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Influence of solvent polarity from water to toluene on the co-ordination of pyridines by the cobalt(III) corrinoid sulfitocobyrinic acid heptamethyl ester ‡

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Equilibrium constants K have been determined by UV/VIS spectrophotometry for co-ordination of 4-cyanopyridine, pyridine and 4-dimethylaminopyridine (pK 1.9, 5.2 and 9.8 respectively) by the uncharged five-co-ordinate sulfitocobyrinic acid heptamethyl ester in six solvents (water, MeOH, PrOH, MeCN, CH_2Cl_2, toluene) at 25 °C in order to establish the solvent dependence of the values of a and b in the linear free-energy relation (l.f.e.r.) $\log K = a\cdot pK + b$, where pK refers to protonation of the free base in aqueous solution. The results reveal a simple pattern in which the decrease in solvent polarity from water to toluene is accompanied by a decrease in a from 0.36 to 0.25 and in b from −0.3 to −1.7. This provides the first direct comparison of the l.f.e.r. for any ligand-binding equilibrium in both protic and aprotic solvents. The UV/VIS spectrum of this ester (in contrast to those of five-co-ordinate alkylcobyrinic acid heptamethyl esters) shows a marked solvent dependence, indicating strong interaction between the solvent and the $^{\delta+}Co–SO_3{}^{\delta-}$ dipole, and it is suggested that the main variable which causes the decrease in a and b with solvent polarity is the dipolar solvation term.

We have been studying the co-ordination of three families of nitrogen bases (amines, azines and azoles) by the d^5 iron(III) porphyrin microperoxidase-8[2–5] and the d^6 cobalt(III) corrinoid aquacyanocobinamide [1,6,7] in aqueous solution in order to identify the main factors which determine the magnitude of the equilibrium constants K for the single-step substitution of co-ordinated H_2O by the base B and the values of a and b in the linear free-energy relation (l.f.e.r.) (1). Here pK refers to

$$\log K = a\cdot pK + b \qquad (1)$$

protonation of the free base in aqueous solution while K may refer to any solvent and may involve the simple binding of the given base to a vacant co-ordination site (see below) as well as substitution of another ligand such as H_2O. For a summary of our main findings in aqueous solution see ref. 1.

We are now interested in establishing the dependence of a and b on changes in relative permittivity and solvent polarity [as measured by the solvent polarity parameter $E_T(30)$ [8]] for metal–ligand binding constants in general and also the possible effect of the low relative permittivity of the protein environment on equilibria involving metalloenzymes. The need for such information in the corrinoid field will increase with the recent availability of the first structural data on any B_{12}-dependent enzymes, *viz.* an active Cbl-containing isomerase (methylmalonyl/succinyl-Coenzyme A isomerase) [9] and an inactive MeCbl-containing fragment of a methionine synthase.[10] The only previous direct comparison of equation (1) for any metal complex in two or more solvents, based on the use of a single-step equilibrium constant, appears to be for the co-ordination of three pyridines (4-cyanopyridine, pyridine and 4-aminopyridine) by a zinc(II) porphyrin in benzene and $CHCl_3$;[11] *cf.* also comparisons of the co-ordination of *N*-methyl- and *N*-acetyl-imidazole by a cobalt(II) porphyrin and of py and 4-methylpyridine by Cby(OMe)$_7$, both in CH_2Cl_2 and toluene,[12] and a comparison of the overall β_2 constants for the simultaneous co-ordination of two pyridine molecules by several iron(II) porphyrins in CCl_4, $CHCl_3$ and benzene.[13] These few comparisons between solvents and the many other studies related to equation (1) in a single non-aqueous solvent have all been carried out using a relatively narrow range of solvents of low polarity parameter $E_T(30)$ from 32.5 (CCl_4) to 41.1 (CH_2Cl_2) compared to 63.1 in water. No clear-cut pattern has yet emerged, probably because of the operation of several factors (ionic and hydrogen-bonding as well as dipolar interactions) and the limited range of solvents used. It would clearly be desirable to minimise the number of variables and to maximise the range of solvents studied to include water and solvents of intermediate polarity, both protic and aprotic, as well as the typical organic solvents of low polarity.

The corrinoids offer several advantages for such solvent studies. First, the seven amide side-chains of the naturally occurring hydrophilic corrinoids can readily be converted into esters with any desired alkyl group. The uncharged $(CN)_2Cby(OMe)_7$, for example, is sufficiently soluble for UV/VIS spectrophotometry in solvents ranging from water (solubility *ca.* 10^{-4} mol dm^{-3}) to CCl_4 [$E_T(30)$ 32.5];[14,15] hydrolysis of one or two ester side-chains to carboxylic acids restricts the solubility to solvents with minimum $E_T(30)$ values of 34.5 (benzene) and 39.1 ($CHCl_3$) respectively,[16] while the hepta-propyl and -butyl esters are virtually insoluble in water.[14] The solubility range can be tuned as desired. Secondly, the absence of any significant change in the spectrum of Me- and C_6H_{11}-Cby(OMe)$_7$ between water and CH_2Cl_2[15] suggests there is little interaction between the conjugated chromophore and the solvent. Much of the corrin ring is, in fact, buried within the protective shell of the exocyclic ring and its substituents; contrast the metal porphyrins. The spectrum of $(CN)_2Cby(OMe)_7$ does, however, show a slight but systematic solvent dependence, which is ascribed to interaction of the solvent with the lone pairs on the cyanide N atoms.[14,15] The corrinoids, in effect, enable one to dissociate studies of the co-ordination chemistry of the central cobalt ion from the problems of solubility which are determined mainly at the periphery.

We have chosen to study the previously unreported $(SO_3)Cby(OMe)_7$ **1**. Its UV/VIS spectrum (see Figs. 1 and 2) is similar or identical to that of $(SO_3)Cbi$, in which the cobalt ion is mainly (≈95%) five-co-ordinate at 25 °C[17] and the

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Abbreviations used: Cbi, Cbl and Cby(OMe)$_7$ denote the corrinoids cobinamide, cobalamin and cobyrinic acid heptamethyl ester; py = pyridine, cnpy = 4-cyanopyridine, dmapy = 4-dimethylaminopyridine.

S-co-ordinated SO_3^{2-} ligand[18] is very firmly held.[19] The co-ordinated S in SO_3^{2-} shares with the isoelectronic P in $P(OR)_2O^-$[20-22] and with C in vinyl and alkyl (but not CN^-)[23] a very strong *trans* effect, which is associated with the ready occurrence of five-co-ordination, while the two negative charges on the co-ordinated SO_3^{2-} and the single negative charge on the corrin ring balance the Co^{3+} ion to provide an uncharged, five-co-ordinate corrinoid. A third advantage of the corrinoids is, therefore, that they allow one to study the solvent dependence of the co-ordination of bases B (pyridines chosen here to avoid complications due to hydrogen bonding) according to the simplified equilibrium (2) involving three

$$B + Co\text{–}SO_3 \rightleftharpoons B\text{–}Co\text{–}SO_3 \quad (2)$$

uncharged species without complications due to the release of any pre-existing ligand (*e.g.* co-ordinated solvent) or the presence of a counter ion.

We report here the determination by UV/VIS spectrophotometry of the stoichiometric equilibrium constants K for co-ordination (for details see Table 1) by the yellow five-co-ordinate **1** of three pyridines (pK ranging from 1.9 to 9.8) in six solvents (protic and aprotic from water to toluene) to give the red six-co-ordinate adducts according to equation (2) with the aim of testing whether *a* and/or *b* of the l.f.e.r. (1) are sensitive to a change in solvent polarity or hydrogen bonding. Owing to the possibility of firm retention of low concentrations of water by the corrinoids [1 molecule of Pr^iOH or water per $(CN)_2Cby(OMe)_7$ established by X-ray analysis of the solids][15] and the difficulty of rigorously drying the corrinoid solutions (due to, *e.g.* adsorption, hydrolysis of the ester side-chains),[15] the solvents used were 'air-equilibrated' and not rigorously dried; such conditions are also more relevant where comparisons need to be made with the hydrophobic (and air-equilibrated) interior of a protein or enzyme. The UV/VIS spectrum of **1** shows an unexpectedly large solvent dependence; a qualitative comparison of its spectrum in a larger number of solvents is therefore also included.

Experimental

Materials

Reagents and solvents were obtained as follows: cyanocobalamin or vitamin B_{12} (Rhône-Poulenc Biochimie, France); Na_2SO_3 anhydrous (BDH, AnalaR); py (BDH, AnalaR); cnpy, dmapy and CF_3CH_2OH (all Aldrich, 99+ %); other solvents from Fisons (≥99% pure). To remove impurities which interfered with the spectrophotometric titration cnpy was recrystallised from a CH_2Cl_2–Et_2O mixture.[27] Other reagents and solvents (air-equilibrated, not specially dried) were used as received.

Preparation and characterisation of compound 1

Compound **1** was prepared by the sequence (CN)Cbl ⟶ $(CN)_2Cby(OMe)_7$[15] ⟶ $(H_2O)_2Cby(OMe)_7$.[28] After increasing the pH to 2–3, the addition of a slight stoichiometric excess of solid Na_2SO_3 immediately gave a solution of yellow **1**; this was extracted into CH_2Cl_2 and the solvent allowed to evaporate to give **1** as a brown solid. Comparison of the spectrum of **1** in water and alcohols (see Figs. 1 and 2) with that of (SO_3)Cbi[17] showed they were essentially identical and established that **1**, like (SO_3)Cbi, is five-co-ordinate with a S-bonded SO_3^{2-} ligand. Thin-layer chromatography[15] established the identity of the purple product of photolysis of an aqueous solution of **1** with $(CN)_2Cby(OMe)_7$ prepared directly as above, hence[16] the presence of seven unhydrolysed ester side-chains in **1**. The difference between axial sites α and β (due to the non-planarity of the corrin ring) allows the occurrence of two stereoisomers if the axial ligands are different.[29] Since SO_3^{2-} is a relatively bulky ligand and the upper (β) co-ordination site is sterically less constrained,[29] we assume that **1** is mainly or entirely the upper (β) isomer. Thin-layer chromatography of yellow **1** in the absence of any potential ligand merely gave a long yellow streak, indicating ready hydrolysis of one or more side chains,[15] but TLC on silica gel with MeOH in the presence of 2 mol dm^{-3} imidazole gave a single slightly elongated reddish spot which supports[29] the presence of only one isomer.

Methods

The UV/VIS spectra were recorded and spectrophotometric titrations carried out on a Philips PU8720 or 8740 spectrophotometer in a 1 cm pathlength cell thermostatted at 25 °C and containing a *ca.* 10^{-5} mol dm^{-3} solution of the corrinoid. For quantitative work in aqueous solutions, the ionic strength was made *ca.* 0.1 mol dm^{-3} using phosphate (pH 7.0) or hydrogencarbonate (pH 10.0) buffers. Compound **1** is light-sensitive and due care must be taken to prevent photolysis. Measurements of pH were made with a Hanna HIB417 pH meter and appropriate glass electrode standardised at pH 7 and 10.

Quantitative determinations of K were carried out in duplicate by spectrophotometric titration of *ca.* 10^{-5} mol dm^{-3} solutions of compound **1** in the given solvent with a concentrated stock solution (1–5 mol dm^{-3}) of the base in the same solvent, following either the rise in absorbance at *ca.* 550 nm or the fall at *ca.* 450 nm. Aqueous buffers of pH 7.0 were used for cnpy and py (pK 1.9 and 5.2 respectively) and 10.0 for dmapy (pK 9.8) and, in the last case, correction was made for partial protonation when calculating the concentration of free base. In the case of MeOH and PrOH, where the pK is not known but assumed to be similar to those in water, no buffer was used; however, a pH-electrode showed that less than 10% of the base added was sufficient to produce an apparent pH of ≥10.5, where we assume that most of the added base is unprotonated, and the error in log K was increased to reflect the increased uncertainty in the concentration of free base. No such corrections were made for the other bases or solvents. For combinations of base and solvent where a value of log $K > 0.5$ allows the spectrum of the product to be deduced with reasonable certainty, it appears that all the species B–Co–SO_3 exhibit similar spectra with λ_α (*ca.* 540 nm) and λ_β (*ca.* 520 nm) varying by less than 10 nm with either the nature of the base or the solvent, and λ_γ 366–367 nm; contrast the marked solvent dependence shown by **1** (Fig. 1). Values of the absorbance (A_∞) corresponding to 100% formation of the product were therefore obtained either by graphical extrapolation of plots of absorbance (corrected for dilution where necessary) *vs.* the concentration of free base or, where values of log K were less than 0.5, by assuming the same final spectrum as obtained with dmapy in aqueous solution. The data were analysed by plotting values of $\log[(A_i - A_x)/(A_x - A_\infty)]$ *vs.* log [B], where A_i is the initial absorbance and A_x that corresponding to the given value of [B], in order to establish the stoichiometry of the equilibrium and the validity of the extrapolated value of A_∞ (slope n = 1.0 ± 0.1 or better in each case) and to obtain the values of log K (= −log [B] when $y = 0$) which are given in Table 1.

Results

Equilibrium constants

Preliminary experiments (*i*) showed that the solubility of compound **1** was just adequate for spectrophotometric studies (in a 1 cm cell) in toluene, too low for accurate work in CCl_4 and undetectable in Et_2O [with $E_T(30)$ values of 33.9, 32.5 and 34.6 respectively] but adequate in solvents of higher polarity and (*ii*) indicated that values of log K decreased as the solvent polarity decreased. The three bases studied and the six solvents used, ranging in polarity from water to toluene, are listed in Table 1 together with the published pK values for protonation of the

Table 1 Equilibrium constants K for the co-ordination of pyridines B by compound **1** in selected solvents

Solvent	log (K/dm^3 mol^{-1}) for B = cnpy	py	dmapy	a[a]	b[a]	$E_T(30)$[b]	D[c]
Water	+0.4 ± 0.1	1.56 ± 0.06	3.20 ± 0.02	0.36	−0.3	63.1	78.54
MeOH	−0.4 ± 0.2	0.74 ± 0.1	2.10 ± 0.05	0.305	−0.8	55.5	32.62
PrOH	≤ −0.5	0.38 ± 0.05	1.54 ± 0.06	0.27	−1.05	50.7	20.1
MeCN	≤ −0.5	0.3 ± 0.1	1.48 ± 0.1	0.265	−1.15	46	37.5
CH_2Cl_2	< −1[d]	−0.1 ± 0.1	1.0 ± 0.1	0.26	−1.5	41.1	9.08
Toluene	< −1[d]	−0.4 ± 0.2	0.7 ± 0.2	0.25	−1.7	33.9	2.38
Pro-ligand pK[e]	1.9	5.17	9.76				

[a] a and b in equation (1); values calculated from linear plots in Fig. 3. [b] Solvent polarity parameter; values from ref. 18. [c] Relative permittivity; values from ref. 24. [d] A value < −1 signifies no detectable co-ordination. [e] In aqueous solution; values from ref. 25 (py, cnpy) and 26 (dmapy).

bases in aqueous solution and the values of $E_T(30)$ and the relative permittivity of the solvents. Initial experiments also revealed an unexpectedly large variation of the UV/VIS spectrum of **1** with solvent (see Fig. 1), which was further studied in several additional solvents (see below). The spectrophotometric titration of the yellow five-co-ordinate **1** with a pyridine to give a red six-co-ordinate product is accompanied by a large change in spectrum (see Fig. 2). Equilibrium is established essentially instantaneously, no further side-reactions are observed during the period of the experiment, and good to excellent isosbestic points can be observed (before corrections for dilution have to be made). Aqueous solutions of **1** in the presence of a low concentration of free sulfite showed no change in spectrum over the whole range of pH 2.5–13. A reversible change above pH 13 can, as with (SO_3)Cbi, be ascribed to co-ordination of HO^- to form the six-co-ordinate HO–Co–SO_3 complex.[19]

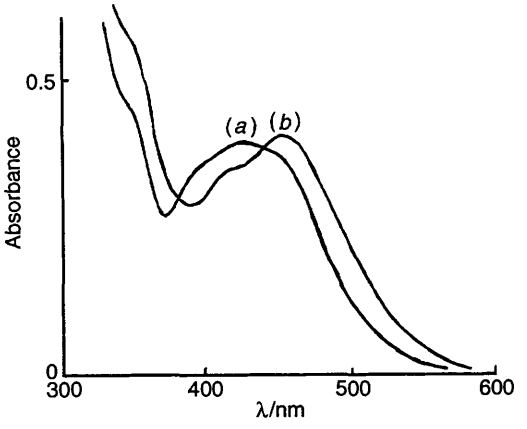

Fig. 1 Comparison of the UV/VIS spectrum of *ca.* 5 × 10^{-5} mol dm^{-3} solutions of compound **1** in (*a*) water and (*b*) toluene

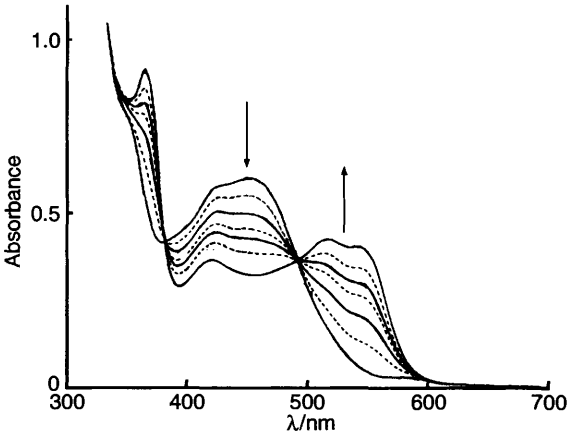

Fig. 2 Spectrophotometric titration of a *ca.* 5 × 10^{-5} mol dm^{-3} solution of compound **1** (λ_{max} *ca.* 450 nm) with dmapy in methanol

UV/VIS spectrum of compound 1

The spectrum of compound **1** has been examined in the solvents listed in Table 2 and in ethyl acetate–methanol mixtures. Typical examples are shown in Figs. 1 (water, toluene) and 2 (MeOH). All the spectra exhibit absorption bands at *ca.* 455 (band I), *ca.* 425 (II) and probably also *ca.* 390 nm (III). Band I is the most intense in solvents of low polarity and increasing polarity causes an increasing shift of intensity from band I into II and eventually into III, which only becomes really noticeable in water and CF_3CH_2OH. The ratio of apparent absorbance of bands I and II (uncorrected for their overlap) in each solvent is given in Table 2. An isosbestic point was observed during the initial stages (before disruption by dilution) of titrating a solution of **1** in ethyl acetate with MeOH, *i.e.* accompanies the shift in intensity from band I to II. Since the spectrum of the six-co-ordinate solvato form of (SO_3)Cbi in ethanol at −180 °C exhibits a maximum at 484 nm with a shoulder at 514 nm,[17] the fact that the spectrum of **1** in the four alcohols and in water shows bands which are more rounded than those in *e.g.* acetone or toluene, and may also show a shoulder *ca.* 520 nm, suggests that there is a small amount of the six-co-ordinate solvato complex present in equilibrium with five-co-ordinate **1** at 25 °C. In all solvents the γ band occurs as a shoulder at 350–360 nm on the steeply rising limb of an intense band at *ca.* 317 nm. Although any trends in the solvent dependence of the wavelength of the γ band would be blurred by solvent dependent changes in the envelope of this intense electronic transition, it appears that there are no major changes in λ or A of the kind observed at longer wavelength.

Discussion

Equilibrium constants

The values of log K determined, together with published values of pK for the pro-ligands and of $E_T(30)$ and relative permittivity for the solvents, are listed in Table 1. Plots of log K for co-ordination in each solvent *vs.* pK for protonation (in aqueous solution) are shown in Fig. 3 and the values of a and b in equation (1), calculated from these plots, are also included in Table 1. Fig. 3 and the values of a and b reveal an unexpectedly simple pattern which shows that, within experimental error including the uncertainty introduced where only maximum values could be obtained, the l.f.e.r. (1) is obeyed in each solvent, the value of b (*i.e.* the intercept at pK = 0) falls with decreasing solvent polarity from −0.3 in water to −1.7 in toluene and that of a (*i.e.* the slope) from 0.36 to 0.25. Using the values of log K for dmapy, which provide the most complete and accurate set of data corresponding to these changes, for a more quantitative analysis shows (see Fig. 4) a reasonably linear dependence of log K on the cube of the value of $E_T(30)$ with no marked discontinuity between protic and aprotic solvents.

Table 2 Solvent dependence of the spectrum of compound **1** in the 400–500 nm region

Solvent	$E_T(30)$[a]	λ[b]/nm Band II	λ[b]/nm Band I	Ratio[c] $A_I:A_{II}$
Toluene	33.9	415	*453*	1.16
Ethyl acetate	38.1	≈422	*452*	1.13
CH_2Cl_2	41.1	≈418	*451*	1.08
Me_2CO	42.2	≈424	*451*	1.08
Me_2SO	45	≈421	*453*	1.03
MeCN	46	≈426	*447*	1.03
PrOH	50.7	≈424	*445*	1.04
EtOH	51.9	≈425	≈*452*	1.02
MeOH	55.5	≈427	≈*453*	1.03
CF_3CH_2OH	59.5	*423*	≈460	0.87
Water	63.1	*430*	≈455	0.92

[a] Solvent polarity parameter; values from ref. 8. [b] Wavelengths in italics denote maxima; others are shoulders. [c] Ratio of absorbances at the wavelengths given under bands I and II.

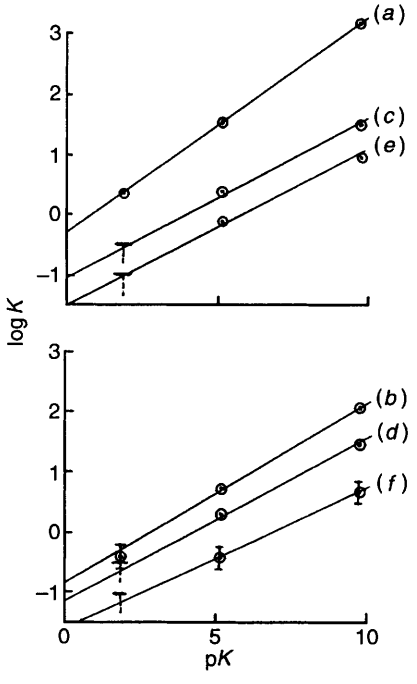

Fig. 3 Plots of the values of log K for the co-ordination of pyridines by compound **1** in the following solvents *vs.* the pK for protonation of the free pro-ligand in aqueous solution: (*a*) water, (*b*) MeOH, (*c*) PrOH, (*d*) MeCN, (*e*) CH_2Cl_2 and (*f*) toluene. Data from Table 1. Note different scales on the x and y axes

These values of log K also show an approximately linear dependence on the square root of the relative permittivity with the exception of a marked discrepancy for MeCN (see Table 1), which may be related to the strong mutual alignment of its dipoles as seen in the crystalline state.[30]

Any observed effect of changing polarity on log K will represent the sum of its separate effects on the solvation and activity of the three individual components of reaction (2). The recent development of techniques for experimentally determining gas-phase proton affinities, coupled with values of pK in solution, has led to the successful analysis of the role of substituents (*e.g.* in pyridines and amines) and identification of the various factors involved in determining both the proton affinities and pK; see, for example, refs. 31 and 32. For the unprotonated pyridines the main effect of a change in solvent or in substituent is on the dipolar solvation term.[32] The facts that the UV/VIS spectrum of the five-co-ordinate compound **1** is very solvent dependent, while those of five-co-ordinate

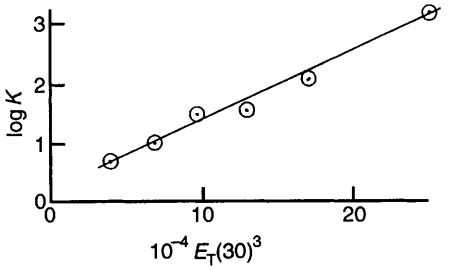

Fig. 4 Plot of the values of log K for the co-ordination of dmapy by compound **1** in various solvents as a function of the cube of the solvent polarity parameter $E_T(30)$. Data from Table 1

alkylcobalt analogues are not,[15] and that isosbestic points are observed when titrating **1** in ethyl acetate with MeOH (see Results) suggest strong localised interaction between the solvent and the axial ligand which will obviously carry a significant dipole $^{\delta+}Co–SO_3{}^{\delta-}$. The positive charge will be partially delocalised onto the equatorial corrin ligand normal to the dipole axis (*cf.* theoretical calculations on charge distribution in various metal porphyrins)[33] with a slight accumulation of positive charge on the C(20) methyl group which interacts with the carbonyl O(62) atom of side-chain g (see discussion in ref. 15). The spectra of the six-co-ordinate products cannot provide such direct evidence of strong dipole–solvent interaction (see below) but it seems reasonable to expect the dipole moment (= charge × separation) to be larger in the six-co-ordinate products; donation of electron density by the co-ordinated N of the pyridine will reduce that donated by the sulfite ligand to the Co, leaving a more negative charge on the sulfite O atoms and moving the positive end of the dipole from the Co to the far end of the co-ordinated pyridine. On the simple basis that the more polar of the two complexes in equilibrium (2), *i.e.* the six-co-ordinate B–Co–SO_3, will be favoured by the more polar solvent, the above analysis predicts qualitatively that equilibrium (2) will be displaced to the right by an increase in solvent polarity, as is found experimentally. Our results support Rillema's suggestion[34] regarding the importance of dipole–solvent interactions in determining ligand-binding equilibria in non-aqueous solvents. It is possible that the cubic term (see Fig. 4) might be related to the presence of the three sulfite O atoms, which would provide the locus of strongest dipole–solvent interaction, but further evidence is needed.

UV/VIS spectra

The spectrum of the five-co-ordinate starting complex **1** is solvent dependent (see Fig. 1 and Table 2). Since all known six-co-ordinate corrinoids with an unmodified corrin ring are red or purple with absorption beyond 500 nm,[29] we assume that the spectra in Fig. 1 represent mainly five-co-ordinate species and that the three apparently analogous bands at *ca.* 455, 425 and 390 nm are vibrational bands within the same electronic transition. To a first approximation the solvent-dependent changes form a single order related to solvent polarity and including both protic and aprotic solvents, with an increasing shift of intensity from the first into the second band (*ca.* 425 nm) and eventually into the third band at *ca.* 395 nm. In solvents of low polarity the spectrum of **1** resembles those of the five-co-ordinate alkyl corrinoids,[35] while in water it resembles those of the five-co-ordinate phosphito corrinoids,[20–22] thereby linking together the spectra of the three groups of ligands which all exert a strong *trans* effect (see Introduction). Changes similar to those produced in the spectrum of **1** by increasing solvent polarity can be induced in the spectra of five-co-ordinate alkyl corrinoids by increasing steric distortion around the Co–C bond with intensity moving increasingly out of the first band at *ca.* 460 nm into the second band at *ca.* 440 nm as the ligand is varied in the order Me, Et, Pr^i and C_6H_{11}.[35] Since changes in

electronic (*i.e.* spin) state have been excluded as a possible cause,[36] the change in relative intensity of the different vibrational bands can be related to changes in their Franck–Condon overlaps associated with differences in the structure of the chromophore (*e.g.* lengthening of the Co–C bond, increasing displacement of the Co out of the mean-square plane of the equatorial N atoms) and hence in the potential-energy curves between the ground and excited states, as already discussed for the resonance-Raman spectrum of the five-co-ordinate cobalt(II) cobalamin (B_{12r})[37] and the emission spectra of certain metal-free corrinoids.[38] In the case of **1** we suggest that analogous changes may be caused by changes in oxygen–oxygen repulsion and O–S–O bond angles associated with changes in oxygen-solvent interactions. By contrast, the spectra of the six-co-ordinate adducts with heterocyclic bases show far less sensitivity in the visible region to solvent in the case of **1** (see Results), to steric compression in the case of alkyl corrinoids and to varying R (Me, Et or Pr^i) in corrinoids with the ligands $P(OR)_2O^-$.[22] It would appear that the five-co-ordinate are more easily distorted or 'polarisable' than the six co-ordinate corrinoids; *cf.* the detailed analysis of the Soret band in the UV/VIS spectra of haemoproteins such as myoglobin, where the five-co-ordinate forms show a marked asymmetry of the Soret band (ascribed to the out-of-plane position of the Fe atom) and a far greater temperature sensitivity in the five- compared to the six-co-ordinate forms (ascribed to the stabilising effect of the sixth ligand on motions around the Fe atom).[39]

Conclusion

Our present results provide the first test of solvent effects on the l.f.e.r. (1) for any set of ligand-binding equilibria, which includes both protic and aprotic solvents and also spans a wider range of solvent polarity than studied previously. They reveal an unexpectedly simple pattern in which the values of a and b in equation (1) both appear to fall with decrease in solvent polarity and show no obvious effects of hydrogen-bonding and which can be explained in terms of changes in dipolar solvation.

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