



Studies on interaction between divalent transition metal ions and some substituted imidazolinone at 0.1M ionic strength pH metrically

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ABSTRACT

The interaction between Ni(II), Cu(II) and Zn(II) metal ions and substituted imidazolinone have been studied at 0.1 M Ionic Strength in 70 % DMF-water mixture by Bjerrum method as adopted by Calvin and Wilson. It is observed that Ni(II), Cu(II) and Zn(II) metal ions form 1:1 and 1:2 complexes with ligands (L1 & L2). The data obtained were used to estimate and compare the values of proton-ligand stability constant (pK) and metal-ligand stability constants (logk). From estimated data (pK and log k), the effects of substituents were studied. Ligand used for present work were (L1) 1-[2-hydroxy-5-(phenyl azo) benzylidene amino]-2-phenyl-4-benzylidene-5-oxoimidazoline (L2) 1-[2-hydroxy-5-(4-methoxy phenyl azo) benzylidene amino]-2-phenyl-4-benzylidene-5-oxoimidazoline

Keywords: 1-[2-hydroxy-5-(substituted phenylazo)benzylidene amino]-2-phenyl-4-benzylidene-5-oxoimidazoline, 70% DMF-water mixture, proton-ligand stability Constants(pK), metal-ligand stability constant(logK).

INTRODUCTION

Coordination compounds play very important role in numerous chemical, biological and biochemical activities e.g. Chlorophyll, a magnesium complex essential for photosynthesis in plants; Haemoglobin, an iron complex, which carries oxygen to living organism cells; Coenzyme-Vitamin B₁₂, a cobalt complex which serves as a prosthetic group in metabolic activities of living organisms. The study of enzyme has revealed that the site of reaction in biological systems is frequently a complexed metal ion. Coordination compounds have also played a very important role in biological activities for removal of undesirable and harmful metals from living organisms. The application of coordination chemistry is varied in the field of biological, biochemistry, medicine, agriculture, organometallic chemistry, solid state chemistry, catalysis and molecular receptors and devices. The metal ion complexes as a catalyst are invariably involved in various industrial processes.

Stability constant is well known tool for solution chemist, biochemist, and chemist. In general to help for determination the properties of metal-ligand reactions in water and biological system [1]. In the study of coordination compound in solution, first and foremost requirement is the knowledge of stability constant of complex. For correct interpretation of complex, the knowledge of stability constant is essential. Reliable information of stability constant is of great importance in analytical and separation procedure. To remove undesirable and harmful metals from living organism, chelating agents are very much useful in biological systems. This gives importance to the study of determination of stability constant of metal complexes.

The complexes have been extensively studied in solution as well as in solid state by many workers, due to its remarkable properties and high stability. With the help of various experimental techniques, the extensive work in

coordination complexes has been made possible and has led in a number of empirical conclusions which have been detailed by Martell[2]. The stability of complex in solutions is depending on nature of central metal ion and ligands. The most important characteristics of the central atom which influence the stability of complex compounds are the degree of oxidation, the radius and electronic structure. Stability is dependent on the same characteristic in the ligand as considered for the cation in the case of complexes with monoatomic ligands. The strength of binding of ligand to the central metal ion is depending on structure of ligand molecule or ions[3- 5].

The stability of complexes is dependent upon the size and number of chelating rings also. The structure of chelating agent determines the size of the chelating rings and the number of rings formed on chelation. Ley[6] has concluded that five and six member rings of amino acid chelates are the most stable. Pfeiffer[7] has observed that, in general the five member ring is more stable when the ring is entirely saturated. But when one or more double bonds are present, the six member ring is favoured. Schwarzenbach *et al.*[8] have observed that there is a decrease in chelate stability with the increase in ring size. Tihile [9] have observed increase in the value of formation constant with the presence of electron donating group. thakur[10] have studied the stability of complex with changing temperature. The stability order of metal complexes of transition metal ion was found by Irving and Williams [11] as $Mn^{2+} < Fe^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$.

Though vast amount of work has been done on stability constant of metal complexes. Many workers study the effect of transition metal on a stability of complex by pH metrically[12-15]. Bendi[16], Janrao[17], Ramteke[18], Thakur[19] has investigated the stability constant of ligand with lanthanide metals. Literature survey reveals that compound bearing azo group exhibit various biological activity, imidazoline-5-(4H)-one exhibit promising biological and pharmacological activity. Interest in the chemistry of imidazoline continuously increases because of their usefulness as antibacterial[20] and anti-inflammatory[21] agents. Some of them may be useful in the polymer chemistry. Moreover imidazoline and 5-oxo imidazoline have great therapeutic importance such as anticonvulsant, potent CNS depressant, sedative and hypnotics, hypotensive and potent antiparkinsonian activity[22] promoted by these observations.

Imidazolinone ring system is of biological and chemical interest since long. The imidazolinones[23] are associated with therapeutic activities such as MAO inhibitory, antihelmintical and herbicidal activities. Some workers have recognized 5-imidazolone as having anticancer activity. The therapeutic importance of the compounds inspired us to synthesize some potential imidazolinones. M. P. Wadekar *et al*[24] gives a method of synthesis of series of 1-(2-hydroxy-5-(substituted phenyl azo) benzylidene amino)-2-phenyl-4-benzylidene-5-oxo imidazolines carrying azo linkages. This gives importance to the study physicochemical properties of substituted imidazolinone.

In the present work, effect of metal ions such as Ni(II), Cu(II) and Zn(II) on the properties of complexes of substituted imidazolinone in 70% DMF+water mixture at 298K had studied.

EXPERIMENTAL SECTION

a. Ligands (Substituted imidazolinone drugs)

(L₁) 1-[2-hydroxy-5-(phenyl azo) benzylidene amino]-2-phenyl-4-benzylidene-5-oxoimidazoline

(L₂) 1-[2-hydroxy-5-(4-methoxy phenyl azo) benzylidene amino]-2-phenyl-4-benzylidene- 5-oxoimidazoline

The ligands (L₁) & (L₂) were synthesized in the laboratory by known literature method[24]. The purity of these compounds exceeds 99.5% and structures were confirmed by NMR, IR and melting points. The stock solutions of the ligand was prepared by dissolving required amount of ligand in a minimum volume of 70% (DMF+water) mixture subsequently diluted to final volume.

b. Metal ions (divalent metalion in nitrates forms)

Ni(II), Cu(II) and Zn(II).

c. Stock solution

1M KNO₃ solution, 0.1M HNO₃ solution, 0.1M NaOH and 0.01M Transition metal ions solution are prepared in double distilled water . 0.01 M ligand (L₁ and L₂) solution in 70% DMF –water mixture. All the chemical used in experimental work are AR grades.

d. Calvin –Bjerrum titration methods

All pH-metric titrations and pH-measurements were carried out with EQUIP-TRONIC DIGITAL pH meter model EQ-610 (accuracy + 0.05 units) with a glass and calomel electrodes assembly. at 25±0.10c in 70% DMF-water mixture and at an inert atmosphere by bubbling nitrogen gas .

General procedure :

Types of Titrations

- i) Free acid HNO₃(0.01 M)
- ii) Free acid HNO₃(0.01 M) and ligand (20 x 10⁻⁴M)
- iii)Free acid HNO₃ (0.01 M) and ligand (20 x 10⁻⁴) and metal ion (4 x 10⁻⁴M) against standard 0.1N NaOH solution.

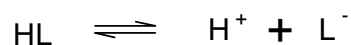
The ionic strength of all the solutions was maintained constant 1M by adding appropriate amount of KNO₃ solution. All the titrations were carried out in 70% DMF-water mixture and the reading were recorded for each 0.2 ml addition. The graphs of volume of alkali added (NaOH) against pH were plotted.

e. Detection Method :

Titration curves are used to estimate the values of \bar{n}_A (proton -ligand formation numbers) which are presented in Table 1 to 2. Formation curve are constructed between \bar{n}_A values and pH. The pH values at 0.5 \bar{n}_A values corresponds the pK values (proton-ligand dissociation constants) of respective ligand. Proton ligand dissociation constants (pK values) are evaluated and presented in Table (3), which are calculated by Half Integraland Pointwise calculations method.

RESULTS AND DISCUSSION

The ligands involved in the present work may be considered as a monobasic acid having only one dissociable H⁺ ion from phenolic-OH group and it can therefore, be represented as HL. The dissociating equilibria can be shown as.



By the law of mass action, we have,

$$k = \frac{[H^+][L^-]}{[HL]} \quad \dots\dots\dots (1)$$

where, the quantities in bracket denote the activities of the species at equilibrium.

Calculation of Proton-Ligand Stability Constant (\bar{n}_A)

The plots between volumes of NaOH and pH of the solutions were used to determine the proton ligand stability constant (representing the replacement of H⁺ from functional group of ligand with respect to pH value) and evaluate the proton-ligand stability constants of the ligands. The horizontal difference (V₂-V₁) was measured accurately between the titration curves of acids and acids + ligands. It was used to calculate the formation number \bar{n}_A at various pH values and fixed ionic strength $\mu = 0.1M$ using Irving and Rossotti's equation[25-26]

$$\bar{n}_A = \gamma \frac{(V_2 - V_1)(N + E^0)}{(V^0 + V_1)T_L^0} \quad \dots\dots\dots (2)$$

where, V₀ is the initial volume of the solution. E₀ and T_{L0} are initial concentrations of the mineral acid and ligand respectively. V₁ and V₂ are the volumes of alkali of normality N during the acid and ligand titration at given pH. γ is the replaceable proton from the ligand.

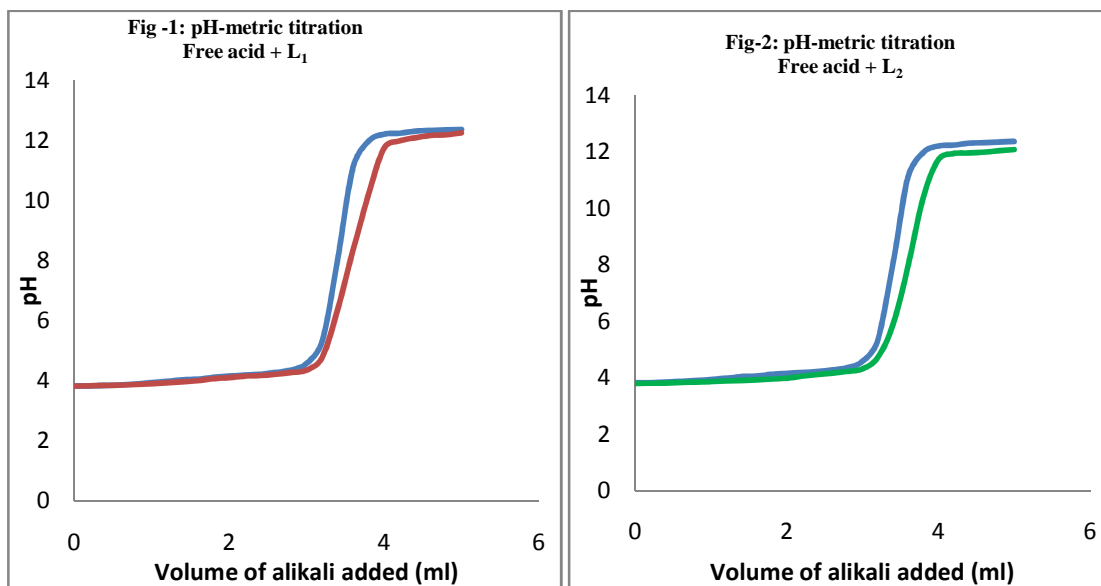
The data of \bar{n}_A values obtained at various pH along with the horizontal difference for some representative systems are presented in Table 1 to 2.

Calculation of Proton-Ligand Stability Constant (logK)

The metal–ligand formation constant (\bar{n}) is estimated by Irving-Rossotti's equation.

$$\bar{n} = \frac{(V_3 - V_2)(N + E^0)}{(V^0 + V_2) n_A T_M^0} \dots\dots\dots (3)$$

where the notations have the same meaning as given in earlier equation in. The horizontal difference (V_3-V_2) between the metal complex (A+M+L) and reagent (A+L) curve is used to evaluate the value of \bar{n} using Irving Rossotti's equation.



pH	V1	V2	V2-V1	\bar{n}_A
4.50	3.00	3.08	0.08	0.7143
5.00	3.15	3.24	0.09	0.6803
5.50	3.21	3.32	0.11	0.6101
6.00	3.25	3.37	0.12	0.5752
6.50	3.28	3.41	0.13	0.5403
7.00	3.33	3.47	0.14	0.5058
7.50	3.36	3.52	0.16	0.4358
8.00	3.40	3.57	0.17	0.4014
8.50	3.43	3.61	0.18	0.3669
9.00	3.46	3.65	0.19	0.3324
9.50	3.49	3.69	0.20	0.2980
10.00	3.53	3.75	0.22	0.2289
10.50	3.56	3.80	0.24	0.1597
11.00	3.59	3.84	0.25	0.1256
11.50	3.65	3.92	0.27	0.0576

pH	V1	V2	V2-V1	\bar{n}_A
4.50	3.00	3.05	0.05	0.8214
5.00	3.15	3.21	0.06	0.7869
5.50	3.21	3.28	0.07	0.7519
6.00	3.25	3.34	0.	0.6814
6.50	3.28	3.38	0.10	0.6464
7.00	3.33	3.45	0.12	0.5764
7.50	3.36	3.49	0.13	0.5416
8.00	3.40	3.55	0.15	0.4718
8.50	3.43	3.59	0.16	0.4372
9.00	3.46	3.64	0.18	0.3675
9.50	3.49	3.68	0.19	0.3331
10.00	3.53	3.74	0.21	0.2639
10.50	3.56	3.78	0.22	0.2297
11.00	3.59	3.83	0.24	0.1605
11.50	3.65	3.90	0.25	0.1274

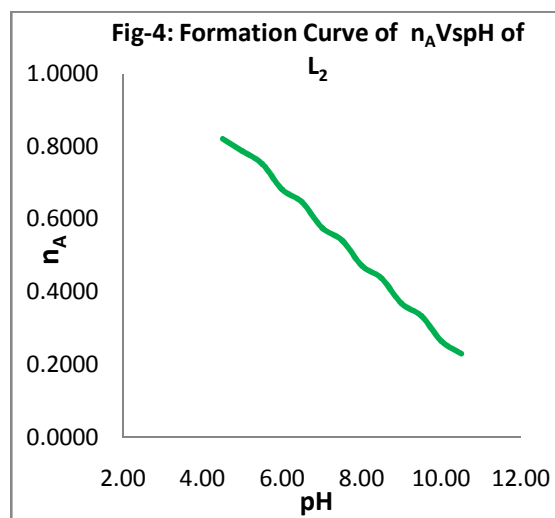
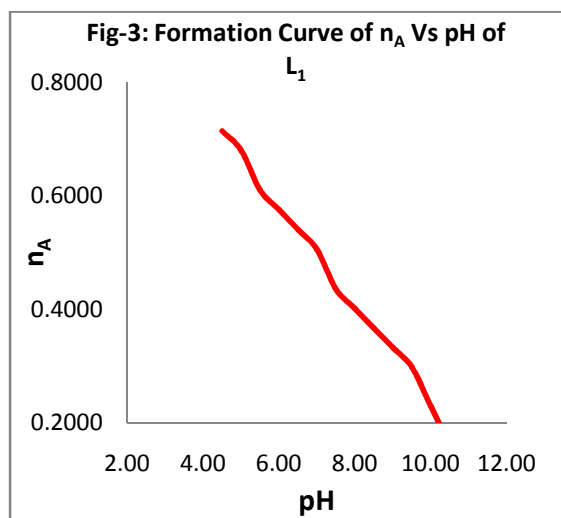


Table 3 : Proton –Ligand stability Constants (pk values)

Ligand	pK (Half Integral Method)	pK (Pointwise Method)
(L ₁) 1-[2-hydroxy-5-(phenyl azo) benzylidene amino]-2-phenyl-4-benzylidene-5-oxoimidazoline	6.80	6.78
(L ₂) 1-[2-hydroxy-5-(4-methoxy phenyl azo) benzylidene amino]-2-phenyl-4-benzylidene- 5-oxoimidazoline	7.80	7.76

Table – 4: Determination of n System $L_1 + Ni(II)$					Table – 5: Determination of n System $L_1 + Cu(II)$					Table – 6: Determination of n System $L_1 + Zn(II)$				
pH	V2	V3	V3-V2	n	pH	V2	V3	V3-V2	n	pH	V2	V3	V3-V2	n
4.50	3.08	3.09	0.01	0.2492	4.50	3.08	3.09	0.01	0.2492	4.50	3.08	3.10	0.02	0.4985
5.00	3.24	3.26	0.02	0.5205	5.00	3.24	3.26	0.02	0.5205	5.00	3.24	3.27	0.03	0.7807
5.50	3.32	3.35	0.03	0.8681	5.50	3.32	3.34	0.02	0.5787	5.50	3.32	3.36	0.04	1.1575
6.00	3.37	3.40	0.03	0.9192	6.00	3.37	3.40	0.03	0.9192	6.00	3.37	3.42	0.05	1.5320
6.50	3.41	3.45	0.04	1.3029	6.50	3.41	3.44	0.03	0.9772	6.50	3.41	3.47	0.06	1.9544
7.00	3.47	3.52	0.05	1.7360	7.00	3.47	3.51	0.04	1.3888	7.00	3.47	3.54	0.07	2.4305
7.50	3.52	3.57	0.05	2.0114	7.50	3.52	3.56	0.04	1.6100	7.50	3.52	3.60	0.08	3.2182
Table – 7: Determination of n System $L_2 + Ni(II)$					Table – 8: Determination of n System $L_2 + Cu(II)$					Table – 9: Determination of n System $L_2 + Zn(II)$				
pH	V2	V3	V3-V2	n	pH	V2	V3	V3-V2	n	pH	V2	V3	V3-V2	n
4.50	3.05	3.07	0.02	0.4340	4.50	3.05	3.06	0.01	0.2170	4.50	3.05	3.06	0.01	0.2170
5.00	3.21	3.24	0.03	0.6757	5.00	3.21	3.23	0.02	0.4504	5.00	3.21	3.23	0.02	0.4504
5.50	3.28	3.32	0.04	0.9405	5.50	3.28	3.31	0.03	0.7054	5.50	3.28	3.31	0.03	0.7054
6.00	3.34	3.39	0.05	1.2946	6.00	3.34	3.37	0.03	0.7767	6.00	3.34	3.38	0.04	1.0356
6.50	3.38	3.44	0.06	1.6353	6.50	3.38	3.42	0.04	1.02	6.50	3.38	3.43	0.05	1.3627
7.00	3.45	3.52	0.07	2.1343	7.00	3.45	3.49	0.04	1.2196	7.00	3.45	3.51	0.06	1.8294
7.50	3.49	3.57	0.08	2.5923	7.50	3.49	3.54	0.05	1.6202	7.50	3.49	3.56	0.07	2.2682

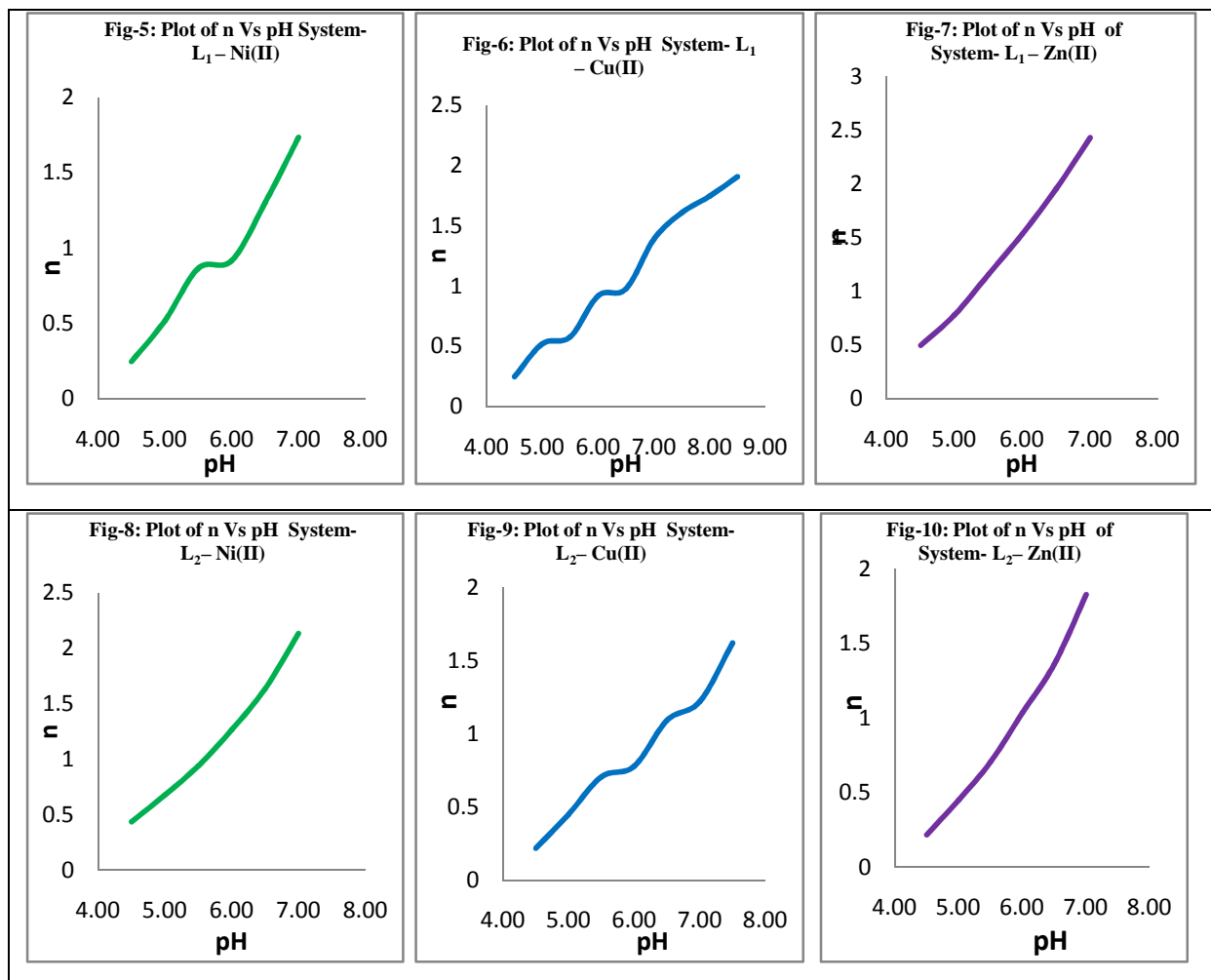


Table 10 : Metal –Ligand stability Constants (LogK values)

System : Ligand +Metal	logK ₁	logK ₂	logK ₁ /logK ₂	logk ₁ -logk ₂	
L ₁	Ni(II)	4.49	2.95	1.52	1.54
	Cu(II)	4.44	2.20	2.01	2.24
	Zn(II)	4.94	3.75	1.31	1.19
L ₂	Ni(II)	5.84	4.45	1.31	1.39
	Cu(II)	5.34	3.15	1.69	2.19
	Zn(II)	5.49	4.00	1.37	1.49

CONCLUSION

From the titration curves, it is observed that the departure between (acid + ligand) curve and (acid +ligand + metal) curve for all systems started from pH = 3.90 this indicated the commencement of complex formation. Also change in colour from yellow to brown in the pH range from 3.90 to 11 during titration showed the complex formation between metal and ligand. The order of pK values of ligands is found to be as (Table-3)

pK ligand (L₂). > pK ligand (L₁).

The increment in pK value of ligand (L₂) is attributed to presence of electron donating –OCH₃ group which enhance the activity of ligand to form more stable complex.

From the table 10 it is observed that small difference between log K₁ and log K₂ values not more than 2.5 indicates the simultaneous formation of complex between metal ion and ligand. But in case of Cu(II) difference of stability constant is nearly 2.5 indicated than there is a stepwise formation of complex.

The order of stability of ligand L₁ and L₂ with metal as

For Ligand L1 : Zn(II) > Ni(II) > Cu(II).

For Ligand L2: Ni(II) > Zn(II) > Cu(II)

If the ratio between metal- ligand stability constant(logK₁/ LogK₂) is greater than 1.5 then in such case there is a stepwise formation of metal ligand complex. From the table-10 it is observed that, in case of Zn(II) ion there is a simultaneous formation of complex with both the ligand L₁ and L₂ and in case of Cu(II) ion there is a stepwise formation of complex with both the ligand. But in case of Ni(II) ion, it shows simultaneous complex formation with Ligand L₂ and Stepwise complex formation with ligand L₁.

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