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NOTE

Proton-Ligand and Metal-Ligand Stability Constants of Newly Synthesised Bis-Chalcones and Their Bromo Derivatives

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The interaction of Cu(II) and Th(IV) with 1,1-bis-[2-hydroxy-3-(3-aryl-prop-2-en-1-one)-5-methyl phenyl] methanes and their bromo derivatives has been investigated by Bjerrum method as adopted by Calvin and Wilson. The stability constants of complexes containing 1 : 1 and 1 : 2 ratio of Cu(II) and Th(IV) to ligand have been estimated at (27 ± 0.1°C) and 0.1 M ionic strength ($NaClO_4$) in 80% DMF-water mixture.

Ligand stability constants of lanthanides with some substituted pyrazolines[1] and diketones were studied by Sawalakhe[1]. Mandakmare *et al.*[2] have studied the metal-ligand stability constant of Cu(II) with some substituted coumarins pH-metrically in 70% dioxane-water mixture. Gudadhe *et al.*[3] carried out the study of stability constants of Th(IV) complexes with some substituted pyrazolines.

In view of the analytical applications of chalcone and their bromo derivatives, it is of interest to know that the physico-chemical properties such as stability of the complexes with Cu(II) and Th(IV) metal ions are still lacking; therefore the present investigation has been undertaken to study the complex formation of Cu(II) and Th(IV) with some bis-chalcones and their bromo derivatives. In 80% DMF-water medium at fixed ionic strength, m = 0.1 M and temperature (27 ± 0.1°C)

The interaction of 1,1-bis-[2-hydroxy-3-(3-phenyl-prop-2-en-1-one)-5-methyl pheny] methane **(1)**, 1,1-bis-{2-hydroxy-3-[3-(4′-methoxy phenyl)-prop-2-en-1-one]-5-methyl phenyl} methane **(2)** and their dibromo derivatives; 1,1-bis-[2-hydroxy-3-(2,3-dibromo-3-phenyl-propan-1-one)-5-methyl phenyl] methane **(3)**, 1,1-bis-{2-hydroxy-3-[2,3-dibromo-3-(4′-methoxy phenyl)-propan-1-one]-5-methyl phenyl} methane **(4)** with Cu(II) and Th(IV) has been studied in our present investigation in 80% DMF-water medium potentiometrically. The stability constants of metal chelates have been determined by Calvin-Bjerrum method.

All chemicals such as sodium hydroxide, sodium perchloride and perchloric acid and metal salts used were of AR grade in the present investigation. Ligands **(1)**, **(2)**, **(3)** and **(4)** were prepared following the literature method.[4] All ligands were crystallised and their purity was checked by TLC before being used. The

solutions of purified ligands were prepared in DMF and standardized by potentiometric techniques.

Systronics microprocessor based pH-meter with accuracy of ± 0.01 unit with glass and saturated calomel electrode was used for the measurement. It was calibrated by buffer solution of pH 4.00, 7.00 and 9.20 at 27°C before proceeding for the titrations.

The experimental procedure involved pH-metric titration of (i) free acid (0.01 M), (ii) free acid (0.01 M) + ligand (20×10^{-4} M), and (iii) free acid + ligand (20×10^{-4} M) + metal ion (4×10^{-4} M) against standard NaOH solution. The ionic strength of all the solutions was maintained constant (0.1 M) by adding an appropriate quantity of 1 M sodium perchlorate.

The titration was carried out in 100 mL pyrex glass beaker kept in water bath maintained at constant temperature (27 ± 0.1°C). Nitrogen gas was slowly purged into the solution to remove oxygen and carbon dioxide. In aqueous-organic mixture, pH values were corrected by use of Van-Ultert and Hass equation[5].

Proton-ligand formation constants: The deviation of acid-ligand curves from acid curve started around pH 2.5 for each ligand and increased continuously up to pH 12. It shows that dissociation of —OH group occurs which is present in the ligand part of the complex structure. The values of nA were calculated by Irving-Rossotti's expression. The pKa values for each system were calculated by half integral method which are presented in Table-1.

TABLE-1

S.N.	System	Constant	
		pK_1	pK_2
1.	1,1-bis-[2-hydroxy-3-(3-phenyl-prop-2-en-1-one)-5-methyl phenyl] methane.	7.05	10.80
2.	1,1-bis-{2-hydroxy-3-[3-(4′-methoxy phenyl)-prop-2-en-1-one]-5-methyl phenyl} methane	9.85	10.90
3.	1,1-bis-[2-hydroxy-3-(2,3-dibromo-3-phenyl-propan-1-one)-5-methyl phenyl] methane	9.71	11.14
4.	1,1-bis-{2-hydroxy-3-[2,3-dibromo-3-(4′-methoxy phenyl)-propan-1-one]-5-methyl phenyl} methane.	10.10	11.07

Metal-Ligand stability constants: The values of n were evaluated from Irving-Rossotti's expression which were used to calculate the metal-ligand stability constants. The metal-ligand stability constants for all the systems were calculated by half integral method. These values are presented in Table-2. It could be seen from Table-2 that there is variation in values of log k for each complex. It showed that there must be stepwise complex formation. The order of stability of metal complex is Th(IV) > Cu(II) in all the ligands.

TABLE-2

S.N.	System	Constant	
		$\log K_1$	$\log K_2$
1.	Cu(II)-1,1-bis-[2-hydroxy-3-(3-phenyl-prop-2-en-1-one)-5-methyl phenyl] methane.	12.96	6.33
2.	Cu(II)-1,1-bis-{2-hydroxy-3-[3-(4′-methoxy phenyl)-prop-2-en-1-one]-5-methyl phenyl} methane.	14.39	10.25
3.	Cu(II)-1,1-bis-[2-hydroxy-3-(2,3-dibromo-3-phenyl-propan-1-one)-5-methyl phenyl] methane.	17.27	8.97
4.	Cu(II)-1,1-bis-{2-hydroxy-3-[2,3-dibromo-3-(4′-methoxy phenyl)-propan-1-one]-5-methyl phenyl} methane.	16.41	13.60
5.	Th(IV)-1,1-bis-[2-hydroxy-3-(3-phenyl-prop-2-en-1-one)-5-methyl phenyl] methane.	14.51	7.80
6.	Th(IV)-1,1-bis-{2-hydroxy-3-[3-(4′-methoxy phenyl)-prop-2-en-1-one]-5-methyl phenyl} methane.	14.80	11.58
7.	Th(IV)-1,1-bis-[2-hydroxy-3-(2,3-dibromo-3-phenyl-propan-1-one)-5-methyl phenyl] methane.	17.51	12.46
8.	Th(IV)-1,1-bis-{2-hydroxy-3-[2,3-dibromo-3-(4′-methoxy phenyl)-propan-1-one]-5-methyl phenyl} methane.	16.64	12.20

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