TABLE 1 — STABILITY CONSTANTS OF AZIDO COMPLEXES OF Ni(II), Zn(II) AND Cd(II)

| Composition of half-cell I [N_3^-] in moles lit.$^{-1}$ | Composition of half-cell II | | e.m.f. (V) | K_1 | K_2 (approx.) |
	N_3^- in moles lit.$^{-1}$	[$M(ClO_4)_2$] in moles lit.$^{-1}$			
		Ni(II) COMPLEX			
0·10	0·020	0·030	0·04971	43·5	1·4
0·10	0·005	0·020	0·08289	39·7	1·8
0·10	0·005	0·005	0·07725	57·4	2·4
0·10	0·01	0·005	0·05943	58·3	3·5
0·05	0·0075	0·01	0·05228	40·1	2·7
0·05	0·0075	0·0075	0·05215	57·2	2·1
0·05	0·0075	0·005	0·05000	47·2	3·3
			Av. 49·1 ± 7·7		~2·5
		Zn(II) COMPLEX			
0·08	0·02	0·09	0·05088	29·2	—
0·08	0·01	0·10	0·06885	26·6	0·4
0·08	0·03	0·08	0·03588	24·4	0·5
0·08	0·015	0·10	0·05940	29·9	0·4
0·08	0·005	0·09	0·08455	23·1	0·6
0·08	0·025	0·08	0·04425	31·6	0·5
0·08	0·01	0·08	0·06724	27·7	0·6
			Av. 27·5 ± 2·8		~0·5
		Cd(II) COMPLEX			
0·03	0·03	0·03	0·02122	202·8	1·3
0·06	0·03	0·03	0·03851	221·3	1·4
0·05	0·04	0·03	0·02526	277·8	1·3
0·07	0·05	0·03	0·02335	207·0	1·2
0·08	0·04	0·04	0·04135	247·2	1·1
0·06	0·03	0·04	0·04315	204·6	1·1
			Av. 226·8 ± 27·4		~1·2

SCN^-, $SeCN^-$ and N_3^- ions can be arranged in the following increasing order of their " softness " on the basis of Pearson classification[7,8], $N_3^- < SCN^- < SeCN^-$.

Among the metal ions studied, Cd(II) ion is a " soft " acceptor of electrons[9] and hence the following order of stabilities is expected[10]: $CdSeCN^+ > CdSCN^+ > CdN_3^+$. A reversal of this sequence here is surprising ($K_{CdSeCN^+} = 96·0$, $K_{CdSCN^+} = 140·8$ and $K_{CdN_3^+} = 226·8$). This anomaly may be due to (a) in solution the stability is not only determined by the affinity between the metal ion and the ligand but also by the hydrational energies of the metal ion, the ligand and the complex species and (b) cadmium forms bonds with SCN^- ion both through S and N atoms[3] forming two types of species with different metal-ligand bond energies. A similar sequence cannot be predicted for complexes with other metal ions studied.

An approximate estimation of the mean ionic diameter ($a°$) of MN_3^+ was made on the basis of Bjerrum's treatment[11]. The value of $a°$ at 25° for the azido complexes were found to be between 1·2 and 2·2 Å (Cd, 1·2 Å; Ni, 1·7 Å, and Zn, 2·2 Å) which are less than the distance of closest approach for the associating ions (calculated from the relationship, $q = Z_1 Z_2 e^2 / 2DkT$), suggesting " inner-sphere " type complexes. It may however be mentioned that such method of distinguishing between " outer-sphere " and " inner-sphere " complexes from their K values on the basis of Bjerrum's theory is not always correct[12] although some authors have done so[13].

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Stability Constants of Complexes of Ni(II), Co(II), Zn(II) & Cd(II) with p-Chlorobenzoylacetone

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The thermodynamic dissociation constant ($pk_D = 11·91 ± 0·05$) of p-chlorobenzoylacetone and overall stability constants (log β_2) of its complexes with Ni(II), Co(II), Zn(II) and Cd(II) have been determined potentiometrically in 75% (v/v) dioxane-water at 30°±0·1° and $\mu = 0·1M$ ($NaClO_4$). The values of log β_2 obtained by the method of least squares came out to be 19·31±0·03, 18·67±0·07, 18·04±0·06 and 15·37±0·06 for Ni(II), Co(II), Zn(II) and Cd(II) complexes respectively. This order is in agreement with the Irving-Williams series. The solid bis(p-chlorobenzoylacetonate) dihydrate complexes of these metals have also been prepared.

THE effect of a substituent at the α- and/or γ-positions in acetylacetone, on its keto-enol equilibrium, chemical reactivity and chelating tendency has been the subject of many investigations[1-4]. But no data have been reported on the Ni(II), Co(II), Zn(II) and Cd(II)-p-chlorobenzoylacetone systems. The results of physico-chemical studies on these systems are presented in this paper.

p-Chlorobenzoylacetone was synthesized by refluxing a mixture containing p-chloroacetophenone (78 g), absolute ether (400 ml), sodium wire (12·5 g) and ethylacetate (110 g). Sodium p-chlorobenzoylacetonate obtained was kept overnight and washed repeatedly with ether and dried in vacuo. The product was dissolved in water and decomposed with acetic acid and recrystallized from methanol in white shining needles, yield 55%, m.p. 67°.

Solvents were purified by standard methods[5]. Metal perchlorates were obtained by decomposing the corresponding carbonates with requisite amount of perchloric acid and their solutions were standardized as pyridine-thiocyanate complexes[6]. Dioxane-water (75% v/v) was used for preparing the solutions.

Procedure — The solutions containing ligand (0·01M) or ligand and metal ions (0·01M and 0·0025M) were titrated potentiometrically at $\mu = 0\cdot1M$ (NaClO$_4$) and $30° \pm 0\cdot1°$ with 0·5M and 0·1M CO$_2$-free sodium hydroxide respectively. The changes in pH were recorded as a function of [OH]$^-$ and suitable corrections were incorporated.

The $\bar{n}$ values were calculated from the pH data obtained prior to the precipitation of metal complex during the titration of the metal-ligand mixture with sodium hydroxide.

Correction term — The relation between pH meter reading (B) in 75% (v/v) dioxane-water mixture and [H$^+$] has been shown by Van Uitert and Hass[7] to be:

$$p\text{H}_{corr.} = -\log [\text{H}^+] = B + \log U_H \quad ...(1)$$

where the value of the correction factor, log U_H, at a given composition of the medium at a fixed temperature can be obtained at any ionic strength from the expression:

$$\log U_H = \log U^°_H - \log (1/\Upsilon_\pm) \quad ...(2)$$

The value of log $U^°_H$ is reported to be independent of the ionic strength but is a function of temperature and dioxane-water composition.

Recently, Rao and Mathur[8] gave an expression for the temperature dependence of log $U^°_H$ for dioxane-water mixture (75% v/v):

$$\log U^°_H = (0\cdot007406)t + 0\cdot828 \quad ...(3)$$

In the present work the value of log $U^°_H$ was calculated from Eq. (3) at 30° which turned out to be 1·05.

The value of log $(1/\Upsilon_\pm)$ was determined either by interpolation of the plot of log $(1/\Upsilon_\pm)$ vs mean molality $(m_\pm)$ in dioxane-water mixture (75% v/v) at 30° from the data given by Harned and Owen[9] for HCl or by employing the polynomial given by Irving *et al.*[10].

In both the cases the value of log $(1/\Upsilon_\pm)$ turned out to be 0·92 and 0·9212 respectively. In the present work the value 0·92 was employed for the evaluation of log U_H by Eq. (2).

Calculation of thermodynamic dissociation constant (pk_D) — The stoichiometric dissociation constant (pq_D) of p-chlorobenzoylacetone was calculated from Eq. (4).

$$-\log q_D = -\log [\text{H}^+]$$
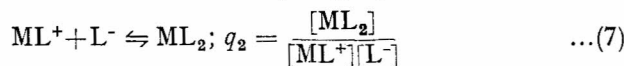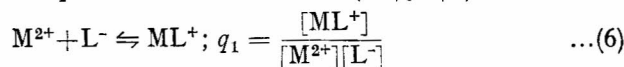$$+ \log \left[\frac{[\text{HL}]}{[\text{NaOH}]+[\text{H}^+]-[\text{OH}^-]} - 1 \right] \quad ...(4)$$

where $-\log$ [H$^+$] is obtained by adding 0·13 to the pH meter reading (B). The thermodynamic dissociation constant, pk_D was calculated from the relationship[8]:

$$pk_D = pq_D + 2 \log (1/\Upsilon_\pm) \quad ...(5)$$

Substituting the values of av. pq_D (10·07 $\pm$ 0·05)

and 2 log $(1/\Upsilon_\pm)$ (1·84), the value of pk_D turned out to be 11·91 $\pm$ 0·05. It is observed that the substitution of the p-chlorophenyl group at the α-carbon in benzoylacetone has decreased the basicity of the ligand as compared to that of acetylacetone (pk_D = 12·75, 12·70)[2,4] and benzoylacetone (pk_D = 12·85)[3]. A comparison of pk_D of benzoylacetone and the present ligand indicates that the inductive effect $(-I)$ of chlorine atom is operative and the p-chlorobenzoyl group is not coplanar with the enolic ring and acts as an electron acceptor.

Calculation of thermodynamic stepwise formation constants — The following equations were used to express the formation of bis-β-diketonato metal complexes in dioxane-water (75% v/v):

$$\text{M}^{2+} + \text{L}^- \leftrightharpoons \text{ML}^+; \quad q_1 = \frac{[\text{ML}^+]}{[\text{M}^{2+}][\text{L}^-]} \quad ...(6)$$

$$\text{ML}^+ + \text{L}^- \leftrightharpoons \text{ML}_2; \quad q_2 = \frac{[\text{ML}_2]}{[\text{ML}^+][\text{L}^-]} \quad ...(7)$$

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

$$\log [\text{L}^-] = \log \left[\frac{[\text{L}_0] - [\text{NaOH}] - [\text{H}^+] + [\text{OH}^-]}{} \right]$$
$$- \log \frac{[\text{H}^+]}{q_D} \quad ...(8)$$

$$\bar{n} = \left[[\text{L}_0] - [\text{L}^-] \left\{ \frac{[\text{H}^+]}{q_D} + 1 \right\} \right] 1/[\text{M}_0] \quad ...(9)$$

$$\frac{\bar{n}}{(\bar{n}-1)[\text{L}^-]} = \frac{(2-\bar{n})[\text{L}^-]}{(\bar{n}-1)} q_1 q_2 - q_1 \quad ...(10)$$

where $\bar{n}$ is the formation number, [L$_0$] and [M$_0$] are total ligand and metal concentrations respectively.

The thermodynamic stepwise formation constants were then evaluated from the relationships[8]:

$$\log k_1 = \log q_1 + 4 \log (1/\Upsilon_\pm) \quad ...(11)$$
$$\log k_2 = \log q_2 + 2 \log (1/\Upsilon_\pm) \quad ...(12)$$

The values of log k_1, log k_2 and log β_2 listed in Table 1 have also been computed, using the correction-term method[11] and linear-plot method[12].

The chelating tendency of p-chlorobenzoylacetone has been found markedly less than for benzoylacetone[3,13,14]. This is in agreement with the conclusion drawn above.

Synthesis and properties of metal bis(p-chlorobenzoylacetonate) dihydrates — To a methanolic solution of the ligand (0·01 mole) was added an aqueous solution of sodium carbonate (0·01 mole). The mixture was then added to an aqueous solution of metal salt (0·005 mole) and the solution stirred for 30 min. The product was filtered, washed repeatedly with water, methanol and ether and dried. Nickel and cobalt complexes were recrystallized from chloroform solution. The zinc and cadmium complexes have little solubilities in common organic solvents like benzene, chloroform and carbon tetrachloride. The characterization data are given in Table 2.

TABLE 1—THERMODYNAMIC STEPWISE FORMATION CONSTANTS OF Ni(II), Co(II), Zn(II) AND Cd(II) COMPLEXES*

[Solvent: dioxane-water (75% v/v); $\mu = 0.1M$ (NaClO$_4$); temp. $30° \pm 0.1°$]

	Ni(II)	Co(II)	Zn(II)	Cd(II)
IRVING-ROSSOTTI[11] (LEAST-SQUARE METHOD)				
$\log k_1$	11·28	10·71	10·31	9·09
	±0·02	±0·03	±0·03	±0·03
$\log k_2$	8·03	7·96	7·73	6·28
	±0·05	±0·10	±0·09	±0·09
$\log \beta_2$	19·31	18·67	18·04	15·37
	±0·03	±0·07	±0·06	±0·06
IRVING-ROSSOTTI[11] (CORRECTION-TERM METHOD)				
$\log k_1$	11·26	10·71	10·33	9·08
$\log k_2$	8·04	7·99	7·73	6·29
$\log \beta_2$	19·30	18·70	18·06	15·37
ROSSOTTI-ROSSOTTI[12] (LINEAR-PLOT METHOD)				
$\log k_1$	11·28	10·72	10·32	9·09
$\log k_2$	8·03	7·95	7·71	6·27
$\log \beta_2$	19·31	18·67	18·03	15·36

*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-chlorobenzoylacetone = 1·97 g)

Metal salt (g)	Product, colour and m.p. (°C)	Metal (%) found (calc.)
Ni(NO$_3$)$_2$.6H$_2$O (1·45)	Ni(L)$_2$.2H$_2$O light green 153-58° (d)	12·03 (12·08)
Co(NO$_3$)$_2$.6H$_2$O (1·46)	Co(L)$_2$.2H$_2$O brown 195-205° (d)	12·07 (12·13)
ZnSO$_4$.7H$_2$O (1·44)	Zn(L)$_2$.2H$_2$O white 97-102°	13·18 (13·26)
3CdSO$_4$.8H$_2$O (1·28)	Cd(L)$_2$.2H$_2$O white 104-8°	20·74 (20·83)

Molecular weights of the Ni(II) and Co(II) complexes in chloroform are 750 and 1012 respectively showing molecular complexities of 1·54 and 2·08. Although the acetylacetonates of Ni(II) and Co(II) are trimeric in benzene and triphenylmethane[15-17], it may be concluded that the replacement of methyl by p-chlorophenyl group introduces steric factors which retards further association.

We are grateful to Prof. K. C. Joshi for providing necessary facilities.

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Studies in Cu(II) Complexes of 8-Amino-1-naphthol-5,7-, 3,6- & 3,5-disulphonic Acids & 8-Amino-1-naphthol-5-sulphonic Acid

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Cu^{2+} forms well defined 1:1 and 1:2 complexes with 8-amino-1-naphthol-5,7-, 3,6- and 3,5-disulphonic acids and 8-amino-1-naphthol-5-sulphonic acid. The role of steric factors during the formation of 1:1 chelate of 8-amino-1-naphthol-5,7-disulphonic acid has also been examined.

TRANSITION metal complexes of 8-amino-1-naphthol have already been reported by a large number of workers[1]. In the present note, we report the results of our investigations on the complexes of Cu(II) with 8-amino-1-naphthol-5,7-(5,7-DSA), 3,6-(3,6-DSA) and 3,5-(3,5-DSA) disulphonic acids and 8-amino-1-naphthol-5-sulphonic acid (5-SA) employing Calvin-Bjerrum titration technique in aqueous medium at $30° \pm 0.1°$ and $\mu = 0.1M$ (NaClO$_4$).

Perchloric acid, sodium perchlorate and sodium hydroxide were of Analar grade. Copper perchlorate and the ligands such as 5,7-DSA, 3,6-DSA, 3,5-DSA and 5-SA of 8-amino-1-naphthol were obtained from Schuchardt, Munchen, Germany. All the solutions were prepared in doubly distilled water and the concentration of Cu(II) in water was estimated by EDTA titration.

The experimental procedure involved the potentiometric titrations of carbonate-free solutions of (i) free HClO$_4$ ($1.0 \times 10^{-2}M$), (ii) free HClO$_4$ ($1.0 \times 10^{-2}M$)+ligand ($2.0 \times 10^{-3}M$), and (iii) free HClO$_4$ ($1.0 \times 10^{-2}M$)+ligand ($2.0 \times 10^{-3}M$)+Cu(II) ($2.0 \times 10^{-3}M$) under N$_2$ atmosphere and at $\mu = 0.1M$ (NaClO$_4$).

The pK values of these ligands were determined using pointwise calculation method and are presented in Table 1. It is observed from Table 1 that the observed pK values for ligands are much higher to that of the literature values[2,3], except for 5-SA, where the agreement is good.