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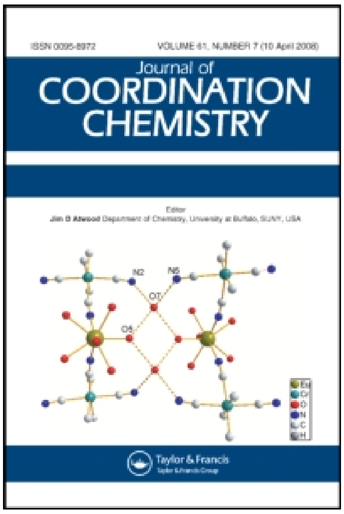

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Equilibrium and Kinetic Studies on Ligand Substitution Reactions of *Trans*-[$\mathrm{CO^{III}(en)_2(Me)H_2O]^{2+}$: A Model for Coenzyme B_{12}

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EQUILIBRIUM AND KINETIC STUDIES ON LIGAND SUBSTITUTION REACTIONS OF *TRANS*-$[CO^{III}(en)_2(Me)H_2O]^{2+}$: A MODEL FOR COENZYME B_{12}

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Ligand substitution of *trans*-$[Co^{III}(en)_2(Me)H_2O]^{2+}$ was studied for pyrazole, 1,2,4-triazole and *N*-acetylimidazole as entering nucleophiles. These displace the coordinated H_2O molecule *trans* to the methyl group to form *trans*-[Co(en)$_2$(Me)azole]. Stability constants at 18°C for the substitution of H_2O by pyrazole, 1,2,4-triazole and *N*-acetylimidazole are 0.7 ± 0.1, 13.8 ± 1.4 and $1.7 \pm 0.2\,M^{-1}$, respectively. Second order rate constants at the same temperature for the reaction of *trans*-$[Co^{III}(en)_2(Me)H_2O]^{2+}$ with pyrazole, 1,2,4-triazole and *N*-acetylimidazole are 161 ± 12, 212 ± 11 and $12.9 \pm 1.6\,M^{-1}\,s^{-1}$, respectively. Activation parameters ($\Delta H^{\neq}$, $\Delta S^{\neq}$) are $67 \pm 6\,kJ\,mol^{-1}$, $+27 \pm 19\,J\,K^{-1}\,mol^{-1}$; $59 \pm 2\,kJ\,mol^{-1}$, $+1 \pm 6\,J\,K^{-1}\,mol^{-1}$ and $72 \pm 4\,kJ\,mol^{-1}$, $+23 \pm 14\,J\,K^{-1}\,mol^{-1}$ for reactions with pyrazole, 1,2,4-triazole and *N*-acetylimidazole, respectively. Substitution of coordinated H_2O by azoles follows an I_d mechanism.

Keywords: Kinetics; Equilibrium; B_{12} model complexes; Azoles; I_d mechanism

INTRODUCTION

Equilibrium and kinetic studies of ligand substitution *trans* to the alkyl group in coenzyme B_{12} and various model complexes are of significant interest since it is known that methylcobalamin and coenzyme B_{12} undergo substitution of axial benzimidazole by a protein histidine residue during complexation to the enzymes methionine synthase, methyl malonyl coenzyme A mutase, and glutamate mutase, respectively [1–3].

Cobalt complexes containing a Co–C -bond can be used as models for coenzyme B_{12} to mimic reactivity and mechanistic behaviour of coenzyme B_{12}. Several complexes were used for this purpose, such as cobalt(III) complexes of dimethlglyoxime, salen and Costa's complex [4–12]. Kofod [13] showed that the Co(III) metal centre surrounded by five ammonia ligands and one methyl group can be used as a simple model for the B_{12} coenzyme. Also, it was mentioned that *cis*-$[Co(NH_3)_4(NH_2)\text{-}(CH_3)]^+$ was used as a model system for coenzyme B_{12} with respect to molecular orbital calculations investigating the overlap population of the Co–C bond by applying a variety of electronic perturbations [14]. Van Eldik *et al.* [15] have studied the kinetics of the reaction of $[Co(NH_3)_5(CH_3)]^{2+}$ with ethylenediamine in details and identified the rapid stepwise

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formation of *cis*-$[Co(en)_2(NH_3)(CH_3)]^{2+}$ and subsequent slower isomerization to the stable *trans*-$[Co(en)_2(NH_3)(CH_3)]^{2+}$ complex. All rate and activation parameters were resolved and strongly support the operation of a limiting dissociative (D) mechanism for all reaction steps [15].

Ligand substitution of *trans*-$[Co^{III}(en)_2(Me)H_2O]^{2+}$ have been studied for cyanide, imidazole and NH_3 as entering nucleophiles [16,17]. These were found to displace the coordinated water molecule *trans* to the methyl group to form *trans*-$[Co(en)_2(Me)L]$. Stability constants for cyanide, imidazole and NH_3 at 25°C were found to be $(8.3 \pm 0.7) \times 10^4$, 24.5 ± 2.2 and $17.4 \pm 1.1\,M^{-1}$, respectively. Second order rate constants for the substitution were found to be 3.3×10^3, 198 and $125\,M^{-1}\,s^{-1}$ at 25°C for cyanide, imidazole and $NH_{3,}$ respectively. From temperature- and pressure-dependence studies, activation parameters ($\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta V^{\neq}$) for the reaction of *trans*-$[Co^{III}(en)_2(Me)H_2O]^{2+}$ with cyanide were found to be $49\,kJ\,mol^{-1}$, $-38\,J\,K^{-1}\,mol^{-1}$ and $+7.0\,cm^3\,mol^{-1}$, respectively, compared to $53\,kJ\,mol^{-1}$, $-22\,J\,K^{-1}\,mol^{-1}$ and $+4.7\,cm^3\,mol^{-1}$, respectively, for the reaction with imidazole. However, those for the reaction *trans*-$[Co^{III}(en)_2(Me)H_2O]^{2+}$ with NH_3 were found to be $62\,kJ\,mol^{-1}$, $+3\,J\,K^{-1}\,mol^{-1}$ and $+5.7\,cm^3\,mol^{-1}$, respectively. Based on these activation volumes, the reactions follow an I_d mechanism in which the entering nucleophile is weakly bound in the transition state [16,17].

It is of interest to study azoles as entering nucleophiles since their action could link studies of metal binding properties of nitrogenous bases with information on proton affinities in the gas phase [18,19], in aqueous solution and aprotic solvents [20,21], and of their H-bonding capacities [22]. It is also of interest from a bioinorganic chemistry point of view, because the imidazole group of histidine occurs as a ligand in most of the known haemoproteins [23].

Recently, it has been shown that azoles react with vitamin B_{12a} and the second order rate constants for the reaction of aquacobalamin with pyrazole, 1,2,4-triazole and *N*-acetylimidazole at 25°C were found to be 35.0, 24.0 and $6.6\,M^{-1}\,s^{-1}$, respectively [24]. The suppression in the rate constant in the case of *N*-acetylimidazole compared to pyrazole and triazole was ascribed to the possibility of hydrogen bond formation between the entering ligands and the acetamide side chain of the corrin ring. Based on the reported kinetic and activation parameters, the substitution of coordinated H_2O in vitamin B_{12a} by these 5-membered heterocyclic azoles follows an I_d mechanism [24].

This study reports equilibrium and kinetic data for the reaction of *trans*-$[Co^{III}(en)_2(Me)H_2O]^{2+}$, as a simple model for coenzyme $B_{12,}$ with pyrazole, 1,2,4-triazole and *N*-acetylimidazole *N*-Ac-ImH.

EXPERIMENTAL

Materials

All chemicals were of analytical grade and used as received. Ultra pure water was used for all measurements. Special care was taken during the preparation and measurements because *trans*-$[Co^{III}(en)_2(Me)H_2O]^{2+}$ was found to be light sensitive akin to other alkylcobalamins and alkyl cobalt complexes [25–27].

Trans-$[Co^{III}(en)_2(Me)NH_3]S_2O_6$ was prepared as described previously by Kofod [28] by reacting Co(II) nitrate with methylhydrazine in the presence of NH_3 to give $[Co(NH_3)_5Me](NO_3)_2$. This was treated with ethylenediamine to give *cis*-$[Co(en)_2(Me)NH_3]^{2+}$, followed by slow isomerization to give *trans*-$[Co(en)_2(Me)NH_3]^{2+}$, which can be isolated in the solid form. This complex gives *trans*-$[Co(en)_2(Me)H_2O]^{2+}$ upon dissolving in buffers [16]. Characterization of the complexes by elemental analysis, electronic and NMR spectroscopy was in agreement with literature data [28].

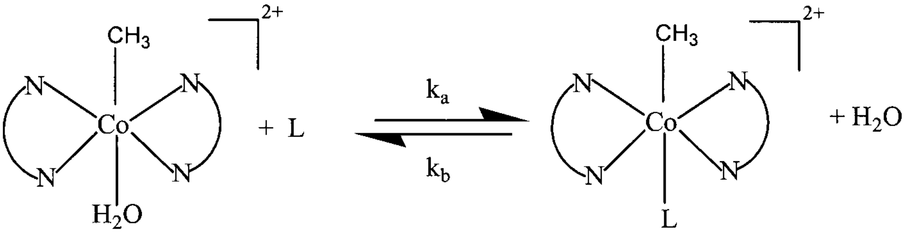
Instrumentation

The pH of the solution was measured using a Mettler Delta 350 pH meter. The meter was calibrated with standard buffer solutions at pH 4.0 and 7.0 Electronic spectra were recorded on Shimadzu UV-2101 and Hewlett-Packard 8452A spectrophotometers.

Kinetic measurements were carried out on an Applied Photophysics SX 18MV stopped-flow instrument coupled to an online data acquisition system. At least eight kinetic runs were recorded under all conditions, and the reported rate constants represent mean values. All kinetic measurements were carried out under *pseudo*-first order conditions, i.e., the ligand concentration was in at least a ten-fold excess. All instruments used were thermostatted to the desired temperature (± 0.1°C).

RESULTS AND DISCUSSION

This study presents kinetic and equilibrium data for the substitution of the axial H_2O molecule in *trans*-$[Co(en)_2(Me)H_2O]^{2+}$ by azoles in comparison with previous work on the reactions of cyanide, imidazole and NH_3 [16,17]. The investigated reaction is shown in Eq. (1), where L = pyrazole, 1,2,4-triazole or *N*–Ac–ImH.



(1)

Electronic Spectra of *trans*-$[Co(en)_2(Me)H_2O]^{2+}$

The electronic spectrum of *trans*-$[Co(en)_2(Me)H_2O]^{2+}$ in bis–tris buffer at pH 6.0 shows characteristic bands at 364 and 472 nm. Increasing temperature shifts these bands slightly to longer wavelength accompanied with good isosbestic points at 330,385,430 and 486 nm. This suggests that this complex exists in an equilibrium between 5- and 6-coordinate species. Increasing temperature shifts this equilibrium towards the 5-coordinate species. This is expected, since the presence of CH_3 in the axial position exerts a strong *trans* influence and the coordination of the other axial ligand (H_2O) is very weak. A similar observation was made in the case of alkylcobaloximes and alkylcobinamide

[7,29,30]. In the case of cobinamide, increasing pressure of decreasing temperature shifts the equilibrium towards the 6-coordinate species. It has been shown in the case of methylcobinamide that the reaction volume for this equilibrium is $-12.4\,\mathrm{cm^3\,mol^{-1}}$. This indicates that a H_2O molecule is coordinated *trans* to the methyl group to form the 6-coordinate species [29].

Equilibrium Measurements

The electronic spectrum of *trans*-$[Co(en)_2(Me)NH_3]^{2+}$ in bis–tris buffer at pH 6.0 shows characteristic bands at 364 and 472 nm, suggesting that the main species in solution is *trans*-$[Co(en)_2(Me)H_2O]^{2+}$ [16,28]. Addition of triazole shifts the bands to 355 and 462 nm, accompanied by good isosbestic points at 364, 420 and 440 nm as shown in Fig. 1. This indicates that a simple equilibrium exists under these conditions and the aqua ligand *trans* to the methyl group is displaced by triazole to form $[Co(en)_2(Me)triazole]^{2+}$. Similar changes in electronic spectra were obtained in the cases of pyrazole and *N*-Ac-ImH. However, in these two cases, λ_{max} for the product was found to be at 358 and 468 nm, with a shoulder at 290 nm. It is clear that the shift in the case of triazole is slightly larger than in the case of pyrazole and *N*-Ac-ImH, since the equilibrium constants for the latter cases are smaller than for triazole. By way of comparison, λ_{max} for the first absorption band of the *trans*-$[Co(en)_2(Me)L]^{2+}$ where L is CN, NH_3, triazole pyrazole, *N*-Ac-ImH and H_2O is 332, 354, 355, 358 and 364 nm, respectively. Also the second absorption band shifted from 445 nm (CN) to 462 nm (triazole), 468 nm (pyrazole and *N*-Ac-ImH) and finally in the case of H_2O, was located at 473 nm. This shift is consistent with the spectrochemical series: $CN^- > NH_3 >$ triazole > pyrazole $\approx$ *N*-Ac-ImH > H_2O.

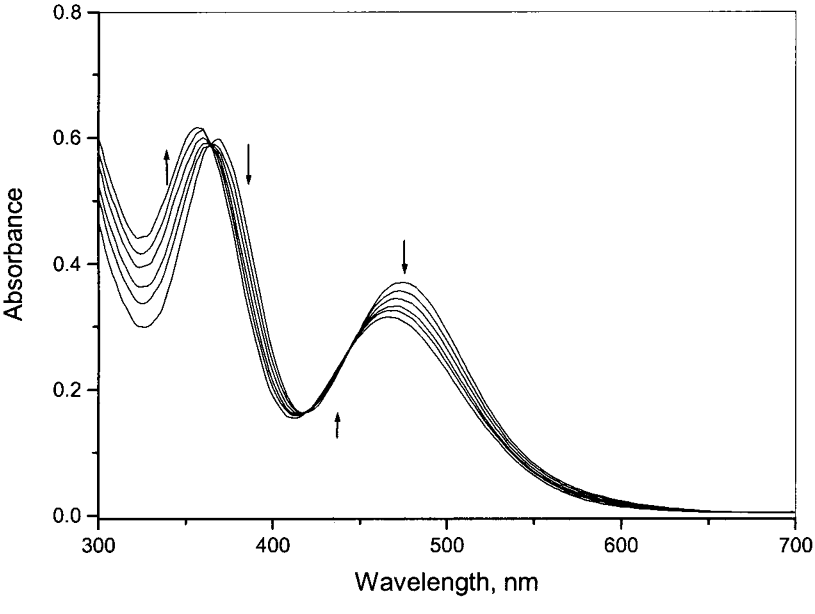


FIGURE 1 Electronic spectra of *trans*-$[Co(en)_2(Me)H_2O]^{2+}$ in the presence of various concentrations (0.015–0.3 M) of triazole at pH 6.0, 18.0°C and I = 0.1 M ($NaClO_4$).

Equilibrium (1) was established within the time required for mixing the solutions and recording the spectra. Spectrophotometric titration of triazole was monitored by following the increase in absorbance at 330 nm or the decrease at 384 nm, where the largest change in absorbance occurred. A solution of 3–5 × 10^{-3} M *trans*-$[Co(en)_2(Me)\text{-}NH_3]^{2+}$ dissolved in bis–tris buffer (pH 6.0) ($I = 0.1$ M using $NaClO_4$), was placed in a 1.0 cm path length cuvette in the thermostatted cell block of the spectrophotometer for *ca* 20 min. This solution was titrated by addition of small volumes of a concentrated stock solution of the azoles using a Hamilton syringe. Values of the equilibrium constant, K, and A_∞ were obtained by fitting the absorbance *versus* concentration curve to Eq. (2) after correction of dilution if necessary.

$$A_x = A_o + (A_\infty - A_o)K[L]/(1 + K[L]) \tag{2}$$

Typical data for the reaction with triazole are shown in Fig. 2. The solid line represents the fit of the experimental data to (2), where A_o and A_∞ represent the absorbance at 0 and 100% formation of *trans*-$[Co(en)_2(Me)triazole]^{2+}$, respectively, and A_x is the absorbance at any given ligand concentration, $[L]$. The data were subsequently analyzed by plotting $\log(A_x - A_o)/(A_\infty - A_x)$ *versus* $\log[L]$, which resulted in a good linear plot with slope of 1.02 ± 0.03 for triazole at 18°C, indicating that only one ligand (L) is coordinated to the cobalt complex. The intercept gives the value of $\log K$, in excellent agreement with the directly determined value described above. The value of K in the case of triazole was found to be $13.8 \pm 1.4\,M^{-1}$ at 18°C (this temperature throughout unless specifically noted).

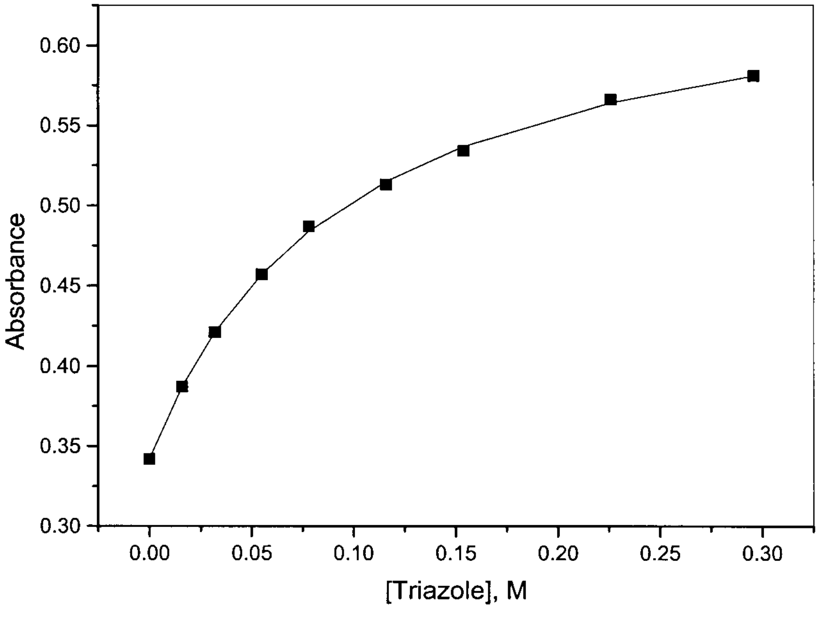


FIGURE 2 Changes in absorbance at 330 nm on addition of triazole to *trans*-$[Co(en)_2(Me)H_2O]^{2+}$; the solid line is a fit of data to Eq. (2).

Similar spectrophotometric titrations were carried out in the case of pyrazole and *N*-Ac-ImH. Values of K in the case of pyrazole and *N*-Ac-ImH were found to be 0.7 ± 0.1 and $1.7 \pm 0.2\,M^{-1}$, respectively. Plotting $\log(A_x - A_o)/(A_\infty - A_x)$ *versus* $\log[L]$ resulted in good linear plots with slopes of 1.08 ± 0.07 for pyrazole and 0.95 ± 0.07 for *N*-Ac-ImH. This indicates that only one entering ligand is coordinated to the cobalt atom.

The value of K for the reaction of *trans*-$[Co(en)_2(Me)H_2O]^{2+}$ with imidazole was found to be $24.5\,M^{-1}$ [16]. This values is higher than that obtained in the case of *N*-Ac-ImH ($1.7\,M^{-1}$) and pyrazole ($0.7\,M^{-1}$). This comparison demonstrates the effect of basicity since the $pK_{BH}{}^{+}$ values of pyrazole, *N*-Ac-ImH and imidazole are 2.48, 3.6 and 7.24, respectively [31]. These values may be used to establish a linear relationship between $\log K$ and $pK_{BH}{}^{+}$ to probe the effect of basicisity. Linear plots between $\log K$ for the coordination of nitrogenous bases (imidazole, pyridines and primary amines and their derivatives) *versus* $pK_{BH}{}^{+}$ were obtained for the coordination of these ligands to Co(III) corrinoids and Fe(III) porphyrins [32–34].

The value of K(triazole) was found to be $13.8 \pm 1.4\,M^{-1}$ and the value for binding of triazole to $[Co(corrin)(Me)H_2O]^{2+}$ was reported to be $2.75\,M^{-1}$ [35], from which it follows that the affinity of triazole for *trans*-$[Co(en)_2(Me)H_2O]^{2+}$ is almost 5 times higher than for $[Co(corrin)(Me)H_2O]^{2+}$. This comparison demonstrates the *cis* effect, i.e., the influence of the equatorial ligand on the substitution reaction of the axial ligand *trans* to the alkyl group. The observed trend in formation constants for the equatorial ligands is corrin $< (en)_2$.

Kinetic Measurements

Reaction of trans-$[Co(en)_2(Me)H_2O]^{2+}$ with Triazole

The reaction between $3 \times 10^{-3}\,M$ *trans*-$[Co(en)_2(Me)H_2O]^{2+}$ and excess triazole at pH 6.0 ([triazole] = 0.05–0.5 M, I = 0.1 M using $NaClO_4$) was studied at different temperatures. The results are shown in Fig. 3, from which good linear plots with significant intercepts were obtained. Furthermore, the plots do not indicate any saturation at high concentrations of triazole. This behaviour can be expressed by the rate law given in (3), where k_a and k_b represent the rate constants for the forward and reverse reactions in (1). Values of k_a and k_b as a function of temperature, along with corresponding activation parameters are summarized in Table I.

$$k_{obs} = k_a[\text{triazole}] + k_b \qquad (3)$$

Values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for the forward reaction (k_a) were found to be $59 \pm 2\,kJ\,mol^{-1}$ and $+1 \pm 6\,J\,K^{-1}\,mol^{-1}$, respectively, whereas those for the reverse reaction (k_b) were $90 \pm 4\,kJ\,mol^{-1}$ and $+87 \pm 13\,J\,K^{-1}\,mol^{-1}$, respectively, suggesting that the reaction is dissociative I_d in nature.

The value of k_a and k_b can be used to calculate K ($= k_a/k_b$), which turns out to be $15.8 \pm 1.6\,M^{-1}$ at 18°C. The kinetically determined value of K is in very good agreement with that obtained spectrophotometrically at the same temperature, $13.8 \pm 1.4\,M^{-1}$.

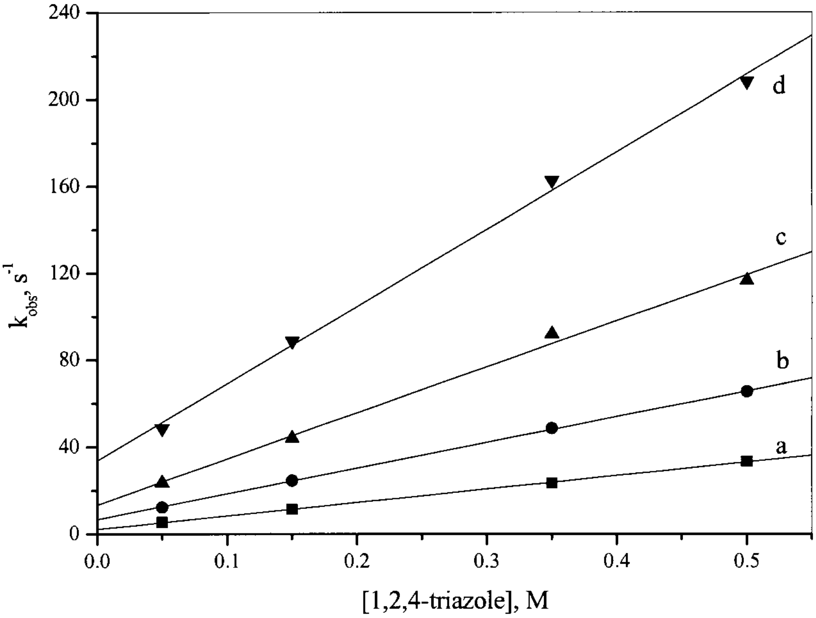


FIGURE 3 Plot of k_{obs} *versus* [triazole] for the reaction between *trans*-$[Co(en)_2(Me)H_2O]^{2+}$ and triazole as a function of temperature. Experimental conditions: [Co(III)] = 0.003 M, pH 6.0, I = 0.1 M ($NaClO_4$) and temperature = 5.0 (a); 12.0 (b); 18.0 (c) and 25.0°C (d).

TABLE I Kinetic data and activation parameters for the reaction of *trans*-$[Co(en)_2(Me)H_2O]^{2+}$ with pyrazole, triazole and *N*-acetylimidazole as a function of temperature

Temp. (°C)	*Pyrazole*		*1,2,4-Triazole*		*N-Ac-ImH*	
	k_a (M^{-1}s^{-1})	k_b (s^{-1})	k_a (M^{-1}s^{-1})	k_b (s^{-1})	k_a (M^{-1}s^{-1})	k_b (s^{-1})
5.0	40.2 ± 3.8	28.2 ± 1.8	62 ± 1	2.20 ± 0.30	2.76 ± 0.70	1.59 ± 0.21
12.0	83 ± 3	88 ± 1	118 ± 1	6.78 ± 0.42	7.03 ± 0.22	4.13 ± 0.07
15.0	102 ± 6	119 ± 3				
18.0	161 ± 12	159 ± 5	212 ± 11	13.4 ± 3.4	12.9 ± 1.6	8.67 ± 0.47
25.0			256 ± 13	33.6 ± 4.2	24.1 ± 0.7	20.4 ± 0.21
$\Delta H^{\neq}$, kJ mol^{-1}	67 ± 6	88 ± 8	59 ± 2	90 ± 4	72 ± 4	85 ± 1
$\Delta S^{\neq}$, JK^{-1}mol^{-1}	+27 ± 19	+102 ± 27	+1 ± 6	+87 ± 13	+23 ± 14	+66 ± 3

Experimental conditions: $[Co(en)_2(Me)H_2O]$ = 3–5 × 10^{-3} M; pH 6.0 (bis–tris buffer), I = 0.1 M $NaClO_4$.

Reaction of trans-$[Co(en)_2(Me)H_2O]^{2+}$ with Pyrazole

Figure 4 shows the effect of [pyrazole] on the reaction of *trans*-$[Co(en)_2(Me)H_2O]^{2+}$ with excess pyrazole at pH 6.0 ([pyrazole] = 0.15–0.7 M, I = 0.1 M using $NaClO_4$) at different temperatures. This figure shows that good linear plots with significant intercepts are obtained and no curvature was observed at high concentrations of pyrazole. This behaviour can be expressed by a rate law similar to that in (3). Values of k_a and k_b as a function of temperature, along with the corresponding activation parameters are summarized in Table I. The values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for the forward reaction (k_a) were found to be 67 ± 6 kJ mol^{-1} and +27 ± 19 J K^{-1}mol^{-1}, respectively, whereas those for the reverse reaction (k_b) were found to be 88 ±8 kJ mol^{-1} and

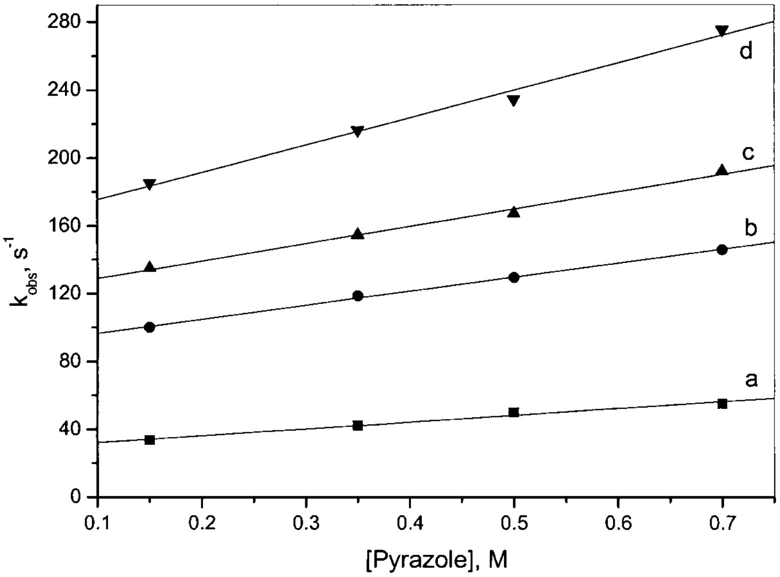


FIGURE 4 Plot of k_{obs} *versus* [pyrazole] for the reaction between *trans*-$[Co(en)_2(Me)H_2O]^{2+}$ and pyrazole as a function of temperature. Experimental conditions: [Co(III)] = 0.005 M, pH 6.0, I = 0.1 M ($NaClO_4$) and temperature = 5.0 (a); 12.0 (b); 15.0 (c) and 18.0°C (d).

$+102 \pm 27\,J\,K^{-1}\,mol^{-1}$, respectively. The derived value of K $(= k_a/k_b)$ is $0.9 \pm 0.1\,M^{-1}$ at 15°C, in good agreement with that obtained spectrophotometrically at the same temperature, $0.7 \pm 0.1\,M^{-1}$.

Reaction of *trans*-$[Co(en)_2(Me)H_2O]^{2+}$ with *N*-Ac-ImH

Similar linear plots to those obtained in the case of pyrazole and 1,2,4-triazole were obtained for the reaction of *trans*-$[Co(en)_2(Me)H_2O]^{2+}$ with excess *N*-Ac-ImH at pH 6.0 ([*N*-Ac-ImH] = 0.075–0.5 M, I = 0.1 M) at different temperatures. These plots are shown in Fig. 5 and show significant intercepts. The same is apparent in this case and rate law values of k_a and k_b as a function of temperature, along with the corresponding activation parameters are summarized in Table I. The values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for the forward reaction (k_a) were found to be $72 \pm 4\,kJ\,mol^{-1}$ and $+23 \pm 14\,J\,K^{-1}\,mol^{-1}$, respectively, whereas those for the reverse reaction (k_b) were found to be $85 \pm 1\,kJ\,mol^{-1}$ and $+66 \pm 3\,J\,K^{-1}\,mol^{-1}$, respectively. K $(= k_a/k_b)$ is $1.48 \pm 0.2\,M^{-1}$ at 18.0°C, in a good agreement with that obtained spectrophotometrically at the same temperature, $1.7 \pm 0.2\,M^{-1}$.

By way of comparison, the second order rate constants (Table I) for pyrazole, triazole and *N*-Ac-ImH at 18.0°C are 161 ± 12, 212 ± 11 and $12.9 \pm 1.6\,M^{-1}\,s^{-1}$, respectively. The significant decrease in k_a ($12.9\,M^{-1}\,s^{-1}$) in the case of *N*-Ac-ImH as compared to the other azoles is ascribed to the possibility of hydrogen-bond formation between *N*-Ac-ImH and ethylenediamine in the equatorial position. It has been suggested recently that *N*-Ac-ImH forms hydrogen bonds with the acetamide side chain of the corrin ring and the suppression in the rate constant in this case too was ascribed to hydrogen bond formation [24].

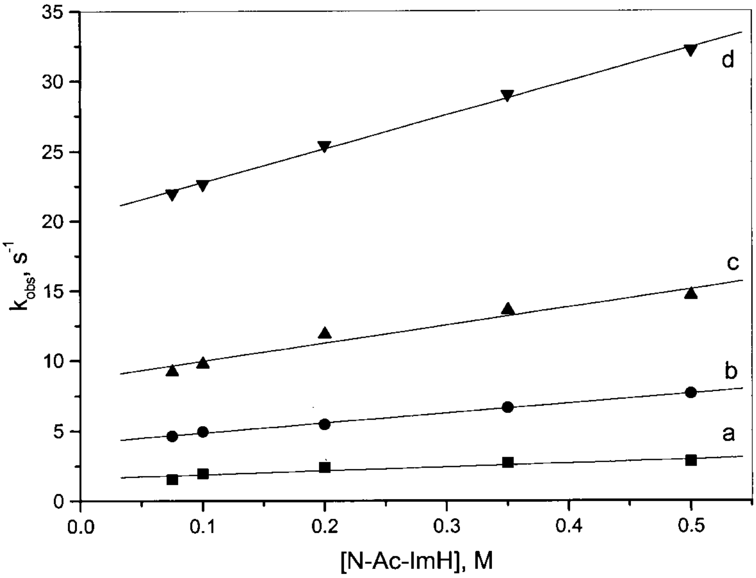


FIGURE 5 Plot of k_{obs} *versus* [*N*-Ac-ImH] for the reaction between *trans*-$[Co(en)_2(Me)H_2O]^{2+}$ and *N*-Ac-ImH as a function of temperature. Experimental conditions: [Co(III)] = 0.003 M, pH 6.0, I = 0.1 M ($NaClO_4$) and temperature = 5.0 (a); 12.0 (b); 18.0 (c) and 25.0°C (d).

The high lability of coordinated water in *trans*-$[Co(en)_2(Me)H_2O]^{2+}$ is seen in the relatively low activation enthalpy for substitution by azoles, as compared to the higher activation enthalpy for the aquation reaction of the azole complexes (i.e., the back reaction). The significantly positive values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for the reverse reaction suggest a dissociatively activated transition state. Values of the activation enthalpy for the reaction with triazole, pyrazole and *N*-Ac-ImH (59 ± 2, 67 ± 6, and $72 \pm 4\,kJ\,mol^{-1}$, respectively) are close to those obtained previously [16,17] for the reaction with CN^-, imidazole and NH_3 (50 ± 4, 53 ± 2 and $62 \pm 1\,kJ\,mol^{-1}$ respectively). Values of activation entropy for the formation of *trans*-$[Co(en)_2(Me)azole]^{2+}$ were found to be close to zero, compared to a significantly positive value for the back reaction. $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for the reaction of *trans*-$[Co(en)_2(Me)H_2O]^{2+}$ with pyrazole, triazole and *N*-Ac-ImH are in a good agreement with those obtained previously for CN^-, NH_3 and Imidazole, where the mechanism was assigned as I_d [16,17]. Thus it can be concluded that the mechanism for the reaction investigated here is an I_d mechanism, where the azoles partially participate in the transition state.

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References

[1] C.L. Drennan, S. Huang, J.T. Drummond, R.G. Matthews and M.L. Ludwig, *Science* **266**, 1669 (1994).
[2] C.L. Drennan, R.G. Matthews and M.L. Ludwig, *Curr. Opin. Struct. Biol.* **4**, 919 (1994).
[3] F. Mancia, N.H. Keep, A Nakagawa, P.F. Leadlay, S. McSweeney, B. Ramussen, P. Boscke, O. Diat and P.R. Evans, *Structure* **4**, 229 (1996).

[4] K.L. Brown and Satyanarayana, *J. Am. Chem.*, *Soc.* **114**, 5674 (1992).
[5] K.L. Brown and A.W. Awtrey, *Inorg. Chem.* **17**, 111 (1978).
[6] A.L. Crumbliss and W.K. Wilmorth, *J. Am. Chem. Soc.* **92**, 2593 (1970).
[7] K.L. Brown, D. Lyles, N. Pencovici and R.G. Kallen, *J. Am. Chem. Soc.* **97**, 7338 (1975).
[8] F. Asaro, R. Dreos, S. Geremia, G. Nardin, G. Pellizer, L. Randaccio, G. Tauzher and S. Vuano, *J. Organomet. Chem.* **548**, 211 (1997).
[9] R. Dreos, A. Felluga, G. Nardin, L. Randaccio, P. Siega and G. Tauzher, *Eur. J. Inorg. Chem.* 267 (2001).
[10] E. Fonda, A. Michalowicz, L. Randaccio, G. Tauzher and G. Vlaic, *Eur. J. Inorg Chem.* 1269 (2001).
[11] (a) R. Dreos Garlatti, G. Tauzher, G. Costa and M. Green, *Inorg. Chim. Acta* **50,** 95 (1981); (b) R. Dreos Garlatti, G. Tauzher and G. Costa, *Inorg. Chim. Acta* **70**, 83 (1983); (c) R. Dreos Garlatti, G. Tauzher and G. Costa, *Inorg. Chim. Acta* **82**, 197 (1984); (d) R. Dreos Garlatti and G. Tauzher, *Inorg. Chim Acta* **142**, 263 (1983).
[12] (a) G. Costa, G. Mestroni and E. de Savorgnani, *Inorg. Chim. Acta* **3**, 323 (1969); (b) G. Costa, *Coord. Chem. Rev.* **8**, 63 (1972); (c) G. Costa, G. Mestroni and L. Stefani, *Organomet. Chem.* **7**, 493 (1967); (d) A. Bigotto, G. Costa, G. Mestroni, G. Pellizer, A. Puxeddu, E. Reisenhofer, L. Stefani and G. Tauzher, *Inorg. Chim. Rev.* **41** (1970).
[13] P. Kofod, *Inorg. Chem.* **34**, 2768 (1995).
[14] D.W. Christianson and W.N. Lipscomb, *J. Am. Chem. Soc.* **107**, 2682 (1985).
[15] C. Dücker-Benfer, M.S.A. Hamza, C. Eckhadt and R. van Eldik, *Eur. J. Inorg. Chem.* 1563 (2000).
[16] M.S.A. Hamza, C. Dückar-Benfer and R. van Eldik, *Inorg. Chem.* **39**, 3777; 6145 (2000).
[17] B.M. Alzoubi, M.S.A. Hamza, C. Ducker-Benfer and R. van Eldik, *Eur. J. Inorg. Chem.* 968 (2002).
[18] R.W. Taft, F. Anvia, M. Taagepera, J. Catalan J. Elguero, *J. Am. Chem. Soc.* **108**, 3237 (1986).
[19] M. Meot-Ner, *J. Am. Chem. Soc.* **110**, 3071 (1988).
[20] J. Catalan and J. Elguero, *J. Chem. Soc. Perkin Trans. II* 1869 (1983).
[21] J. Catalan, M. Menendez and J. Elguero, *Bull. Soc. Chim. France* 30 (1985).
[22] M.H. Ibraham, P.P. Duce, D.V. Prior, D.G. Barratt, J.J. Morris and P.J. Taylor, *J. Chem. Soc. Perkin Trans. II* 1355 (1989).
[23] R.J. Sundberg and R.B. Martin, *Chem. Rev.* **74**, 471 (1974).
[24] M.S.A. Hamza, *J. Chem. Soc. Dalton Trans.* 2831 (2002).
[25] J.M. Pratt, Inorganic Chemistry of Vitamin B_{12}. (Academic Press, London, 1972).
[26] R. Banerjee (Ed.), Chemistry and Biochemistry of B_{12}. (Wiley and Sons, New York, 1999).
[27] G.N. Schrauzer, *Acc. Chem. Res.* **1**, 97 (1968).
[28] P. Kofod, P. Harris and S. Larsen, *Inorg. Chem.* **36**, 2258 (1997).
[29] M.S.A. Hamza, R. van Eldik, P.L.S. Harper, J.M. Pratt and E.A. Betterton, *Eur. J. Inorg. Chem.* 580 (2002).
[30] R.A. Firth, H.A.O. Hill, B.E. Mann, J.M. Pratt, R.G. Throp and R.J.P. Williams, *J. Chem. Soc. A* 2419 (1968).
[31] (a) G.D. Fasman, Handbook of Biochemistry and Molecular Biology, 3rd Edn., Vol. 1. (CRC Press, Cleveland, 1976), and references therein; (b) C.F. Kroger and W. Freiberg, *Z. Chem.* **10**, 381 (1965); (c) W.P. Jencks and L. Carriuolo, *J. Boil. Chem.* **234**, 1272 (1959).
[32] (a) M.P. Byfield, M.S.A. Hamza and J.M. Pratt, *J. Chem. Soc.*, *Dalton Trans.* 1641 (1993); (b) M.S.A. Hamza and J.M. Pratt, *J. Chem. Soc.*, *Dalton Trans.* 1647 (1993).
[33] M.S.A. Hamza and J.M. Pratt, *J. Chem. Soc.*, *Dalton Trans.* 1367 (1994).
[34] M.S.A. Hamza and J.M. Pratt. *J. Chem Soc.*, *Dalton Trans.* 1373; 1377 (1994).
[35] M.S.A. Hamza and J.M. Pratt, unpublished data.