Study of proton & Metal ligand stability constant of Schiff base complexes in 70% DMF solvent media pH metrically

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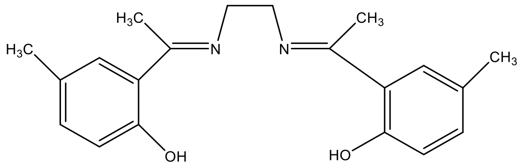
Abstract

Stability constant of some transition metals like Cu(II) & Co (III) complexes with Schiff bases 2,2’(ethane-1,2-diybis(azanylyliden)bis(ethan-1-yl-1-ylidene)bis(4-methylphenol) and 2,2’-(ethane-1,2-diylbis(azanylylidene)bis(ethan-1-yl-1-ylidene)bis(4-chlorophenol),an anti-diabetic drugs have been evaluated at (27^0c± 0.1^0c) & fixed 0.1 M ionic strength in 70% DMF-Water have been carried out by pH metrically . Proton ligand stability constants & metal ligand stability constants were determined by using Calvin Bjerrum titration technique as modified by Irving & Rossoti. Stability constants were discussed in terms of order of stability, basicity of ligands & correlated with atomic number, ionization potential, electronegativity and reciprocal of ionic radii.

Keywords: Schiff base H_2L^1, H_2L^2, pH metry, Metal-ligand Stability Constants.

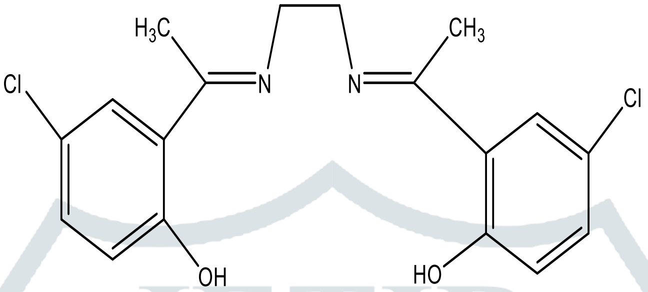
Introduction

The Schiff bases and their metal complexes have more importance recently [1-5] because of their application as biological, biochemical, analytical, antimicrobial, anticancer, antibacterial, antifungal and antitumor activity. They have been studied as a class of ligands [6-8].Schiff bases and their complexes have a variety of applications in biological clinical and analytical fields[9]. Recently there has been a considerable interest in the chemistry of Schiff base compounds because of their potential pharmacological applications.



2,2'-(ethane-1,2-diylbis(azanylylidene))bis(ethan-1-yl-1-ylidene))bis(4-methylphenol)

H_2L^1



2,2'-(ethane-1,2-diylbis(azanylylidene))bis(ethan-1-yl-1-ylidene))bis(4-chlorophenol)

H_2L^2

Experimental Method

Materials

All chemicals were used as obtained from Rankem and Sd fine chemicals. Anal. Grade solvent from Sd Fine chemicals was used without further purification. The diamine and acetophenones were purified before use. Freshly prepared triple distilled water was used for making reagents.Ligands solution was prepared in DMF solvent. For determination of metal ligand stability constants of Cu (II) & Co (III)-H_2L^1 and Cu (II) & Co(III) -H_2L^2 complexes pH metrically, three titrations, acids titration, ligand titration and metal titration are carried out at 0.1 ionic strength in 70%DMF-water mixture using Bjerrium titration Process.

Calculation

The values of pK are calculated from fornation curves (i.e.half integral method). The pH at nA=0.5 corresponds the proton-ligands stability constant (pK). The correct value is also calculated by pointwise calculation method. The pK values for L1 to L2 are given in table -2

Table 1: Determination of $\bar{n}_A$ Values

System – L_1 Medium – 70% DMF-water

T_L^0 = 2 x 10^{-3} E^0 = 0.01 M μ = 0.1 M

N = 0.1 M V^0 = 25 ml Temp. = 27 ± 0.1°C

pH	V_1 (ml)	V_2 (ml)	$V_2 - V_1$ (ml)	$\bar{n}_A$
4.2	3.16	3.25	0.09	1.8242
4.4	3.21	3.31	0.1	1.8050
4.6	3.25	3.36	0.11	1.7858
4.8	3.3	3.42	0.12	1.7668
5	3.34	3.5	0.16	1.6895
5.2	3.36	3.6	0.25	1.5346
5.4	3.39	3.78	0.38	1.2444
5.6	3.42	3.95	0.53	0.9743
5.8	3.45	4.07	0.62	0.8014
6.0	3.5	4.2	0.7	0.6491
6.2	3.52	4.29	0.77	0.5150
6.4	3.55	4.4	0.85	0.3625
6.6	3.56	4.49	0.93	0.2090
6.8	3.59	4.55	0.97	0.1333
7.0	3.6	4.6	1	0.0769

Table 2: Determination of $\bar{n}_A$ Values

System – L_2 Medium – 70% DMF-water

$T_L^0 = 2 \times 10^{-3}$ $E^0 = 0.01$ M $\mu = 0.1$ M

N = 0.1 M $V^0 = 25$ ml Temp. = 27 ± 0.1°C

pH	V_1 (ml)	V_2 (ml)	$V_2 - V_1$ (ml)	$\bar{n}_A$
4	3.02	3.08	0.06	1.882227
4.2	3.14	3.21	0.07	1.863184
4.4	3.2	3.28	0.08	1.843972
4.6	3.25	3.35	0.1	1.80531
4.8	3.3	3.43	0.13	1.74735
5	3.31	3.53	0.22	1.572589
5.2	3.35	3.65	0.3	1.417989
5.4	3.4	3.78	0.38	1.264085
5.6	3.42	3.9	0.48	1.071077
5.8	3.45	4.08	0.63	0.782074
6	3.5	4.25	0.75	0.552632
6.2	3.51	4.34	0.83	0.398807
6.4	3.55	4.4	0.85	0.362522
6.6	3.56	4.46	0.9	0.266807
6.8	3.58	4.52	0.94	0.191043

The titration data were used to construct the curves [acid curve (A), acid + ligand curve (A + L) and acid + ligand + metal ion curve (A + L + M)] between volume of NaOH against pH. The proton-ligand formation number nA were calculated by Irving and Rossotti expression (Table 1 and 2).

$$n_A = \gamma - \frac{(V_2 - V_1)(N - E^0)}{(V^0 + V_1)\, T_L^0}$$

Where γ denotes the number of dissociable protons, N is the concentration of sodium hydroxide (0.1 mol.dm-3), (V2-V1) is the measure of displacement of the ligand curve relative to acid curve, where V2 and V1 are the volume of alkali added to reach the same pH reading to get accurate values of (V2-V1): the titration curves were drawn on an enlarged scale: E0 and TL0 are the resultant concentration of KNO and concentration of ligand, respectively. V0 is the initial volume of reaction mixture (25 cm3). Protonligand stability constant pk values of Ligand were calculated by algebraic method point wise calculation and also, estimated from formation curve nA Vs pH (Half integral method) by noting pH at which nA = 0.5 [Bjerrum 1957] (Table 3).

Table 3: Proton-Ligand stability constants (pK)

T_L^0 = 20 x 10^{-3} E^0 = 0.01 M μ= 0.1 M
N = 0.196 M V^0 = 12.5 ml Temp. = 27±0.1°C

System	Proton-Ligand stability constants (pK)			
	Half Integral Method		Pointwise Calculation	
	pK1	pK2	pK1	pK2
L_1	5.20	6.20	5.126	6.215
L_2	5.02	6.01	5.07	5.93

Determination of metal ligand stability constants

Table 4: Determination of $\bar{n}$ Values

System – L_1 - Cu (II) Medium – 70% DMF-water
T_L^0 = 2x 10^{-3} E^0 = 0.01 M μ = 0.1 M
N = 0.1 M V^0 = 25 ml Temp. = 27 ± 0.1°C

pH	V_2 (ml)	V_3 (ml)	$V_3 - V_2$ (ml)	$\bar{n}$
4.3	3.29	3.37	0.08	0.430862
4.4	3.31	3.4	0.09	0.48434
4.5	3.35	3.44	0.09	0.488875
4.6	3.36	3.46	0.1	0.54298
4.7	3.4	3.51	0.11	0.609669
4.8	3.42	3.55	0.13	0.711981
4.9	3.45	3.6	0.15	0.839064

5.0	3.5	3.67	0.17	0.970918
5.1	3.55	3.72	0.17	1.19581
5.2	3.6	3.84	0.24	1.503818
5.3	3.69	3.94	0.25	1.736923
5.4	3.78	4.03	0.25	1.969569
5.5	3.95	4.2	0.25	2.437391

Table 5: Determination of $\overline{n}$ Values

System – L_1 - Co (III) Medium – 70% DMF-water
$T_L^0 = 2x\ 10^{-3}$ $E^0 = 0.01$ M $\mu = 0.1$ M
N = 0.1 M $V^0 = 25$ ml Temp. = 27 ± 0.1°C

pH	V_2 (ml)	V_3 (ml)	$V_3 - V_2$ (ml)	$\overline{n}$
4	3.19	3.25	0.06	0.316447
4.2	3.25	3.32	0.07	0.373538
4.3	3.29	3.37	0.08	0.430862
4.4	3.31	3.4	0.09	0.48434
4.5	3.35	3.44	0.09	0.498875
4.6	3.36	3.47	0.11	0.597278
4.7	3.4	3.51	0.11	0.649669
4.8	3.42	3.55	0.13	0.711981
4.9	3.45	3.6	0.15	0.809064
5	3.5	3.65	0.15	0.856692
5.1	3.55	3.7	0.15	0.956303
5.2	3.6	3.79	0.19	1.190522
5.3	3.69	3.89	0.2	0.316447

Table 6: Determination of $\bar{n}$ Values

System – L_2 - Cu (II) Medium – 70% DMF-water
T_L^0 = 2x 10^{-3} E^0 = 0.01 M μ = 0.1 M
N = 0.1 M V^0 = 25 ml Temp. = 27 ± 0.1°C

pH	V_2 (ml)	V_3 (ml)	$V_3 - V_2$ (ml)	$\bar{n}$
4	3.08	3.16	0.08	0.416249
4.1	3.15	3.24	0.09	0.471964
4.2	3.21	3.31	0.1	0.523207
4.3	3.25	3.37	0.12	0.633549
4.4	3.28	3.41	0.13	0.685555
4.5	3.31	3.45	0.14	0.745341
4.6	3.35	3.5	0.15	0.805971
4.7	3.39	3.55	0.16	0.877333
4.8	3.43	3.6	0.17	0.941076
4.9	3.5	3.68	0.18	1.064977
5	3.53	3.72	0.19	1.16458
5.1	3.6	3.8	0.2	1.303056
5.2	3.65	3.88	0.23	1.556908

Table 7: Determination of $\bar{n}$ Values

System – L_2 - Co (III) Medium – 70% DMF-water
T_L^0 = 2x 10^{-3} E^0 = 0.01 M μ = 0.1 M
N = 0.1 M V^0 = 25 ml Temp. = 27 ± 0.1°C

pH	V_2 (ml)	V_3 (ml)	$V_3 - V_2$ (ml)	$\bar{n}$
4.2	3.21	3.28	0.07	0.357501
4.3	3.25	3.33	0.08	0.422366
4.4	3.28	3.37	0.09	0.474615
4.5	3.31	3.4	0.09	0.479148
4.6	3.35	3.45	0.1	0.537314
4.7	3.39	3.5	0.11	0.603167
4.8	3.43	3.56	0.13	0.719647
4.9	3.5	3.64	0.14	0.838316
5	3.53	3.67	0.14	0.858111
5.1	3.6	3.75	0.15	0.957292

5.2	3.65	3.8	0.15	1.015375
5.3	3.7	3.86	0.16	1.127082
5.4	3.78	3.95	0.17	1.285034
5.5	3.84	4.01	0.17	1.388392
5.6	3.9	4.08	0.18	1.599141
5.7	3.99	4.17	0.18	1.82354
5.8	4.08	4.27	0.19	2.29744
6	4.25	4.45	0.2	3.40252

Metal-Ligand stability constants (log k) were determined by the half integral method by plotting $\bar{n}$ Vs pL. The experimental values determined using expression

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

Where N, E0, Vo and V2 have same significance as in equation (1), V3 is the volume of NaOH added in the metal ion titration to attain the given pH reading and TM 0 (4 × 10-4 mol dm-3) is the concentration of metal ion in reaction mixture. The stability constants for various binary complexes have been calculated

Table 8: Value of log K_1 and log K_2 of the complexes with ligand (L_1 to L_2)

System	log K_1	log K_2
Cu(II) –L_1	5.06	4.52
Co(III)–L_1	5.36	4.08
Cu(II) –L_1	5.56	4.07
Co(III)–L_1	4.87	3.66

Results and Discussion

The extent of deviation may be the dissociation of -OH group. L_1, L_2, may be considered as a monobasic acid having one replaceable H+ ion from phenolic -OH group and can be represented as –

HL $H^+ + L$

The titration data were used to construct the curves [acid curve (A), acid + ligand curve (A + L) and acid + ligand + metal ion curve (A + L + M)] between volume of NaOH against pH. The proton-ligand formation number nA were calculated by Irving and Rossotti expression (Table 1).

$$\bar{n}A = \gamma \frac{(V_3 - V_2)(N + E^0)}{(V^0 + V_2) \times T^0_M}$$

Where γ denotes the number of dissociable protons, N is the concentration of sodium hydroxide (0.15 mol.dm-3), (V2-V1) is the measure of displacement of the ligand curve relative to acid curve, where V2 and V1 are the volume of alkali added to reach the same pH reading to get accurate values of (V2-V1) titration curves were drawn on an enlarged scale: E_0 and TL_0 are the resultant concentration of perchloric acid and concentration of ligand, respectively. V0 is the initial volume of reaction mixture (50 cm3). Proton ligand stability constant pk values of Ligand were calculated by algebraic method point wise calculation and also, estimated from formation curves (Fig. 4-6) nA Vs pH (Half integral method) by noting pH at which nA = 0.5 [Bjerrum 1957] (Table 2).

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