Binuclear Complexes from Trans-$[Co(en)_2ClgyH]^{2+}$ and Trans-$[Co(en)_2Cl/\beta$ alaH$]^{2+}$ with Transition Metal Ions

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The proton ligand association constant $logK_{11}$ of trans-$[Co(en)_2Clgly]^+$ (6.04 - 6.45) and trans-$[Co(en)_2Cl$ β -ala$]^+$ (6.09-6.50) and stability constant of mixed metal binuclear complexes of trans-$[Co(en)_2Clgly\ H]^{2+}$ and trans-$[Co(en)Cl$ β ala $H]^{2+}$ with divalent metal ions Cu^{2+}, Ni^{2+} and Co^{2+} have been determined using pH titration method in aquo ethanol mixtures of varying composition. The proton and metal ion binding site is the unbound primary amine group of cobalt(III) substrate. log K_M *vs* $logK_{11}$ plots are linear for glycinato and β-alaninato complexes with slopes 1.36, 1.33 (Cu^{2+}), 1.46, 1.28 (Ni^{2+}) and 1.40, 1.21 (Co^{2+}). The thermodynamic parameters (ΔH° and ΔS°) of the complexation reaction have also been calculated.

Formation of various oxo and hydroxo bridged binuclear complexes of metal ions has been investigated [1-5] but measurement of formation constants of such binuclear species with two different metal ions has been rarely attempted. Recently Cannon and Benjarvongkulchai [6] studied the complex formation of $[Co(en)_2(OH)_2]^+$ with Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} and reported the formation constants of the respective hydroxo bridged binuclear complexes.

This prompted us to determine the stability constants of the binuclear species and also the proton ligand association constant of trans-$[Co(en)_2$-$Clgly]^+$ and trans-$[Co(en)_2Cl$ βala$]^+$ in ethanol water mixtures of varying composition.

EXPERIMENTAL

The two Co(III) complexes trans$[Co(en)_2Cl$ gly $H]^{2+}$ and trans-$[Co(en)_2Cl$ β ala $H]^{2+}$ were prepared by the reported method [7] and characterised by elemental and spectral analysis. Stock solutions of Co^{2+}, Ni^{2+} and Cu^{2+} were prepared using AR grade metal nitrates and standardised.

The following solutions containing 0.1 M sodium nitrate were prepared and titrated pH metrically against 0.4 M NaOH

a. 0.004 M HNO_3
b. 0.003 M Co(III) complex + 0.004 M HNO_3
c. 0.003 M Co(III) complex + 0.004 M

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HNO_3 + 0.001 M Co^{2+}
d. 0.003 M Co(III) complex + 0.004 M HNO_3 + 0.001 M Ni^{2+} and
e. 0.003 M Co(III) complex + 0.004 M HNO_3 + 0.001 M Cu^{2+}

Titration were repeated at 4 temperatures in the range 25-40° C and aquo-ethanol media with ethanol content varying from 0 to 60%. Each titration was repeated twice to check reproducibility.

Toshniwal digital pH meter (model Cl-46) with combination electrode (glass-Ag/AgCl) was standardised using NBS buffer and used for following the titration. Conversion of pH readings to hydrogen ion concentration has been done by the method of van Uitert [8]. A suitable computer programme was developed to calculate the proton-ligand association constant and formation constant using Irving - Rossotti method [9].

RESULTS

The acid dissociation equilibria of the N-protonated glycinato and alaninato complexes are given by equation 1 and 2 respectively.

$$\text{Trans } [Co(en)_2 Cl \text{ gly } H]^{2+} \overset{K_{II}}{\rightleftharpoons} \text{Trans } [Co(en)_2 Cl \text{ gly}]^{+} + H^{+} \quad .....(1)$$

$$\text{Trans } [Co(en)_2 Cl \ \beta \text{ alaH}]^{2+} \overset{K_{II}}{\rightleftharpoons} \text{Trans } [Co(en)_2 Cl \ \beta \text{ ala}]^{+} + H^{+} \quad .....(2)$$

The n_A (average no of protons bound per Co(III) complex by the amino function) were evaluated at various pH values from titration curves for complex + HNO_3 solution (b) and HNO_3 solution (a) using the formula of Irving and Rossotti [9]. The values are collected in Table 1. The stability constants of the binuclear complexes trans- $[Co(en)_2 Cl \text{ gly } M]^{3+}$ and trans-$[Co(en)_2 Cl \ \beta \text{ ala } M]^{3+}$ [M=Co^{2+}, Ni^{2+} and Cu^{2+}] were calculated from titrations

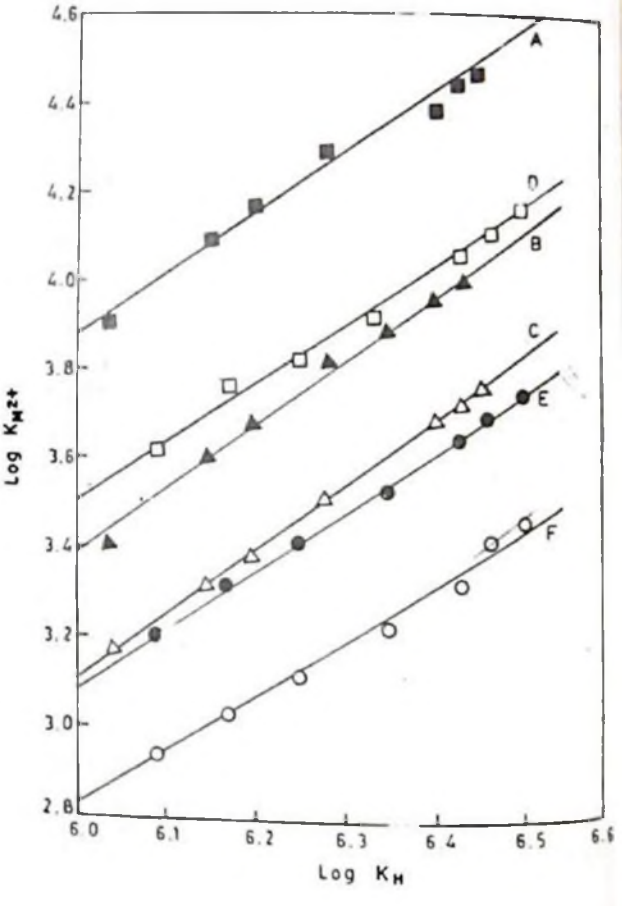


Fig.1 log K_M^{2+} vs Log K_H
(-60% v/v EtOH), temp=30 C and I=0.1 mol dm^{-3}
A,B,C are for Cu(II), Ni(II) and Co(II) complexes of trans- $[Co(en)_2 Cl \text{ gly}]^{+}$ respectively.
D,E,F are Cu(II), Ni(II) and Co(II) complexes of trans- $[Co(en)_2 Cl \ \beta \text{ ala}]^{+}$ respectively.

Table 1

Proton Ligand Stability Constants of Trans [Co(en)$_2$ Cl glyH] and Trans [Co(en)2 Cl ß alaH] and Formation Constants of Binuclear Complexes I = 0.1 mol dm-3

Temp ±0.1° C	<- Trans [Co(en)$_2$ Cl glyH] ->				<-Trans [Co(en)$_2$ Cl ß alaH]->			
	H^+	Cu^{2+}	Ni^{2+}	Co^{2+}	H^+	Cu^{2+}	Ni^{2+}	Co^{2+}
0% Ethanol								
25	6.02	3.88	3.39	3.16	6.07	3.61	3.18	2.91
30	6.04	3.89	3.40	3.17	6.09	3.63	3.20	2.94
35	6.05	3.90	3.43	3.18	6.11	3.68	3.27	2.96
40	6.06	3.91	3.44	3.19	6.12	3.72	3.30	3.00
10 % Ethanol								
30	6.15	4.10	3.61	3.31	6.17	3.78	3.32	3.03
20 % Ethanol								
30	6.20	4.17	3.67	3.38	6.25	3.82	3.41	3.12
30% Ethanol								
25	6.22	4.24	3.78	3.47	6.30	3.83	3.47	3.18
30	6.28	4.29	3.83	3.51	6.35	3.88	3.52	3.22
35	6.34	4.34	3.87	3.54	6.39	3.93	3.56	3.26
40	6.39	4.39	3.92	3.59	6.44	3.97	3.61	3.31
40 % Ethanol								
30	6.40	4.37	3.96	3.68	6.43	4.03	3.64	3.32
50 % Ethanol								
30	6.43	4.43	3.99	3.72	6.46	4.12	3.69	3.42
60 % Ethanol								
25	6.40	4.39	3.94	3.73	6.45	4.14	3.70	3.43
30	6.45	4.45	4.01	3.76	6.50	4.18	3.74	3.47
35	6.50	4.50	4.06	3.80	6.55	4.23	3.78	3.51
40	6.55	4.57	4.11	3.83	6.59	4.26	3.82	3.55

Average Deviation in log K values are ± 0.01

of solutions c,d and e in various ethanol water mixtures by determining $\bar{n}$ and PL values at different pH using a suitable computer program. It is worth noting that the stability of the (1:1) binuclear species of M^{2+} with trans- [Co(en)$_2$ Cl glyH]$^+$ and trans- [Co(en)$_2$ Cl ß alaH]$^+$ follow Irving Williams order; $Co^{2+} < Ni^{2+} < Cu^{2+}$. The proton ligand association constant increases from 6.04 to 6.45.

Table 2

Thermodynamic Parameters of complexation equilibria of Glycinato and alaninato Complexes with Co^{2+}, Ni^{2+} and Cu^{2+}

	<- Trans $[Co(en)_2$ Cl glyH] ->			<-Trans $[Co(en)_2$ Cl ß alaH]->		
	Cu^{2+}	Ni^{2+}	Co^{2+}	Cu^{2+}	Ni^{2+}	Co^{2+}
0% Ethanol						
ΔH	3.57±0.046	3.60±1.0	3.57±0.046	13.5±1.6	15.3±2.4	10.4±0.04
ΔS	86.3±0.15	86.7±3.4	72.5±0.15	114.0±5.4	112.0±8	90.7±3.7
30% Ethanol						
ΔH	18.0±0.34	16.4±0.52	13.0±1.0	16.8±0.45	16.4±0.51	15.3±0.8
ΔS	142.0±1.1	128.0±2	113±3.4	130±1.5	122±2	112±2.6
60 % Ethanol						
ΔH	21.0±1.1	19.7±1.9	12.1±0.54	14.6±0.86	14.3±0.2	14.3±0.18
ΔS	155.0±3.6	142.0±6	112.0±2	128.0±3.0	119.0±0.6	114±0.6

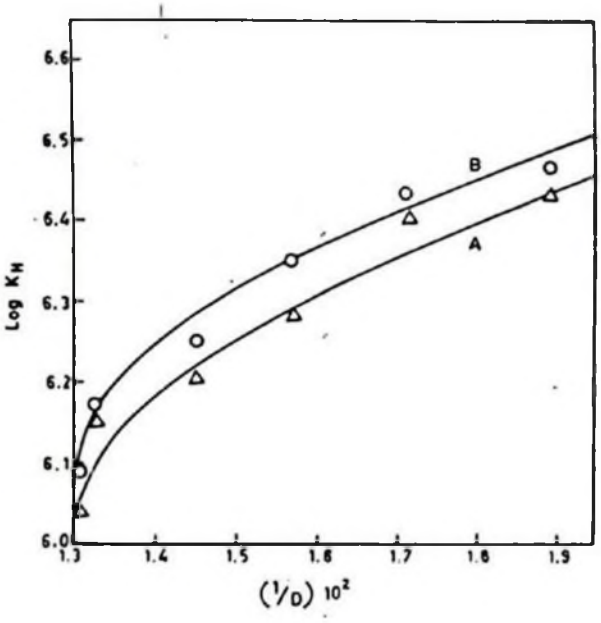


Fig.2 **Log K_M *vs* (I/D)10^2**
temp=30 and I=0.1 mol dm^{-3}
A for trans- $[Co(en)_2$ Cl gly H$]^{2+}$
B for trans- $[Co(en)_2$ Cl ß ala H$]^{2+}$

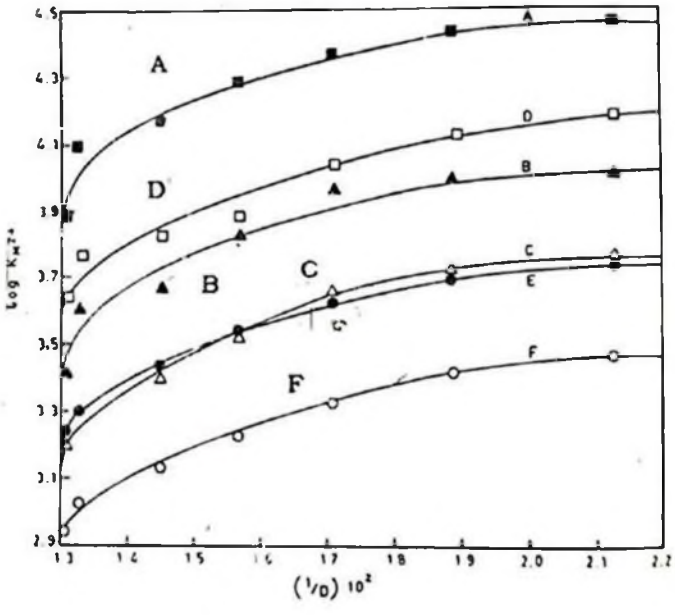


Fig.3 **Log $K_{M2.}$ *vs* (1/D) 10^2**
Temp=30°C ±0.1°C and I=0.1mol dm^{-3}
A,B, C are for Cu(II), Ni(II) and Co(II) complexes of trans-$[Co(en)_2$ Cl gly$]^+$ respectively.
D.E,F are for Cu(II), Ni(II) and Co(II) complexes of trans-$[Co(en)_2Cl$ ß ala$]^+$ respectively.

The values of the overall changes in enthalpy (ΔH°) and entropy (ΔS°) for the complexation equilibria given in Table 2 were calculated using a suitable computer program. The correlation coefficient in each case was found to be 0.99

The K'_{II} values of the chloro ß -alaninato complex were found to be greater than that of the K_{II} values of chloroglycinato complex. Chloro ß -alaninato complex is less acidic because $-NH_2$ group is on the ß-carbon atom unlike in chloroglycinato complex. Favourable electrostatic repulsion effect of the protonated amine and cobalt(III) centre in glycinato complex also could be the cause of higher acidity of this complex.

Values of dielectric constant of ethanol water mixture were obtained from literature [10] and were used to construct the plot of log K_{II} and log K_{M2+} *vs* $1/D\ 10^2$ (Fig 2). The plots in both the cases were found to be nonlinear. The proton-ligand association constant is found to increase with the decrease of the dielectric constant of the medium for both chloroglycinato and chloro ß-alaninato complexes. This is also expected because the association of the proton with the conjugate base will increase with the decrease of dielectric constant of the medium.

The formation constant of the binuclear species increases with decreasing dielectric constant of the medium; this is perfectly in agreement with the fact that the electrostatic attraction (ion dipole) between the unbound amino group and M^{n+} ions has the major contribution to the overall free energy change associated with the formation of the binuclear species. The formation constants further reflect that the complexing ability of the half bonded glycine in trans-$[Co(en)_2Cl\ gly]^+$ is higher than that of ß-alanine in trans-$[Co(en)_2Cl$ ß-ala$]^+$ as observed in the corresponding mono nuclear metal ligand chelate complexes due to ring size effect.

The fact that the stability sequence of these binulear species is opposite to that of the K_{II} of the corresponding Co(III) substrate suggest that the binuclear species have chelate structures involving the amino group and carboxylate group already bound to Co(III) centre.

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