The Ligand-substitution Reactions of Aquahydroxocobinamide proceed through a Dissociative Interchange Mechanism†

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The dependence of the second-order rate constants for replacement of H_2O in aquahydroxocobinamide by azide at 25.0 °C, ionic strength $I = 1.0$ mol dm^{-3} (KCl) in the range pH 9–12 showed that dihydroxocobinamide is inert to substitution. The kinetics of substitution of bound H_2O in aquahydroxocobinamide by L = cyanide, azide, pyridine, *N*-methylimidazole or 3-aminopropan-1-ol was investigated as a function of ligand concentration and temperature by stopped-flow spectrophotometry at pH 12.0 and a constant I of 2.0 mol dm^{-3} (except for 3-aminopropan-1-ol where $I = 1.0$ mol dm^{-3} because of the limited solubility of the ligand). The observed pseudo-first-order rate constants (corrected, where appropriate, for protonation of the N-donor atom of L, and the presence of inert dihydroxocobinamide) showed the onset of saturation with ligand concentration for all ligands, with the exception of 3-aminopropan-1-ol. The saturation effect proves that the reaction proceeds through a dissociative activation pathway. Furthermore, the observation that the saturation rate constant, k_{sat} (and its activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$), depends on the identity of L indicates that incoming L participates in the transition state. This allows the mechanism of the reaction to be identified as a dissociative interchange.

The mechanism of the ligand-substitution reactions of the cobalt corrinoids continues to attract considerable attention;[1-5] our interest[5-11] has focused primarily on the mechanism of substitution of bound H_2O in vitamin B_{12a}.‡ It was demonstrated recently[3] that at high (*i.e.* > 0.5 mol dm^{-3}) concentration of L = pyridine as incoming ligand the observed rate constants saturate to a limiting value, k_{sat}. It was subsequently shown that for L = pyridine, 4-methylpyridine, histamine (imidazole-4-ethanamine), imidazole or methyl glycinate the values of k_{sat} are all different,[5] and it was concluded that, contrary to the generally held view,[12-17] the reactions do not proceed through a limiting dissociative (D) mechanism (for which k_{sat} would correspond to the rate constant for the unimolecular release of water from Co^{III} and hence be independent of L) but through a dissociative interchange (I_d) mechanism which accommodates nucleophilic participation by L in the transition state.

The position along the reaction coordinate of, and hence the extent of ingression by, L into the transition state may be influenced by the nature of the *trans* ligand, Z. The *trans* effect is a well established phenomenon in the chemistry of cobalt corrinoids. For example, as the donor power of Z increases: (*i*) a five-co-ordinate ground state in which dmbzim is displaced from the co-ordination sphere becomes progressively more favoured;[18] (*ii*) in a series of CN^-–Co–Z complexes, the stretching frequency of co-ordinated CN^- decreases;[19] and (*iii*) the stability constants for L–Co–Z, where L = cyanide, azide, pyridine, *N*-methylimidazole or 3-aminopropan-1-ol, decrease.[20]

Aquahydroxocobinamide provides an opportunity for studying the kinetic *trans* effect of OH^-. Apparently the only comprehensive study on the kinetics of substitution of H_2O *trans* to OH^- in this compound has been reported by Pratt and co-workers.[21] Using CN^-, I^- or $[Co(CN)_6]^{3-}$ as entering ligand they found that the reactions were complex, showing bi- and even tri-phasic kinetics. They attributed this to the presence of slowly interconverting conformational isomers of diaqua- and aquahydroxo-cobinamide in solution and suggested that these isomers arose from different orientations of the axial ligands relative to, and hydrogen bonding with, the amide side-chains of the corrin ring. This is unprecedented in B_{12} chemistry and clearly merits further study. They were also able to demonstrate, by studying the effect of pH on the reactions, that dihydroxocobinamide is inert to substitution by all incoming ligands, including cyanide. Unfortunately, only a very modest range of ligand concentration was used (0.1–40 mmol dm^{-3}). In this range, pseudo-first-order rate constants will almost certainly vary linearly with [L] and saturation effects, which are important for the elucidation of the mechanism in these systems, will be missed. We have therefore reinvestigated the kinetics of substitution of H_2O in aquahydroxocobinamide [equation (1)]

$$HO\text{–}Co\text{–}OH_2 + L \xrightarrow{k} HO\text{–}Co\text{–}L + H_2O \quad (1)$$

using five ligands, CN^-, N_3^-, pyridine, *N*-methylimidazole and 3-aminopropan-1-ol, *i.e.* two anionic ligands which have, respectively, very high and very modest affinities for this compound (the formation constants[20] are $\log K_1K_2 = 19.0 \pm 0.1$; $\log K = 3.45 \pm 0.04$), and three N-donors, pyridine ($\log K = 4.19 \pm 0.01$), *N*-methylimidazole ($\log K = 6.06 \pm 0.04$), and a primary amine, 3-aminopropan-1-ol ($\log K = 4.66 \pm 0.04$), and report here on the results.

† *Supplementary data available* (No. SUP 56969, 36 pp.): primary kinetic data, see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

‡ In B_{12a} (aquacobalamin) Co^{III} is co-ordinated in the equatorial plane by the corrin ring, and in the axial positions by 5,6-dimethylbenzimidazole (dmbzim) and H_2O. For convenience B_{12a} is abbreviated dmbzim–Co–H_2O with only the axial ligands shown and the overall charge neglected. The cobinamides lack the dmbzim-containing nucleotide side chain.

Experimental

Diaquacobinamide was prepared from aquacyanocobinamide as previously reported.[20] Sodium cyanide, sodium azide, *N*-methylimidazole and pyridine were obtained from Merck; 3-aminopropan-1-ol was obtained from Aldrich. All other solvents and reagents were of the highest purity available and used as received. The instrumentation used has been described.[5]

The kinetics of the reactions was studied under pseudo-first-order conditions. The concentration of cobinamide was *ca.* 10 μmol dm^{-3}, buffered with phosphate (0.1 mol dm^{-3}), and the total ionic strength was adjusted to 2.0 mol dm^{-3} (KCl) for pyridine, *N*-methylimidazole, CN^- and N_3^-, and 1.0 mol dm^{-3} (KCl) for 3-aminopropan-1-ol (which is appreciably less miscible with water at high ionic strengths). Ligand solutions were also buffered with phosphate (0.1 mol dm^{-3}) and the pH and ionic strength adjusted to the same values as for the cobinamide solution by addition of HCl or NaOH, as appropriate, and KCl, respectively. The reactions were monitored for at least four half-lives at 340 (CN^-), 364 (3-aminopropan-1-ol), 365 (*N*-methylimidazole), 367 (pyridine) and 370 nm (N_3^-) by mixing equal volumes (100 cm^3) of the two solutions using the stopped-flow spectrometer. The experimentally determined pseudo-first-order rate constants, k^I_{obs}, were found by fitting the absorbance *vs.* time trace to an equation of the form $A_1\exp(-k^I_{obs}t) + A_2$ using a non-linear least-squares technique employing a Newton–Raphson procedure. Apparent second-order rate constants, k^{II}_{obs}, were determined from the slopes of plots of k^I_{obs} against ligand concentration using standard linear least-squares methods. The activation parameters $\Delta H^‡$ and $\Delta S^‡$ were determined from the slopes and intercepts, respectively, of plots of $\ln(kh/k_BT)$ against T^{-1} where h and k_B are the Planck and Boltzman constants, respectively, and k is the appropriate rate constant (k^{II}_{obs} or k_{sat}, see below). The temperature of the system was maintained (±0.1 °C) with an external circulating water-bath. Primary kinetic data are available as supplementary material (SUP 56969).

Results and Discussion

Dihydroxocobinamide, but not aquahydroxocobinamide, is reported to be inert to substitution by I^-, CN^-, and $[Co(CN)_6]^{3-}$.[21] As part of a study (unpublished) into the chemistry of co-ordinated hydroxide in macrocycle complexes of Fe^{III} and Co^{III}, we have verified this conclusion by investigating the influence of pH on the apparent second-order rate constant, k^{II}_{obs}, for the reaction of azide with aquahydroxocobinamide in the range pH 9–12 (25 °C, I = 1.0 mol dm^{-3}, KCl). At each pH, k^I_{obs} was determined for five solutions of different concentrations of azide (ranging from 0.5 to 10 mmol dm^{-3} after mixing with the cobinamide solution). Plots of k^I_{obs} against azide concentration gave good straight lines (not shown) with intercepts never significantly different from zero. Values of k^{II}_{obs} are plotted against pH in Fig. 1. The pK_a of azide at 25 °C, I = 1 mol dm^{-3}, is 4.38;[10] between pH 9 and 12, therefore, essentially all azide is present as the anion. Assuming that hydroxide in both aquahydroxo- and dihydroxocobinamide is inert to substitution, the apparent second-order rate constants, k^{II}_{obs}, should depend on pH and be related by equation (2) (where pK_{Co2} is the acid dissociation constant

$$k^{II}_{obs} = \frac{[H^+]k^{II}}{[H^+] + K_{Co2}} \quad (2)$$

of co-ordinated H_2O in aquahydroxocobinamide) to the pH-independent apparent second-order rate constant, k^{II}, which is defined by equation (3). A non-linear least-squares fit of

$$HO\text{–}Co\text{–}OH_2 + N_3^- \xrightarrow{k^{II}} HO\text{–}Co\text{–}N_3 + H_2O \quad (3)$$

the data by equation (2) as the objective function with pK_{Co2}

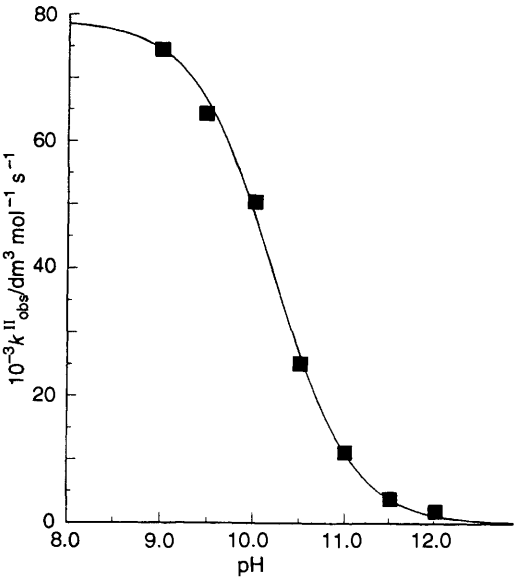

Fig. 1 Dependence of k^{II}_{obs} on pH for the anation of aquahydroxocobinamide by azide at 25.0 °C (I = 1.0 mol dm^{-3}). The solid line is a fit of equation (2) to the data (see text)

and k^{II} as parameters gave pK_{Co2} = 10.21 ± 0.3 (in good agreement with the value of 10.30 ± 0.24 determined spectrophotometrically[20]) and k^{II} = 7.9 ± 0.1 × 10^4 dm^3 mol^{-1} s^{-1}. The acceptable fit of the line to the experimental data confirms the previous observation[21] that OH^- in aquahydroxo- and dihydroxo-cobinamide is inert to substitution. Much of the work reported here was done at an ionic strength of 2.0 mol dm^{-3} (because high ligand concentrations were needed to observe saturation and two of the ligands are charged). A determination of the second-order rate constants for the reaction of azide with aquahydroxocobinamide at pH 9 and 12 but with I = 2.0 mol dm^{-3} showed that ionic strength had little effect on the kinetics and the dependence of rate on pH shown in Fig. 1 persists at the higher ionic strength.

Aquahydroxocobinamide presumably exists in solution as a mixture of two diastereoisomers depending on whether the hydroxide ligand is co-ordinated on the α or β face of the corrin. In contrast to a previous study[21] we found no evidence of bi- or tri-phasic kinetics in the reactions with azide (pH 9–12) or other ligands (pH 12), and the reactions proceeded with well defined isosbestic points.[20] We have therefore found no evidence for the existence of kinetically distinguishable mixed species in solution. Furthermore, our failure to observe even biphasic kinetics suggests that either both α- and β-OH^- diastereomers react at similar rates, or only one reacts, but interconverts rapidly with the second.

Since the rate of substitution of H_2O on aquahydroxocobinamide is fast and we were primarily interested in looking for evidence of saturation effects, the reactions were studied at pH 12 where the fraction of kinetically labile aquahydroxocobinamide is small. As we have discussed previously,[5] at sufficiently high ligand concentrations, k^I_{obs} will saturate to reach a limiting value, k_{sat}, for any dissociative mechanism of ligand substitution. If a limiting D mechanism is operative [equations (4) and (5)] then the microscopic rate constants k_1,

$$HO\text{–}Co\text{–}OH_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HO\text{–}Co + H_2O \quad (4)$$

$$HO\text{–}Co + L \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HO\text{–}Co\text{–}L \quad (5)$$

$$k^I_{obs} = \frac{(k_1k_2/k_{-1})[L] + k_{-2}}{1 + k_2[L]} \quad (6)$$

k_{-1} and k_2 are related to k^1_{obs} by equation (6) (where $k_{-2} = 0$ if the rate of the reverse reaction is insignificant), and $k_1 = k_{sat}$. In the case of an I_d mechanism [equations (7) and (8)], equation (9) applies and $k_4 = k_{sat}$.

$$HO\text{–}Co\text{–}OH_2 + L \overset{K}{\rightleftharpoons} \{H_2O \cdots HO\text{–}Co \cdots L\} \quad (7)$$

$$\{H_2O \cdots HO\text{–}Co \cdots L\} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} HO\text{–}Co\text{–}L + H_2O \quad (8)$$

$$k^1_{obs} = \frac{(k_4 + k_{-4})K[L] + k_{-4}}{1 + K[L]} \quad (9)$$

Although we attempted to study the reactions over a wide range of ligand concentrations (1 mmol dm^{-3} to 1.0 mol dm^{-3}) collection of data at high concentrations of *N*-methylimidazole and pyridine proved impossible. At above about 0.5 mol dm^{-3} the signal changes arising from the mixing of solutions of different refractive indices interfered with the observation of the signal changes due to the reaction and the results became unreliable. We were therefore limited to concentrations of $\leqslant$0.45 mol dm^{-3} *N*-methylimidazole and $\leqslant$0.55 mol dm^{-3} pyridine.

The experimentally determined rate constants were converted into pH-independent rate constants by applying equation (2); further, in the case of 3-aminopropan-1-ol (acid dissociation constant at 25 °C, $pK_L = 10.44$; $\Delta H = 58.1$ kJ mol^{-1} and $\Delta S = -5$ J K^{-1} mol^{-1}),[9] k^{II}_{obs} was multiplied by a factor $(1 + [H^+]/K_L)$ to account for the fraction of protonated (and hence unreactive) amine in solution.

When determining the equilibrium constants for the reaction of pyridine, *N*-methylimidazole, azide, and 3-aminopropan-1-ol with aquahydroxocobinamide, we found that only one ligand is co-ordinated;[20] in the case of cyanide, however, two ligands bind to dicyanocobinamide, and only the overall equilibrium constant, β_2, could be determined. It is therefore obvious that the process of which the kinetics we measured for all ligands, L, other than CN^-, is the replacement of H_2O in aquahydroxocobinamide by L. This may not be the case for L = CN^-, however. We only observed monophasic kinetics, so either replacement of H_2O in aquahydroxocobinamide is rate-limiting, or faster than the dead-time of the instrument used (*ca.* 2 ms). Reenstra and Jencks[22] have determined that the rate constants for reaction of CN^- with the two isomers (α-cyano-β-aqua and β-cyano-α-aqua, respectively) of aquacyanocobinamide are 2.9×10^6 and 2.1×10^6 dm^{-3} mol^{-1} s^{-1}; at pH 12.0, therefore, the apparent second-order rate constants would be 2.4×10^5 and 1.7×10^5 dm^{-3} mol^{-1} s^{-1}, respectively, since the pK_a of aquacyanocobinamide is 10.95[23] and cyanohydroxocobinamide is inert.[22] At pH 12 we observed an apparent second-order rate constant of 2.3×10^3 dm^{-3} mol^{-1} s^{-1} for the reaction with aquahydroxocobinamide. Clearly, the reaction to produce the intermediate aquacyanocobinamide is rate-limiting. This is not unexpected since CN^- has a greater thermodynamic *trans* effect than OH^-,[20] and there is a direct correlation between the thermodynamic and kinetic *trans* effects.[19]

For cyanide, *N*-methylimidazole, pyridine and azide, plots of k^1_{obs} against ligand concentration showed curvature (Fig. 2) with zero intercepts (except for N_3^-). The experimental data were fitted by equation (9) and the results are listed in Table 1. Even up to concentrations of 1 mol dm^{-3} (close to the solubility limit of the ligand), no saturation effects were seen with 3-aminopropan-1-ol. For this ligand, therefore, the second-order rate constant, k^{II}_{obs}, was obtained from the slope of a plot of k^1_{obs} against ligand concentration (Fig. 2 and Table 1). The activation parameters $\Delta H^‡$ and $\Delta S^‡$ for k_{sat} and k^{II}_{obs} are also listed in Table 1.

The occurrence of saturation does not depend on pH. Saturation was found at pH 11.51, 11.92 and 12.51 (25 °C) with

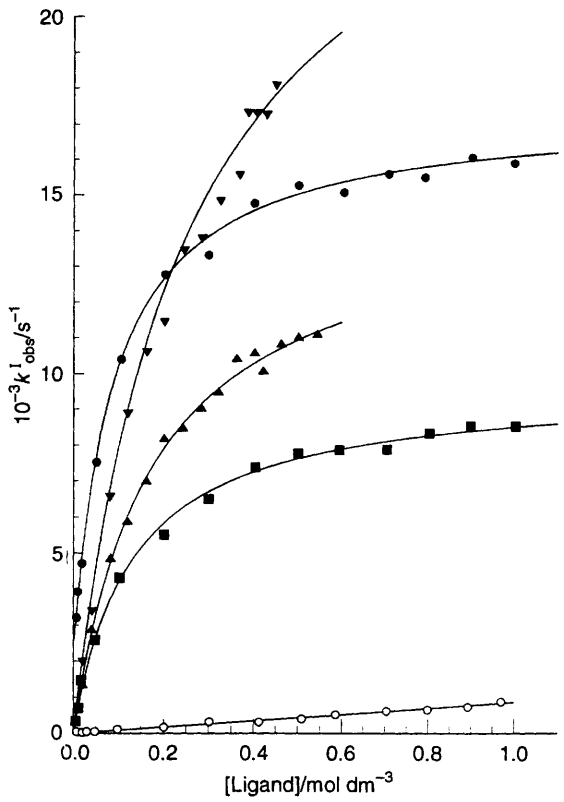

Fig. 2 Dependence of the pseudo-first-order rate constant, k^1_{obs}, on the concentration of the incoming ligand, L, for substitution of H_2O in aquahydroxocobinamide (25 °C) for L = azide (●), *N*-methylimidazole (▼), pyridine (▲) cyanide (■) or 3-aminopropan-1-ol (○). The solid lines are fits to the data using equation (9) of the text except for 3-aminopropan-1-ol where a straight line was fitted to the data

CN^- as entering ligand. The studies could not be extended to lower pH values because the reaction became too fast for the instrument available. On correcting for the effect of pH [equation (2)], virtually identical values of k_{sat} were obtained [$(9.8 \pm 0.5) \times 10^3$, $(9.6 \pm 0.6) \times 10^3$, and $(9.8 \pm 0.2) \times 10^3$ s^{-1}, respectively].

Fig. 2 shows that the saturating rate constant, k_{sat}, depends on the incoming ligand and therefore corresponds to k_4 [or $k_4 + k_{-4}$ if (as for N_3^-) the reverse reaction is significant] in an I_d process. Furthermore, the values of the activation parameters for k_{sat} also argue against D mechanism; if k_{sat} corresponded to k_1 [equation (4)], then $\Delta H^‡$ and $\Delta S^‡$ should be independent of the identity of the incoming ligand. That k_{sat} values are not more dissimilar stems from a compensation effect between the two activation parameters (Fig. 3).

The saturation rate constant for 3-aminopropan-1-ol is unknown; even up to concentrations of 1 mol dm^{-3} the rate increased linearly with ligand concentration.

Hydroxide has a greater *trans* effect than dmbzim; this does not preclude participation of L in the transition state, although there has been a considerable increase in the value of k_4. For example, for substitution of H_2O in B_{12a} by pyridine, imidazole and histamine, k_4 was found to be 7.1, 43 and 0.49 s^{-1}, respectively, at 25 °C;[20] *trans* to hydroxide, k_4 for pyridine and *N*-methylimidazole are 1.5×10^4 and 2.8×10^4 s^{-1}, respectively, *i.e.* a *ca.* 10^3 rate enhancement. Values of *K*, the pre-equilibrium constant are not dissimilar (at 25 °C, 2.4 and 5.8 dm^3 mol^{-1} for pyridine with B_{12a} and aquahydroxocobinamide, respectively; 0.7 and 4 dm^3 mol^{-1} for imidazole with B_{12a} and *N*-methylimidazole with aquahydroxocobinamide, respectively). The rate enhancement is due to a substantial increase in the exchange rate constant, k_4. Presumably the greater *trans* effect of OH^- compared to dmbzim allows the incoming ligand to compete more effectively for the metal ion.

Table 1 Rate constants and activation parameters for ligand-substitution reactions of aquahydroxocobinamide[a]

Ligand	T/°C	$10^{-3}k_4$/s^{-1}	$10^{-3}k_{-4}$/s^{-1}	K/dm^3 mol	$\Delta H^{\ddagger}$ (k_4)/ kJ mol^{-1}	$\Delta S^{\ddagger}$ (k_4)/ J K^{-1} mol^{-1}	$10^{-3}k^{II}_{obs}$/dm^3 mol^{-1} s^{-1}
Cyanide	5.2	1.93 ± 0.07		4.93 ± 0.08			
	10	2.92 ± 0.07		5.6 ± 0.2			
	15	4.2 ± 0.2		6.1 ± 0.4			
	20	6.3 ± 0.2		6.6 ± 0.8			
	22	7.5 ± 0.4		6.9 ± 0.8			
	25	9.6 ± 0.6		7.8 ± 0.8	53.0 ± 0.9	9 ± 3	
3-Aminopropan-1-ol	5						0.20 ± 0.01
	12						0.34 ± 0.01
	18						0.55 ± 0.01
	25						1.15 ± 0.03[b]
Azide	5	3.8 ± 0.2	0.21 ± 0.02	3.0 ± 0.3			
	10	5.8 ± 0.2	0.30 ± 0.03	4.9 ± 0.7			
	15	7.5 ± 0.3	1.0 ± 0.1	6 ± 1			
	20	11.2 ± 0.3	1.8 ± 0.2	7 ± 1			
	25	14.9 ± 0.7	2.4 ± 0.5	11 ± 3	45 ± 2	−14 ± 6	
Pyridine	5.5	1.43 ± 0.08		1.9 ± 0.1			
	10	2.8 ± 0.4		3.1 ± 0.7			
	15.1	5.0 ± 0.3		4.5 ± 0.6			
	20	9.8 ± 0.8		5 ± 1			
	25	15 ± 1		6 ± 1	81 ± 4	106 ± 13	
N-Methylimidazole	5.2	2.9 ± 0.4		1.7 ± 0.3			
	10.1	4.0 ± 0.8		2.1 ± 0.6			
	15.0	9 ± 2		3 ± 1			
	20.0	15 ± 4		3 ± 1			
	25.0	28 ± 5		4 ± 1	79 ± 5	106 ± 18	

[a] Errors are standard errors of estimate. [b] $\Delta H^{\ddagger}(k^{II}_{obs})$ = 57 ± 5 kJ mol^{-1}, $\Delta S^{\ddagger}(k^{II}_{obs})$ = 6 ± 14 J K^{-1} mol^{-1}.

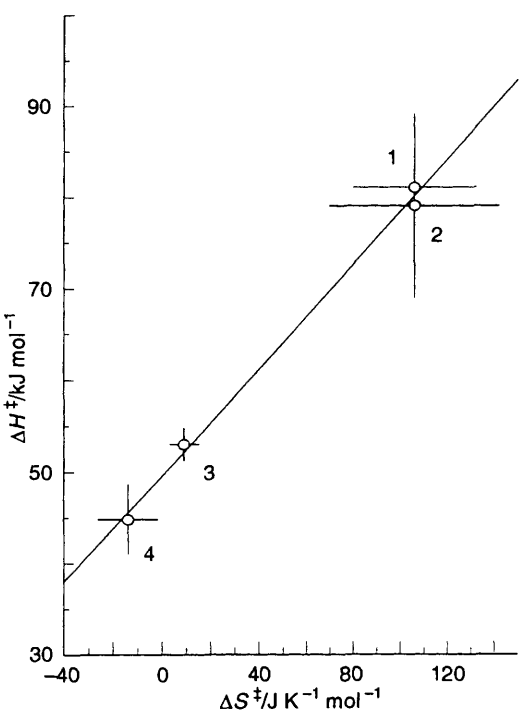

Fig. 3 Correlation between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the substitution of H_2O in aquahydroxocobinamide, 25 °C, pH 12. L = Pyridine (1), *N*-methylimidazole (2), cyanide (3) or azide (4). The error bars are 95% confidence limits

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