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NOTE

pH-Metric Method for Ligand Dissociation Constants of Mercaptotriazoles and Their Reactions

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The proton ligand dissociation constants, log K_L of a few mercaptotriazoles and the stability constants of their complexes with bivalent metal ions have been determined using Bjerrum-Calvin pH titration technique as extended by Irving and Rossotti. The order of stability constants of metal complexes follows Irving-William series and the acid dissociation constant values of ligands are in the order $L_1 > L_2 > L_3 > L_4$.

The organic thio compounds are known for their reactivity with metal ions. The complexing ability through sulphur and other groups containing nitrogen and/or oxygen is well documented. Mercapto triazole complexes of UO_2^{2+} have already been reported in our earlier paper[1]. The stability constants are shown to be related to dissociation constants of these ligands which in turn are dependant on other electron influencing properties of groups attached to the organic moiety. These are explained in the present paper using transition metal ions to verify further the order of reactivity of these ligands and the role of nature of metal ions on stability constant values calculated by pH-metric method.

The preparation of the ligands,

L_1 = [3-(methyl phenyl)-5-mercapto-1,2,4-triazole]

L_2 = [3-(phenyl)-5-mercapto-1,2,4-triazole]

L_3 = [4-amino-3-(*p*-chlorophenoxy methyl)-5-mercapto-1,2,4 triazole)

L_4 = [4-amino-3-(phenoxy methyl)-5-mercapto-1,2,4 triazole]

was reported in our earlier paper[1]. The solutions are stored in double distilled water and ethanol. All the metal ions, potassium nitrate, sodium hydroxide and nitric acid solutions are from AR samples.

A digital pH meter (Model LI-120) along with 0–13 glass electrode and SCE supplied by Elico (Pvt.) Ltd., India are used for collecting pH data. The composition of the solutions used in the titrations with 0.1 M sodium hydroxide in order are:

(1) 5 mL (0.01 M) nitric acid + 30 mL of ethanol + 15 mL (0.04 M) potassium nitrate.

(2) 1 mL (0.01 M) ligand + 5 mL (0.01 M) nitric acid + 29 mL ethanol + 15 mL (0.04 M) potassium nitrate.

(3) 1 mL (0.001 M) metal ions + 1 mL (0.01 M) ligand + 5 mL (0.01 M) nitric acid + 28 mL ethanol + 15 mL (0.04 M) potassium nitrate.

The temperature of the solution is maintained at 25° ± 0.1°C and Bjerrum-Calvin[2] pH metric method as modified by Irving and Rossotti[3] is used for the dissociation constant values of the ligands and the stability constant calculations of metal complexes.

The dissociation constant values of all four ligands (log K_L) are obtained from the formation curves of proton-ligand systems drawn between $\bar{n}A$ and pH. These values are found to be the same (L_1 9.6, L_2 9.2, L_3 8.3, L_4 7.8) as reported earlier. From the solutions (2) and (3) $\bar{n}$ and p^L values are calculated and the metal ligand stability constants are obtained by applying least square method to the $\bar{n}$, p^L data.

TABLE-1
STABILITY CONSTANTS OF METAL-MERCAPTOTRIAZOLE COMPLEXES IN 60% ETHANOL MEDIUM

Ligand	log K_1	log K_2	log β_2	log K_1	log K_2	log β_2	log K_1	log K_2	log β_2
	Mn(II)			Fe(II)			Co(II)		
L_1	3.4	—	3.4	8.2	—	—	13.7	9.4	23.1
L_2	3.0	—	3.0	6.8	—	—	6.0	2.1	9.1
L_3	2.8	—	2.8	5.9	1.4	6.3	5.8	1.7	7.6
L_4	2.3	—	2.3	3.0	1.2	4.2	3.5	1.8	5.3
	Ni(II)			Cu(II)			Zn(II)		
L_1	14.5	12.7	27.2	15.2	14.5	29.7	14.7	9.4	24.1
L_2	13.0	5.4	18.4	14.0	12.9	26.9	8.5	5.3	13.8
L_3	5.9	3.8	9.7	10.2	5.9	16.1	7.2	5.3	12.5
L_4	4.0	2.7	6.7	4.0	5.0	7.0	3.5	1.5	5.0

The relative strengths of ligands are $L_1 > L_2 > L_3 > L_4$ because of replacement of imino hydrogen atom by amino group. Among L_2 and L_1, it is due to –I effect of aryl group. Similarly the strength of L_3 is greater than L_4 because of +M effect of halogen. It is also observed from the results shown in Table-1 that the overall stability constants of the bivalent metal ions follow the Irving-William order

$$Zn(II) < Cu(II) > Ni(II) > Co(II) > Fe(II) > Mn(II)$$

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