Formation of Ternary Complex of Cu(II) with Tridentate Schiff Base and Dipeptide as Primary and Secondary Ligand

Sarika Manohar Jadhav

Assistant Professor,
Department of Chemistry
Siddharth Arts, Commerce and Science College Jafrabad,
Dist. Jalna 431206, Maharashtra State, India.

***Abstract*: The stability of 1:1:1 ternary chelates of bivalent Cu(II) metal ion with Schiff base 4-hydroxy-3-(1-{2(4-fluroenzylideneamino)phenylimino)ethyl)--6-methyl-2H-pyran-2-one MF:$C_{21}H_{17}N_2O_3F$) as primary ligand (L) and DL-Glycyl DL-Phenylalanyl as secondary ligand (R) have been carried out in 60% (v/v) THF-Water medium pH metrically at 30° C and 0.1 MNaClO$_4$ ionic strength. The stability constants of ternary complexes ML and MR are also determined under similar experimental conditions. The stability constants of ternary complexes are evaluated and their relative stabilities compared to the corresponding binary complexes are evaluated and their relative stabilities compared to the corresponding binary complexes are expressed in terms of statistical parameter Δ logk, K_R,K_L and K_r values. The species distribution curves are used to explain the variation in concentration of these as function of pH. The pH have been discussed by Irving-Rossotti technique and evaluated by using the computer SCOGS program.**

***Keywords*: Ternary Complex, Dipeptide, Schiff base, Potentiometry, Tridentate ligand.**

I. INTRODUCTION

Schiff Bases and their metal complexes studied for their use in antimicrobial activity.[1,2] Metal Complexes of Containing first row elements like Copper (Cu), Cobalt(Co), Nickel(Ni), and Zincn (Zn) as they are associated with various bio molecules related to essential physiological activities.[3] Schiff bases of o-phenyldiamine reported to have variety of applications including biological clinical and analytical fields.[4-6] How ever much less attension has been focused on Schiff bases of o-phynelene diamine, So we have synthesised Schiff bases of OPD and DHA (Dehydro Acetic Acid) with various aldehydes. The ternary complex formation equilibria of tetradentate Schiff base with 4-hydroxy-3(1-{2-[(4-chlorobenzylideneamino) phenylimino) ethyl) – 6 methyl-2H-Pyran2-one as primary ligand and DL- Alanyl Glycyl (R_1), Glycyl- DL-Valine(R_2) dipeptides as secondary ligands with Cu, reported earlier.[7,8] Also we report about ternary complex formation of Cu(II) metal with tridentate Schiff base 4-hydroxy-3-(1-{2(4-fluroenzylideneamino) phenylimino)ethyl)--6-methyl-2H-pyran-2-one as primary ligand(L) and DL-Alanyl-DL-Valine as secondary ligand (R)[8] In continuation of our earlier work we have prepared tri dentate Schiff base with known method.[9]

II. EXPERIMENTAL

All the reagents used were of AR grade. Schiff Base was found insoluble in water there for 60% (THF: Water) used as a solvent in present investigation. AR grade THF used further purified by Known literature method.[10] Ligand was synthesized by known method of ligand reported. The ligand solution (0.1M) was prepared in distilled THF. A standard 0.2N NaOH solution was used for titrations prepared in distilled water. Standard solutions of AR grade $HClO_4$, $NaClO_4$ (1.0 M) were prepared in distilled water and standardized by known methods.[10] Experimental procedure by potentiometric titration technique performed in inert atmosphere (nitrogen) at ionic strength of 0.1 M ($NaClO_4$). The potentiometric technique for study of the mixed ligand complexes include following titrations.

1) 2 ml $HClO_4$ (0.2N) + 5 ml $NaClO_4$ (1M) + 13 (ml) Water + 30 ml THF **(A).**
2) 2 ml $HClO_4$ (0.2N) + 5 ml $NaClO_4$ (1M) + 10 ml Ligand 13 ml (0.1M) + 20ml THF **(A+R)**.
3) 2 ml $HClO_4$(0.2N) + 5 ml $NaClO_4$(1M) + 10 ml ligand + 2 ml Metal solution(0.01M) + 11 ml Water + 20 ml THF **(A+R+M).**
4) 2ml $HClO_4$(0.2N) + 5 ml $NaClO_4$(1M) + 10 ml ligand (L) + 10 ml secondary Ligand (R) + 2 ml Metal solution (0.01M) + 11 ml Water + 10 ml THF **(A+L+R+M).**

The solutions were titrated pH metrically against (0.2N) NaOH. All other solvents used during the entire research work were of AR grade

III. APPARATUS

The titrations were carried out using Elico digital pH meter (model LI-127) equipped with a CL-51B combined electrode for pH measurements. Before titrations pH meter was calibrated against standard buffers (pH 4.02 and 9.18) readings were corrected for THF: water media. The pH and volume of NaOH piloted to determine protonation constants and stability constants of the Schiff bases and their complexes were determined. Throughout the experimental work glass distilled water was used. This was obtained by double distillation of deionised water in presence of crystals of potassium per magnate and potassium hydroxide pallets. For synthesis of Schiff bases, ethanol and methanol were used as commercial solvents. Structure of Ligand is as follow.

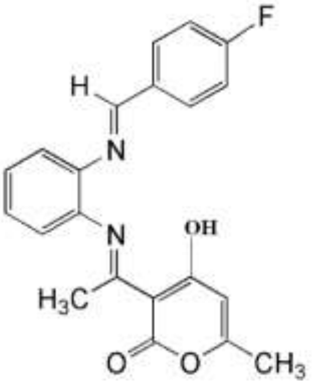

Figure 1. 4-hydroxy-3-(1-{2(4-fluroenzylideneamino)phenylimino)ethyl)--6-methyl-2H-pyran-2-one

IV. POTENTIOMETRIC MEASUREMENT

Stock solutions of ligand (0.1M) was prepared in THF. The protonation constants of primary ligand (L) and secondary ligands DL- Glycyl DL lphenylalanyl (R) with Cu ions determined in 60% (v/v) THF: Water medium. The Irving-Rossetti technique was used after appropriate pH corrections determined by using method suggested by Van Uitert.[11] The protonation constant and metal-ligand stability constant of ligands is given in the (Table 1). The pH values of titrations were found in between pH 3 to 11 from pH metric data the stoichiometry, deprotonation and stability constants were calculated. Primary and secondary ligands form both 1:1 and 1:2 complexes with Cu(II) ions. Here two systems are represented in the above work. The Concentration of various species HL, L, R, CuL, CuR, CuLR, at different pH were obtained by using SCOGS computer programme.[12,13] The concentration of these species were plotted against pH values to study complexing equilibria and predominance of mixed ligand complexes over binary complexes. Equilibrium constant β_{111} for the reaction

$$\mathrm{M + R + L \rightleftharpoons MRL}$$
$$\beta_{111} \rightleftharpoons [\mathrm{MRL}]\ [\mathrm{M}]^{-1}\ [\mathrm{R}]^{-1}[\mathrm{L}]^{-1}$$

V. RESULT AND DISCUSSION

TERNARY COMPLEXATION

The pH titration curves for systems Cu(II)-L-R is represented in (Fig.2). The possible equilibria in the ternary chelation was done by analyzing the graph. The precipitation pH of mixed ligand complex was about 6.9. The mixed ligand curves coincide with A+L curve at pH 1.4 and then deviates. The mixed ligand curve from the theoretical composite curve towards left indicate the formation of ternary complex. The mixed ligand curve did not coincide with A+L+M and A+R+M metal complex titration curves, indicates the formation of 1:1:1 complex by a simultaneous equilibria.

The species distribution curves as a function of pH were generated using SCOGS computer programme. The initial percentage of free metal at pH = 3.2 is very less i.e. 2.45 which indicates the maximum consumption of metal ions in the complex formation at this pH. It sharply decreases up to pH 5.2 after which the concentration remains constant indicating the maximum complexation in the pH- range 3.2 to 5.2. The percentage of free ligands L and R though extremely low (~0.03%) found to increase with increasing pH. The percentage of F_L and F_R reaches to 0.1 and 36 % percent respectively at pH 5.3 and then remains constant. Due to the dissociation of excess ligands present in the system increase in free ligand concentrations. The values of β_{111}, β_{20}, β_{02}, K_L, K_R, K_r and Δ logK are presented in (Table. 2).These values express relative stabilities of binary and ternary complexes. The comparative study of β_{111} with the product of β_{20} and β_{02} i.e.K_R of the system confirm formation of ternary complexes over binary complexes of primary as well as secondary ligands. Since they show positive value. Relatively higher positive value of K_R than K_L reveals greater stability of ternary complexes with respect to the binary complexes of secondary ligand than that of primary ligand.

$$C_1 = \mathrm{H_2R} \rightleftharpoons \mathrm{HR + H} \ \ldots\ldots\ ..(1a)$$
$$C_2 = \mathrm{HR} \rightleftharpoons \mathrm{H + R} \ \ldots\ldots\ldots\ldots\ldots (1b)$$
$$C_3 = \mathrm{H2L} \rightleftharpoons \mathrm{HL + L} \ \ldots\ldots\ldots\ldots (2a)$$
$$C_4 = \mathrm{HL} \rightleftharpoons \mathrm{H + L} \ \ldots\ldots\ldots\ldots\ldots\ (2b)$$
$$C_5 = \mathrm{M + R} \rightleftharpoons \mathrm{MR} \ \ldots\ldots\ldots\ldots\ldots (3a)$$
$$C_6 = \mathrm{MR + R} \rightleftharpoons \mathrm{MR2} \ \ldots\ldots\ldots\ldots (3b)$$
$$C_7 = \mathrm{M + L} \rightleftharpoons \mathrm{ML} \ \ldots\ldots\ldots (4a)$$
$$C_8 = \mathrm{ML + L} \rightleftharpoons \mathrm{ML_2} \ \ldots\ldots\ldots\ldots\ldots (4b)$$
$$C_9 = \mathrm{M + R + L} \rightleftharpoons \mathrm{MLR} \ \ldots\ldots\ldots (5a)$$

To understand mechanism and extent of ternary complex formation at different pH the species distribution curves are most useful. The speciation diagram obtained for Cu(II)LR is presented in Figure 2. From C_9 curve it can be observed that initially ternary species is near about 2.64% at pH 3.2 it increases sharply upto 62 % at pH 5.9 then after it remains constant thus more than 62% metal ion is present in the form of ternary complex at pH 5.9.

The reaction 1b and 2b represent formation of R(C_2) and L(C_4) their continuous decrease in pH indicate the formation of CuLR by reaction 5a (C_9). It can be seen that concentration of HL and HR at initial pH 3.2 are 1.83 % and 88.34 % respectively which sharply decreases up to pH 5.9 and then remains constant. The formation of ternary complex also takes place to maximum extent i.e. 62% in the same pH range which support possibility of C_9. The possibility of formation of CuLR in the present investigation is also possible by following equilibria

$$\mathrm{ML} + \mathrm{R} \rightarrow \mathrm{MLR} \quad \ldots \ldots (6)$$

$$\mathrm{MR} + \mathrm{L} \rightarrow \mathrm{MLR} \ldots \ldots (7)$$

The other way of characterizing the ternary complexes is by following disproportionation reactions.

$$\mathrm{CuR_2} + \mathrm{CuL_2} \rightarrow 2\mathrm{CuLR} \ldots \ldots (8)$$

This reaction is possible if both ligands form 1:1 and 1:2 complexes individually with the metal ion. Otherwise disproportionation reactions are

$$\mathrm{ML_2} + \mathrm{MR} \rightarrow \mathrm{MLR} + \mathrm{ML} \ldots \ldots (9)$$

$$\mathrm{MR_2} + \mathrm{ML} \rightarrow \mathrm{MLR} + \mathrm{MR} \ldots (10)$$

$$\mathrm{ML} + \mathrm{MR} \rightarrow \mathrm{MLR} + \mathrm{M} \ldots \ldots (11)$$

The reaction 9 and 10 are possible when both ligands forms 1:1 and 1:2 binary complexes. The reaction 11 indicates ligand which form only 1:1 binary complex with metal ion

From species distribution curve it shows that initial concentration of primary C_4 and secondary ligands C_5 decreases sharply up to pH 5.2 and 5.9. The percentage distribution curves of free metal (F_M), free primary ligand (F_L) and free Secondary Ligand (F_R) are shown in Figure (3-5). The initial percentage of free metal is 1.02 at pH 3.2 which indicates the maximum consumption of metal ions in the complex formation at this pH. Concentration of free metal sharply decreases up to pH 4.2 then after it remains constant this indicates the maximum complexation in the pH range of 3.2 to 5.9. The percentage of free ligand F_L and F_R initially is very low near about 0.0005% and 0.5% and increases with increase in pH. The percentage of free primary ligand (F_L) and free secondary ligand (F_R) reaches to 0.1 and 36% respectively at pH4.4 and 5.9 and then remains constant. This increase in free ligand concentration may be due to the dissociation of excess of ligands present in the system.

The relative stabilities of the binary and ternary complexes are expressed in terms of β_{111}, β_{20}, β_{02}, K_L, K_R, K_r and Δ logK are presented in (Table. 2).These values express relative stabilities of binary and ternary complexes. The K_R value more than K_L indicates that ternary complexes with respect to binary complexes of primary ligand than binary complex of secondary ligand. The negative value of Δlogk complex indicates that the ternary complex is less stable than binary complexes of primary and secondary ligand and also due to reduced number of coordinating sites. From ternary complex curve

Table1. pK and logk values of Cu(II) chelates of ligand and dipeptide in 60 %(v/v) THF-water medium at Temp: 30 °C and ionic strength μ= 0.1 M $NaClO_4$

Ligands(L) / peptide(R)	***pK_1***	***pK_2***	***$logk_1$***	***$Logk_2$***	***logβ***
Ligand (L)	3.01	9.98	9.39	8.84	18.23
DL -Glycine Phenylalanyl (R)	4.5666	8.5700	8.900	3.8700	12.77

Table. 2 Parameters of formations of mixed ligand complexes of Cu(II) with primary Ligand (L) and dipeptides (R)

Dipeptides	***Log β_{20}***	***β_{02}***	***β_{11}***	***k_L***	***k_R***	***k_r***	***Δlogk***
DL-Glycyl Phenylalanyl(R)	17.4501	12.7700	17.0786	7.1034	8.1786	0.1532	-1.7966

VI. Conclusion

Present investigation include the study of Ternary complex formation equilibria of Cu(II) metal involving tridentate Schiff base ligand (L) 4-hydroxy-3-(1-{2(4-fluroenzylideneamino)phenylimino)ethyl)--6-methyl-2H-pyran-2-one MF:$C_{21}H_{17}N_2O_3F$) as primary ligand(L) and DL--Glycyl Phenylalanyl as secondary ligand (R). From Complexometric curve it is concluded that ternary complex formation is upto 62 % at pH 5.9 then after it remains constant. The curve C_2 shows that concentration of free secondary ligand is 1.84 it decreases to 0.001 which indicate dissociation of secondary ligand. From curve C_5 initial concentration of binary complex of secondary ligand I.e. MR is near about 95% it sharply decreases to 37% at pH 5.8 and then remains constant. From C_4 it shows that initial concentration of initialy primary ligand concentration is 88% it decreases contiguously with increase in upto 0.01 at pH 5.8 . The less percentage of free primary ligand indicate involvement of primary ligand in the complex formation. C_9 curve indicate that percentage of ternary complex is 2.4% at initial pH 3.2 percentage of ternary complex continuously increases with increase in pH upto 62% at pH 5.8 and then after remains constant. From complexometric curve it is concluded that involvement of primary ligand more than secondary ligand in ternary complex formation. The less formatation of ternary complex may be due to less involvement of secondary ligand than primary ligand.

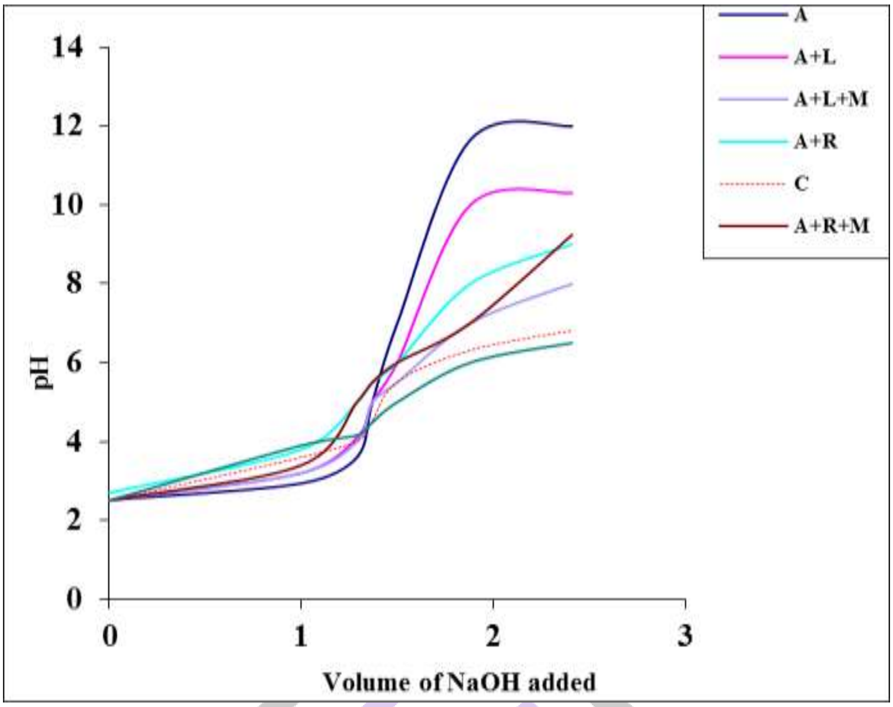

Figure 1. Potentiometric titration curve in CuLR system

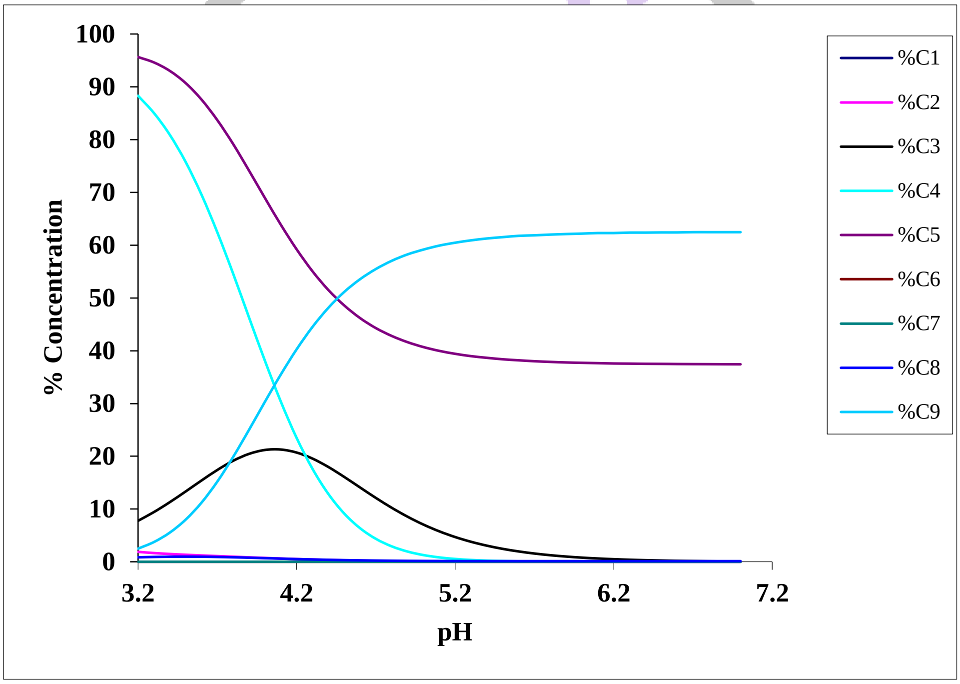

Figure 2. Species distribution diagram in CuLR system

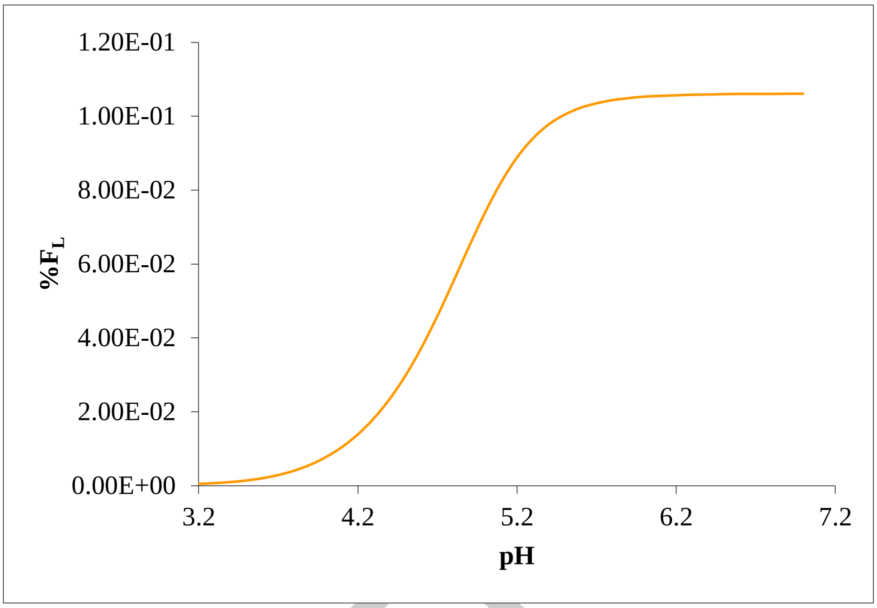

Figure 3. Percentage distribution curve of F_L in CuLR

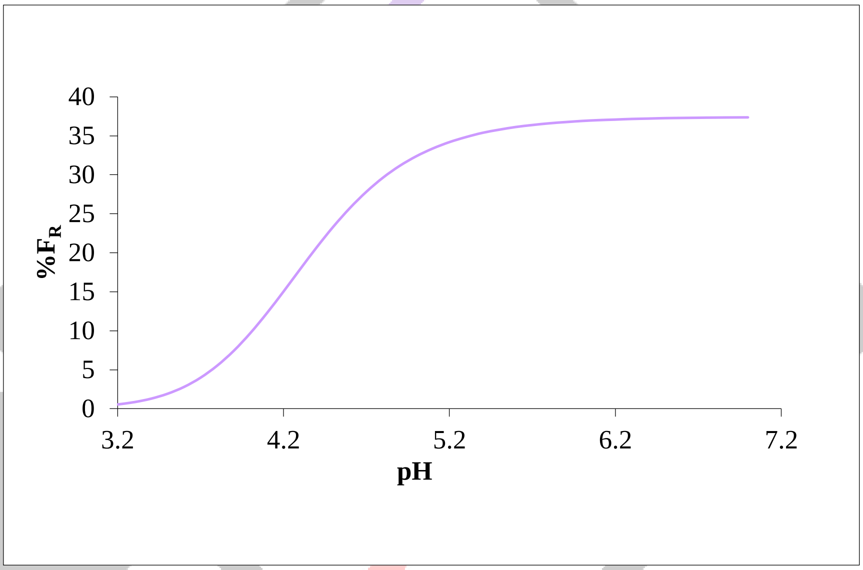

Figure 4. Percentage distribution curve of F_R in CuLR

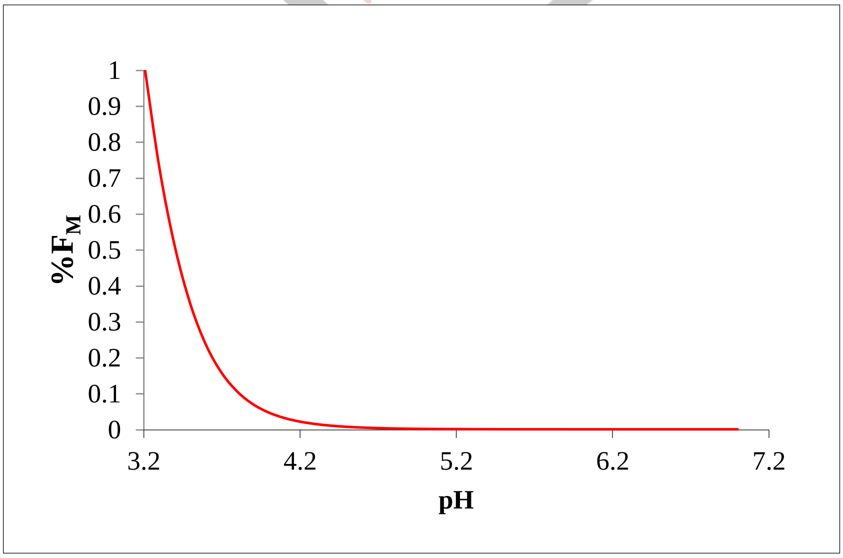

Figure 5. Percentage distribution curve of F_M in CuLR

References

[1] M. C. Rodriguez-Arguelles, S. Mosquera- Vazquez, P. TouronTouxeda, J. Sanmartin-Matalobos, A. M. Garcia-Deibe, M. Belicchi- Ferrari et.al. “ Complexes of 2-thiophenecarbonyl and isonicotinyl hydrazones of 3-(N-mrthyl)isatin. A study of their antimicrobial activity, J. Inorg Biochem. Vol. 101, pp-138-147, 2007.

[2] P. Kamalakannan and D. Venkappayya, “ Synthesis and characterisation of cobalt and nickel chelates of 5-dimethylaminomethyl- 2-thiuracil and their evaluation as antimicrobial and anticancer agents, J. Inorg Biochem , vol. 90, pp- 22-37, 2002.

[3] M. C. Lanier, M. Feher, N. J. Ashweek, C. J. Loweth, J. K. Rueter D. H. Slee. Et.al, Synthesis and structure activity relationship of tetrahydropyridol{4,3-dlpyrimidine-2,4-diones as human Gn RH receptor antagonists ,Biorg Med Chem. Vol. 15, pp-5590-5603,2007.

[4] P. Singh, R. L. Geol , B. P. Singh,” Synthesis Characterisation and Biological actvity of Schiff Bases”, J. Indian Chem. Soc, .vol. 52, pp-958, 1975.

[5] A. M. Mahindra, J. M. Fisher, M. Rabinovitz,” A Tissue Culture Compatible Indicator of Copper Mediated Toxicity”, Nature, vol. 64, pp-303, 1983.

[6] P. R. Patel, B. T. Thakar, S. Zele,Preparation and Characterisation of some Lanthanide Complexes involving a Heterocyclic Beta Diketone”, Indian J. Chem. Vol. 38 A, pp-563, 1999.

[7] S. M. Jadhav. V. A. shelke ,U.P. Shaikh,”Ternary Complex formation Equilibria of tetradentate Schiff Base ligand with Zn (II) and Dipeptides” .International Journal of All Research education and Scientific Methods ,Vol. 9, Issue. 5, pp- 2562-2568, 2021.

[8] S. M. Jadhav, V. A. Shelke, S. G. shankarwar and T. K. Chondhekar, “Synthesis Charecterisation, Potentiometry and Antimicrobial Studies of Transition Metal Complexes of Tridentate Schiff Base Ligand”, *Journal of Coordination Chemistry*, Vol. 63, No. 23, pp-4153-4163, 2010.

[9] S. M. Jadhav “ Formation of Binary and Ternary Complex of Cu(II) wth Tridentate schiff Base and Dipeptide as Primary and Secondary Ligand, International Journal of Chemical Science”,Vol. 5, Issue 4, pp-20-24, 2021.

[10] A. I. Vogel,” A *Text Book of practical Organic Chemistry*” 3rd Edn, publisher, Longmans, London, pp-177, 1959.

[11] L. G. Van-Uitert, W. C. Ferrelius, B.E. Douglass, “Studies On Coordination Compounds III Chelating Tendencies of β-Diketones with the Chlorides of Copper (II) , Nickel and Bariumin Water- Dioxane Solutions*“,* Journal of American Chemical Society, Vol. 75, No. 2, pp- 457-460, 1953.

[12] I. G. Sayce, *Talenta*, Vol. 15, no.19, pp-831,1972.

[13] I. G. Sayce, Talenta, 1988:15:1397, 1988.