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Potentiometric Studies on Complexes of 3d Transition Metal (II) and Lanthanides (III) with 2-Carboxyphenylhydrazo-p-Methoxy-Acetoacetanilide and Other Derivatives in 75% (V/V) Dioxan-Water

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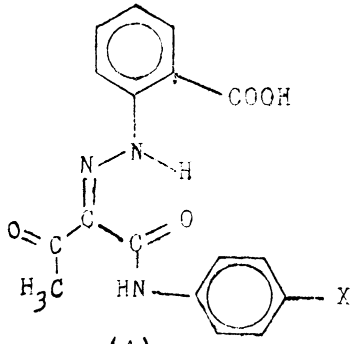
The synthesis, acid-base equilibria and metal-ion chelating tendencies of 2-Cl-AAA, 2-OCH_3-AAA and 2-CPH-p-OCH_3-AAA are reported. From potentiometric measurements of hydrogen ion concentration at 30°C and ionic strength 0.10M (KNO_3), in 75% (v/v) dioxan-water medium. The values of stability constants of p-Cl-AAA, p-OCH_3-AAA, 2-CPH-p-Cl-AAA and 2-CPH-p-OCH_3-AAA with lanthanide(III) ions have been evaluated. The theoretical relationship derived by Irving and Rosotti between the logarithms of stability constants for metal complexes of a similar pair of ligands was discussed.

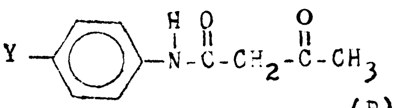
INTRODUCTION

In the previous papers[1,2], we have discussed the complex equilibria of 2-CPHAAA and 2-CPH-p-Cl-AAA (structures in A) with proton,



(A)

2–CPHAAA (−X = H)
2–CPH–p–Cl–AAA (−X = Cl)
2–CPh–p–OCH_3–AAA (−X = OCH_3)



$Y{-}C_6H_4{-}\overset{H}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}CH_3$

(B)

p–Cl–AAA (−Y = −Cl)
p–OCH_3–AAA (−Y = −OCH_3)

divalent ions[1] of Ni, Co, Zn, Mn, Cd, Cu and tervalent lanthanide ions (2). The studies show that these ligands behave as diprotic species through the dissociation of carboxylate proton first followed by hydrazo proton. The infrared spectra of the solid complexes indicate that the ligands act as tridentate using carboxylate oxygen, hydrazo nitrogen and ketonic oxygen as coordinating sites[1]. The role of proton and metal ion solvation by organic solvent has been discussed in view of results obtained for lanthanide-(III)-2-CPHAAA system in different media[2].

Continuing our studies we proceed now to investigation of complex equilibria of 2-carboxyphenylhydrazo-para-methoxy-acetoacetanilide (2–CPH-p-OCH_3-AAA) (structure A), p-Cl-AAA and p-OCH_3-AAA (structures in B) with proton, 3d transition metals(II) and lanthanide(III). In addition to the chelating ability of 2–CPH–p–Cl–AAA towards lanthanide (III) which is not done in the previous investigations[1,2].

EXPERIMENTAL

2-CPH-p-OCH_3-AAA was prepared as described previously[1]. The pure organic product is obtained after crystallization several times from acetic acid as yellowish needle crystals, the elemental analyses of which are: Found: C, 60.78; H 4.75; N 11.85%; calculated for $C_{18}H_{17}N_3O_5$: C 60.85; H 4.79; N 11.83%. The other compounds were prepared as reported earlier[1,2].

All reagents were of analytical grade. Rare earth oxides 99.9% purity (BDH) were dissolved in nitric acid, the excess acid was removed by evaporation, and the concentrations of $Ln(NO_3)_3$ were determined complexometrically with EDTA using hexamine buffer and xylenol orange serves as indicator[3]. Other metal ion solutions were prepared from the corresponding nitrate salts and standardized by conventional method (3). Dioxan was purified and distilled prior to each use as described elsewhere[4]. The base used was carbonate free KOH kept under nitrogen atmosphere and standardized against primary standard potassium hydrogen phthalate.

The potentiometric titrations were carried out using a Beckman SSR 2 pH-meter fitted with a combined glass-calomel electrode. In each run 30 ml aliquots of the metal ligand mixture in 75%(v/v) dioxan-water solvent were titrated with standard base. Solutions were adjusted to 0.1M ionic strength by the addition of KNO_3 and maintained at 30°C with constant-temperature water circulated through a sealed jacket cell. Purified nitrogen gas passed through the solution during the measurements. The correction for the measured pH values in 75%(v/v) dioxan-water was taken as 0.28[5].

All titrations were repeated at least twice and the titration curves agreed within ±0.02 pH unit.

RESULTS AND DISCUSSION

Ligands Protonation constants

The titration curve of 2-CPH-p-OCH_3-AAA (Fig. 1) is characterized by two well-defined buffer regions: pH 2.5–5.5 and pH 8–12 corresponding to the deprotonation of –COOH and hydrazo –NH groups. This indicates that 2-CPH-p-OCH_3-AAA behaves as diprotic ligand. This observation is further confirmed from the titration of the ligand in the presence of various metal ions only two protons liberates. For the general protonation equilibrium:

$$H^+ + H_{n-1}L \overset{K_n^H}{\rightleftharpoons} H_nL \ (n = 1 \text{ or } 2)$$

the constants, K_n^H were determined from the hydrogen ion concentrations of the ligand solution for each increment of the base added. The values of these constants were calculated using the general relationship:

$$\log K_n^H = \frac{(1 - a + m - n)C_L - [H^+] + [OH^-]}{(a - m + n)C_L + [H^+] - [OH^-]} + pH + 0.28 \qquad (1)$$

where m is the ligand basically, and a is the number of moles of base added per mole of ligand present. The value of ionic product, pK_w, of water in 75%(v/v) dioxan-water medium was taken as 18.7[6]. The results obtained are given in Table (1).

TABLE 1

STABILITY CONSTANTS log K_1 AND log K_2 FOR PROTON AND DIVALENT METAL COMPLEXES OF 2-CPH-p-Cl-AAA(1) AND 2-CPH-p-OCH_3-AAA. $t = 30°$, $\mu = 0.10$, 75%(v/v) DIOXAN-WATER

Cation	2-CPH-p-Cl-AAA		2-CPH-p-OCH_3-AAA	
	log K_1	log K_2	log K_1	log K_2
H^+	6.44	10.97	6.21	12.43
	±0.06	±0.06	±0.03	±0.05
Cu^{2+}	12.45		15.05	10.25
Ni^{2+}	9.25	7.30	11.60	8.10
Co^{2+}	8.15	6.50	10.65	7.25
Zn^{2+}	7.15	6.70	8.10	6.50
Mn^{2+}	7.05	6.30	7.60	6.30
Cd^{2+}	6.60	5.90	7.25	6.20

Ligand Metal Ion Interaction

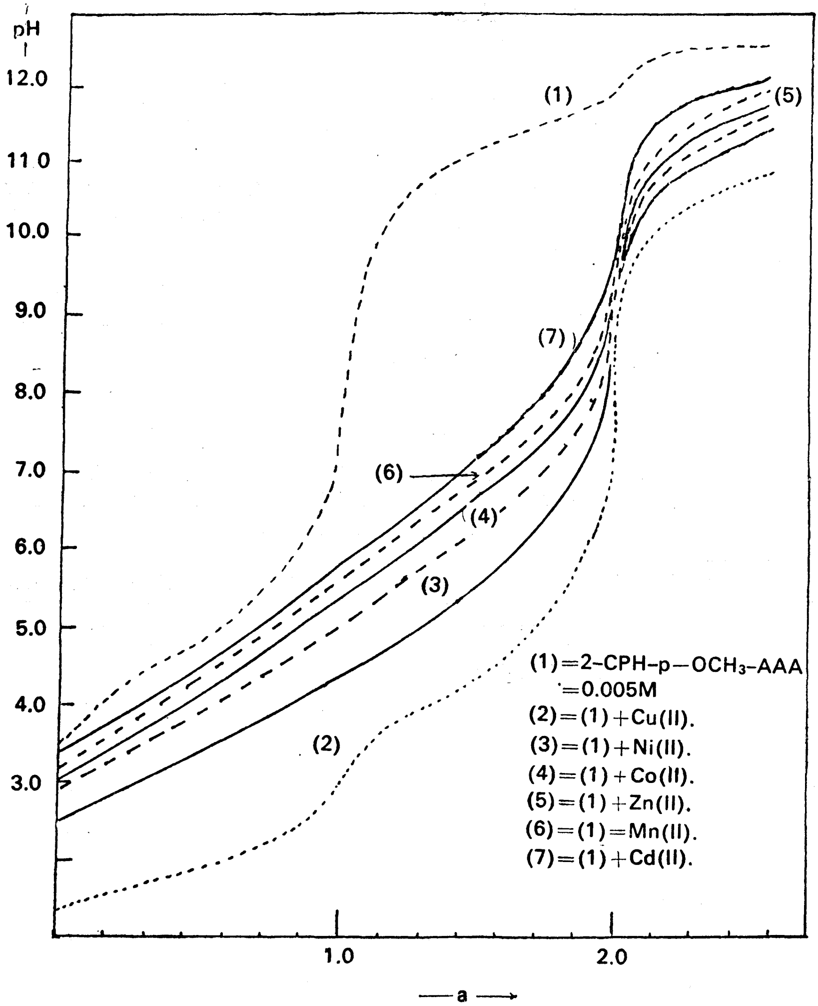


Fig. 1. Potentiometric titration curves of 2-CPH-p-OCH$_3$-AAA in absence and presence of 0.0025M divalent metal ions. (t = 30°C; μ = 0.10M KNO$_3$; 75%(v/v) dioxan-water).

The 2-CPH-p-OCH$_3$-AAA curves obtained with 2 : 1 molar ratios of ligand to Cd(II), Mn(II), Zn(II), Co(II), Ni(II) and Cu(II) ions are shown in Fig. 1. The curves show the presence of long buffer region from $a = 0$ to $a = 2$ corresponding to the formation of bis-chelates. The constants for the overlapping equilibria:

$$M^{Z+} + H_2L \rightleftharpoons ML^{(Z-2)+} + 2H^+ \qquad (2)$$

$$ML^{(Z+2)+} + H_2L \rightleftharpoons ML_2^{(Z-4)+} + 2H^+ \qquad (3)$$

are calculated with the help of expressions given by Irving and Rossoffi[7]:

$$\log \frac{\bar{n}}{1-\bar{n}} = \log K_1 + pA \tag{4}$$

$$\log \frac{\bar{n}-1}{2-\bar{n}} = \log K_2 + pA \tag{5}$$

These expressions are solved by the graphic relation in the plots of log $\bar{n}/1 - \bar{n}$ versus pA and log $1 - \bar{n}/2 - \bar{n}$ versus pA; these give straight lines. The interception of these lines with pA axis is taken as log K_1 and log K_2 respectively. The values of the constants obtained are refined using the method of least squares. With lanthanide ions, slight hydrolysis was observed beyond the completion of the buffer region between $a = 1$ and $a = 2$. For this reason, only the values of log K_1 are quoted in Table (2) for the lanthanide complex with p-Cl-AAA, p-OCH_3-AAA, 2-CPH-p-Cl-AAA and 2-CPH-p-OCH_3-AAA ligands.

TABLE 2

STABILITY CONSTANTS FOR LANTHANIDE (III) COMPLEXES OF p-Cl-AAA, p-OCH_3-AAA, 2-CPH-p-Cl-AAA and 2-CPH-p-OCH_3-AAA, $t = 30°C$, $\mu = 0.10$, 75% (v/v) DIOXAN-WATER

Ln^{3+}	p-Cl-AAA	p-OCH_3-AAA	2-CPH-p-Cl-AAA	2-CPH-p-OCH_3-AAA
	log K_1	log K_1	log K_1	log K_1
H^+	10.43 ± 0.06	11.13 ± 0.05		
La	5.50	6.25	9.65	11.70
Ce	6.00	6.65	10.05	12.08
Pr	6.20	6.95	10.15	12.40
Nd	6.40	6.85	10.55	12.50
Sm	6.50	7.10	10.80	12.88
Eu	6.60	7.10	11.15	12.98
Gd	6.30	6.90	10.95	12.70
Tb	6.70	7.15	10.65	13.00
Dy	6.75	7.29	10.46	12.80
Ho	6.90	7.30	10.50	12.60
Er	7.29	7.55	10.80	12.90
Tm	7.30	7.65	10.90	13.11
Yb	7.38	8.05	10.95	13.15
Lu	7.35	7.65	10.80	13.00

The values of protonation constants given in Table (I) indicate that the dissociation of enolate proton in p-Cl-AAA($pK^H = 10.43$) is higher than in the case of p-OCH_3-AAA($pK^H = 11.13$). This may be due to the strong withdrawing effect of chlorine atom compared to methoxy group. This also could account for the higher acidity of hydrazo proton in 2-CPH-p-Cl-AAA($pK_2^H = 10.97$) compared to the corresponding in 2-CPH-p-OCH_3-AAA($pK_2^H = 12.43$).

The complex forming abilities of transitional metal ions are frequently characterized by stability orders. This is displayed graphically in Fig. 2.

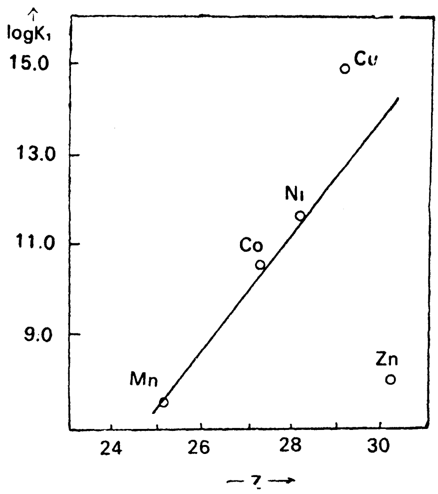


Fig. 2. Plots of log K_1 vs. atomic number (Z) of divalent metal ions.

It can be seen that log K_1 and log K_2 order Zn < Cu > Ni > Co > Mn > Cd is in agreement with Irving and Williams order.[8] As is clear from Fig. 2, the points of Zn and Cu lie below and above the straight line respectively. The lower value for log K_1 for Zn complex compared to Cu complex may be explained on the basis of the following factors: (1) the *d* orbital which is not taking part in homopolar bond formation, (2) the ionic radii, and (3) the higher charge density of electrons around the metal ion. The higher value of log K_1 for Cu-2-CPH-p-OCH_3-AAA complex may be attributed to the unique electronic configuration of Cu(II) ion which is capable of additional stabilization due to tetragonal distortion of the octahedral symmetry as a result of Jahn-Teller effect.

Considering that in most cases the formation of complexes means a competetion between metal ions and protons, it is reasonable to expect that there is some correlation between the stability of the complex and acidic dissociation constants of the ligands. Irving and Rossotti[9] derived the theoretical relationship between the logarithms of the stability constants for metal complexes of a similar pair of ligands A and B, as follows:

$$\log K_{MA} = \log K_{MB} + (\log K_{HA} - \log K_{HB}) \qquad (6)$$

This equation is based on the assumption that the term including the partial-molar free energy of each species S, denoted; $\overline{G}^{o}_{S} \cdot 1/RT(\overline{G}^{o}_{MB} - \overline{G}^{o}_{MA}) - (\overline{G}^{o}_{HB} - \overline{G}^{o}_{HA})$, and the term including the activity coefficient can be neglected when ligand A and B are similar in character. In our system this equation is valid. The plots of stability constants of metal complexes of p-Cl-AAA or 2-CPH-Cl-AAA against those of the same metals and p-OCH_3-AAA or 2-CPH-p-OCH_3-AAA respectively is linear (Figs. 3 and 4). The intercept (Δ log K_1) of the line for the first system (p-Cl-AAA-and p-OCH_3-AAA) is 0.70 and equals 1.25 for the second system (2-CPH-p-Cl-AAA and 2-CPH-p-OCH_3-AAA). These values are expected from log K^H, from 10.43 to 11.13 and from 17.41 to 18.64 for the first and second systems respectively.

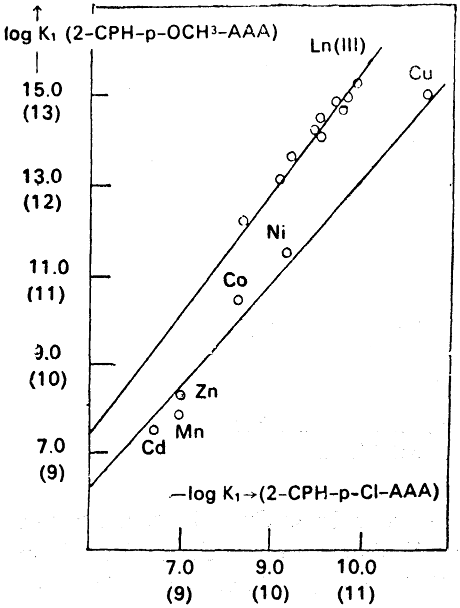


Fig. 3. Relationship between stability constants for divalent and trivalent metal complexes with 2-CPH-p-Cl-AAA and 2-CPH-p-OCH_3-AAA.

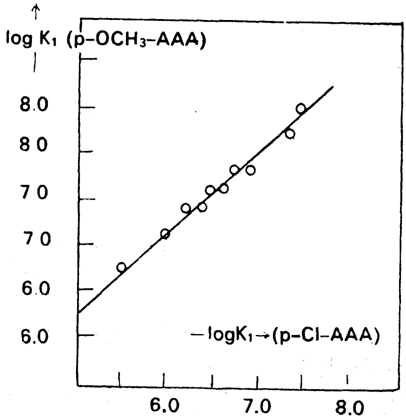


Fig. 4. Relatlonship between stability constants for lanthanide (III) complexes with p-Cl-AAA and p-OCH_3-AAA.

log K_1 values for lanthanon p-Cl-AAA, p-OCH_3-AAA, 2-CPH-p-Cl-AAA and 2-CPH-p-OCH_3-AAA chelate species are plotted for comparison in Fig. 5, versus the ionic potential Z^2/r of Ln (III) cations. This relation indicates that the log K_I for Ln (III) complexes follows the order, p-Cl-AAA < p-OCH_3-AAA < 2-CPH-p-Cl-AAA < 2-CPH-p-OCH_3-AAA which is the same order of the basicity of these ligands. As is clear from Fig. 5, the variation of log K_I as a function of ionic potential is not linear as was expected from the ionic theory. Instead, a curve is obtained with a gradual increase in stability between lanthanum and europium followed by a plateau in the region of gadolinium-terbium and slight increase for

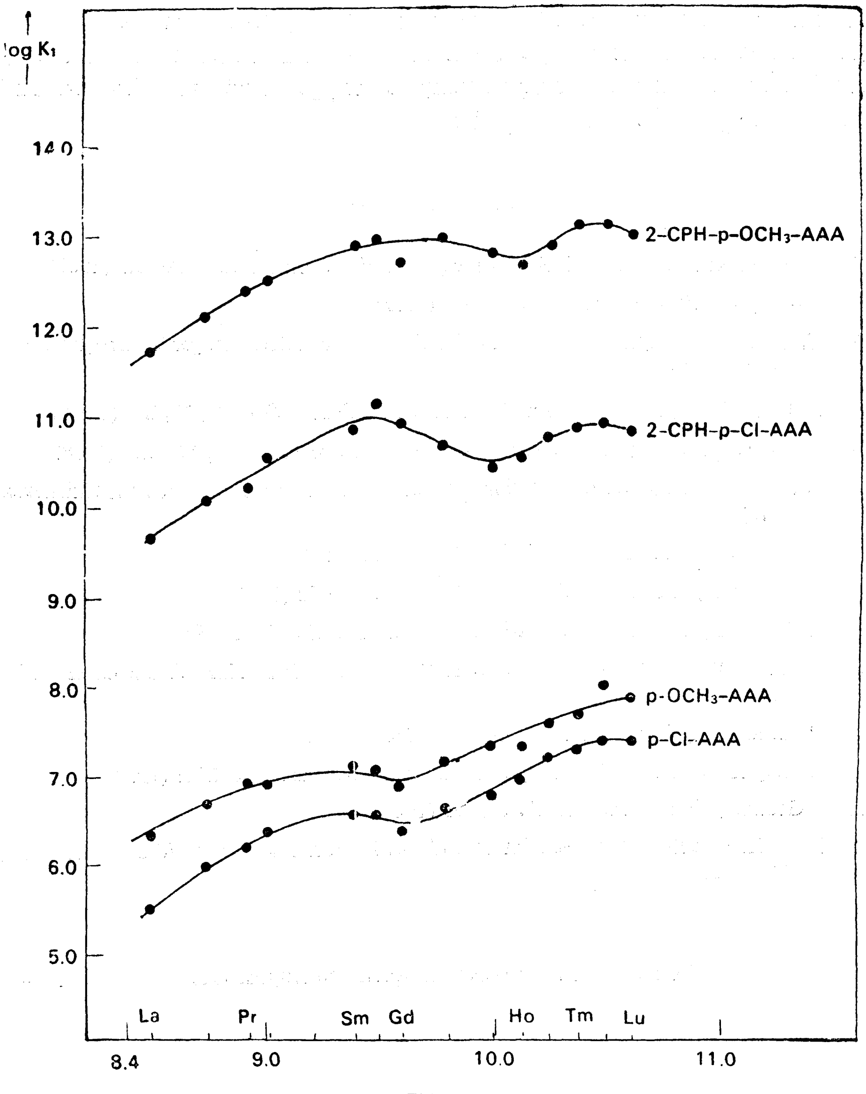


Fig. 5. Log K_1 as a function of ionic potential, Z^2/r, for various rare-earth complexes.

the earlier heavy lanthanides. This kind of behaviour has been observed for variety of ligands among which are quoted here those 8-hydroxyquinoline[10] and 8-hydroxy-5,7-di-iodo-quinoline.[11] This deviation from linearity beyond gadolinium has been attributed by various authors to change in hydration along the cationic series[12-14].

An attempt to rationalize the trend of log K_1 values for particular lanthanide ion with the various chelating agents terms of ligands basicity Σ pK^H is unsuccessful. This is ascribed to the difference in the dentate character of the ligands. p-Cl-AAA and p-OCH_3-AAA act as bidentate (enolic and ketonic oxygen) while 2-CPH-p-Cl-AAA and 2-CPH-p-OCH_3-AAA act as tridentate[1] using carboxylate oxygen, hydrazo nitrogen and ketonic oxygen as coordinating sites.

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