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Physico-Chemical Studies of Ni(II), Co(II), Zn(II), and Cd(II) Ions with p-Fluorobenzoylacetone

By

B. P. Bachlas, A. K. Rai, and B. P. Gupta

Chemical Laboratories, University of Rajasthan, Jaipur, India

With 2 Figures

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Incorporation of pH correction, in data obtained from the potentiometric titration of p-fluorobenzoylacetone with NaOH solution in dioxane—water (3 : 1, *V*/*V*) at 30 ± 0.1 °C in a medium of constant ionic strength, $\mu = 0.1 M$ ($NaClO_4$) gave the value of thermodynamic dissociation constant (pk_D) as 12.06 ± 0.02. Under similar conditions of solvent composition, temperature and ionic strength the thermodynamic stepwise formation constants of the complexes formed between Ni(II), Co(II), Zn(II) and Cd(II) ions and the above ligand, using method of least squares, gave $\log \beta_2$ as 19.50 ± 0.05, 18.89 ± 0.05, 18.61 ± 0.04 and 16.16 ± 0.08 resp. This order is in accordance with the *Irving—Williams* series. Derivatives of the above metals have also been synthesised and characterised.

Thermodynamic stepwise formation constants of complexes obtained by the interaction of several bi- and trivalent metal ions with various β-diketones and the effect of substituents at α- and/or γ-positions on their chelating tendency have been investigated in detail[1–3]. In the literature, there is no mention of any such study for the complexes of Ni(II), Co(II), Zn(II) and Cd(II) ions with p-halobenzoylacetones. In the present communication the thermodynamic stepwise formation constants of the complexes formed by the interaction between p-fluorobenzoylacetone and the above metal-ions are reported.

Experimental

Materials

p-Fluorobenzoylacetone was synthesised by the method of *Joshi* and *Pathak*[4]. Dioxane was purified by a standard procedure[5]. Metal perchlorates were prepared by decomposing the corresponding carbonates with the requisite amount of $HClO_4$ and their solutions were standardised as pyridine thiocyanate complexes[6]. Dioxane—water mixture (3 : 1, *V/V*) was used in preparing metal salt, ligand and $NaClO_4$ solutions.

Procedure

The solutions containing ligand (0.01*M*) or ligand and metal-ions (0.01*M* and 0.0025*M*) were titrated potentiometrically at $\mu = 0.1M$ ($NaClO_4$) and 30 ± 0.1 °C with 0.5*M* and 0.1*M* carbonate-free NaOH solutions. The changes in pH were recorded as a function of $[OH^-]$ and suitable pH corrections were incorporated.

Calibration of Glass Electrode

According to *Van Uitert* and *Haas*[7] the pH meter reading (**B**) in an aqueous dioxane medium is related to the hydrogen ion concentration

$$-\log [H^+] = \mathbf{B} + \log \mathbf{U}_H \tag{1}$$

where the value of the correction factor, $\log \mathbf{U}_H$, at a fixed temperature and composition of the medium is related to the activity coefficient by the relation:

$$\log \mathbf{U}_H = \log \mathbf{U}_H{}^\circ - \log (1/\gamma_\pm). \tag{2}$$

The value of $\log \mathbf{U}_H{}^\circ$ was calculated by using an expression given by *Rao* and *Mathur*[8] for the temperature dependence in dioxane—water mixture (3 : 1, *V/V*):

$$\log \mathbf{U}_H{}^\circ = (0.007406)\, t + 0.828 \tag{3}$$

where t is the temp. in °C.

The value of $\log (1/\gamma_\pm)$ was determined either by interpolation of the plot of $\log (1/\gamma_\pm)$ vs. mean molality ($m_\pm$) in dioxane—water mixture (3 : 1, *V/V*) at 30 °C from the data given by *Harned* and *Owen*[9] for HCl or by employing the following polynomial given by *Irving* and *Mahnot*[10].

$$\log (1/\gamma_\pm)_{30\,^\circ\mathrm{C}} = 0.0933 + 1.0351\, n_2 + 0.3142\, n_2^2 + 6.6350\, n_2^3 \tag{4}$$

where n_2 is the mole fraction of dioxane recalculated with the atomic weights C = 12.01, H = 1.008.

The value of $\log (1/\gamma_\pm)$ turned out to be 0.920 and 0.9212 resp. by using the above two methods. In the present work the value 0.920 was employed for the evaluation of $\log \mathbf{U}_H$ by using Eq. (2) [1.050—0.920 = 0.130].

Calculation of Thermodynamic Dissociation Constant and Stepwise Formation Constants

The stoichiometric dissociation constant ($\mathrm{p}\, q_D$) of p-fluorobenzoylacetone was calculated by the following expression:

$$-\log q_D = -\log [H^+] + \log \left[\frac{[HL]}{[NaOH] + [H^+] - [OH^-]} - 1\right] \tag{5}$$

where the correct pH was obtained by adding 0.130 to the pH meter reading (**B**). The thermodynamic dissociation constant $\mathrm{p}k_D$ was calculated from the relationship[8]:

$$\mathrm{p}\,k_D = \mathrm{p}\,q_D + 2 \log (1/\gamma_{\pm}). \tag{6}$$

Substituting the values of av. $\mathrm{p}\,q_D$ (10.22 ± 0.02) and $2 \log (1/\gamma_{\pm})$ (1.84), the value of $\mathrm{p}\,k_D$ turned out to be 12.06 ± 0.02.

The following equations were used to express the formation of 1 : 2 metal—ligand complexes in dioxane—water (3 : 1, V/V):

$$M^{2+} + L^{-} \leftrightharpoons ML^{+};\; q_1 = \frac{[ML^{+}]}{[M^{2+}]\,[L^{-}]} \tag{7}$$

$$ML^{+} + L^{-} \leftrightharpoons ML_2;\; q_2 = \frac{[ML_2]}{[ML^{+}]\,[L^{-}]} \tag{8}$$

The values of $\log q_1$ and $\log q_2$ for the complexes of Ni(II), Co(II), Zn(II) and Cd(II) ions with p-fluorobenzoylacetone systems were computed from the data for $\bar{n}$ and $[L^{-}]$, using the *Irving—Rossotti*[11] equation and the following expressions:

$$\log [L^{-}] = \log \left[[L_0] - [\mathrm{NaOH}] - [\mathrm{H}^{+}] + [\mathrm{OH}^{-}]\right] - \log \frac{[\mathrm{H}^{+}]}{q_D} \tag{9}$$

$$\bar{n} = \left[[L_0] - [L^{-}] \left\{\frac{[\mathrm{H}^{+}]}{q_D} + 1\right\}\right] 1/[M_0] \tag{10}$$

$$\frac{\bar{n}}{(\bar{n} - 1)\,[L^{-}]} = \frac{(2 - \bar{n})\,[L^{-}]}{(\bar{n} - 1)}\, q_1\, q_2 - q_1 \tag{11}$$

where $[L_0]$, $[M_0]$ are total ligand and metal concentrations and $\bar{n}$ is the formation number calculated from the pH data obtained prior to the precipitation of metal complex during the titration of the metal—ligand mixture with NaOH.

Calculation of Stepwise Formation Constants by Correction-Term and Linear-Plot Method

The values of $\log q_1$ and $\log q_2$ for the above metal complexes have been computed by the equation given by *Irving* and *Rossotti*[11].

$$\mathrm{p}L_{1-d} + \mathrm{p}\,L_{1+d} = 2\,\mathrm{p}\,L_1 = \log q_1\, q_2 \tag{12}$$

$$\log q_1 = \mathrm{p}L_{1-d} + y \tag{13a}$$

$$\log q_2 = \mathrm{p}L_{1+d} - y \tag{13b}$$

where the "correction term" y is given by

$$y = \frac{2\,(1 - d)}{d + \sqrt{d^2 + 4\,(1 - d^2)\, q_2/q_1}} \tag{14}$$

If $\mathrm{p}\,L_{1-d}$ and $\mathrm{p}\,L_{1+d}$ are two points on the formation curve disposed symmetrically about the mid-point, then from Eqs. (12) and (13)

$$\Delta\, \mathrm{p}L_d = \mathrm{p}L_{1-d} - \mathrm{p}L_{1+d} = \log (q_1/q_2) + 2\,y \tag{15}$$

By using Eqs. (14) and (15), corresponding values of y and $\Delta\, \mathrm{p}L$ have been calculated for nine values of d for each of series of values of q_1/q_2 ranging from 10^5 to 10^{-2}. The relationship between y and Δ pL was shown graphically for which the necessary data were given by *Irving* and *Rossotti*[11]. The correction-term method was applied to pairs of values ($\bar{n}$, pL) symmetrically disposed about the mid-point. The process was repeated for several values of d and the mean value of the calculated stepwise formation constants was taken. The formation curves for metal chelates of p-fluorobenzoylacetone was shown in Fig. 1.

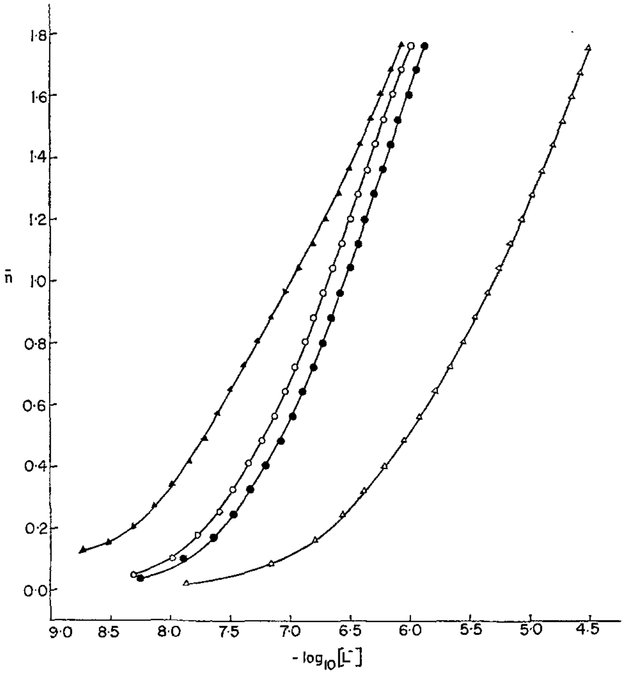

Fig. 1. Formation curves for metal chelates of p-fluorobenzoylacetone. ▲ = Ni, ○ = Co, ● = Zn, Δ = Cd

The values of $\log q_1$ and $\log q_2$ for the same metals have also been computed by linear-plot method using the following equation given by *Rossotti* and *Rossotti*[12].

$$\frac{(1-\bar{n})\,[L^-]}{\bar{n}}\,q_1 + \frac{(2-\bar{n})\,[L^-]^2}{\bar{n}}\,q_1\,q_2 = 1. \qquad (16)$$

The plot of $(2-\bar{n})\,[L^-]^2/\bar{n}$ against $(\bar{n}-1)\,[L^-]/\bar{n}$ always gives a straight line (Fig. 2). The slopes and intercepts of these lines provide the values for $q_1/q_1\,q_2$ and $1/q_1\,q_2$ resp. which are used for calculating the values for $\log q_1$ and $\log q_2$.

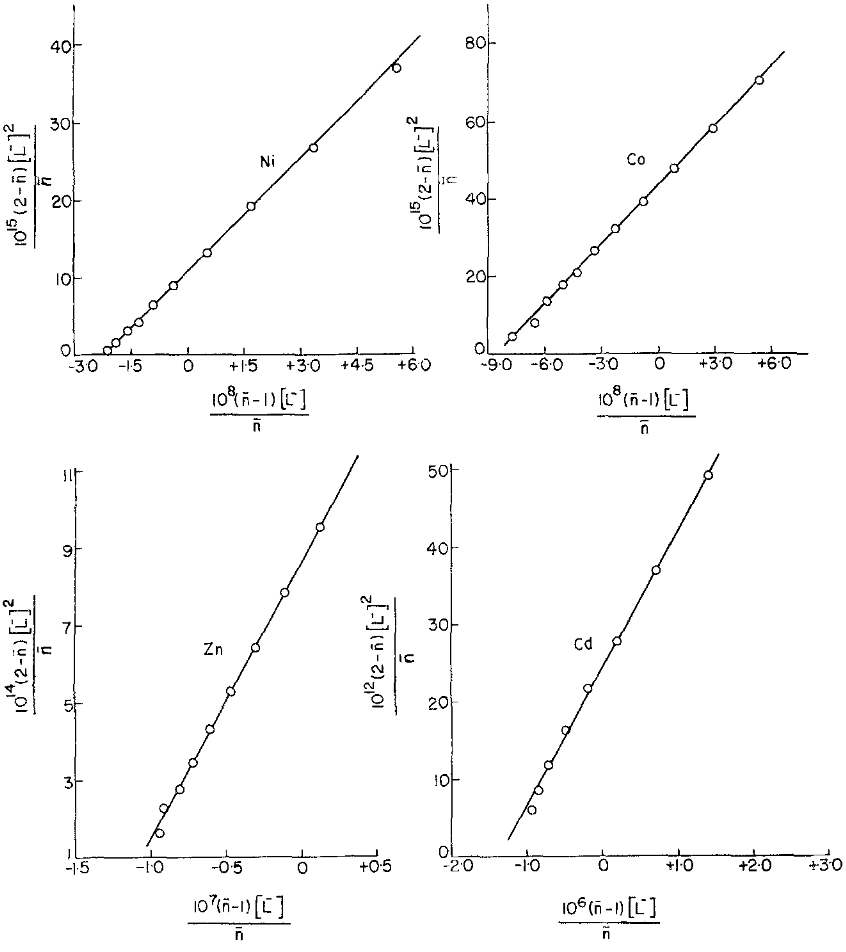

Fig. 2. Computation of $\log q_1$ and $\log q_2$ by linear-plot method[12] [Eq. 16] of Ni(II), Co(II), Zn(II) and Cd(II) with p-fluorobenzoylacetone

The thermodynamic stepwise formation constants then computed from the relationship[8]:

$$\log k_1 = \log q_1 + 4 \log (1/\gamma_\pm), \qquad (17)$$

$$\log k_2 = \log q_2 + 2 \log (1/\gamma_\pm). \qquad (18)$$

The values of $\log k_1$, $\log k_2$ and $\log \beta_2$ have been listed in Table 1.

Results and Discussion

The effect of substitution of the fluorine atom at the para position of the phenyl group in benzoylacetone has been found to decrease the

Table 1. *Thermodynamic Stepwise Formation Constants of* Ni(II), Co(II), Zn(II), *and* Cd(II) *Complexes**. [Solvent: Dioxane—Water (3 : 1, *V*/*V*); $\mu = 0.1M$ ($NaClO_4$); Temp. 30 ± 0.1 °C]

		Ni(II)	Co(II)	Zn(II)	Cd(II)
Irving—Rossotti[11] (least square method)					
	log k_1	11.33 ± 0.03	10.74 ± 0.03	10.56 ± 0.03	9.59 ± 0.03
	log k_2	8.17 ± 0.08	8.15 ± 0.08	8.05 ± 0.07	6.57 ± 0.11
	log β_2	19.50 ± 0.05	18.89 ± 0.05	18.61 ± 0.04	16.16 ± 0.08
Irving—Rossotti[11] (correction-term method)					
	log k_1	11.33	10.74	10.58	9.61
	log k_2	8.22	8.20	8.07	6.61
	log β_2	19.55	18.94	18.65	16.22
Rossotti—Rossotti[12] (linear-plot method)					
	log k_1	11.33	10.74	10.59	9.56
	log k_2	8.16	8.14	8.00	6.56
	log β_2	19.49	18.88	18.59	16.12

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* Metal perchlorate concentration $2.5 \times 10^{-3}M$ and ligand concentration $1 \times 10^{-2}M$.

Table 2. *Complexes of* Ni(II), Co(II), Zn(II), *and* Cd(II). (Amount of p-fluorobenzoylacetone = 1.80 g)

Metal salt (g)	Product, colour and m.p. (°C)	Yield, %	Metal assay % Found (Calc.)	Mol. weight* Found (Calc.)
$Ni(NO_3)_2 \cdot 6\,H_2O$ (1.45)	$Ni(p\text{-}FC_6H_4COCHCOCH_3)_2 \cdot 2\,H_2O$ light green; (152–158°)**	85	12.90 (12.96)	678 (453)
$Co(NO_3)_2 \cdot 6\,H_2O$ (1.46)	$Co(p\text{-}FC_6H_4COCHCOCH_3)_2 \cdot 2\,H_2O$ brown; (107–111°)**	86	12.95 (13.00)	476 (453)
$ZnSO_4 \cdot 7\,H_2O$ (1.44)	$Zn(p\text{-}FC_6H_4COCHCOCH_3)_2 \cdot 2\,H_2O$ white; (76–80°)	71	14.15 (14.22)	—
$3\,CdSO_4 \cdot 8\,H_2O$ (1.28)	$Cd(p\text{-}FC_6H_4COCHCOCH_3)_2 \cdot 2\,H_2O$ white; (120–125°)	62	22.10 (22.18)	—

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* (Average.)

** Product melts with decomposition.

basicity of the ligand (p$k_D = 12.06 \pm 0.02$) as compared to that of benzoylacetone (p$k_D = 12.85$)[13]. These results are in close agreement with our earlier work reported on p-bromobenzoylacetone[14] and p-chlorobenzoylacetone[15]. It appears that the substitution of halogen atom at p-position of the phenyl nucleus results in the non-coplanarity of the molecule with respect to enolic ring. The latter acts as an electron donor through resonance.

Synthesis and Properties of Metal bis (p-Fluorobenzoylacetonate) Dihydrates

Equi-molar mixture of a methanolic solution of p-fluorobenzoylacetone (0.01*M*) and aqueous sodium carbonate (0.01*M*) were mixed slowly with continuous stirring to the aqueous solutions of metal salts (0.005*M*). The precipitates obtained on mixing were filtered, washed repeatedly with water, methanol and finally with ether. These products were dried under reduced pressure and on analyses found to have the composition, $M\,(\text{ligand})_2 \cdot 2\,H_2O$, where M = Ni, Co, Zn, Cd and ligand = p-fluorobenzoylacetone. Nickel and cobalt complexes were found to have appreciable solubility in common organic solvents and have been recrystallised from chloroform. However, zinc and cadmium complexes were found to be sparingly soluble. Their melting points and molecular weights are given in Table 2.

The molecular complexities of the Ni(II) and Co(II) complexes in chloroform are found to be 1.5 and 1.05 resp. The acetylacetonates of Ni(II) and Co(II) are reported to be trimeric in benzene and triphenylmethane[16–18] and therefore it may be concluded that the replacement of methyl by the p-fluorobenzoyl group introduces steric factors which retard further association of the molecules.

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Correspondence and reprints:
Dr. B. P. Bachlas
Department of Chemistry
University of Rajasthan
IND-302004 Jaipur
India