

Synthesis, Spectral Studies & Stabilities of Ternary Complexes of Nickel(II) Containing Histidine & Diols

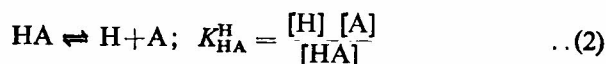
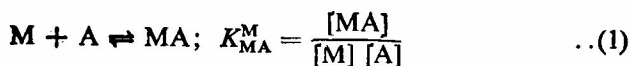
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Received 11 May 1981; revised 1 August 1981; accepted 14 December 1981

Ternary complexes of nickel(II) of the type MAB, MA₂B and MAB₂ (where A=histidine and B=diols, viz. ethane diol, propane-1,2-diol, 2-butene-1,4-diol, butane-1,3-diol, pentane-2,4-diol and hexane-1,6-diol) have been prepared. The complexes have been characterized on the basis of the elemental analyses, magnetic moment and spectral studies. The stability constants of the mixed ligand complexes have been determined by potentiometric method and have been correlated with spectral data (Dq/B) (Dq = splitting energy, B = inter-electronic repulsion parameter). The differences in the stability constants of binary and ternary complexes ($\Delta \log K$) and total enhancement of stability due to mixed complex formation ($\log X$) are of greater magnitude in MA₂B systems than those in MAB₂ systems. This appears to be due to the greater number of nitrogen atoms coordinating to metal ion in the species of the type MA₂B. Some changes in the stability constants have been found to be due to the variation in the size of the ring formed by diols.

SIGEL¹ and coworkers^{2,3} have observed that the stability of the ternary complexes is higher if the ligand contains a hetero atom (basic nature) like nitrogen in contrast to oxygen. The complexes containing N-atom as donor have higher stabilities and the values of $\log X$ are higher as compared to those in the case of complexes where oxygen is the donor atom. This was explained in terms of cooperative effect^{4,5} and π -bond formation in the system.

In the present paper we report the results of our studies on the ternary systems containing histidine (pseudo-aromatic system with N- and O-donor sites) and some diols (with oxygen as the donor atom) as the ligands. We have observed a greater stability for complexes containing two histidine and one diol molecules as compared to complexes containing one histidine and two diols. In the case of binary complexes, for a given structurally related ligand series, a straight line is observed if $\log K_{MA}^M$ (Eq. 1) is plotted against pK_{HA}^H (Eq. 2)^{6,7}.



The same linear correlation was observed in the case of the ternary complexes on plotting $\log K_{MA_2B}^M$, $\log K_{MA_2B}^M$ and $\log X$ against pK_{HA}^H . The stabilities of binary complexes are strongly dependent upon the size of chelate ring⁸ also, and this too is expected for the mixed ligand complexes, specially when one of the ligands is aromatic⁹. For the sake of an unequivocal generalization we have studied systems

involving aliphatic ligands only. The ternary complexes described in the present study contain pseudo-aromatic imidazole moiety which coordinates via secondary imidazole nitrogen and carboxylic oxygen^{9,10} forming a seven membered ring. The diols coordinate through both the oxygens and form rings of varying sizes.

Materials and Methods

L-Histidine monohydrochloride and various diols were Fluka reagents. The diols were purified by distillation under reduced pressure. Nickel(II) chloride hexahydrate and KNO₃ used were of AR (BDH) grade.

Synthesis of the ternary complexes—To an aqueous solution of nickel(II) chloride (0.01 M) were simultaneously added aqueous solutions of histidine (0.01 or 0.02 M) and diols (0.02 or 0.01 M). The reaction mixture was well stirred in nitrogen atmosphere and a standard solution of lithium hydroxide was slowly added to maintain the pH around 7. The turbidity due to lithium chloride was filtered off and the excess solvent was distilled off *in vacuo*. A crystalline product was obtained after keeping the concentrated solution *in vacuo*.

The stability constants $\beta_{MAB_2}^M$, $\beta_{MA_2B}^M$ of the ternary complexes were calculated from the data obtained from alkalimetric titrations¹¹⁻¹³ ($I = 0.2$, KNO₃; 30°C) of the solution containing nickel (II) (0.005 M), histidine (0.005 M) and diols (0.005 M) in the ratios 1:1, 1:2, 1:3, 1:1:1, 1:1:2, and 1:2:1 by taking into account the formation of the species H₂A, HA, A, MA, MA₂, MA₃, H₂B, HB, B, MB, MB₂, MB₃, M, MAB, MAB₂ and MA₂B. The acidity constants of the ligands and stability constants of the binary (1:1, 1:2, 1:3) and ternary complexes

(1:1:1) were calculated¹⁴. These were used for the calculation of $\beta_{MAB_2}^M$ and $\beta_{MA_2B}^M$ (Table 1).

Nickel(II) was estimated by EDTA titration, nitrogen using micro Kjeldahl assembly¹⁵ and magnetic moments by Gouy's method. The electronic spectra of the complexes were recorded in aqueous medium on a Carl-Zeiss spectrophotometer. These spectra were used for the calculation of various spectral parameters¹⁶ viz. Racah interelectronic repulsion parameter (B), crystal field splitting energy (Dq), nephelauxetic ratio (β) and the ratio Dq/B (Table 2).

Results and Discussion

It is observed that mixed ligand ternary complexes have higher stabilities than the corresponding binary complexes in agreement with the observations of

Martin and Paris¹⁷, Sigel⁸ and coworkers who found that complexes containing a hetero aromatic nitrogen base and an oxygen donor have high stabilities. This most probably is due to the cooperative effects and π -bond formation in the system. Irving and Williams⁸ expressed that stability of binary chelate complexes is strongly dependent upon the size of the ring but not of their side chain and the same may be expected for the mixed ligand complexes also.

The complexes of the ring type MAB_2 contain one histidine moiety and two diol rings whereas MA_2B system contains ligands in the reverse order. Histidine moiety contains one five membered ring of imidazole unit; it coordinates through its secondary nitrogen atom and carboxylic oxygen forming a seven membered ring. The diols coordinate through both the oxygens forming another ring which varies in size from diol to diol. Thus, all the complexes of the type MA_2B have more nitrogen donor atoms and some additional pseudo aromatic character due to imidazole moiety than the complexes of MAB_2 type. Thus MA_2B type of complexes should be more stable than those of the MAB_2 type. All the expectations are fulfilled in the case of present complexes as shown by the stability constant data presented in Table (1). The values of $\Delta \log K$ and $\log X$ are higher in the case of MA_2B type of complexes (Table 3). Though factors determining the stability of a complex species are many but it appears from the data observed in the present study that size of the chelate ring formed

TABLE 1 — STABILITY CONSTANTS OF TERNARY COMPLEXES OF NICKEL(II)

(A = Histidine, B = Diols)

Ligand B	$\log K_{MB_2}^{MB_2}$	$\log \beta_{MAB_2}^M$	$\log \beta_{MA_2B}^M$	$\log K_{MAB_2}^{MAB_2}$	$\log K_{MA_2B}^{MA_2B}$
Ethane diol	4.19	21.15	16.94	6.53	6.53
Propane-1,2-diol	4.48	21.82	22.69	6.17	6.67
2-Butene-1,4-diol	4.84	23.81	26.59	6.15	6.17
Butane-1,3-diol	4.59	22.58	23.57	6.93	6.71
Pentane-2,4-diol	4.82	22.60	24.72	6.42	6.42
Hexane-1,6-diol	4.01	23.05	25.00	7.22	7.24

TABLE 2 — ANALYTICAL MAGNETIC MOMENT AND ELECTRONIC SPECTRAL DATA OF SOME TERNARY COMPLEXES OF NICKEL(II)

[M = Nickel, A = Histidine, B = Diol]

Ligand B	Mol. wt	Found (Calc.) %		μ_{eff} B.M.	ν_1		ν_2		B	β	Dq/B	$\delta\nu$		
		Ni	N		Exp.	Obs.	Exp.	Obs.						
Ethane diol	*337.7	17.4	12.4	3.45	9803.9	10Dq.	16393	16063	27026	27356	933.6	0.897	1.056	±330
	×430.7	13.6	19.4	3.46	10582	..	17391	17069	27777	28099	894.8	0.859	1.183	±322
Propane-1,2 diol	*365.6	16.0	11.4	3.43	9756	..	16393	16014	27028	27405	943.2	0.906	1.034	±37.7
	×444.5	13.1	18.8	3.45	10416	..	17543	17006	28169	28705	964.2	0.926	1.080	±536
2-Butene-1,4 diol	* 389.6	15.1	10.8	3.46	10000	..	16528	16441	28169	28256	979.6	0.941	1.021	±87
	×456.8	12.9	18.4	3.43	10638	..	17857	17391	28985	29451	995.2	0.956	1.069	±466
Butane-1,3-diol	* 393.5	14.9	10.6	3.46	9661	..	16181	15887	27030	27322	968.2	0.911	1.020	±292
	×458.7	12.8	13.3	4.41	10402	..	17664	17212	28585	29037	988.4	0.950	1.062	±452
Pentane-2,4 diol	* 421.8	13.8	10.0	3.49	9615.3	..	16528	15881	27027	27633	944.5	0.942	1.018	±646
	× 472.6	12.4	17.8	3.47	10495	..	18018	17471	28985	29531	994.5	0.955	1.045	±546
Hexane-1,6 diol	* 449.7	13.1	9.0	3.48	9689.9	..	16666	15903	27027	27202	974.8	0.899	0.994	±175
	×486.6	12.0	17.2	3.47	10471	..	17699	17083	28169	28784	993.6	0.926	1.036	±615

* MAB_2 type system.

× MA_2B type system.

TABLE 3 — VALUES OF $\Delta \log K$, $\log X$ AND Dq/B OF TERNARY COMPLEXES OF NICKEL(II) WITH HISTIDINE (A) AND DIOLS (B)

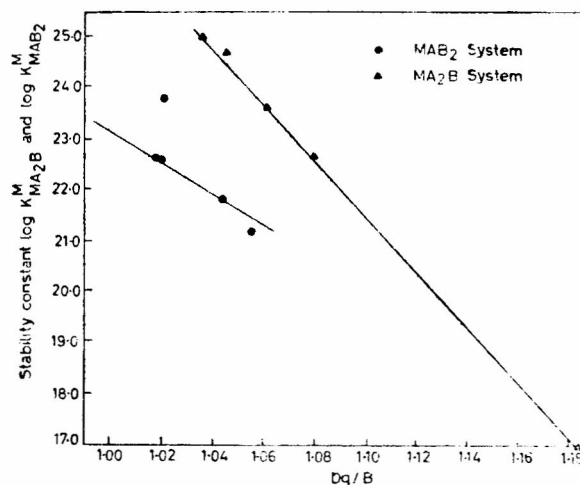
Ligand (B)	$\Delta \log K_{MAB_2}$	$\Delta \log K_{MA_2B}$	$\log X_{MAB_2}$	$\log X_{MA_2B}$	$(Dq/B)_{MAB_2}$	$(Dq/B)_{MA_2B}$
Ethane diol	-3.04	-0.36	14.06	20.63	23.43	1.183
Propane-1,2-diol	-3.16	-0.28	11.81	20.84	19.20	1.080
2-Butene-1,4-diol	-3.18	-0.98	14.74	23.45	21.18	1.069
Butane-1,3-diol	-1.85	-0.91	14.57	15.14	21.11	1.062
Pentane-2,4-diol	-1.41	-1.10	9.92	17.18	26.34	1.045
Hexane-1,6-diol	-3.22	-0.7	13.20	16.70	27.59	1.036

by the diol moiety has some effect on the overall stability constant. Ethane-diol and propane-1,2-diol form five membered ring by co-ordination through diol oxygens to the nickel. In MA_2B & MAB_2 species these diols will form three five membered chelate rings and thus the stability of complexes is expected to be high. But 1, 3-diol and pent-2, 4-diol form six membered chelate rings, thus the stability of MA_2B species will be lower than the stability of MA_2B formed by ethane-diol and propane-1, 2-diol. The stability of hexane-diol which forms the nine membered ring is unusually high. 2-Butene-1,4-diol exhibits the highest stability in this series. Such type of behaviour can be explained on the basis of the participation of π -electrons of 2-butene-1, 4-diol in these complexes. The anomalous behaviour of 2-butene-1,4-diol was also observed in our earlier studies on ternary complexes of praseodymium¹⁸.

In the electronic spectra of present complexes three spin allowed transitions occur around the regions, 9600-10700 cm^{-1} , ${}^3A_{2g} \rightarrow {}^3T_{2g}$ (ν_1), 16100-18000 cm^{-1} , ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (F), (ν_2), and 27000-29000 cm^{-1} , ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (P) (ν_3).

Konig¹³ has calculated the values for parameters B and Dq using different sets of transition energies. In the present study we have calculated the values of electronic spectral parameters by employing Konig's method using the sum of ν_2 and ν_3 transitions, where all the three spin-allowed $d-d$ transitions are observed. The magnetic moment μ_{eff} varies from 2.96 to 3.10 B. M. showing the presence of two unpaired electrons. The value of transition energy ratio ν_2/ν_1 varies from 1.62 to 1.65 and ν_3/B 28.0-30.0 and Dq/B lies between 0.99 and 1.05 in all these complexes. The magnitude of Dq/B for MA_2B complexes was larger than that for the corresponding MAB_2 species. This is in agreement with the higher magnitude $\Delta \log K$ and $\log X$ for MA_2B species as compared to those for the corresponding MAB_2 species. The negative values for $\Delta \log K$ indicate the reverse direction for binary to ternary equilibria. Such type of values of spectral parameters indicate octahedral stereochemistry in these ternary complexes.

A plot of Dq/B values against stability constants of these complexes (Fig. 1) is linear, but it shows a negative slope suggesting that the quantities are related inversely to each other i.e. increase in the stability of the species decreases the magnitude of Dq/B . The data for 2-butene-1,4-diol chelate

Fig. 1 — Plot of Dq/B against $\log K_{MA_2B}^M$ and $\log K_{MAB_2}^M$

do not fall on this line. It appears that the behaviour of 2-butene-1,4-diol is different from other diols which may be due to the presence of a double bond in this system.

Acknowledgement

The authors are grateful to Prof. R. C. Kapoor, Head of the Chemistry Department, for encouragement and for providing laboratory facilities. One of them (A. A.) thanks the CSIR, New Delhi for a junior research fellowship.

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