

TABLE 1—STABILITY CONSTANTS OF SOME MIXED LIGAND COMPLEXES OF Th(IV)

($\mu = 0.2 M$; temp. = $30^\circ \pm 0.1^\circ$)

System	log K_{MAL}^{MA}	System	log K_{AML}^{AM}
Th(IV)-NTA-NAP	7.30	Th(IV)-NTA-ARS	13.50
Th(IV)-HEDTA-NAP	7.05	Th(IV)-HEDTA-ARS	12.70
Th(IV)-EDTA-NAP	5.80	Th(IV)-EDTA-ARS	8.50

where T_{CM}° is the concentration of [Th(IV)-A] which is the concentration of Th(IV); \bar{n}_A = proton-ligand stability constant at particular pH value; V^0 = total volume of the system; V_1 = volume of alkali required at curve A; and $(V_3 - V_2)$ = volume of alkali required for secondary complexation at certain pH value. It is calculated by subtracting the difference of the volume of alkali required between curves A and B (V_2) from the volume of alkali required between curves C and D (V_3).

\bar{n} and pL values were calculated at different pH values. At $\bar{n} = 0.5$ in the formation curve, $pL = \log K_{MAL}^{MA}$. The values of $\log K_{MAL}^{MA}$ have been summarized in Table 1. The error limits are ± 0.05 log units.

The stability sequence of the ternary complexes of Th(IV) with change in primary complex is NTA > HEDTA > EDTA. Both the secondary ligands chosen are bidentate and coordination takes place through two oxygen atoms. The [Th(IV)-NTA]⁺ has an electrostatic attraction for the incoming secondary ligands (anion form). [Th(IV)-HEDTA]⁺ behaves similarly. However, because of neutral nature of [Th(IV)-EDTA] chelate the incoming secondary ligand faces comparatively lesser electrostatic force of attraction and thus the stability of the ternary complex of EDTA is less. This order of the formation constant of ternary complexes, with change in the primary ligands can also be explained on the basis of the vacant coordination sites of Th(IV) after its reaction with primary ligands. For Th(IV), NTA acts as tetradentate, HEDTA as pentadentate while EDTA acts as hexadentate leaving respectively four, three and two coordination positions available for bidentate secondary ligands (considering the coordination number of Th(IV) as 8). As per statistical effect the expected sequence of NTA > HEDTA > EDTA ternary complexes are observed in the present case.

The order of the stability constants of ternary complexes with respect to secondary ligand is ARS > NAP. It can be explained on the basis of ring size of chelates formed by these ligands; ARS forms a five-membered chelate ring, while NAP forms a six-membered chelate ring.

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Metal Chelates of

3-(*o*-Hydroxyphenyl)-5-phenylisoxazole with Be(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) & Dioxouranium(VI)

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The interaction of 3-(*o*-hydroxyphenyl)-5-phenylisoxazole with some bivalent metal ions like Be(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and dioxouranium(VI) has been investigated potentiometrically in 75% v/v methanol-water mixture at 35° and at an ionic strength of 0.1M KNO₃. The stability constants of the metal chelates have been determined by Bjerrum-Calvin pH titration technique followed by Irving and Rossotti. The stability constants of the metal chelates follow the order UO₂²⁺ > Cu(II) > Be(II) > Zn(II) > Ni(II) > Cd(II) > Co(II) > Mn(II).

RECENTLY Rao and Rao¹ reported the synthesis of a number of 3,5-disubstituted isoxazoles, some of which have shown appreciable antibacterial and antifungal activities. The spectral properties of 3-(*o*-hydroxyphenyl)-5-phenylisoxazole^{2,3} were reported by Murthy *et al.*⁴ However, the chelating tendencies of the above ligand have not been studied. Presently we have determined the stability constants of the metal chelates of 3-(*o*-hydroxyphenyl)-5-phenylisoxazole with different bivalent metal ions, viz. Be(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and UO₂²⁺, in 75% methanol-water mixture using pH titration technique. The correction factor for converting the pH reading in methanol-water to aqueous medium is -0.12 as calculated by Van Uitert and Haas⁵ procedure.

The ligand was prepared by the literature method³. Metal nitrates (AR) were dissolved in doubly distilled water and the metal contents estimated volumetrically by titrating against standard EDTA solution using suitable indicators. Uranyl nitrate was of AR grade and the methanol used was distilled before use. In all experiments ionic strength was kept constant as 0.1M (KNO₃).

The experimental method employed consists of pH titrations of the following solutions, thermostated at 35°, against 0.2M NaOH: (i) 10 ml of

TABLE 1 — STABILITY CONSTANTS OF THE METAL CHELATES OF 3-(*o*-HYDROXYPHENYL)-5-PHENYLISOXAZOLE WITH DIFFERENT BIVALENT METAL IONS

Metal ions	log K_1	Metal ions	log K_1
H ⁺	10.25	Zn(II)	7.0
Mn(II)	5.6	Cd(II)	6.0
Co(II)	5.7	Be(II)	8.0
Ni(II)	6.9	UO ₂ ²⁺	9.1
Cu(II)	8.2		

0.1M HNO₃ + 9 ml of 1M KNO₃ + 75 ml of methanol + 6 ml of water; (ii) 10 ml of 0.1M HNO₃ + 9 ml of 1M KNO₃ + 10 ml of 0.01M of the ligand in 100% methanol + 65 ml of methanol + 6 ml of water; and (iii) 10 ml of 0.1M HNO₃ + 9 ml of 1M KNO₃ + 10 ml of 0.01M metal ion solution + 65 ml of methanol + 4 ml of water.

The dissociation constant of the ligand and the stability constants of the metal chelates were determined using Bjerrum-Calvin *pH* titration technique as adapted by Irving and Rossotti⁶. From the plots of \bar{n} versus *pL*, stability constants log K_1 were obtained and are given in Table 1. The standard deviation for the stability constants is found to be the order of ± 0.05 .

The stability order enunciated by Irving-Williams has been extended by Basolo and Pearson⁷ to include among others the bivalent metal ions UO₂²⁺ and Be(II). Their order is UO₂²⁺ > Be(II) > Cu(II) and is subject to variation with the nature of the ligand. For the ligands like EDTA, oxine, etc., the order is Cu(II) > UO₂²⁺ > Be(II). One obvious reason for the variation is the difference in the relative affinities of these ions for nitrogen and oxygen donors⁸. It appears that the relative stabilities of five- and six-membered rings are influenced by the size of the metal ion in the ring. The stability constants of the present metal chelates follow the order: UO₂²⁺ > Cu(II) > Be(II) > Zn(II) > Ni(II) > Cd(II) > Co(II) > Mn(II). The greater stability of Cu(II) chelate is due to the π bond formation as has been observed in the case of Cu-acetylacetonate chelate. The order of stability constants of bivalent transition metal ions can be explained in terms of crystal field stabilization energy. There is a gradual rise in the crystal field stabilization energy (CFSE) values from Mn(II) to Ni(II) and decrease in Cu(II) aquo complexes or complexes with weak field ligands. The stability order from Mn(II) to Ni(II) can therefore be attributed to the gradually increasing CFSE values. Though the crystal field stabilization energy for Cu(II) is lower than Ni(II) the complex stability order is Cu(II) > Ni(II). This is because of the fact that the stability is the measure of free energy change and the enthalpy a measure of crystal field stabilization. The lower stability of Cd(II) chelate as compared to Zn(II) chelate is due to the decrease in ionic potential (e^2/r).

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Formation Constants of Metal Chelates of 2'-Hydroxychalkone & 2'-Hydroxy-5'-methylchalkone with Some Bivalent Metal Ions

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The interaction of 2'-hydroxychalkone and 2'-hydroxy-5'-methylchalkone with some bivalent metal ions like Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) has been investigated potentiometrically in 70% v/v ethanol-water mixture at 35° and an ionic strength $\mu = 0.1M$ (KNO₃). The stability constants have been determined by Bjerrum's method as adopted by Calvin and Wilson. The order of stability constants of metal chelates is found to be Mn(II) < Co(II) > Ni(II) > Cu(II) > Zn(II) > Cd(II).

THE formation constants of Al(III), Cr(III), Be(II), Cu(II), Zn(II), Co(II) and Ni(II) chelates with 2'-hydroxychalkone in 60% v/v dioxane-water mixture at 30° were reported by Khadikar *et al.*¹. The present note deals with the potentiometric determination of stability constants of chelates of 2'-hydroxychalkone and 2'-hydroxy-5'-methylchalkone with Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) in 70% ethanol-water mixture at 35° and $\mu = 0.1M$ KNO₃.

The ligands were prepared by the literature methods^{2,3} and their purity checked. An ELICO *pH* meter model LI-10 fitted with glass and calomel electrode assembly and having an accuracy ± 0.02 *pH* unit was employed and standardized using standard buffers of *pH* 4.00 and 9.00. The solutions of metal nitrates were prepared in doubly distilled CO₂-free water, and standardized by standard methods. The *pH* meter readings in 70% ethanol-water mixture were corrected using the method of Van Uitert and Haas⁴. The experimental method and the method of calculation were reported in our earlier publication⁵.

The proton-ligand stability constants of 2'-hydroxychalkone and 2'-hydroxy-5'-methylchalkone