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Equilibria and kinetics for pH-dependent axial ligation of ethylester and methylester(aquo)cobaloximes with aromatic and aliphatic N-donor ligands and a molecular mechanistic study of the Co–C bond

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Abstract. Equilibrium constants are determined for the reaction of ethylester and methyl ester (aquo) cobaloximes with histamine, histidine, glycine and ethyl glycine ester as a function of pH at 25°C, using spectrophotometric technique. The functional dependence of pK_a on the substitution rate of H_2O varies with the pK_a of the incoming ligand, establishing the existence of nucleophilic participation of the ligand in the transition state. This data is interpreted with the help of kinetic data where dissociation kinetic reactions were also studied as a function of pH. Binding and kinetic data were correlated based on the basicity, steric hindrance of the entering ligand and HSAB principle. To compare the rate constants of the entering ligands pH-independent second-order rate constants were calculated. The effect of incoming ligand on Co–C bond is studied using molecular mechanics.

Keywords. Cobaloximes; equilibrium constants; ligand substitution reactions; molecular mechanics.

1. Introduction

The chemistry and biochemistry of vitamin B_{12} model compounds is of great significance for the methodological understanding of the biological function of vit B_{12}.[1–3] Vitamin B_{12} coenzymes are octahedral Co(III) compounds containing direct Co–C bonds which occupy an axial coordination position relative to a corrinoid ring system.[4,5] The cobaloximes, $RCo(DH)_2OH_2$ (chart 1, where DH = mono anion of dimethyl glyoxime), are often studied as models for B_{12} coenzyme and have furnished significant amounts of data[6,7] that have provided a foundation for understanding the behaviour of cobalamins[8]. The ligand-substitution reactions of vitamin B_{12}, and its derivatives,[9–13] and B_{12} model compounds, the cobaloximes[14–16] are of interest from the point of view of the mechanisms of inorganic ligand substitution reactions and the possibility that such reactions may play an important role in the coenzyme B_{12}-catalysed reactions. This activity has been motivated by the possibility that axial base release may be involved in biological mechanisms.

The axial ligation reactions of metalloporphyrin ions in aqueous solution are dependent upon the particular metal ion,[17–22] equatorial ligands[23] and axial ligands.[24–26] The $(DH)_2$ equatorial ligand system is not as electron-donating as the corrin in coenzyme B_{12} or the Schiff-base equtorial ligands of other B_{12} models.[27] Compared to both cobalamins and other model systems, cobaloximes have stronger Co–C bonds and shorter Co–L (L = pyridine or substituted pyridines) bonds.[28,29] van Eldik *et al*[30,31] studied the ligand-substitution reactions of *trans*-$[Co(en)_2Me(H_2O)]^{+2}$, a simple model for coenzyme B_{12}, with cyanide and imidazole as incoming ligands where they found that these ligands displace the coordinated water molecule *trans* to the methyl group forming the six coordinate complex. Hence, it is important to study ligand substitution reactions *trans*

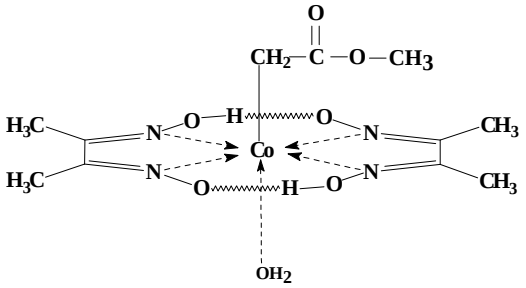

Chart 1. Structure of methylester(aquo)cobaloxime.

*For correspondence

to the axial alkyl ligand in coenzyme B_{12} and related model complexes. Binding of cobaloximes with amino acids, and histamine is remniscent of the structural and bonding characteristics of corrin systems involved in biological mechanisms. In this work, we have made an attempt to explore the kinetics and equilibria of the axial ligation of methyl ester(aquo)cobaloxime and ethylester(aquo)cobaloxime with aromatic (histamine and histidine) and aliphatic (glycine and ethylglycine ester) ligands. Molecular mechanics (using Bio Med CAChe 5·02 software) is used for optimising the geometry of the structure of various substituted cobaloximes. Bond length and bond strain values are evaluated and are correlated to the experimental results.

2. Materials and methods

Histamine (histamine dihydrochloride), histidine (histidine monohydrochloride), glycine, and ethyl glycine ester, were obtained from Sigma. KCl, HPLC grade methanol, acetic acid, HCl, phosphoric acid, formic acid was obtained from Fluka. Dipotassium hydrogen phosphate, potassium dihydrogen phosphate, potassium phosphate, tris(hydroxymethyl) aminomethane (tris), sodium acetate, potassium hydroxide were obtained from Acros. Double-distilled, deionized water was used during our experimental investigations. To maintain appropriate pH, 0·2 M buffers of HCl (0–1·5 pH), KH_2PO_4 and H_3PO_4 (2·0 pH), HCOOH and KOH (2·5–3·0 pH), CH_3COOH and CH_3COONa (3·5–5·5 pH), K_2HPO_4 and KH_2PO_4 (6·0–8·0 pH), tris and HCl (8·5–9·0 pH) were used. Ethylester(aquo) and methylester(aquo) cobaloximes were prepared by the procedure of Brown *et al.*[32] All manipulations were performed under minimal illuminations due to photolability of the carbon–cobalt bond.[13] These alkyl(aquo)cobaloximes are photolabile, particularly in solution. They are soluble in alcohols and DMSO, less so in chloroform or water and virtually insoluble in ether and hydrocarbon solvents.

pH values were determined with a Digisun digital pH-meter equipped with a combined glass electrode. The electrode was standardized at two pH values (pH = 4·0 and 9·2) with standard buffer solutions. UV and visible spectra were recorded on a Hitachi *U*–3410, the sample compartment of which is provided with a thermostat and the concentration of both ethylester(aquo) and methylester(aquo)cobaloximes is 0·00125 M and the wavelength was fixed at 436 nm. For axial ligation single wavelength measurements were made on an Elico single beam spectrophotometer SL 171 model and the sample compartment was thermostated at 25 ± 0·1°C.

3. Results and discussion

3.1 *Determination of equilibrium constants*

Apparent equilibrium constants (K_{app} values, see (1) below) for the axial ligation of ethylester (aquo) and methyl ester (aquo) cobaloximes were determined by spetrophotometric measurements. Solutions containing $EtCOOCH_2Co(DH)_2(OH_2)$ and $MeCOOCH_2$-$Co(DH)_2(OH_2)$, an appropriate buffer (0·2 M) to maintain pH, KCl to maintain ionic strength (1·0 M) and varying concentrations of ligand are taken in 3 mm cuvettes and allowed to equilibrate in a thermostated holder at 25 ± 0·1°C for 15 min prior to addition of cobaloxime. Figure 1 demonstrates the binding of histidine to methyl ester(aquo)cobaloxime with varying concentrations of histidine at pH 5·5;

$$K_{app} = [RCo(DH)_2L]/[RCo(DH)_2H_2O][L]_{free}. \quad (1)$$

Final absorbance readings are taken after equilibrium is established as indicated by the time independence of the readings. The difference in the absorbance at a given pH is calculated using,

$$\Delta A = \Delta A_{max}[L]_f/(1/K_{app} + [L]_f), \quad (2)$$

where ΔA is the difference in absorbance between solutions containing cobaloxime along with added ligand (L) and solutions containing only cobaloxime at the same concentration, ΔA_{max} is the maximum

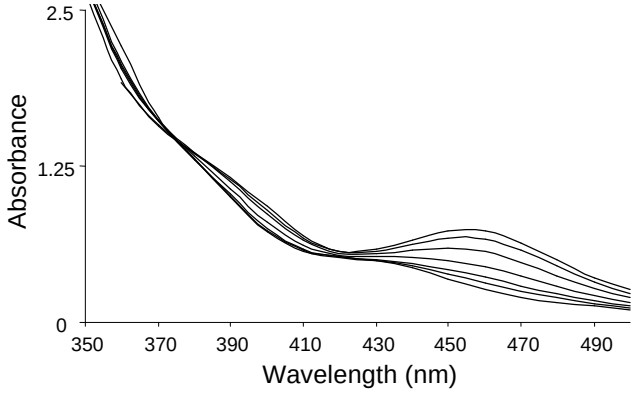

Figure 1. Binding of $CH_3COOCH_2Co(DH)_2OH_2$ with varying concentrations of histidine at pH 5·5 and 25°C.

absorbance change thus obtained at high [L], $[L]_f$ is the concentration of the unbound ligand. The data are analysed using a least squares fit to (2) where the slope and intercept are given by

$$\Delta A = \Delta A_{max} - \{1/K_{app}\ (\Delta A/[L]_f)\}, \quad (3)$$

$$[L]_f = [L]_T - (C_T \Delta A/\Delta A_{max}). \quad (4)$$

$[L]_f$ is calculated from (4) using the measured value of ΔA_{max}, $[L]_T$ is the total concentration of added ligand and C_T is the total concentration of cobaloxime. Values of K_{app} are obtained from the least squares fit of (3) i.e., the plot of ΔA vs $\Delta A/[L]_f$ and the slope is $-1/K_{app}$.

Histamine, histidine, glycine and ethyl glycine ester undergo protonation of N-atom with acid dissociation constants, p*Ka* in the range of 6–10. The values of the equilibrium constant K_{app} for the reaction of the glycine (gly), ethyl glycine ester (glyest), histidine (hisdn) and histamine (hisamn) with ethyl ester (aquo) and methyl ester (aquo)cobaloximes is given in table 1. Logarithmic plots of log K_{app} vs pH for ethyl ester(aquo)cobaloxime and methyl ester(aquo)cobaloxime are shown in figures 2 and 3 respectively, which indicates that as the pH increases the K_{app} increases and the affinity for ligands increases in the order glyest < gly < hisamn < hisdn for both the cobaloximes.

From the above plot it is evident that for both glycine and ethyl glycine ester, K_{app} increases with increase in pH. In the case of histamine and histidine, there is no increase in K_{app} at the pH above the p*Ka* of the ligand. This clearly indicates that in these ligands the binding is through the endocyclic nitrogen. In histidine, the coordination is through the nitrogen of the imidazole ring, though there is a possibility of COO^- and NH_2 coordination, the NH_2 is mostly protonated below pH 8·0, hence it is not available for binding.

3.2 *Determination of ligation rates (k_{on})*

For each ligand L, at various pH values, first order rate constants (k_{obs}) are determined from the absorbance measurements at the same wavelength used for K_{app} determinations under pseudo first-order condition with L being at least in 10-fold excess over cobaloxime concentration. Reaction progress is monitored by measurements of the change in the absorbance upon addition of alkyl(aquo)cobaloxime to a 3·0 ml cuvette, which contains KCl to maintain pH and ligand in the thermostated (25 ± 0·1°C) cell compartment of Elico SL 171 model. First-order rate constants (k_{obs}) are obtained by least squares fits of the data to (5) below

$$\ln[A]_0/[A]_t = k_{obs}t, \quad (5)$$

where A_t is the absorbance at the time t and A_0 is the initial absorbance.

Second-order rate constants, k'_{on} at a given pH for a given ligand are obtained from the slopes of least squares fits of the data,

$$k_{obs} = k'_{on}\ [L]_T + k_{off}, \quad (6)$$

where $[L]_T$ is the total concentration of L present. Values of k_{on}, the pH-independent second-order ligation rate constant are calculated from $k_{on} = k'_{on}/a_L$, where $a_L = (Ka + [H^+])$.

The plot of pseudo first-order rate constant k_{obs} against histidine, concentration is linear with a very small intercept, which may indicate that a small dis-

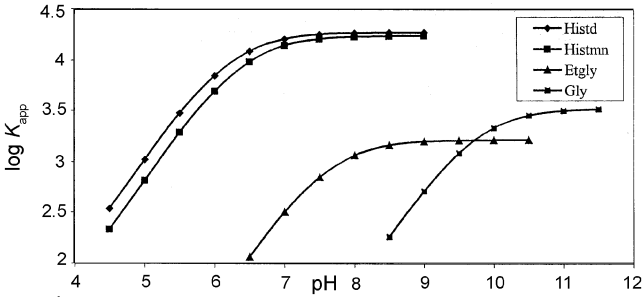

Figure 2. Dependence of log K_{app} on pH for the axial ligation of $C_2H_5COOCH_2Co(DH)_2OH_2$ by different ligands at 25°C.

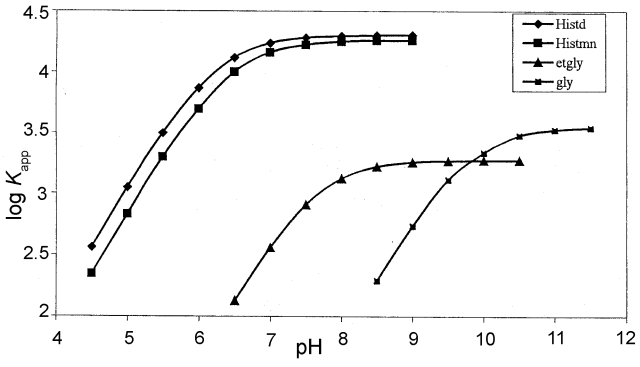

Figure 3. Dependence of log K_{app} on pH for the axial ligation of $CH_3COOCH_2Co(DH)_2OH_2$ by different ligands at 25°C.

Table 1. Formation constants log K_{app} for the axial ligation of $CH_3COOCH_2Co(DH)_2OH_2$ and $C_2H_5COOCH_2Co(DH)_2OH_2$ by L at 25°C.

	pH															
L	4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0	10.5	11.0	11.5	K_{eq}
Hisdn	2.565	3.048	3.499	3.872	4.116	4.235	4.280	4.295	4.300	4.302	–	–	–	–	–	20100
Hisdn*	2.539	3.022	3.473	3.846	4.091	4.209	4.255	4.270	4.275	4.277	–	–	–	–	–	18960
Hisamn	2.345	2.834	3.3	3.7	4.002	4.16	4.22	4.25	4.257	4.259	–	–	–	–	–	18240
Hisamn*	2.33	2.818	3.285	3.692	3.987	4.146	4.211	4.234	4.241	4.244	–	–	–	–	–	17600
EtGlyest	–	–	–	–	2.123	2.561	2.910	3.123	3.221	3.257	3.269	3.273	3.274	–	–	1885
EtGlyest*	–	–	–	–	2.065	2.504	2.852	3.066	3.163	3.199	3.211	3.215	3.216	–	–	1650
Gly	–	–	–	–	–	–	–	–	2.287	2.739	3.114	3.336	3.48	3.528	3.544	3565
Gly*	–	–	–	–	–	–	–	–	2.260	2.712	3.087	3.334	3.455	3.501	3.517	3350

*Binding of L with $C_2H_5COOCH_2Co(DH)_2OH_2$

sociation is accompanied by the complex formation (figure 4.)

The plots of k_{obs} vs concentration of glycine and ethyl glycine ester gave straight lines with non-zero intercepts.

3.3 *Determination of k_{off}*

Ligand dissociation rate constants, k_{off} are measured spectrophotometriclly by addition of a small volume of a solution containing preformed $EtCOOCH_2Co(DH)_2L$ and $MeCOOCH_2Co(DH)_2L$ to cuvettes containing KCl buffer (0·2 M) in the thermostated (25 ± 0·1°C) cell compartment of the spectrophotometer.

Absorbance is continuously monitored at the same wavelength (436 nm) used for K_{app} and k_{obs} measurements. Triplicate measurements are made at each pH value and first-order rate constants, k_{off}, are determined as above, (5). In all cases, the ligand dissociation proceeds to ≥ 99% completion at both pH values. All plots of (5) are satisfactorily linear (correlation coefficients ≥ 0·998). All determinations were averaged to obtain a final value of k_{off}. Pseudo first-order rate constants at different pH values for the formation and dissociation of $[EtCOOCH_2Co(DH)_2Hisdn]$ and $[MeCOOCH_2Co(DH)_2Hisdn]$ at 25°C in aqueous solution are given in figures 5 and 6 respectively.

For histidine and histamine there is not much change in the k_{obs} values upto pH 7·5 but afterwards k_{obs} increases as pH increases. Whereas for glycine and ethylglycine ester, k_{obs} increases as pH increases but after pH 8·5, there is not much change in k_{obs}. This can be explained by the fact that at pH 8·5 it reaches saturation, which means that there is no effect of further increase in pH on the rate of formation.

A soft or class b character has been assigned to cobaloximes (III)[33] and is consistent with its observed greater ligand affinity of cyanide, imidazole[34–37] histidine or histamine than for hard glycine or ethyl glycine ester. The order of binding of various ligands to methyl and ethyl estercobaloximes is of the order, histidine > histamine > glycine > ethylesterglycine. The order of $CH_3COOCH_2Co(DH)_2L$ and $C_2H_5COOCH_2Co(DH)_2L$ attributed to the ability of histidine or histamine to accept electrons into higher energy unfilled p^* anti-bonding orbitals through $dp \rightarrow pp$ back bonding, whereas primary amine (glycine or ethyl glycine ester) cannot accept electrons in either fashion. The reverse order for the dependence of $EtCOOCH_2Co(DH)_2L$ and $CH_3COOCH_2Co(DH)_2L$ stability on ligand basicity among two series of ligands, aromatic (histamine, histidine) and aliphatic (glycine and ethyl glycine ester) is not unexpected based on the following reasons.

(i) An increase in basicity is associated with increased ability for *s* donation, for example glycine forms more stable complexes than ethyl glycine ester, since glycine is more basic (p*Ka* 9·74) than ethyl glycine ester (p*Ka* 7·62).

(ii) An increase in basicity is associated with decreased ability for the aromatic ligands to function as *p* acceptors. Hence, though histamine is more basic than histidine it forms less stable complexes than histidine.

Histidine and histamine binds to Co(III) via N → Co(III) donor as well as Co(III) → N*p* bond. Histidine is a better *p* acceptor than histamine, hence histidine forms more stable complexes than histamine. When we compare the binding constants of

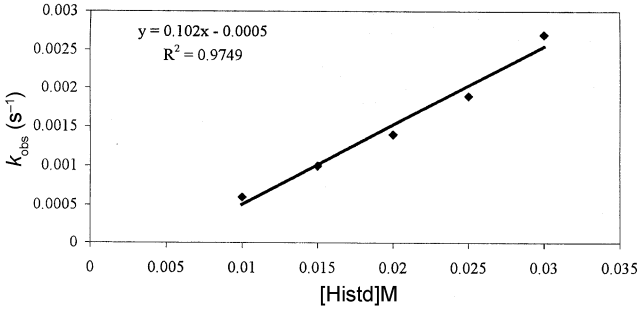

Figure 4. Dependence of [Histd] on pseudo first-order rate constants (k_{obs}) for the formation of $EtCOOCH_2Co(DH)_2L$ at 25°C, ionic strength 1·0 M KCl.

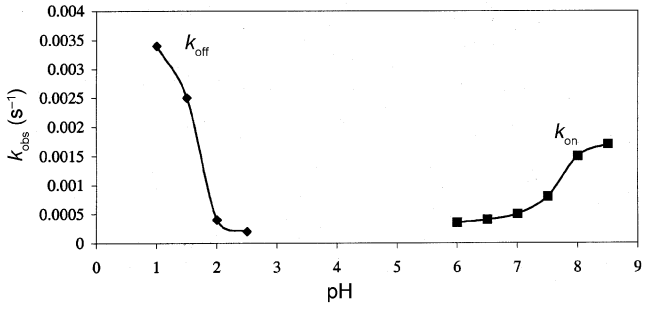

Figure 5. Dependence of pH on pseudo first-order rate constants for the formation and dissociation of $[EtCOOCH_2Co(DH)_2(Histm)]$ at 25°C in aqueous solution, ionic strength 1·0 M KCl.

methyl and ethyl estercobaloximes, methyl ester forms the more stable complex. In case of histidine and histamine, as the pH increases the rate of formation of complex increases. In case of histamine there is not much change in the k_{obs} even when the pH is increased up to 7·0.

The plot of pseudo first-order rate constants k_{obs} against histidine, histamine concentrations is linear with a very small intercept, which may indicate that small dissociation is accompanied by complex formation (figure 4). This appears to be more likely at lower pH. This is probably due to the protonation of the ligand.

Figure 5 shows the pseudo first-order rate constant for the formation (k_{obs}) and dissociation (k_{off}) of $C_2H_5COOCH_2Co(DH)_2$(Histmn) complex as a function of pH (table 2). For all the ligands studied k_{obs} increases slowly between 6 and 8 pH and then increases sharply. The rate of dissociation of L from the [$RCo(DH)_2L$] complex (where R = CH_3COOCH_2 or $CH_3CH_2COOCH_2$) increases with decrease in pH.

To compare the rate constants of the various ligands for the formation of complex with $RCo(DH)_2OH_2$, we have calculated the second-order rate constants k'_{on} from the slopes of the pseudo first-order rate constants as a function of concentration of the ligand. Since this is also pH dependent, for better comparison we have calculated k_{on}, the pH-independent second-order rate constant by dividing k'_{on} by a_L ($k_{on} = k'_{on}/a_L$) where a_L is the degree of dissociation of the ligand at a given pH (tables 2 and 3). Though the basicities of glycine and glycine ester are larger than that of histidine or histamine the second-order rate constants (k_{on}) are much smaller. However, between glycine and ethylglycine ester, they again follow the basicity order: k_{on} of glycine > glycine ester.

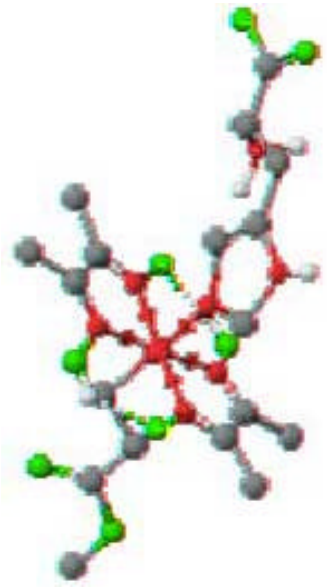

Figure 6. A ball and stick representation of the minimum energy structure of $C_2H_5COOCH_2Co(DH)_2$Histd obtained by MM calculations.
Colours: Centre dark blue: cobalt, light blue: nitrogen, red: oxygen, grey: carbon, white: hydrogen

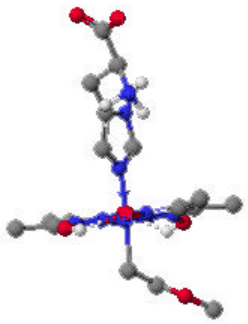

Figure 7. A ball and stick representation of the minimum energy structure of $CH_3COOCH_2Co(DH)_2$Histd obtained by MM calculations.
Colours as in figure 6.

3.4 *Molecular mechanistic study*

In molecular mechanics (MM), mathematical equations are used to simulate all the components that contribute to the strain energy of a molecule, which is then minimized to find a low energy conformation.[38] The total (steric) energy of a molecule is considered to be the sum of steric and non-bonded interactions:

$$E_{total} = E_s + E_b + E_t + E_{VDW},$$

where, E_s is the bond stretching energy, E_b is the angle bending energy, E_t is the torsional energy and E_{VDW} is the energy arising from van der Waals interactions of non-bonded pairs of atoms.

Bio Med CAChe 5·02 software is used for carrying out molecular mechanistic studies. Initially, the structures are drawn in the workspace provided and are geometrically optimized by applying MM2 parametrization.[39] Figures 6 and 7 are the structures of ethylester (histidine) cobaloxime and methyl ester (histidine) cobaloxime respectively. Bond lengths

Table 2. Kinetic data for the axial ligation of $C_2H_5COOCH_2Co(DH)_2OH_2$ by different ligands at 25∘C.

	k_{obs} (s^{-1})				k_{off} (s^{-1})				k_{obs} (s^{-1})			
pH	Histd	Hisamn	EtGlyest	Gly	pH	Histd	Hisamn	C : L*	Histd	Hisamn	EtGlyest	Gly
5.5	–	–	–	–	1.0	0.0035	0.0034	1 : 10	0.0006	0.0005	0.0004	0.00035
6.0	–	0.00035	0.0003	–	1.5	0.0027	0.0025	1 : 15	0.001	0.0009	0.0005	0.00058
6.5	–	0.0004	0.0004	–	2.0	0.0005	0.0004	1 : 20	0.0014	0.0014	0.0006	0.00077
7.0	0.005	0.0005	0.0005	0.00008	2.5	0.0003	0.0002	1 : 25	0.0019	0.0017	0.0007	0.0008
7.5	0.006	0.0008	0.0008	0.00009	3.0	0.001	–	1 : 30	0.0027	0.002	0.0008	0.001
8.0	0.008	0.0015	0.0009	0.0002				k'_{on} (s^{-1})	0.102	0.0796	0.020	0.0304
8.5	0.009	0.0017	–	0.0003		0.3						
9.0	0.011	–	–	0.0004		0.5		k_{on} ($dm^3\ mol^{-1}\ s^{-1}$)	1.838	0.696	0.0283	0.551
									pH = 5	pH = 5.5	pH = 8.5	pH = 6.5

*Ratio of $[C_2H_5COOCH_2Co(DH)_2OH_2]$ and [L]

Table 3. Kinetic data for the axial ligation of $CH_3COOCH_2Co(DH)_2OH_2$ by different ligands at 25∘C.

	k_{obs} (s^{-1}) $\times 10^{-3}$				k_{off} (s^{-1})				k_{obs} (s^{-1})			
pH	Histd	Hisamn	EtGlyest	Gly	pH	Histd	Hisamn	C : L*	Histd	Hisamn	EtGlyest	Gly
5.5	0.2	–	–	–	1.0	0.004	0.0035	1 : 10	0.0008	0.0004	0.00035	0.0006
6.0	0.4	0.3	0.2	–	1.5		0.0026	1 : 15	0.001	0.00062	0.00044	0.0007
6.5	0.6	0.3	0.3	–	2.0	0.0006	0.0003	1 : 20	0.0012	0.0008	0.0005	0.0008
7.0	0.8	0.5	0.5	0.07	2.5		0.0002	1 : 25	0.0014	0.00095	0.00055	0.0009
7.5	0.9	0.7	0.7	0.09	3.0	0.001	–	1 : 30	0.0016	0.0012	–	0.001
8.0	1.0	0.9	–	0.1				k'_{on} (s^{-1})	0.04	0.038	0.0132	0.0162
8.5	1.2	–	–	0.3								
9.0	–	1.5	–	0.5				k_{on} ($dm^3\ mol^{-1}\ s^{-1}$)	0.720	0.348	0.0187	0.2977
9.5	1.5	–	–	0.6								
									pH = 5	pH = 5.5	pH = 8.5	pH = 6.5

*Ratio of $[CH_3COOCH_2Co(DH)_2OH_2]$ and [L]

and bond strains of the molecules are evaluated and are reported in table 3. From table 3 it is evident that the data confirms the kinetic and binding data. The variations in bond length and bond strains are in accordance with the experimental data. When the formation constant is large the bond length and the bond strain are low and vice versa. The Co–N bond lengths provide an insight to the *ð*-bonding character and about the *trans* influence. The Co–C and Co–N bond lengths and bond strains show that histidine binds to the cobaloxime more strongly than histamine, and glycine binds more strongly than ethylglycine ester.

4. Conclusions

In this study we have observed that the values of formation constant reveal the trend histidine > histamine > glycine > glycine ester. This is explained based on the *p*-bonding and basicity of the ligands (p*Ka* values). Kinetic data are also evaluated to support the formation constants. Second-order rate constants which are pH-independent are calculated from the pH-dependent pseudo first-order rate constants. Co(III) being assigned a soft character binds more strongly to histidine and histamine as compared to glycine and ethyl glycine ester, which is explained based on the HSAB concept. It is observed that methyl ester forms more stable complexes than ethylester cobaloximes. Finally, molecular mechanistic studies reveal the effect of incoming ligand on Co–C bond length variation and strain on the bond.

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