were calculated at various pH values from the titration curves. The pH values were calculated by the half-integral and mid-point methods[4, 5] from the pH *vs.* $\bar{n}$ plots (Fig. 1). The mean values are presented in Table-1.

TABLE-1
VALUES OF PROTON-LIGAND STABILITY CONSTANTS

Compounds	pK (enolic)	pK(phenolic)
1a	10.98	—
1b	11.88	—
1c	12.15	10.70
1d	12.95	10.75
1e	13.10	—

The pK (enolic) values of these compounds are significantly higher than the corresponding values reported for saturated analogues such as acetylacetone, benzoylacetone and dibenzoylmethane.[1, 6, 7] This indicates that the extended conjugation increases the stability of the enolic anion. The observed increase in the pK(enolic) values from 1a to 1e can be attributed to the increasing electron releasing tendencies of the aryl substituents.

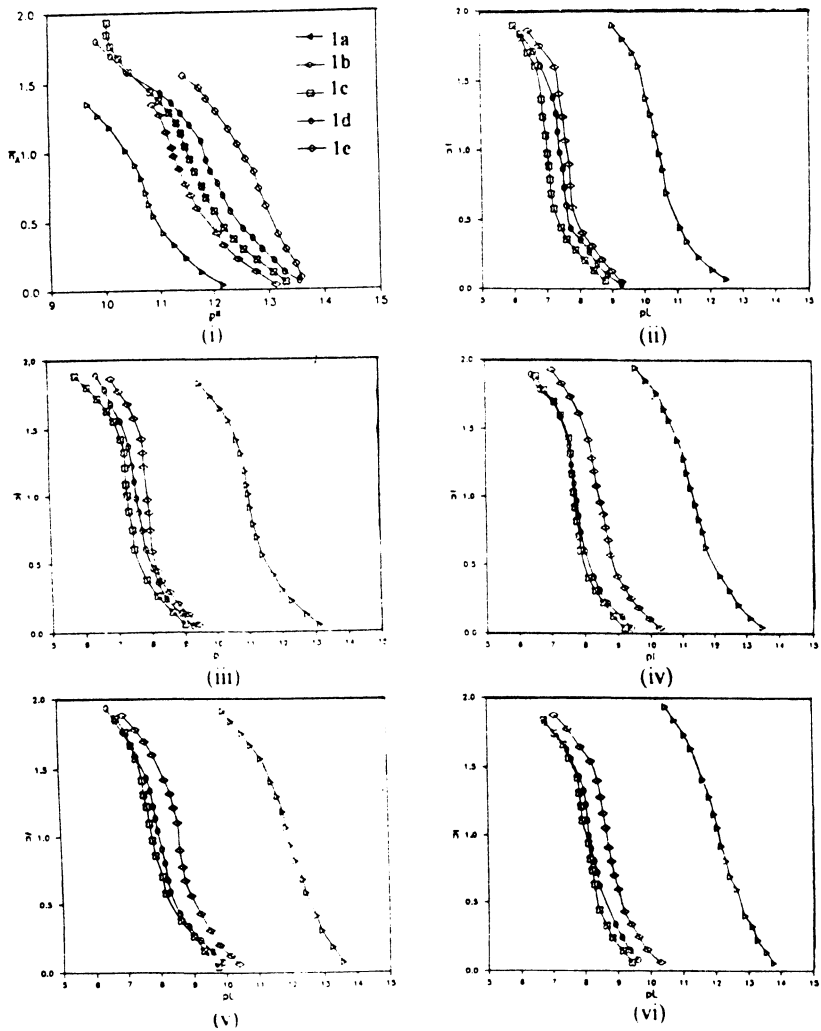

Fig. 1. Proton-ligand formation curves: (i) for 6-aryl-5-hexene-2,4-diones (1a–e) and metal-ligand formation curves for Co(II), Ni(II), Cu(II) and Zn(II) ions with respect to the ligands 1a–e. (ii) 1a, (iii) 1b, (iv) 1c, (v) 1d, (vi) 1e

(Zn(II) Co(II) Ni(II) Cu(II))

In the case of metal-ligand formation studies, the $\bar{n}$ (average metal-ligand formation number) and pL values were calculated from the titration curves. The formation curves of metal complexes were obtained by plotting pL against $\bar{n}$. The $\bar{n}$ values extend up to 2.0, indicating the formation of [ML] and [ML_2] complexes. The overall stability constants are brought out in Table-2.

TABLE-2
VALUES OF METAL-LIGAND STABILITY CONSTANTS

Metal(II) ions	Stability constants	Ligands				
		1a	1b	1c	1d	1e
Cu	$\log K_1$	10.88	11.56	11.95	12.58	12.74
	$\log K_2$	9.96	10.60	10.68	11.30	11.42
	$\log \beta$	20.84	22.16	22.63	23.88	21.16
Ni	$\log K_1$	7.88	8.10	8.85	9.00	9.10
	$\log K_2$	7.32	7.70	8.00	8.10	8.21
	$\log \beta$	15.20	15.80	16.85	17.10	17.31
Co	$\log K_1$	7.35	7.62	7.95	8..24	8.36
	$\log K_2$	6.80	7.08	7.45	7.50	7.58
	$\log \beta$	14.15	14.70	15.40	15.74	15.94
Zn	$\log K_1$	7.65	7.95	8.12	8.45	8.52
	$\log K_2$	7.05	7.23	7.45	7.55	7.70
	$\log \beta$	14.70	15.18	15.57	16.00	16.22

The stability constants of the metal ions considered follow the natural order of stability.[8] The observed variaions in log K_n values can be correlated with the electron releasing effect of the aryl substituents in the ligand molecule. The order of formation constants $\log K_1 > \log K_2$ is in agreement with the weakening of metal-ligand bond strength by the successive attachment of ligand molecules and the observed small differences between the two values suggest *trans* configuration of the chelates.

The metal-ligand formation curves obtained with respect to the ligands are also included in Fig.1. The observed values of metal-ligand stability constants of these compounds far exceed those reported for simple 1,3-diketones such as acetylacetone, benzoylacetone, dibenzoylmethane, etc.[1,6] This indicates that the chelating ability of 1,3-diketonyl function is enhanced by α,β-unsaturation as reported in the case of certain unsaturated 1,3-diketones.[9,10]

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