

Ternary Complexes of Ni (II) with Histidine or Nitrilotriacetic Acid as Primary Ligand & Thioglycollic Acid, Thiolactic Acid, Thiomalic Acid, Aspartic Acid, Glycine or α -Alanine as Secondary Ligand

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The modified form of Irving-Rossotti titration technique has been used to determine the formation constants of ternary complexes of Ni(II) with histidine or nitrilotriacetic acid as primary ligand (A) and thioglycollic acid, thiolactic acid, glycine, α -alanine or aspartic acid as secondary ligand (L). It has been observed that mixed ligand formation constant values $\log K_{Ni.A.L}^{Ni.A}$ are lower than $\log K_{Ni.L}^{Ni}$ and $\log K_{Ni.L_2}^{Ni}$. This has been ascribed to electrostatic repulsion between primary ligand (A) and secondary ligand (L).

Ternary systems (MAL) involving bivalent metal ions like Cu(II), Ni(II), Zn(II) and histidine, iminodiacetic acid or nitrilotriacetic acid as primary ligands and poly hydroxy phenols or amino acids as secondary ligands have already been reported^{1,2}. In the present note, mixed ligand complexes of Ni(II) with nitrilotriacetic acid (NTA) or histidine (Hist.) as primary ligand and thioglycollic acid (TGA), thiolactic acid (TLA), thiomalic acid (TMA), aspartic acid, glycine or α -alanine as secondary ligand have been studied employing modified Irving-Rossotti titration technique³. Histidine⁴ and NTA⁵ are known to form 1:1 complexes with Cu(II) and Ni(II) at low pH and the complexes are stable at higher pH where the combination of secondary ligand starts.

The reagents used were of AR grade. The Ni(II) perchlorate was prepared from nickel carbonate and the metal contents were determined by standard methods. All the solutions were prepared in

conductivity water. All the titrations were carried out at 30° using constant temperature bath. The potentiometric curves were interpreted as reported earlier⁶. \bar{n} and P_L were calculated as reported earlier⁷.

The $\log K_{Ni.A.L}^{Ni.A}$ values were obtained by method of averages⁸; the values are presented in Table 1.

It is observed that in all the cases $\log K_{M.A.L}^{M.A.}$ values are lower than $\log K_{ML}^M$. This may be ascribed to the electrostatic repulsion between the charged primary ligand (A) and secondary ligand (L). Histidine has two negative charges while NTA has three negative charges and is sterically bulkier. Therefore, $\log K_{Ni.NTA.L}^{Ni.NTA}$ values are lower than $\log K_{Ni.Hist.L}^{Ni.Hist.}$ values. The systems Ni-Hist-TMA and Ni-NTA-TMA could not be studied, due to very small separation between secondary ligand curve and metal + primary ligand + secondary ligand curve. The behaviour of thio acids and corresponding amino acids is alike with the systems, where A = 2, 2'-bipyridyl or 1,10 phenanthroline^{9,10}. Thio acid ion has two negative charges, whereas, amino acid ion has one negative charge, and hence thio acid ion faces greater electrostatic repulsion resulting in higher Δ values.

References

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Table 1—Mixed Ligand Formation Constants of Various Thio and Corresponding Amino Acids at 30° + 0.1°C

Ligand (L)	$\log K_{Ni.L}^{Ni}$	$\log K_{Ni.Hist.L}^{Ni.Hist.}$	Δ	$\log K_{Ni.NTA.L}^{Ni.NTA}$	Δ
Thioglycollic acid	6.78 ± 0.02	5.87 ± 0.05	0.91	4.83 ± 0.06*	1.85
Thiolactic acid	7.31 ± 0.05	6.41 ± 0.03	0.90	4.59 ± 0.04*	2.72
Thiomalic acid	7.68 ± 0.07	—	—	—	—
Glycine	5.90 ± 0.06	4.89 ± 0.02	1.01	4.88 ± 0.04**	1.02
α -Alanine	5.05 ± 0.07	4.64 ± 0.02	0.41	4.72 ± 0.04**	0.33
Aspartic acid	7.12 ± 0.02	4.78 ± 0.05	2.34	4.19 ± 0.06	3.93

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$\Delta = \log K_{Ni.L}^{Ni} - \log K_{Ni.A.L}^{Ni.A}$