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A COMPARATIVE STUDY ON BINARY AND TERNARY COMPLEXES OF Ni(H) WITH N–N, N–Ō, S–Ō, Ō–Ō DONOR 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' 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.
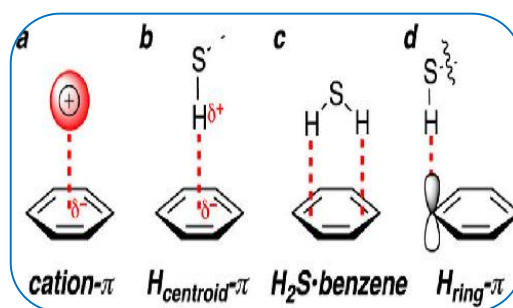
KEYWORDS : π interaction, Ternary and Binary Complexes.

INTRODUCTION :

Metal complexes have been extensively studied due to their biological[1], antitumour[2] and anticancer[3] activities. The formation stabilities and reactivities of complexes is a very active and challenging field of research [4–5]. 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[6]. Amino acid are well known chelating agents[7-12].

MATERIALS AND METHODS

Potentiometric titration of ligands were carried out in absence and in presence of 2,2' bipyriadyl 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 ^{0}C in 0.2M $NaClO_4$ solution. Calculation of stability constant was done by Excel Programme on basis of modified form of Irving–Rossotti titration technique. Various values of formation constant of Log K_{NiL}^{NiL} & Log K_{NiA}^{NiA} are presented in the table as comparison among primary and secondary ligands with Nickel(II) heterochelates.

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| Donor Atoms	Ligand	Log K^{Ni}_{NiL}	Log $K^{NiL_1}_{NiL_2}$	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	7.60	5.93	7.22	7.30
	1,2 diamino propane	8.02	7.02	7.34	7.45
(S–Ō) thioacids	Thioglycolic acid	6.76	6.60	6.56	6.70
	Thiolactic acid	7.30	6.93	6.76	6.85
(N–Ō) amino acids	Glycine	5.90	5.03	5.46	5.50
	α–alanine	5.58	4.51	5.12	5.12
(Ō–Ō) oxy acids	Glycolic acid	4.72	4.33	4.32	5.06
	lactic acid	5.01	4.56	5.05	5.11

2,2' bpA   = 2,2' bipyridyl amine

2,2' bp   = 2,2' bipyridyl

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
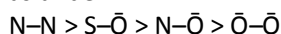
The order of formation of mixed ligand complexes is same as binary complexes. The order is explained in terms of basicity of both primary and Secondary ligands. Besides, basicity other factor like,

(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^{NiL}_{NiAL} is significantly higher.

The values of log K^{NiL}_{NiAL} is higher than log K^{NiL}_{NiL} and lower than log K^{Ni}_{NiL}. The value of log K^{NiA}_{NiAL} are slightly higher than log K^{NiL}_{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)$^{2-n}$ 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 σ- bonding, presence of aromatic ring in them 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 electron density' around metal ion in [Ni (2,2 bipyridyl amine)]$^{2+}$ or [Ni(2,2' bipyridyl)]$^{2+}$ is almost same as [Ni(aq)$^{2+}$] so tendency of [Ni(2,2' bipyridyl amine)]$^{2+}$ or [Ni (2,2' bipyridyl)]$^{2+}$ to bind ligands L is al same. Proton ligand formation constant values of various donor ligands is in the following order.

N–N > S–Ō > N–Ō > Ō–Ō
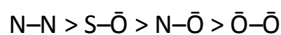
The formation constant values for N–N donor ligands is highest, the reason may be presence of two electron donating nitrogen atoms. Amongst S–Ō (thio acids) N–Ō (amino acids) & Ō–Ō (hydroxy acids) donor ligands differ only in terms of S,N,O atoms, while other associated donor atoms i.e. oxygen is common. Stability constant are having higher values for S–Ō donor ligands than for N–Ō and Ō–Ō donor ligands. Sulphur 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 constants of S–Ō donor ligands

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in binary as well as in ternary complexes. The strengthening of Ni–S bound in mercapto complexes is due to σ interaction. 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 acids) arise from greater tendency if Ni(II) to bind with a nitrogen containing ligand then to oxygen containing ligand. Binary and ternary complexes of Ni(H) with N–N, N–Ō, S–Ō, Ō– Ō donar atoms....

CONCLUSION

The binary MA and ternary MAL complexes of Ni(II) with A 2,2' bipyridyl amine or 2,2' bipyridl as primary ligands and L = diamines (N–N), thio acids S– Ō), amino acids (N– Ō and oxy acids (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 systems.

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