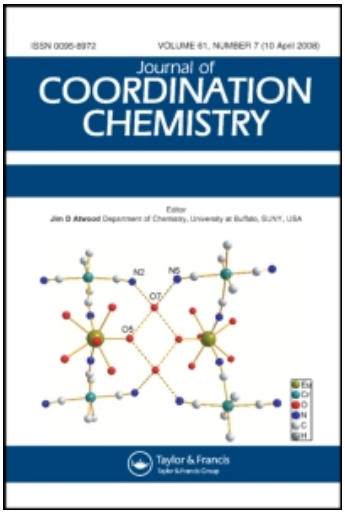

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Ligand-substitution reactions of hydrophobic vitamin B_{12} derivatives: reaction of cobyric acid heptamethyl ester with azoles

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Ligand-substitution reactions of hydrophobic vitamin B_{12} derivatives: reaction of cobyric acid heptamethyl ester with azoles

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Hydrophobic cobyrinic acid heptamethyl ester corrinoids XCbs–Me (axial ligand $X = CN^-$, SO_3^{2-}, and vinyl) have been prepared from vitamin B_{12} by hydrolysis of the seven-amide chain and conversion to methyl ester. The solvents affect both the Soret band and the shape of the UV-Vis spectra of the hydrophobic corrinoids. The equilibrium constant, *K*, for the reactions of XCbs–Me ($X = CN^-$, SO_3^{2-}, and vinyl) with pyrazole (Pz) and imidazole (ImH) have been determined spectrophotometrically at 25°C. Value of *K* for Pz was less than that obtained for ImH in all the solvents used in the present study. The values of *K* increase as the solvent polarity increases, water > methanol > DMSO > DMF. The values of *K* for the two azoles decreases in the order $X = CN^- > SO_3^{2-} >$ vinyl. This shows that the ligands coordinated at the *trans* position in the substitution site have a significant effect on the value of *K*.

Keywords: Equilibrium; Ligand substitution; Azoles; Vitamin B12; Ester side chain

1. Introduction

Hydrophobic cobalt corrinoids "cobesters" are a class of vitamin B_{12} derivatives obtained by converting the seven-amide side chains of the naturally occurring hydrophilic corrinoids into ester groups with a desirable alkyl group.

The properties of hydrophobic vitamin B_{12} are affected by the nature of the reaction media [1, 2]. The effect of solvent polarity on electronic absorption of dicyanocobyrinic acid heptamethyl ester (DCCbs, figure 1) was studied by Pratt *et al.* [3], and found that the main Soret (γ) band varied from 374 nm in non-polar solvents (benzene and CCl_4), through 371 nm in more polar solvents (MeCN and MeCOOMe) to *ca* 368 nm in protic solvents (H_2O and ROH), accompanied by an increase in the CN stretching frequency. They also revealed through X-ray diffraction that one of the coordinated CN's is hydrogen bonded to Pr^iOH, while the other interacts with two methyl groups of the ester side chain on neighboring molecules.

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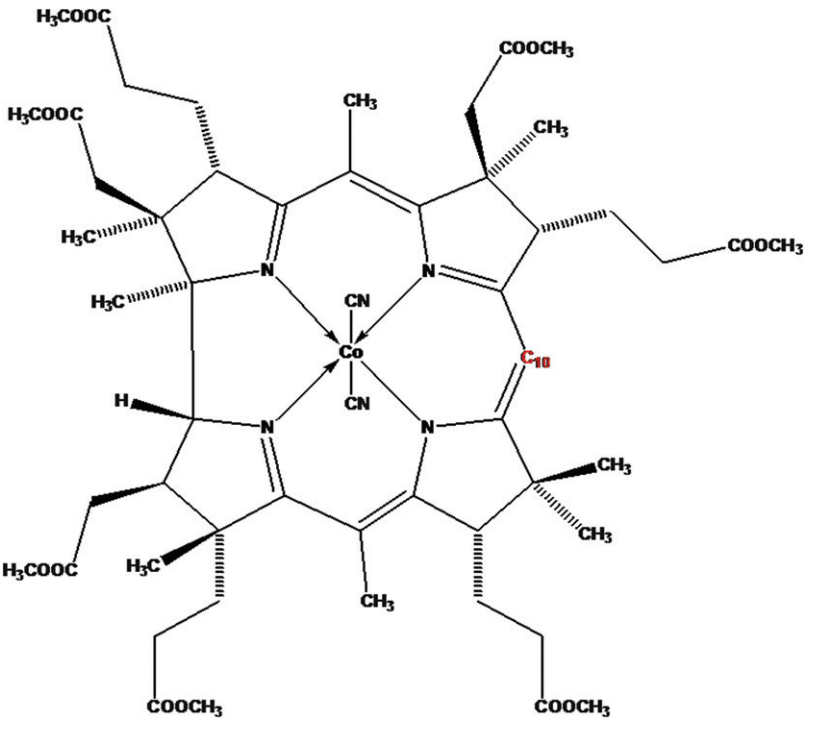


Figure 1. The structure of dicyanocobyrinic acid heptamethyl ester (DCCbs).

There is interest in studying azoles which contain two or three nitrogens in the five-membered ring because the ImH group of histidine occurs as a ligand in most of the known hemoproteins [4]. Interest in five-membered heterocycles has also been stimulated by the success of many agricultural and medical fungicides, which inhibit steroid synthases by acting as ligands to Fe(III) porphyrins in certain P-450 enzymes [5, 6]. ImH derivatives are of interest to the coordination chemists because these compounds can be used to link studies on the metal-binding properties of nitrogen bases [7].

The equilibrium constants for coordination of pyridine and its 4-substituted derivatives by five-coordinate sulfitocobyrinic acid heptamethyl ester (SCbs–Me) in six solvents have been determined spectrophotometrically, and show that the solvent polarity has an influence both on the UV-Vis spectrum of SCbs and on the equilibrium constants for the formation of six-coordinate SCbs [8].

Hydrophobic cobyrinic acid heptapropyl ester corrinoids were prepared from vitamin B_{12}. The equilibrium constant, K, for the reaction of hydrophobic cobyrinic acid heptapropyl ester corrinoids with five-membered heterocyclic nitrogen bases in different solvents were determined spectrophotometrically. Values of K are dependent on the identity of the ligand in the *trans* position, increasing with the basicity of the azoles and the solvent polarity [9].

This article is concerned with preparing different cobesters, which contains seven ester groups in the side chains (XCbs–Me), to study the effect of solvent polarity on the UV-Vis spectrum of the different methyl cobesters and to determine the equilibrium

constants for the coordination of various five-membered heterocyclic compounds containing nitrogen (azoles).

2. Experimental

2.1. *Materials and chemicals*

Vitamin B_{12} (cyanocobalamin) was purchased from Sigma-Aldrich. Pyrazole and imidazole were purchased from Sigma-Aldrich and used as received. Methanol and *N*,*N*-dimethylformamide (DMF) were obtained from ADWIC. *N*,*N*-dimethylsulfoxide (DMSO) was purchased from Fluka. All the salts used were of analytical grade, where $NaBH_4$ and Na_2SO_3 were purchased from Merck, NaOH and $NaHCO_3$ from Biochemicals. Buffer solutions were of analytical grade supplied by BDH and used to cover 1–13 pH range using ACOH/ACONa (pH 3.5–5.5), phosphate buffer (pH 8.5–11), and borate buffer (pH > 11). The ionic strength was kept constant at $I = 0.1\,\text{mol}\,\text{L}^{-1}$ unless otherwise stated. The pH was always checked after dissolving the ligand and adjusted if necessary with hydrochloric acid or sodium hydroxide.

2.2. *Instrumentation*

UV-Vis measurements were made on a Shimadzu UV-1601 (Kyoto, Japan) double beam UV-Vis spectrophotometer equipped with 10 mm matched cells. The temperature of the cell compartment was kept constant at $(25.0 \pm 0.01)^{\circ}\text{C}$ by circulating water from thermostated water bath.

The equilibrium constant *K* of the reaction was measured by pipetting a fixed volume of corrinoid solution of the desired pH and ionic strength into 2.5 mL quartz cell and recording the absorbance change at fixed wavelength associated with the injection of a known volume of standard ligand solution into the cell using Eppendorf micropipettes (5–100 μL). The absorbance was monitored after each addition to ensure that the equilibrium had been reached. All the absorbance measurements and the ligand concentrations were corrected for known dilution effects.

pH measurements were made on a calibrated E.D.T. (Dover Kent, UK) pH-mV meter model GP353 equipped with an E.D.T.-combined glass electrode with an accuracy of ± 0.01 and calibrated against standard buffer solutions (pH 4 and 7).

For quick qualitative experiments, photolysis was achieved by exposing the sample to a 60 W tungsten lamp at a distance of *ca* 20 cm to avoid excessive heating.

2.3. *Synthesis of corrinoids*

The dicyano cobyrinic acid heptamethylester (DCCbs–Me) was prepared as described previously [10] by refluxing a $6 \times 10^{-3}\,\text{mol}\,\text{dm}^{-3}$ solution of vitamin B_{12} in methanol containing $1.0\,\text{mol}\,\text{dm}^{-3}$ H_2SO_4 under N_2 for four days. The reaction mixture was concentrated, diluted with water, neutralized with $NaHCO_3$, and treated with excess KCN to give DCCbs–Me. DCCbs–Me was extracted first with CCl_4 and then with CH_2Cl_2, and finally the solvents were removed by evaporation.

Diaquacobester was prepared as described before for diaquacobinamide [11]. A solution of the aquacyanohepta methyl cobester (ACCbs–Me) was adjusted to pH 2–3 with acetic acid. The cobester was then allowed to photolyze and the volatile hydrogen cyanide was swept out with purging nitrogen until the reaction was complete. After about 3 h the sample of DACbs–Me was carefully neutralized with dilute NaOH. ACCbs–Me was prepared as described previously [12]. The dicyanocobster was dissolved in suitable solvent, to which acetic acid was added to adjust the pH to *ca* 3 and a stream of nitrogen was passed through for 24 h. Sulfitocobyrinic acid heptamethyl ester (SCbs–Me) was prepared by reacting the sodium sulfite with diaquacobester as described before [8]; the color of the orange red diquacobester changed to yellow within few seconds upon adding sodium sulfite.

Vinylcobyrinic acid heptamethyl ester (vinylCbs–Me) was prepared as described in the case of vinylcobinamide [11, 13]. DACbs–Me was reduced by $NaBH_4$ under N_2 to give the yellow cob(II)ester, which slowly changed to the grey-green cob(I)ester, followed by bubbling acetylene gas to cob(I)ester solution until we get the yellow vinylCbs–Me.

2.4. *Equilibrium measurements*

The hydrophobic corrinoids (ACCbs–Me, SCbs–Me, vinylCbs–Me, 1.0×10^{-5} mol L^{-1}) dissolved either in a 2.5 mL buffer solution of ionic strength 0.1 mol L^{-1}, or in an organic solvent placed in a cuvette in the thermostated cell block of the spectrophotometer for 30 min. The solution was titrated by the addition of small volumes of concentrated stock solution of an azole, prepared in the same solvent, using an Eppendorf micropipette. The reaction was followed by observing the change in absorbance at the wavelength that gave the greatest change during the course of the reaction. All titrations were carried out at least in duplicate. The values of the equilibrium constants, K, were obtained by fitting the absorbance *versus* concentration curve, after correction for dilution, to a binding hyperbola (Equation 1, where A_0 and A_∞ are the initial absorbance in the absence of the ligand and upon complete conversion to the product (L)(X)Cbs–Me, respectively, and A_x is the absorbance at any ligand concentration [L]) using standard non-linear least-square method.

$$A_x = (A_0 + A_\infty K[L])(1 + K[L]) \quad (1)$$

As $\log K$ values are small, the assumption was made that $[\text{ligand}]_{\text{total}} = [\text{ligand}]_{\text{free}}$. The linear plot obtained has a slope equal to the number of ligand molecules bound to the cobalt center, and the intercept gives the value of $\log K$. Analysis of the data was also carried out by plotting $\log[(A_0 - A_x)/(A_x - A_\infty)]$ against log [ligand]. The slope gives the number of ligands that coordinate to the Co(III) center.

3. Results and discussion

3.1. *Effect of solvent polarity on the UV-Vis spectra of hydrophobic corrinoids*

The effect of solvent polarity was studied by scanning the UV-Vis spectrum (300–700 nm) on changing solvent polarity. Several solvents over a wide range of

polarity have been used. Figure 2(a) shows the UV-Vis spectrum of ACCbs–Me in water, DMSO, and DMF. Solvent polarity has a significant effect of the shape and position of the three (α, β, and γ) absorption bands of ACCbs–Me.

The Soret band has been found to be 353 nm in H_2O, 359 nm in DMSO, and 360 nm in DMF. The shift in the three bands with increasing $E_T(30)$ from DMF < DMSO < MeOH < H_2O is also accompanied by the systematic movement of intensity from the low into the high bands within α, β regions and also a decrease in the intensity around 400 nm. These changes could be attributed to the formation of hydrogen bonds as investigated previously [12].

The Soret band of ACCbs–Pr (prepared from DCCbs–Pr) shifts to longer wavelength as the solvent polarity increases. The Soret band was at 352, 358, and 360 nm for toluene, acetonitrile, and H_2O, respectively [9].

Varying the polarity of the solvent has been shown to have a significant effect on the d–d transition of $[Co^{III}(CN)_6]^{3-}$ (e.g., from 311 nm in water to 318 nm in MeCN and 321 nm in DMSO) with accompanying changes in the CN stretching frequency (from 2127 cm^{-1} in water to 2111 cm^{-1} in DMSO) [14]. It also has an effect on the NMR and the electronic spectra of dicyanoiron(III) porphyrin complexes [15] and the electronic spectra of dicyanocobalt(III) corrinoid [2] and dicyanocobalt(III) tetrahydrocorrinoid complexes [16, 17].

There is crystallographic evidence that the coordinated CN^- in DCCbs is hydrogen bonded to an isopropanol [3]. Hydrogen bonding to CN^- in DCCbs is associated with a shift in λ_γ from 374 nm in CCl_4 to 369.9 nm in *ca* 20% MeOH for one hydrogen bond ($K = 7$ dm^3 mol^{-1}) and to <368 nm in water on formation of a second hydrogen bond.

Figure 2(B) shows solvent effects on the UV-Vis spectra of SCbs-Me in H_2O, DMSO, and DMF. For DMSO and DMF there is an increase in absorbance at 500–550 nm, suggesting a small amount of the six-coordinate solvate complex present in equilibrium with five-coordinate SCbs–Me; marked solvent dependence shows a strong interaction between the solvent and the Co–SO_3 dipole. UV-Vis spectra of SCbs–Me were examined previously in different solvents covering a wide range of solvent polarity (from H_2O to toluene) and it was found that the spectrum of the five-coordinate SCbs is solvent dependent [8]. UV-Vis spectra of SCb–Me (figure 2b) are similar to those reported for SCbs–Pr [9].

In all solvents, the Soret band occurs as a shoulder at 350–360 nm. The spectrum of the five-coordinate SCbs–Me is solvent dependent (figure 2b). As all known six-coordinate

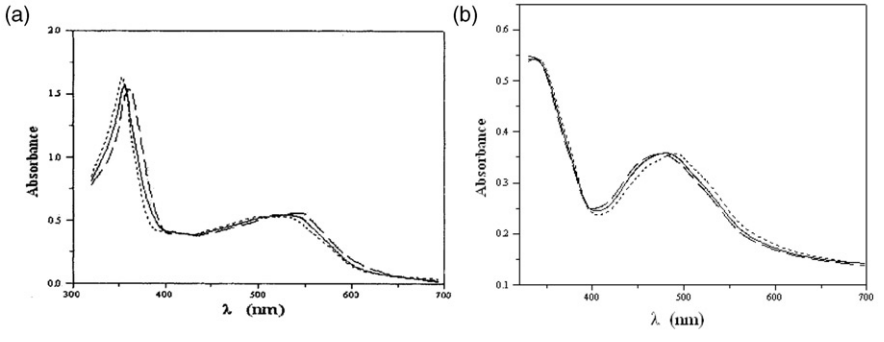
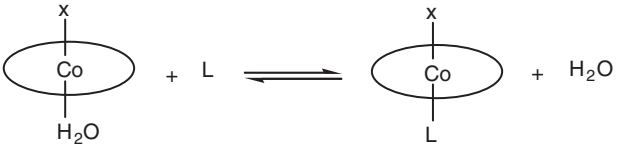


Figure 2. UV-Vis spectra of (a) ACCbs–Me and (b) SCbs in H_2O (...), DMSO (), and DMF (—).



Scheme 1. The reaction of corrinoid derivatives with ligand L.

corrinoids are red or purple with absorption beyond 500 nm, we assume that the spectra in figure 2(b) represent mainly five-coordinate species. In solvents of low polarity the spectra of SCbs–Me resemble those of five-coordinate alkyl corrinoids, while in water it resembles those of five-coordinate phosphito corrinoids. The equilibrium between five and six-coordinate species in the case of sulfitocobester has been studied using high-pressure techniques [8]. Increasing pressure displaces the equilibrium from five-coordinate toward six-coordinate complexes. A significant increase in the absorbance at *ca* 490 nm was observed, accompanied by sharp isobestic points, suggesting that conversion of five-coordinate to the six-coordinate form involves coordination of one water to the five-coordinate form [18]. UV-Vis absorption changes obtained upon increasing the pressure ascribed to the equilibrium between five-coordinate and six-coordinate are similar to the changes obtained when methanol and DMSO were used as solvents, for which there is increase in absorbance at 500–550 nm.

3.2. *Equilibrium studies*

Two ligands of the azole family (ImH, $pK_a = 7.1$) and (Pz, $pK_a = 2.28$) [19] were selected for the equilibrium study with three derivatives of the hydrophobic corrinoids [aquacyanocobyrinic acid heptamethyl ester (ACCbs–Me), sulfitocobyrinic acid heptamethyl ester (SCbs–Me), and vinylcobyrinic acid heptamethyl ester (vinylCbs–Me)]. The equilibrium studies for each corrinoid were carried out in four different solvents with different polarities (water, methanol, DMSO, and DMF).

The reaction between the different corrinoid complexes and the azoles is represented in scheme 1, where X is the ligand in the β-axial position ($X = CN^-$, SO_3^-, and CH_2CH) and L is the incoming ligand (L = ImH and Pz) (scheme 1).

Preliminary experiments on the reaction of XCbs–Me in H_2O or in organic solvents showed that the equilibria are established rapidly with well-defined isosbestic points observed in the 300–700 nm range. The Soret band of the product was found at 357 and 360 nm for (Pz)(CN)Cbs–Me and (ImH)(CN)Cbs–Me, respectively. Hence, the Soret band shifts to longer wavelength as the basicity of the ligand increase. A similar trend was observed in the other solvents used in the present study.

3.3. *Reactions of ACCbs–Me with azoles*

Figure 3 shows a typical UV-Vis spectral change accompanying the spectrophotometric titration of ACCbs–Me in water by ImH. It is clear from the figure that there is a significant shift in the UV-Vis spectrum of ACCbs–Me upon the formation of

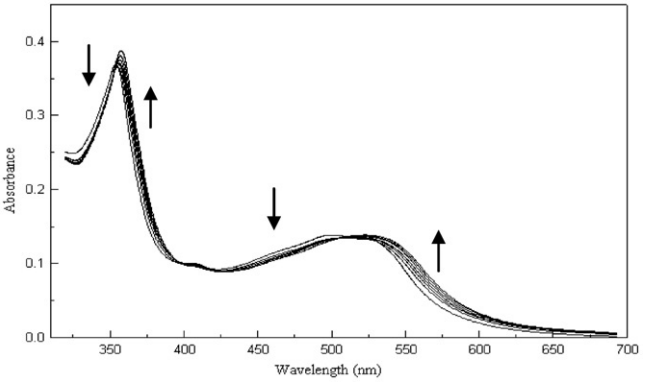


Figure 3. UV-Vis spectral change accompanying the titration of ACCbs–Me with ImH in water at 25.0°C.

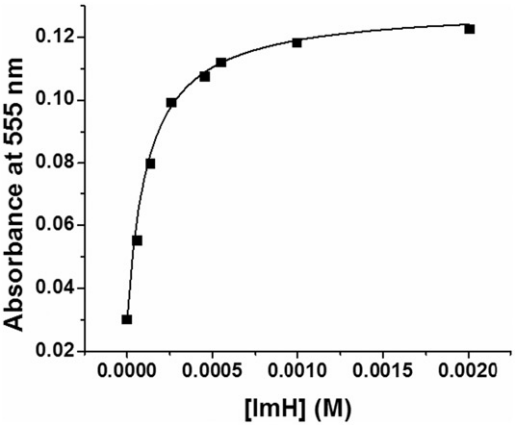


Figure 4. Change in absorbance of ACCbs–Me in H_2O at 555 nm upon addition of ImH in water at 25°C.

CN(ImH)Cbs with λ_{max} occurring at 560, 517, and 357 nm. The shift in spectrum is accompanied by good isosbestic points at 510, 396, and 356 nm.

The spectrophotometric titrations of ACCbs–Me were monitored by following the increase in absorbance at 555 nm. Figure 4 gives a typical plot for the data obtained for the titration of ACCbs–Me with ImH in aqueous solution. The solid line represents the fit of equation (1) to the experimental data, which can be used to obtain the exact value of K.

The plot of $\log(A_i - A_x)/(A_x - A_\infty)$ *versus* log [ImH] gives a straight line (figure S1) with slope $n = 1 \pm 0.02$, which indicates that only one molecule of the ligand binds to Co(III) in ACCbs–Me. Similar plots were observed in the case of Pz in different solvents.

The values of K were found to be 8913 ± 160 and 155 ± 20 for ImH and Pz, respectively. These values show that K_{ImH} is greater than Pz_l. This was ascribed to the difference in basicity.

The same reaction was studied in three other solvents (methanol, DMSO, and DMF). Similar spectral changes to those obtained in aqueous solution were observed. Table 1 summarizes the values of K obtained for the reaction of ACCbs–Me with azoles.

Table 1. Values of K for coordination of XCbs-Me by azoles in different solvents at 25°C.

Solvent $E_T(30)$	Water 63		Methanol 55.5		DMSO 45		DMF 43.8	
L (X)	Pz	ImH	Pz	ImH	Pz	ImH	Pz	ImH
CN^-	1545 ± 20	8913 ± 160	79 ± 5	1584 ± 95	9 ± 0.5	1271 ± 60	7 ± 0.5	937 ± 30
SO_3^{2-}	9 ± 0.5	133 ± 10	6 ± 0.5	58 ± 2	2 ± 0.1	17 ± 1	<-1	6 ± 0.4
$CHCH_2$	2.3 ± 0.1	21 ± 1	2 ± 0.1	17 ± 1	0.55 ± 0.01	14 ± 1	<-1	<-1

The equilibrium constant values for coordination of ImH to ACCbi (amide side chain), ACCbs (methyl ester side chain) and ACCbs–Pr (propyl ester side chain) were found to be 13804, 8913, and 3737 $(\text{mol L}^{-1})^{-1}$, respectively [9, 12, 20, 21]. This comparison shows that the presence of the seven ester groups (methyl or propyl) in the microenvironment of Co(III) leads to a suppression of values of K than that obtained if the side chain is amide. The value of K in case of propyl ester side chain is less than that obtained with methyl ester. This suggests that the bulky propyl group in the side chain affects the entering ImH to coordinate with cobalt.

3.4. *Reactions of SCbs–Me and vinylCbs–Me with azoles*

As with ACCbs–Me, the azoles reacted rapidly with SCbs–Me and vinylCbs–Me in four different solvents used in the present study, with well-defined isosbestic points. Typical spectral changes accompanying the spectrophotometric titration of SCbs–Me with Pz in methanol and vinylCbs–Me with Pz in H_2O are shown in figures S2 and S3 in the supporting information. Equilibrium constant values show similar trends to those observed in case of ACCbs–Me for SCbs–Me and vinylCbs–Me (table 1).

Table 1 summarizes all the data obtained in the present study, showing that the value of K for Pz is less than that for ImH. This clearly shows the effect of basicity on the value of K. The basicity effect was studied before and linear plot between the value of pK and log K was obtained in the case of Co(III) corrinoids and Fe(III) porphyrins [8, 22]. Solvents have a significant effect on the value of K and it is clear that as the solvent polarity increases the value of K increases and the trend was water > methanol > DMSO > DMF.

The data also show that the values of K for the two azoles decrease in the order of $X = CN^- > SO_3^{2-} >$ vinyl, showing that the ligands coordinated at the *trans* position in the substitution site have a significant effect on the value of K.

Pratt [23] showed that by varying only the ligand in the series CN^- to $CH_2CH_3^-$, the positive charge on cobalt changed from typical Co(III) to low spin cobalt(II). Co(III) complexes are characterized by an octahedral configuration and high formation constants for the substitution of H_2O by CN^- or NH_3. Low spin Co(II) complex shows a balance between six- and five- (and four) coordination and the formation constant for the substitution of H_2O by CN^- in $[Co^{II}(CN)_5H_2O)]$ is very low. The usual correlation between stereochemistry and valency and the division into valencies clearly break down in the case of the very polarizable ligands such as alkyls, whose oxidation state is not well-defined.

4. Conclusions

This work provides further evidence that hydrogen bonding between axial ligands and solvent has a significant effect on the UV-Vis spectra of Co(III) corrinoids. The equilibrium constants for coordination of azoles were found to depend on the polarizability of the *trans* ligand ($CN^- > SO_3^{2-} >$ vinyl). The values of K for Pz were less than those obtained for ImH in all solvents used in the present study. The values of K increase as the solvent polarity increases, water > methanol > DMSO > DMF. The presence of the seven ester groups (methyl or propyl) in the microenvironment of Co(III) leads to more suppression of values of K than that obtained if the side chain is amide.

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