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Coenzyme B_{12} model studies: Equilibrium constants for the *p*H-dependent axial ligation of benzyl(aquo)cobaloxime by various N- and S-donor ligands

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Abstract. Equilibria of the axial ligation of benzyl(aquo)cobaloximes by imidazole, 1-methyl imidazole, histidine, histamine, glycine, ethyl glycine ester, thiourea and urea have been spectrophotometrically measured in aqueous solutions of ionic strength 1·0 M (KCl) at 25°C as a function of *p*H. The equilibrium constants are in the order CN^- > 1-methyl imidazole > imidazole > histidine > histamine > glycine > ethyl glycine ester > thiourea > urea. The order of stability of benzyl(ligand)cobaloxime is explained based on the basicity of the ligand, Co(III) → *L dp–pp* back bonding and soft–soft and soft–hard interaction. Imidazole, substituted imidazoles, histidine and histamine form more stable complexes than glycine, ethyl glycine ester in contrast to the basicity of the ligands. Benzyl(ligand)cobaloximes were isolated and characterized by elemental analysis, IR and ^{1}H NMR spectra.

Keywords. Benzyl(aquo)cobaloxime; dimethylglyoxime; soft–soft interaction; *dp–pp* back bonding; imidazole; primary amine.

1. Introduction

In ligand substitution reactions of vitamin B_{12}, its derivatives[1–3] and B_{12} model compounds, cobaloximes[4] 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 coenzyme B_{12}-catalysed reactions. Such ligation changes may indeed be important in the enzymatic reactions involving B_{12}[5–7]. Randaccio *et al*[8–10] compared the properties of rhodoximes and cobaloximes on the basis of electronic and steric effects. These studies were useful in understanding the mechanism of Co–C bond cleavage in the vitamin B_{12} coenzyme. Marques *et al*[11] and Randaccio *et al*[12] studied the molecular mechanism of modelling of cobaloximes. Halpern *et al*[13] studied the hydrolytic dealkylation of organo-cobaloximes related to coenzyme B_{12}. Brown *et al*[14,15] have carried out thermochemical studies on benzyl(ligand)cobaloximes, ($C_6H_5CH_2Co(DH)_2L$). The cobalt carbon bond in cobaloximes, though relatively weak[16], is known to be stabilized by a wide range of equatorial ligands. Thermochemical studies of alkylcobaloximes has so far been limited to species with either pyridine or water as the base ligands[17]. Eldik *et al*[18] reported ligand substitution reactions of

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trans$[Co(en)_2(CH_3)(H_2O)]^{2+}$ with cyanide and imidazoles. Complex formation constants were determined[19] for the reaction of cobalt(II) tripodal-tetramine coplex with different pyridine and imidazole-based nucleophiles and the kinetics of these reactions were studied as a function of entering ligand concentration temperature and pressure. We have chosen imidazole-containing ligands because imidazole rings are important in biological systems[20]. Sridhar and Satyanarayana[21,22] reported on the kinetics and equilibria of bromomethyl(aquo) cobaloximes with CN^- and substituted imidazoles.

2. Materials and methods

Imidazole, 1-methyl imidazole, glycine, thiourea and urea, were obtained in highest purity from Across. Histamine, histidine, ethylglycine ester and benzylbromide were from Sigma, USA.. KCl, HPLC grade methanol, acetic acid, HCl, phosphoric acid and formic acid were obtained from Fluka. Double-distilled and deionized water was used throughout. Acetate (0·2 M), phosphate, or tris-HCl buffers were used to maintain *p*H between 4·5 and 10·0. $C_6H_5CH_2Co(DH)_2OH_2$ was synthesized directly from dimethyl-glyoxime(DH)-cobalt acetate, benzylbromide by the procedure of Brown *et al*[23]. The compound obtained was confirmed by ^{1}H NMR in DMSO-d_6. Benzyl(aquo)cobaloximes, ($C_6H_5CH_2Co(DH)_2OH_2$), are photolabile, particularly in solution. They are soluble in alcohol and DMSO, less soluble in chloroform or water and virtually insoluble in ether and hydrocarbon solvents. All work with the benzyl(aquo) cobaloximes was carried out in dim light (in dark room) and solutions were covered with aluminium foil. *p*H measurements were made with a Digisun digital *p*H meter equipped with a combined glass electrode. The electrode was standardized at two *p*H values (*p*H = 4 and 9·2) with standard buffer solutions.

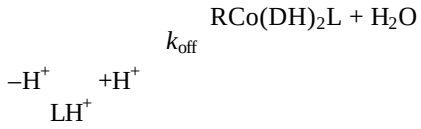
UV and visible spectra were recorded on a Hitachi U-3410 spectrometer, the sample compartment of which is provided with a thermostat and the concentrations of benzyl (aquo) cobaloximes (0·000837 M) were measured at λ_{max} 463 nm. Single wavelength measurements were made on an Elico single beam spectrophotometer SL 171 model, the sample compartment of which was thermostated at 25° ± 0·1°C.

3. Preparation of $C_6H_5CH_2Co(DH)_2L$

The complexes were prepared by mixing 1:3 ratio of benzyl(aquo)cobaloxime and the desired base ligand(L) in ethanol. ^{1}H NMR spectra were recorded on a varian Gemini 200 MHz NMR spectrometer. Samples were prepared by dissolving then in DMSO-d_6. Infrared spectra were obtained on a Perkin-Elmer FTIR-1605 spectrometer using KBr pellets. The molar conductivities of 0·001 M solutions of the complexes in methanol show that they are non-electrolytes.

4. Equilibrium measurements

Apparent equilibrium constants for the axial ligation of benzyl(aquo)cobaloximes were (scheme 1) determined by spectrophotometric measurements[24] at the λ_{max} 463 nm of the $C_6H_5CH_2Co(DH)_2OH_2$. In a 3 ml cuvette, solutions containing $C_6H_5CH_2Co(DH)_2OH_2$, an appropriate buffer (0·2 M) to maintain *p*H, KCl (1·0 M) to maintain ionic strength, and varying concentrations of ligand were taken in a cell compartment maintained at



(2)

Scheme 1.

Final absorbance readings were taken after equilibrium was established as indicated by the time independence of the readings. For such experimental setups, at a given *p*H, (3) is applied.

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

where ΔA is the difference in absorbance between solutions containing both cobaloxime and added ligand (L) and solutions containing only cobaloxime at the same concentration, ΔA_{max} is the maximum absorbance change thus obtained at high [L], and $[L]_f$ is the equilibrium concentration of the ligand in both ionization states ($LH^+ + L$). The data were analysed by a least-squares fit to the rearranged form of (3) to give (4).

$$\Delta A = \Delta A_{max} - 1/K_{app}.\Delta A/[L]_f, \quad (4)$$

$$[L]_f = [L]_{tot} - C_T.\Delta A/\Delta A_{max}. \quad (5)$$

$[L]_f$ calculated from (5) using measured value of ΔA_{max}, where $[L]_{tot}$ is the total concentration of added ligand and C_T is the total concentration of cobaloxime. The data were analysed by a least-squares fit to the rearranged form of (4). ΔA is plotted as a function of $\Delta A/[L]_f$ and the slope is $-1/K_{app}$. The values for the equilibrium constants for axial ligation with respect to unprotonated ligand were calculated from the relation $K_{eq} = K_{app}/\alpha_L$, where α_L (fraction of ligand as free base) was calculated from,

$$\alpha_L = K_a/[K_a + [H^+]], \quad (6)$$

K_a being the dissociation constant of the ligand.

5. Results and discussion

IR spectra of the complexes investigated contain a weak broad band in the range of 1630–1680 cm^{-1} (table 1). It has been proved that the absorption is attributable to an intra-molecular hydrogen bridge[25]. The peaks around 1235 cm^{-1} and 1087 cm^{-1} were assigned[26] to N–O stretching vibration. These two bands are shifted to lower wave numbers when the fifth ligand changes in the order 1-Me IMD > IMD > H_2O, which is in the approximate order of electron-donating strength. The band around 515 cm^{-1} is assignable to Co–N stretching frequency between Co(III) and nitrogen atoms of

Table 1. IR spectral data of benzyl(ligand)cobaloximes.

Complex	*n* Co–N (ligand)	νCo–N (DMG)	νC=N–O (DMG)	*n*-OH (DMG)	*n* O–N (DMG)	*n* O–N (DMG)	*n* CH_3 (equitorial) (DMG)	*n*CH_3	*n* C=N (DMG ligand)	*n* H-O..H (Hydrogen bond)	*n* H-O..H	*n*H-O..H	*n* CH_2 (ligand)	*n* CH_2 (ligand)
$[C_6H_5CH_2Co(DH)_2OH_2]$		514	763	971	1086	1230	1376	1449	1573	1652	2361	≈3255	≈2900	≈3000
$[C_6H_5CH_2Co(DH)_2$ IMD]	475	515	764	999	1085	1234	1333	1488	1558	1645	2368		2922	3111
$[C_6H_5CH_2Co(DH)_2$ 1-Me IMD]	470	518	760	974.8	1089	1236	1352	1422	1561	1659	2362		2620	3109
$[C_6H_5CH_2Co(DH)_2$ 2-Me IMD]	465	515	752	1006	1085	1230	1366	1425	1561	1638	2363		2920	3119
$[C_6H_5CH_2Co(DH)_2$ 2-Et IMD]	462	516	764	1001	1085	1230	1325	1438	1561	1685	2361		2919	3119
$[C_6H_5CH_2Co(DH)_2$ 1,2-Di Me IMD]	468	515	764	1003	1085	1230	1368	1433	1561	1654	2365		2919	3138

dimethylglyoxime[26]. All the complexes show a weak broad band around 2360 cm^{-1} corresponding to another hydrogen-bonded O–H frequency of $(DH)_2$ moiety[27]. The bands at around 1440 cm^{-1} are due to asymmetric and symmetric deformation vibrations respectively, corresponding to methyl groups in dimethylglyoxime. The bands at around 975 cm^{-1} may be attributed to deformation vibrations of OH on $(DH)_2$ moiety and the band at around 760 cm^{-1} due to C=N–O deformation vibration. Characteristic absorption bands due to the axial ligands are also observed. Imidazole derivatives show weak bands at 3000–3150 cm^{-1} to C=N stretching of the ring, bands at 750–780 cm^{-1} due to C–H stretching vibration, bands due to benzyl CH_2 attached to Co(III) occurring at 2920 cm^{-1}. Benzyl(aquo)cobaloxime shows characteristic bands due to H_2O molecule coordinating to Co(III) atom at 3255 cm^{-1}. Disappearance of this band in benzyl ligand cobaloximes, indicates that H_2O is replaced by ligand (L). In addition bands between 460 and 475 cm^{-1} are attributable to Co–N (of L) stretching vibrations. Appearance of the new band is evidence for the coordination of the imidazole to Co(III) of benzyl cobaloxime. Further there is a significant shift of ligational frequencies of νC=C and νC=N modes to lower frequencies, compared to the frequencies of the free ligands indicating the involvement of ring nitrogen in coordination to the metal ion. The alkyl(ligand)cobaloximes are stable and show no signs of loss of imidazole or any other ligand and are non-electrolytic in different solutions[28] (10^{-3} M) of methanol, conductances being in the range of 10–20 mhos cm^2 mol^{-1}.

Electronic spectra of alkyl(aquo)cobaloximes in MeOH or H_2O show spin allowed $^1A_1g \rightarrow {}^1T_1g$ transition[29] in the region 22,000 cm^{-1} due to R^- to Co(III) σ-donation. This band disappears or intensity is drastically decreased in alkyl(ligand)cobaloximes. The $^1A_1g \rightarrow {}^1T_2g$ band is marked by the intense charge-transfer bands. The charge-transfer spectra of the *trans*[$RCo(DH)_2L$] complexes show bands at about 33,000 cm^{-1} due to intra ligand π–π^* transition of the coordinated DH, bands occurring at 27,500 cm^{-1} are assigned to the imidazole to Co(III) (LMCT) and those at 33,000 cm^{-1} are due to the $d\pi$ (Co(III)) $\rightarrow \pi^*$ (DH) (MLCT) transition. The σ DH to σ^* Co(III) (LMCT) is marked by the intense short wavelength bands of alkyl(ligand)cobaloximes[30]. The data presented in table 2 show the ^{1}H NMR chemical shifts of benzyl(aquo)cobaloximes and benzyl (ligand)cobaloximes. In all these complexes a peak around 2 ppm corresponds to methyl

Table 2. ^{1}H NMR spectral data of benzyl(ligand)cobaloximes in DMSO-d_6.

Complex	C_4-H	C_5-H	C_2-H	N–H	CH_3*(eq)	C_6H_5	CH_2-Co
$[C_6H_5CH_2Co(DH)_2OH_2]$					2·0	6·9 (*m*)	2·70
$[C_6H_5CH_2Co(DH)_2$ IMD]	7·22 (*d*) (1·28 Hz)	6·95 (*d*) (1·2 Hz)	7·20 (*s*)	10·05	1·98	6·96 (*m*)	2·75
$[C_6H_5CH_2Co(DH)_2$ 1-Me IMD]	7·22 (*d*) (1·4 Hz)	6·80 (*d*) (0·5Hz)	7·45	3·70 (N_1-CH_3)	2·0	6·99 (*m*)	2·75
$[C_6H_5CH_2Co(DH)_2$ 2-Me IMD]	7·27 (*d*) (1·5 Hz)	7·10 (*d*) (1·4 Hz)	2·75 (C-CH_3)	9·20	1·99	6·97 (*m*)	2·68
$[C_6H_5CH_2Co(DH)_2$ 2-Et IMD]	6·91 (*d*) (2 Hz)	6·62 (*d*) (2·1 Hz)	1·00 *t* CH_3 (3 Hz) 2·64 *q* CH_2	11·6	2·40	7·0 (*m*)	2·72
$[C_6H_5CH_2Co(DH)_2$ 1,2-DM IMD]	7·02 (*d*) (2 Hz)	6·65 (*d*) (2·5 Hz)	2·15 C_2-CH_3	3·45 (N_1-CH_3)	2·20	7·0 (*m*)	2·66

groups of (DH), a multiplet at 7·0 ppm is due to C_6H_5 of benzyl and a peak around 2·7 ppm is due to CH_2 group of benzyl. All the hydrogens in the imidazole are ∝ to the heteroatoms. Hence they are shifted downfield upon coordination to Co(III) of cobaloxime. The H-2 is ∝ to both nitrogens and is observed farthest downfield (7·40). In the free ligand the H-4 and H-5 are averaged by rapid proton exchange and the H-4 and H-5 are together appear at 6·82 ppm with double the intensity. Similarly, in the substituted imidazole, in addition to H-2, H-4 and H-5, the substituent signals like C_2-CH_3 (2·75 ppm) N_1-CH_3 (3·70 ppm) and C_2-CH_2-CH_3 (1·04*t*, 2·65*q*) are also observed in the upfield region. However coordination of imidazole to the Co(III) centre of alkyl cobaloxime render the H-4 and H-5 non-equivalent and separate signals are observed at 7·22 and 6·95 ppm respectively. The N_1-H signal of imidazole appears at 10·05 ppm. The characteristic signals for the various substituted imidazoles are assigned and reported in table 2.

Figure 1 shows the *p*H dependence binding of imidazole to $C_6H_5CH_2Co(DH)_2OH_2$. For the same concentration of imidazole as the *p*H is increased the absorbance decreases. Figure 2 shows the *p*H dependence of apparent equilibrium constants K_{app} for ligation of various ligands from 3·5 to 10·5 *p*H. This indicates that free base is the sole ligating species. The equilibrium constants for the ligation of $C_6H_5CH_2Co(DH)_2OH_2$ by imidazole and 1-methyl imidazole are dependent upon the pK_a's of the conjugate acid of the ligands; as the *p*H increases, the apparent binding constant increases. Similarly, for the other ligands studied, histamine, histidine, glycine and ethylglycine ester, the binding constants are *p*H dependent. This *p*H dependence binding may be because of the competition of H^+ with Co(III) to bind with the N_3 (nitrogen atom in the third position of the imidazole ring) of imidazole and the imidazole ring nitrogen of histamine, histidine and NH_2 of glycine or ethyl glycine ester. Below the pK_a of the ligands, most of them are protonated and not much free base is available for binding to cobalt(III). In case of

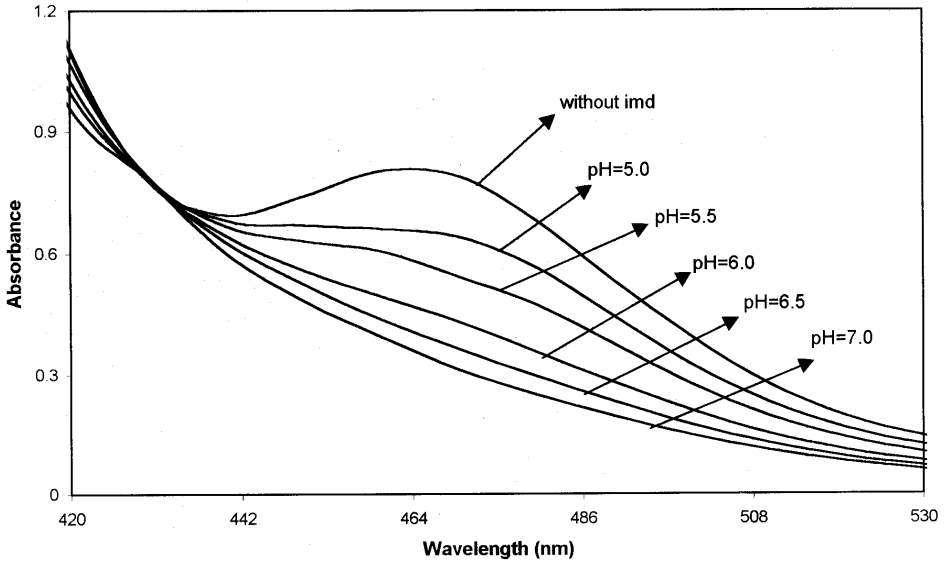


Figure 1. Dependence of *p*H on the binding of $C_6H_5CH_2Co(DH)_2OH_2$ with imidazole at 25°C, isosbestic point = 436 nm.

Table 3. Formation constants for the $C_6H_5CH_2Co(DH)_2L$ complexes.

		K_{app} values at different *p*H's of														
	pKa	3·5	4·0	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	K_{eq}
CN^-	9·04	605	1915	6049	19150												$2{\cdot}1 \times 10^8$
1-Me IMD	7·35						5128·6	14791	37153	70794							$1{\cdot}2 \times 10^5$
IMD	7·2			58·88	186·6	583·4	1778·2	5023·4	11912								$3{\cdot}2 \times 10^4$
Histidine	6·231			79·43	245·47	719·44	1840·7	3622·4	5236	6095·3							$7{\cdot}6 \times 10^3$
His	6·41									1584·8	3467	5888	10000	13182			$6{\cdot}5 \times 10^3$
Gly	9·74										55·08	167	473.1	1124	1986	2624	$3{\cdot}0 \times 10^3$
GlyEt ester	7·62										519·9	941	1318	2238	3162	3630	$2{\cdot}1 \times 10^3$
Thiourea	0·3								9·63	16·71	25·11	39·8	60·25				30·22
Urea	0·1													4·178	6·32	8·75	3·22

imidazole, histidine, or histamine, the free base available is maximum above *p*H 7·0 (above the *pKa* of the ligands), whereas in case of glycine or ethylglycine ester it is above 9·0 *p*H, hence they all bind strongly at *p*H above the pK_a of the corresponding ligands and bind weakly at *p*H values below the pK_a of the ligand. When K_{eq}, the *p*H-independent equilibrium constants, are compared the stabilities are in the order $CN^- > 1$-Meimd > Imd > histidine > histamine > glycine > ethylglycine ester > thiourea > urea, which are shown in table 3. K_{CN} however exceeds $K_{1Me\text{-}IMD}$ by $1{\cdot}1 \times 10^3$-fold. Co(III) in cobaloximes is a soft acid and imidazoles, histamine or histidine are borderline bases, while glycine and ethyl glycine ester are hard bases. Comparison of equilibrium constants of CN^- with that of other ligands studied indicates cyanide forms much stronger complexes than the other ligands. This can be explained as being due to three reasons, (1) cyanide is more basic than most of the other ligands, (2) cyanide is a better p acceptor than imidazole and other ligands, (3) cyanide is a soft base, whereas others are borderline or hard bases.The soft–soft interaction between Co(III) of cobaloxime and CN^- facilitates the stronger and more stable complex formation. Most of the Co(III) complexes, e.g. $[Co(NH_3)_5OH_2]^{+3}$, are hard acids with the exception of the soft acids $[Co(CN)_5H_2O]^{-2}$ and $[Co(NH_3)_5SO_3]^{+}$ [31]. Thus it appears that the presence of one or more soft or unsaturated ligands is sufficient to cause the characteristic softness of a cobalt complex. Due to this the Co(III) in the cobaloximes and vitamin B_{12} is soft. Furthermore the softness appears to be directly related to the ability of a cobalt complex to stabilize the carbon–cobalt bond as seen in cobaloximes and cobalt corrins. The observed greater affinity of CN^-, imidazoles, histamine and histidine compared to glycine and ethyl glycine esters confirms the softness of Co(III). Comparison of binding constants of thiourea and urea tells that the larger value of K_{app} for thiourea than for urea is due to the soft–soft interaction between S of thiourea and Co(III) of cobaloxime. The concept of metal to ligand p bonding explains both the order and strength of ligation. The order of $C_6H_5CH_2Co(DH)_2L$ stabilities are attributed to the ability of imidazole or histamine or histidine to accept electrons into higher energy unfilled p^* antibonding orbitals [31], whereas primary amines

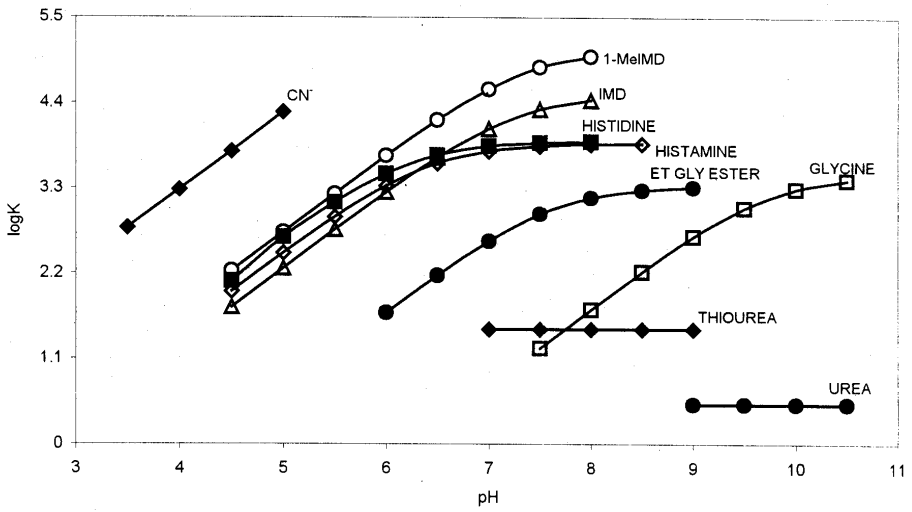


Figure 2. Dependence of log *K* on *p*H for the formation of $C_6H_5CH_2Co(DH)_2L$ at 25°C.

(glycine or ethyl glycine ester) cannot accept electrons by back-donation, they can only form σ bonds by donating electrons to Co(III). This ligand stability order is the same as the order previously established for the *trans* direction of substituents into the square planar complexes[32] of ^{195}Pt and for the stabilization of low valent states of numerous transition metals[33]. The decreasing or increasing of $C_6H_5CH_2Co(DH)_2L$ stabilities on ligand basicity among two series of ligands (imidazole, imidazole containing ligands and glycine or ethyl glycine ester) are not unexpected based on the following considerations.An increase in basicity is associated with an increased ability for σ donation, hence glycine forms a more stable complex than ethyl glycine ester since glycine is more basic (pK_a = 9·74) than ethyl glycine ester (pK_a = 7·62), an increase in basicity is associated with a decreased ability for the imidazole ligands and CN^- to function as π acceptor, but in CN^- and imidazole π bonding is more important than σ bonding, though the pK_a values of CN^- (9·04) and imidazole (7·20) are less than that of glycine (9·74). CN^-, imidazole, histamine or histidine form stronger complexes than glycine or ethyl glycine ester. Metal to ligand π bonding has been firmly established in a number of transition metal complexes[31–33]. Walker[34] has reported that straight lines are obtained when log K vs pK_a is plotted for the coordination of imidazoles, pyridine and non-aromatic cyclic amines to a cobalt porphyrin. The coordination of an imidazoles is stronger than a pyridine which in turn is stronger than a non-aromatic amine (glycine or ethyl glycine ester). Another interpretation of the higher stability is due to d–π back bonding in imidazoles and pyridines, no such stabilization is possible with non aromatic amine ligands (glycine, ethyl glycine ester, thiourea or urea), hence they form less stable complexes.

6. Conclusions

Benzyl(aquo)cobaloxime is prepared and their binding constants with imidazole, substituted imidazoles, glycine, glycine ester, urea and thiourea are studied as a function of *p*H. These were explained based on the basicity of the ligand. It is observed that σ donor ligand stability increases with basicity. Though ligands like imidazole and substituted imidazoles are less basic than glycine and ethyl glycine ester, they formed more stable complexes. This is explained based on dπ–pπ back bonding.

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