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A comparative study of Ni(II) with N-H, N-ō, S-ō, ō-ō donar atoms as secondary ligand

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Abstract

In this paper a comparative study is carried out on binary, NiL_2, and ternary NiAL complexes. Where A=2, 2^4 bipyridyl amine or 2.2 bipyridyl and L=N-N or N-Ō or S-Ō or Ō-Ō donating ligand. The order of stabilities of binary & ternary complexes is explained on the basicities of the ligand & ring size of the chelate. The sequence in order is explained in terms of M→L π interaction, size of chelate ring & steric factor. The same order is followed both by ternary complexes and binary complexes.

Keywords: A comparative study NiAL ternary, binary complexes

Introduction

The formation, stabilities and reactivities of complexes is a very active and challenging field of research (Agrawal and Manoharlal, 1977; Gurnale, *et al.*, 2000; Mukerjee and Ghosh, 1998; Nair and Neelakanatan, 200).

A review of literature reveals that there is considerable interest in under taking systematic studies on N and O/S donor atoms because of their biological significance (Adams, *et al.*, 1987; Singh and Tandon, 1980; Saxena and Hubber, 1989; Singh *et at.*, 1990) [6]. Amino acids are well known chelating agents (Morrism and Boyd, 1959; Stack and Skinner, 1967; Jain and Khan, 1996) [3, 10].

Material and Method

Potentiometric titration of ligands were carried out in absence and in presence of 2.2' bipyridyl amine in 1:1 binary & 1:1:1 ternary mixtures with carbonate free, standard NaOH solution. The pH measurements were made with 301μ pH meter with reasonability ± 0.01 at 30 ± 0.1^{o} C in 0.2M $NaCl0_4$ solution.

Calculation of stability constant was done by Excel Programme on basis of modified form of Irving-Rossotti titration technique (Irving and Rossotti, 1954; Mavani, *et al.*, 1972) [2, 9].

Various values of formation constant of Log K $\frac{N\bar{i}L}{Nil}$ & Log K $\frac{N\bar{i}L}{Nil}$ are presented in the table. For comparison some values are taken from literature.

Result and Discussion

The order of formation constant of binary (NiL_2) & (NiAL) complexes in terms of secondary ligands is as under

N-N>S-Ō>N-Ō>Ō-Ō

The order of formation of mixed ligand complexes is same as binary complexes (Chidambaram and Bhattacharya, 1970; Childambaram and Bhattachrya, 1969) [9]. The order is explained in terms of basicity of both primary and secondary ligands. Besides, basicity other factor like (i) Steric hinderance (ii) Charge on the complex ion (iii) Changes in the thermodynamic factor (iv) Charge size ratio of metal ion also play an important role. It is observed that mixed ligands formation constant log K $\frac{N\bar{i}L}{Nil}$ is significant higher than what is expected from statistical considerations (Griesser and Sigle, 1970; Nakamoto, 1963). The values of log K $\frac{N\bar{i}L}{Nil}$ is higher than log K $\frac{N\bar{i}L}{Nil}$, and lower than log K $\frac{N\bar{i}}{Nil}$. The value of

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log K $\frac{N\bar{i}L}{Nil}$ are slightly higher than log K $\frac{N\bar{i}L}{Nil}$, due to the fact that tendency of ligands L to get bound to aquated metal [M(aq)$^{2+}$] is more than to combine with metal ion already bound with A. From statistical considerations also deriving force for the binding of secondary ligand with (MA)^{2m} should be less than for binding of L with [M(aq)]$^{2+}$ in binding systems.

2.2’ bipyridyl & 2, 2 bipyridyl amine are neutral molecules and are bound metal atoms by ō bonding, presence of aromatic ring in then makes them more selective and discriminating towards incoming ligands. Besides this, there is dπ-pπ interaction between metal ion and 2, 2’ bipyridyl amine or 2, 2’ bipyridyl, which does not allow concentration of electron density on metal ion to increase significantly.

Due to M N π-interaction (Sexena and Dhawa, 1983) electron density around metal ion in [Nil(2, 2 bipyriyl amine)$^{2+}$] or [Nil(2, 2^{+} bipyridyl)]$^{2+}$ is almost same as [Nil(aq)$^{2+}$] so tendency of [Nil(2, 2)$^{+}$ bipyridyl amine]$^{2+}$ or [Nil(2, 2’ bipyridl)]$^{2+}$ to bind ligands L is also same. Proton ligand formation constant values of various donor ligands is in the following order.

N-N> S-Ō> N-Ō > Ō-Ō

The formation constant values for N-N donor ligands is higest, the reason may be presence of two electron donating nitrogen atoms.

Amongest S-Ō (thio acid) N-Ō (amino acis) & Ō-Ō (hydroxy acid) donor ligands differ only in terms of S, N, O atoms, while other associated dono atoms i.e. oxygen is common.

Stability constant are having values for S-Ō donor ligands than for N-Ō and Ō-Ō donor ligands. Sulphar has vacant d-orbital, which can be used for dπ-pπ bonding. The charge transfer in orbital as Oxygen or Nitrogen.

These two factors are responsible for higher values of formation constant of S-Ō donor ligands in binary as well as in ternary complex. The strengthening of Ni-S bound in mercapto complexex is due to Ō interaction (Jorgensen, 1967); Kolpman, 1968) [4].

Oxygen is more electronegative than nitrogen, but formation constant values for N-Ō donor ligands higher than Ō-Ō donor ligands.

The higher value of Ni(II) complexes with N-Ō (amino acid) arise from greater tendency if Ni(II) to bind with a nitrogen containing ligand then to oxygen containing ligand (Joshi, 1988) [7].

Table 1: Comparison among primary and secondary ligands with nickel(ii) heterochelates. Binary and ternary complexes of nil (ii) with N-N> S-Ō> N-Ō > Ō-Ō donor atoms

Donor atoms	**Ligand**	**log** K^{Ni}_{Nil}	**log** $K^{Nil,}_{Nil,}$	**log** $K^{Ni-2,2'bpA}_{Ni-2,2'bpA.L}$	**log** $K^{Ni-2,2'bp}_{Ni-2,2'bp.L}$
(N-N) diamines	Ethylenediamine 1.2 diamino propane	7.61 8.02	5.93 7.04	7.22 7.34	7.31 7.45
S-Ō thioacids	Thioglycolic acid Thioalatic acid	6.78 7.31	6.63 6.95	6.57 6.76	6.71 6.85
N-Ō amino acids	Glycine α-alanine	5.90 5.55	5.05 4.51	5.46 5.14	5.50 5.14
Ō-Ō oxy acids	Glycolic acid lactic acid	4.74 5.01	4.38 4.57	4.34 5.05	5.07 5.12

2.2’ bpA = 2.2’ bipyridyl amine; 2, 2’ bp = 2, 2’ bipyridyl

Conclusion

The binary MA and ternary MAL complexes of Ni(II) with A= 2, 2’ hipyridyl amine or 2,2’ bipyridyl as primary ligands and L = diamines (N-N), thio acids S-Ō), amino acids (N-Ō and oxy acid (Ō-Ō) have been studied to find out their stability, hence stability order. It is interesting, because the order of the stability is governed by various factors and it is same for binary and ternary system.

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