

SYNTHESIS, STABILITY CONSTANTS AND ELECTRONIC SPECTRAL STUDIES OF TERNARY COMPLEXES OF Pr(III) WITH HISTIDINE AND DIOLS

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ABSTRACT

The mixed ligand complexes of the type MAB, MA₂B and MAB₂ where M = Pr(III), A = histidine and B = ethanediol, prop-1,2-diol, 2-butene-1,4-diol, but-2,3-diol, pent-1,5-diol and hex-1,6-diol have been investigated by alkalimetric titrations. The overall stability constants have been evaluated at 30 ± 1°C. ($\mu = 0.2$ M KNO₃). The absorption spectra of some praseodymium (III) ternary complexes in solution have been used to calculate energy interaction and intensity parameters. The low intensity of the pseudohypersensitive transition suggests higher coordination number.

INTRODUCTION

In the present article data on mixed ligand complexes of praseodymium with histidine and diols are reported. The stability of binary complexes is strongly dependent upon the size of the chelate ring¹. A similar behaviour is observed in the ternary complexes². The ternary complexes now described contain a pseudoaromatic imidazole ring, six-membered ring formed by carboxylic oxygen and the side chain of the amino acid and the ring of varying sizes due to diol molecule.

EXPERIMENTAL

L-Histidine monohydrochloride and diols were from Fluka A. G. and B. D. H. Ltd., respectively. Praseodymium chloride six hydrate (99.9%) was obtained from Indian Rare Earths, Alwaye, Kerala.

SYNTHESIS

A solution (0.01 M) of praseodymium chloride in 50% aqueous alcohol was added to alcoholic solution of histidine (0.01 M, 0.02 M, 0.01 M) and diols (0.01 M, 0.01 M, 0.02 M). The reaction mixture was well stirred under nitrogen atmosphere and a standard solution (0.1 N) of lithium hydroxide was slowly added to maintain pH around 7. Wherever precipitation was observed, the solution was filtered and the filtrate was concentrated on a water bath then in vacuum. The crystalline product obtained was washed with anhydrous methanol and ether and dried in vacuo.

PHYSICAL MEASUREMENTS

The pH was measured at 30 ± 1°C with a digital pH meter NIG 333 (accuracy: ± 0.02 pH) and titrated at 30 ± 1°C against 0.1 M sodium hydroxide maintaining the ionic strength $\mu = 0.2$ M. The stability constants β_{MAB}^M , $\beta_{MAB_2}^M$ and $\beta_{MA_2B}^M$ of the ternary complexes were calculated from the data obtained from alkalimetric titrations³⁻⁵. The species H₂A, HA, A, MA, MA₂, MA₃, HB, B, MB, MB₂, MB₃, M, MAB, MA₂B and MAB₂ have been considered for calculation.

The absorption spectra of these complexes were recorded in methanol solution using a spectrophotometer (Carl-Zeiss VSU-2) in the visible region.

The stability constant K_{MAB}^M , $K_{MA_2B}^M$ and $K_{MAB_2}^M$ and the overall stability constants β_{MAB}^M , $\beta_{MA_2B}^M$ and $\beta_{MAB_2}^M$ for the ternary complexes MAB, MA₂B and MAB₂ have been calculated using various equilibria².

RESULTS AND DISCUSSION

From the structure of histidine (HL) it is clear that there are four possible sites of coordination to the metal (M). These are (i) carboxylic oxygen (ii) α -amino nitrogen (iii) the tertiary imidazole nitrogen and (iv) the secondary imidazole nitrogen. It is quite clear that all these four sites cannot lie in the same plane⁶ around the metal ion and thus all cannot interact simultaneously. However, site (i)-(iii) can interact with the three non-planar positions of the octahedron. The possibility of the protonated complexes arise if bonding occurs via (i) and (iii) and the amino nitrogen is protonated. Praseodymium, because of the large size,

can form polyhedron where the coordination number of the metal is more than six. At lower pH, this type of interaction can be prevalent. At pH below 4 it has been suggested that it is the zwitterion which interacts with praseodymium⁷. But as the pH of the reaction mixture increases the carboxylic group gets deprotonated. Around pH 7 the proton from secondary imidazole group is removed.

Sigel⁸ has reported that the stability of ternary complexes increases when ligands contain a hetero nitrogen and an oxygen donor ligand. The complexes of the type MA₂B contain two histidine moieties and one diol ring but MAB₂ system contains the reverse order. Histidine moiety contains one five-membered pseudoaromatic imidazole unit in which the nitrogen atom participates in the formation of the bond while the side chain participates in the ring formation. The diols have two oxygen atoms as potential donor atoms and form rings of various sizes by substituting coordinated water molecules from the praseodymium aquo ion⁹.

The stability constants of ternary complexes of praseodymium(III) with histidine and diols are given in table 1. The species of the type MA₂B, have more bonding nitrogen atoms and some aromatic character due to the imidazole moiety than MAB₂ type, and thus show greater stability. With 2-butene-1,4-diol, the stability constant values are the highest in the series, perhaps owing to the presence of π -electrons which might be involved in the metal ligand interaction.

Absorption spectra: Energy Bonding and Intensity Parameters

The calculation and significance of the energy, bonding and intensity parameters derived from intra- f^N transitions of various binary lanthanide complexes have been discussed earlier^{9, 15}, however, the ternary complexes are briefly discussed below.

The values of F_k , E^k , ζ_{4f} , β and $b^{1/2}$ have been computed by using ΔF_2 and $\Delta\zeta_{4f}$ reported earlier^{9, 15}.

The values of ΔF_k 's and $\Delta\zeta_{4f}$ have been computed from the four equations obtained and using partial and multiple regression method¹⁴.

$$E_{\text{obs}} = E_{0j} + \sum_{k=2,4,6} \frac{\partial E_j}{\partial F_k} F_k + \frac{\partial E_j}{\partial \zeta_{4f}} \Delta\zeta_{4f}$$

The values of E_{0j} and partial derivatives reported by Carnall *et al*¹⁰ have been used in this work. The experimental value of oscillator strength is obtained from:

$$P_{\text{exp}} = 4.318 \times 10^{-9} \times \epsilon_m \times \Delta\nu_{1/2}$$

where ϵ_m is the molar extinction coefficient corresponding to energy ν in wavenumber.

The values of T_λ parameters have been compared from the four equations obtained by using the Judd-Ofelt relationship given below:

$$P_{\text{obs}} = U^{(2)^2} \times T_2 + U^{(4)^2} \times T_4 + U^{(6)^2} \times T_6$$

The values of matrix-elements $U^{(\lambda)^2}$ have been used as given by Carnall *et al*¹¹.

The decrease in the values of F_k , $E^k\beta$ and ζ_{4f} (table 1) and the increase in the values of P for praseodymium ternary complexes compared to the corresponding values of Pr(III) free ion or aquo ion, indicates a sufficient degree of complexation in the methanolic solution.

The magnitude of the ratio T_4/T_6 for each series *i.e.* for MAB or MA₂B and MAB₂ remains almost constant. The magnitude T_4/T_6 is abnormal in complexes with 2-butane-1,4-diol. This appears to be due to the presence of an additional double bond in diol.

The T_2 values which are both negative as well as positive have no physical significance. This may be due to the appearance of $f \rightarrow f$ transition in the visible region.

It is important to note that the ${}^3P_2 \leftarrow {}^3H_4$ transition (which is quite sensitive to environmental changes) exhibits significant increase in the intensity (P) with the increase in the covalent nature ($b^{1/2}$) of the complexes.

Table 1 Stability constants of ternary complexes of Pr(III) of the type MAB, MA₂B and MAB₂ (M = Pr(III), A = histidine, B = diols)

Ligand (B)	Log B _{MAB} ^M	Log B _{MAB₂} ^M	Log B _{MA₂B} ^M	Log K _{MAB} ^{MA}	Log K _{MAB₂} ^{MAB}	Log K _{MA₂B} ^{MAB}
Ethandiol	16.54	22.96	23.06	6.92	6.42	6.51
Prop-1,2-diol	15.97	23.11	23.13	6.35	7.14	7.16
2-butene-1,4-diol	19.12	23.54	25.84	9.50	4.41	6.72
But-2,3-diol	16.66	23.00	23.05	7.04	6.34	6.39
Pent-1,5-diol	15.50	23.36	24.14	5.87	7.87	8.65
Hex-1,6-diol	16.25	23.53	24.96	6.63	7.28	8.71

This increase in (P) is proportional to the magnitude of nephelauxetic effect $(1 - \beta)$. Contrary to this the observed intensities of these ternary complexes are very low ($P = 15.67 \times 10^{-6}$ to 17.76×10^{-6}). No doubt, amino acids are expected to form inner sphere complexes by forming an ionic linkage with carboxylic oxygen and an additional linkage due to the amino group. The infrared spectra in the solid state of these compounds also indicate inner sphere complexation but on dissolution it appears that amino group does not participate in coordination to the metal ion⁷.

The RMS deviation computed for energies and oscillator strength of all the four levels in the complexes varies from ± 96.75 to 126.5 and from $\pm 0.006 \times 10^{-6}$ to 1.63×10^{-6} respectively. The high values of RMS deviations may be attributed to the assumption of radial eigenfunction to be hydrogenic while deriving the energy relation.

The magnitude of $b^{1/2}$ which signifies the amount of $4f$ -ligand mixing has been correlated with the oscillator strength of the pseudohypersensitive transition (${}^3P_2 \leftarrow {}^3H_4$). It has been found that a linear relationship exists between p and $b^{1/2}$. The shift in the band, which determines the magnitude of $b^{1/2}$ is thus accompanied with increase in the intensity of the band. Since $b^{1/2}$ is related to nephelauxetic effect $(1 - \beta)$, $b^{1/2} = [(1 - \beta)/2]^{1/2}$ the magnitude of $(1 - \beta)$ is a measure of the extent of covalency in the metal ligand bond. Hence it may be concluded that the increase in the degree of covalency brings about the intensification of the band. The magnitude of $b^{1/2}$ was higher in MA_2B species as compared to the corresponding MAB_2 species showing that the covalency in the metal ligand bond is more when amino acid content in complexes is higher. A parallel behaviour is observed, i.e. the magnitude of oscillator strength was higher in MA_2B species as compared to that in MAB_2 species.

ACKNOWLEDGEMENT

Thanks are due to UGC, India for awarding fellowship to AK. Authors also thank Prof. R. C. Kapoor for necessary facilities.

20 December 1982; Revised 27 February 1984

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ANNOUNCEMENT

SOVIET HONOUR TO ICMR HEAD

Prof. V. Ramalingaswamy, Director General of the Indian Council of Medical Research, New Delhi, has been elected an honorary member of the Soviet

Academy of Medical Sciences. The only other foreign scientist to be so honoured is the eminent urologist Moritz Bebel.