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# ANATION REACTIONS OF COBALT(III) COMPLEXES

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## CONTENTS

## LIGAND ABBREVIATIONS

| | |
|---|---|
| AO | 2-amino-2-methyl-3-butanone oxime |
| BigH | biguanide |
| Cyclam | 1,4,8,11-tetraazacyclotetradecane |
| DEA | dimethoxyethylamine |
| DMF | dimethylformamide |
| DMSO | dimethylsulphoxide |
| EDDA | ethylenediamine-*N*,*N*′-diacetic acid |
| en | ethylenediamine |
| GlyOH | glycianic acid |
| Hpic | picolinic acid |
| $H_2dmg$ | dimethylglyoxime |

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| | |
|---|---|
| $H_2$ida | iminodiacetic acid |
| $H_2$Mal | malonic acid |
| $H_2$mida | *N*-methyliminodiacetic acid |
| $H_2$P | 5,10,15,20-tetrakis(*N*-methylpyridyl)porphine |
| $H_2$ph | phthalic acid |
| $H_2$sal | salicylic acid |
| $H_2$succ | succinic acid |
| nta | nitrilotriacetic acid |
| $Ph_3P$ | triphenylphosphine |
| PnAO–H | 2,2′-(1,3-diaminopropane)bis(2-methyl-3-butanone)dioxime |
| py | pyridine |
| salen | *N*,*N*′-ethylenebis(salicylimine) |
| TEP | triethylphosphate |
| tetren | tetraethylenepentaamine |
| TMpyP | $\alpha,\beta,\gamma,\delta$-tetra(4-*N*-methylpyridyl)porphine |
| tmtu | 1,1,3,3-tetramethyl-2-thiourea |
| tn | trimethylenediamine |
| $TPPS_4$ | $\alpha,\beta,\gamma,\delta$-tetra(*p*-sulphonatophenyl)porphine |
| tren | triaminotriethylamine |
| trien | triethylenetetraamine |
| tu | thiourea |

## A. INTRODUCTION

Ligand substitution reactions have long been a central focus of mechanistic inorganic chemistry because of their importance in defining the limiting conditions for a preparative or analytical procedure in coordination chemistry. Cobalt complexes occupy a prominent place in this context, having been accorded the ultimate philosophical accolade of paradigm [1].

In recent years work has continued on the anation reactions of various aquacobalt(III) complexes. The anation reaction involves the replacement of coordinated water molecule(s) and is the reverse of an acid hydrolytic reaction. Normally this proceeds as follows:

$$CoL_5(OH_2)^{m+} + X^{n-} \rightarrow CoL_5X^{(m-n)+} + H_2O \qquad (1)$$

through the formation of an ion pair followed by an interchange process:

$$CoL_5(OH_2)^{m+} + X^{n-} \overset{Q}{\rightleftharpoons} CoL_5(OH_2)^{m+},X^{n-} \qquad (2)$$

$$CoL_5(OH_2)^{m+},X^{n-} \xrightarrow{k_i} CoL_5X^{(m-n)+} + H_2O \qquad (3)$$

Detailed considerations of the rate laws for a purely dissociative (D) or a dissociative interchange ($I_d$) process have been dealt with elsewhere [2,3]. The magnitude of $k_i$ in eqn. (3) must necessarily be less than or equal to $k_{ex}$ (the rate constant for the exchange of coordinated water with solvent water) in an $I_d$ process, and unless some special effects are operative, $k_i$ values should be similar for a variety of entering species X.

Although a large number of anation reactions involving cobalt(III) complexes have been reported in the last few years, no review has appeared to systematize such studies. We have attempted to categorize the reactions mainly with regard to the type of aqua complex chosen for such anation studies.

## B. FORMATION OF LIGANDOPENTAAMMINECOBALT(III) COMPLEXES

### (i) *Reactions of $Co(NH_3)_5(OH_2)^{3+}$*

Most studies have been devoted to aquapentaamminecobalt(III) in this category of reactions. The kinetics of anation of $Co(NH_3)_5(OH_2)^{3+}$ with bromide ion have been studied [4(a)] over the range $0.10\ M < [Br^-] < 0.75\ M$. Although no rate saturation with increasing $[Br^-]$ is observed, an $I_d$ mechanism has been proposed for the reaction path. The researcher's view is justified from the observed anation rate which is about 22% of the rate of water exchange [4(b)] of the aquapentaamminecobalt(III) ion (Table 1). This comparison indicates, in turn, a process in which the reaction occurs through outer-sphere association between the complex and the $Br^-$ ion, followed by a slow (rate-determining) interchange between the aqua ligand in the inner sphere and $Br^-$ in the outer sphere in an essentially dissociative process in which the rupture of the Co(III)–$OH_2$ bond is of primary importance in the transition state. However, the absence of thermodynamic data prevents a comparison with the water exchange parameters. The kinetically determined equilibrium constant for the formation of $Co(NH_3)_5Br^{2+}$ is in satisfactory agreement with an independently measured concentration quotient for the formation of the inner-sphere bromo complex ($K = 0.283 \pm 0.30$ M). A similar mechanism has been suggested for the water substitution reaction of this complex by $Cl^-$ in mixed aqueous–organic solvents [5]. The operation of an $I_d$ mechanism has been established by van Eldik et al. [6] for the anation of $Co(NH_3)_5(OH_2)^{3+}$ with $Cl^-$ and $SO_4^{2-}$ using the high pressure kinetic method. However, the results of a similar study on nitrite anation have been interpreted to proceed through the formation of a nitrito intermediate, i.e. without the cleavage of the Co–O bond [7]. A very recent study [8] on the reaction of $Co(NH_3)_5(OH_2)^{3+}$ with $SCN^-$ has shown that it involves the hitherto unrecognized formation of an unstable S-bonded

TABLE 1

Summary of rate and activation parameters for the reaction $Co(NH_3)_5OH_2^{3+} + L^{n-} \rightarrow Co(NH_3)_5L^{(3-n)+} + H_2O$

| L | $T$ (°C) | $I$ (M) | $k \times 10^5$ ($M^{-1}$ $s^{-1}$) | $10^5 k_i$ ($s^{-1}$) | $Q$ ($M^{-1}$) | $\Delta H^{\neq}$ (kcal $M^{-1}$) | $\Delta S^{\neq}$ (e.u.) | Ref. |
|---|---|---|---|---|---|---|---|---|
| $Br^-$ | 25 | 1.00 | 0.13 | | | | | 4 (a) |
| $NCS^-$ | 25 | 1.00 | 0.086 | | | | | 8 |
| $NH_2CH_2COOH$ | 50 | 1.00 | 2.46 | | | 27.60 | 5.20 | 9 |
| $Hph^-$ | 50 | 0.30 | | 7.38 | 3.28 | 28.40 | 10.30 | 10 |
| $ph^{2-}$ | 50 | 0.30 | | 11.50 | 22.50 | 24.50 | −0.70 | 10 |
| $H_2C_2O_4$ | 60 | 1.00 | 6.60 | | | 14.30 | −35.00 | 11 |
| | | | 8.10 | | | 13.70 | −35.50 | 17 |
| $HC_2O_4^-$ | 60 | 1.00 | | 18.00 | 1.80 | 22.40 | −8.60 | 11 |
| $C_2O_4^{2-}$ | 60 | 1.00 | | 12.50 | 9.20 | 24.80 | −2.10 | 11 |
| HCOOH | 60 | 1.00 | 4.20 | | | 21.70 | −13.50 | 12 |
| $HCOO^-$ | 60 | 1.00 | | 19.80 | 0.85 | 20.40 | −14.50 | 12 |
| | | | | 30.00 | 0.50 | 17.60 | −22.10 | 17 |
| $CH_3COOH$ | 60 | 1.00 | 1.70 | | | 22.40 | −13.00 | 13 |
| $CH_3COO^-$ | 60 | 1.00 | | 5.00 | 5.10 | 22.80 | −9.80 | 13 |
| | | | | 5.00 | 5.30 | 25.90 | −0.40 | 17 |
| $CH_3CH_2COOH$ | 60 | 1.00 | 1.08 | | | 25.30 | −5.40 | 14 |
| $CH_3CH_2COO^-$ | 60 | 1.00 | | 6.60 | 4.38 | 24.10 | −5.30 | 14 |
| | | | | 6.00 | 5.00 | 25.40 | −1.50 | 17 |
| $H_6C_4O_4$ | 60 | 0.30 | 2.10 | | | 23.70 | −9.00 | 18 |
| $H_5C_4O_4^-$ | 60 | 0.30 | | 52.00 | 1.00 | 25.10 | 1.00 | 18 |
| $H_4C_4O_4^{2-}$ | 60 | 0.30 | | 7.60 | 30.00 | 20.30 | −16.00 | 18 |
| $H_2Mal$ | 70 | 1.00 | 8.00 | | | 23.40 | −9.30 | 19 |
| $HMal^-$ | 70 | 1.00 | | 53.00 | 1.30 | 30.30 | 14.60 | 19 |
| $Mal^{2-}$ | 70 | 1.00 | | 73.00 | 5.40 | 24.90 | 2.70 | 19 |
| $H_2PO_4^-$ | 50 | 1.00 | 4.50 | | | 26.90 | 4.20 | 20 |
| $H_2PO_3^-$ | 60 | 1.00 | | 2.90 | 2.16 | 33.70 | 19.80 | 21 |

$k_{ex}$ ($s^{-1}$) = $5.89 \times 10^{-6}$ at 25.1° C, $2.58 \times 10^{-5}$ at 35.0° C and $9.31 \times 10^{-5}$ at 44.7° C.
$\Delta H_{ex}^{\neq} = 26.60$ kcal $M^{-1}$; $\Delta S_{ex}^{\neq} = 6.70$ e.u. [4(b)].

$Co(NH_3)_5SCN^{2+}$ ion (26%) in parallel with the stable N-bonded complex $Co(NH_3)_5NCS^{2+}$ (74%). The kinetic S-isomer to N-isomer ratio ($0.36 \pm 0.01$) at 25 °C is the same for $0.5\ M < [SCN^-] < 3.1\ M$. Second-order total and individual rate constants have been evaluated, by ion exchange analyses early in the reaction times, without interference from the ensuing S- to N-linkage isomerization process. An $I_d$ mechanism has been proposed for the reaction of $Co(NH_3)_5(OH_2)^{3+}$ with glycine [9] because of the close similarity between the activation parameters obtained for the anation process and those for the water exchange reaction (Table 1). The results of Dash and Ray [10] for the water substitution reaction of this complex with the deprotonated forms ($Hph^-$ and $ph^{2-}$) of phthalic acid illustrate well the ion pair dissociative mechanism. They explain the observed faster interchange rate of the $Co(NH_3)_5(OH_2)^{3+},ph^{2-}$ ion pair in comparison with that of its $Hph^-$ analogue by assuming that $ph^{2-}$ exerts a stronger labilizing action on the coordinated water molecule than $Hph^-$. Comparing their thermodynamic parameters with those for similar systems and water exchange reactions (Table 1), the researchers have established their suggested path. Extensive studies have been carried out by van Eldik and coworkers on the anation reactions of the aquapentaamminecobalt(III) ion with several carboxylic acids, e.g. oxalic [11], formic [12], acetic [13] and propionic [14] acids and their conjugate bases. The results of such investigations indicate that the anation with the molecular forms of the organic acids follow second-order kinetics in which ion pair formation is not kinetically identifiable, whereas basic (anionic) forms of the acids react by an $I_d$ path [15,16]. The general reaction patterns of these monocarboxylic and dicarboxylic acids may be delineated as follows:

$$R(OH_2)^{3+} + H_xL \xrightarrow{k_0} R(H_{x-1}L)^{2+} + H_3O^+ \tag{4}$$

$$K_1 \downarrow\uparrow$$

$$R(OH_2)^{3+} + H_{x-1}L^- \overset{Q_1}{\rightleftharpoons} \left[R(OH_2)^{3+},H_{x-1}L^-\right] \xrightarrow{k_1} R(H_{x-2}L)^+ + H_3O^+ \tag{5}$$

$$K_2 \downarrow\uparrow$$

$$R(OH_2)^{3+} + H_{x-2}L^{2-} \overset{Q_2}{\rightleftharpoons} \left[R(OH_2)^{3+},H_{x-2}L^{2-}\right] \xrightarrow{k_2} R(H_{x-2}L)^+ + H_2O \tag{6}$$

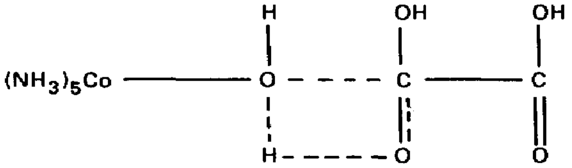
where $R = Co(NH_3)_5$ and $x = 1$ or $2$. The general rate expression for such a reaction scheme is given by

$$k_{obs} = k_0[H_xL] + \frac{k_1Q_1[H_{x-1}L^-]}{1 + Q_1[H_{x-1}L^-]} + \frac{k_2Q_2[H_{x-2}L^{2-}]}{1 + Q_2[H_{x-2}L^{2-}]} \tag{7}$$

The third term of the right-hand side vanishes for monobasic acids. In one of his later reports [17] van Eldik has recalculated the kinetic parameters reported in his earlier papers [11–14] to take into account more than one simultaneous pathway and has shown that the overall rate expression is better represented by eqn. (8) than by eqn. (7):

$$k_{\mathrm{obs}} = \frac{k_0[\mathrm{H}_x\mathrm{L}] + k_1Q_1[\mathrm{H}_{x-1}\mathrm{L}^-] + k_2Q_2[\mathrm{H}_{x-2}\mathrm{L}^{2-}]}{1 + Q_1[\mathrm{H}_{x-1}\mathrm{L}^-] + Q_2[\mathrm{H}_{x-2}\mathrm{L}^{2-}]} \tag{8}$$

This rate expression is equally applicable to the formation of succinatopentaamminecobalt(III) and malonatopentaamminecobalt(III) from the aqua analogue [18,19]. In the succinate anation the reactivity sequence of the ion pairs ($k_1/k_2 \approx 5$) has quite logically been attributed to the transformation of $\mathrm{Co(NH_3)_5(OH_2)^{3+}}$,succ$^{2-}$, to its less reactive hydroxo form, $\mathrm{Co(NH_3)_5}$-$\mathrm{(OH)^{2+}}$,Hsucc$^-$, in a fast internal acid–base equilibrium step. An interesting feature of the oxalic acid anation [11] is the probable $\mathrm{H_2C_2O_4}$ addition mechanism (pseudo-substitution) instead of the conventional water ligand dissociation. On the basis of the thermodynamic parameters and the results of a study of the solvent $\mathrm{D_2O}$ effect the researchers have suggested, though not unambiguously, a four-centre transition state (A) which can achieve oxalate addition without Co(III)–$\mathrm{OH_2}$ bond cleavage. The reactivity order for the molecular forms of



(A)

the aforementioned carboxylic acids is oxalic > formic > succinic ≈ acetic > propionic. Ferrer and coworkers [20,21] have reported the anation of the aquapentaamminecobalt(III) ion with phosphoric acid/dihydrogen phosphate and phosphorous acid/hydrogen phosphite respectively. Undissociated forms of both the phosphoric and phosphorous acids take no part in the reaction sequence. Having established the anions $\mathrm{H_2PO_4^-}$ and $\mathrm{H_2PO_3^-}$ as the reactive species, the researchers proposed an $\mathrm{I_d}$ path for the latter but a D mechanism for the former from the observed linear plot of $k_{\mathrm{obs}}$ vs. $[\mathrm{H_2PO_4^-}]$. This is contrary to the substitution reactions of $\mathrm{Co(NH_3)_5}$-$\mathrm{(OH_2)^{3+}}$, especially with anionic nucleophiles. The researchers experimented up to $[\mathrm{H_3PO_4}]_T = 0.75$ M, in which the molecular form is also a contributing factor. Thus it would be more informative to see the nature of the rate–$[\mathrm{H_2PO_4^-}]$ profile at a higher nucleophile concentration. Also the anation

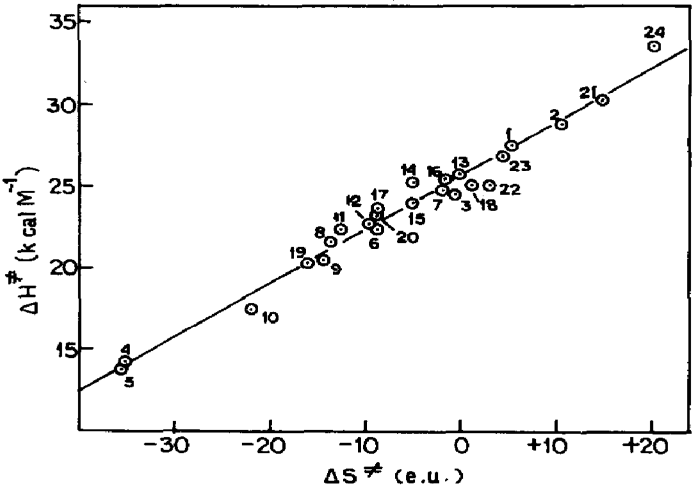


Fig. 1. Isokinetic plot for the anation of $Co(NH_3)_5(OH_2)^{3+}$ with 1, $NH_2CH_2COOH$; 2, $Hph^-$; 3, $ph^{2-}$; 4 and 5, $H_2C_2O_4$; 6, $HC_2O_4^-$; 7, $C_2O_4^{2-}$; 8, HCOOH; 9 and 10, $HCOO^-$; 11, $CH_3COOH$; 12 and 13, $CH_3COO^-$; 14, $CH_3CH_2COOH$; 15 and 16, $CH_3CH_2COO^-$; 17, $H_6C_4O_4$; 18, $H_5C_4O_4^-$; 19, $H_4C_4O_4^{2-}$; 20 $H_2Mal$; 21, $HMal^-$; 22, $Mal^{2-}$; 23, $H_2PO_4^-$; 24, $H_2PO_3^-$.

rate ($1.54 \times 10^{-4}$ $M^{-1}$ $s^{-1}$ at 60°C) lies below the water exchange rate (about $7 \times 10^{-4}$ $s^{-1}$) under comparable conditions. In the formation of the fluoropentaamminecobalt(III) ion by the reaction of fluoride ion with Co $(NH_3)_5X^{n+}$ ($X = H_2O$, $NO_3^-$, $CO_3^{2-}$, $NO_2^-$, $ONO^-$ and $N_3^-$), $F^-$ has been found to be displaced to give $Co(NH_3)_5Cl^{2+}$ in the presence of HCl [22]. The interchange reaction between $Co(NH_3)_5(OH_2)^{3+}$ and DMSO in acidic aqueous DMSO solution has been investigated, emphasizing the evaluation of the dependence of rate coefficients and equilibrium quotients upon the solvent composition [23]. A dominant outer-sphere interaction between the solvent DMSO and the coordinated water molecule of $Co(NH_3)_5(OH_2)^{3+}$ is believed to occur. The rate and activation parameters of all these reactions are collected in Table 1. An excellent linear relationship exists between the activation energies and entropies over a wide range of values for a series of entering nucleophiles in the anation of $Co(NH_3)_5(OH_2)^{3+}$, demonstrating a common $I_d$ mechanism (Fig. 1).

### *(ii) Reactions of $Co(NH_3)_5(DMSO)^{3+}$*

A large collection of data is now available on the substitution and solvent exchange reactions of the $Co(NH_3)_5(DMSO)^{3+}$ ion. Studies [24] on the anation and solvent exchange reactions of $Co(NH_3)_5(DMSO)^{3+}$ in DMSO reveal that these reactions are accompanied by processes in which the conjugate base of this complex undergoes either internal reduction to cobalt(II) or relatively rapid substitution through an $I_d$ path under neutral conditions, the latter speculation being strongly supported by the high positive $\Delta V_{ex}^{\neq}$ value ($10.0 \pm 1.2$ cm$^3$ M$^{-1}$) and the apparent equality of $\Delta H_{ex}^{\neq}$ (123 kJ mol$^{-1}$) with $\Delta H_i^{\neq}$ (about 126 kJ mol$^{-1}$ for $Cl^-$ and 121 kJ mol$^{-1}$ for $Br^-$ anation). The addition of acid eliminates the conjugate base path, but a minor redox path exists for ion pairs with $Cl^-$ and $Br^-$ ions. The rate of exchange of water and DMSO with triethylphosphate, $Cl^-$ and pyridine in $Co(NH_3)_5(OH_2)^{3+}$ and $Co(NH_3)_5(DMSO)^{3+}$ follows a unimolecular path [25]. The substituted products have been characterised. An $I_d$ mechanism has been proposed for the reaction of $Co(NH_3)_5(DMSO)^{3+}$ with nitrate ion [26]. A comparison of the solvent (DMSO) exchange rate, nitrate anation rate and rate of solvolysis of $Co(NH_3)_5(ONO)^{2+}$ by DMSO justifies the proposed mechanism. Reynolds and El-Nasr [27,28] have extended their studies on the $Co(NH_3)_5(DMSO)^{3+}$ ion by performing anation reactions with various nucleophiles, e.g. $N_3^-$, $NCS^-$, $Cl^-$ and $Br^-$. With the change in ionic strength of the medium the ion-pair interchange rate constants remain unaltered, while the ion-pair formation constants change in an inverse manner. In the presence of the entering ligand $X^-$, solvent displacement from $Co(NH_3)_5(DMSO)^{3+}$ also occurs within the ion pair $Co(NH_3)_5(DMSO)^{3+},X^-$ by both solvent exchange and anation reactions, the latter reaction being prominent. Most ion pairs lose coordinated DMSO by interchange with the $X^-$ ion rather than by solvent interchange. The researchers have quite logically argued their observed larger values of the anation rate constant ($k_i$) in comparison with those of solvent exchange rate constant ($k_{ex}$) in the suggested $I_d$ process in terms of the prevention of internal return by the entering ligand, as has been demonstrated earlier by Lo et al. [24]. In the reaction of $Co(NH_3)_5S^{3+}$ ions ($S = H_2O$ or DMSO) with $SeO_3^{2-}$, linkage isomers are formed [29]. The Se-bonded complex is formed when S is DMSO, whereas the O-bonded isomer results, without the

TABLE 2

Kinetic and thermodynamic data for the reaction $Co(NH_3)_5DMSO^{3+} + L^{n-} \rightarrow Co(NH_3)_5L^{(3-n)+} + DMSO$

| L | $T$ (°C) | $I$ (M) | $k \times 10^5$ (s$^{-1}$) | $k_i \times 10^5$ (s$^{-1}$) | $Q$ (M$^{-1}$) | $\Delta H^{\neq}$ (kcal M$^{-1}$) | $\Delta S^{\neq}$ (e.u.) | Ref. |
|---|---|---|---|---|---|---|---|---|
| TEP | 40 | | 25.59 | | | 23.50 | 26.90 | 25 |
| $Cl^-$ | 40 | | 12.79 | | | 29.30 | −4.00 | 25 |
| | 45.2 | 0.10 | | 28.00 | 21.60 | | | 27 |
| $N_3^-$ | 45.2 | 0.25 | | 15.00 | 5.80 | | | 27 |
| $NCS^-$ | 45.2 | 0.10 | | 3.00 | 7.20 | | | 27 |
| $Br^-$ | 45.3 | 1.00 | | 7.00 | 5.50 | | | 28 |

cleavage of the Co–O bond, when S is $H_2O$. The latter reaction can be regarded as nucleophilic attack by the coordinated water at the Se(IV) centre via an associative interchange ($I_a$) mechanism. The results [30] of the solvent interchange of pentaamminecobalt(III) complexes in water–acetonitrile and in DMSO–acetonitrile media have shown that the rate constants for the reaction of acetonitrile with aqua and DMSO complexes depend strongly on the mole fraction of the acetonitrile in the solvent mixture, but those for the reverse reactions, i.e. for the loss of acetonitrile from the acetonitrile complex, depend slightly on this factor. The interpretation of the results given by the researchers is that the $Co(NH_3)_5^{3+}$ group in the activated complex of the $I_d$ path for solvent interchange does not undergo any significant real rotation or pseudo-rotation within its solvent cage. The existing kinetic and thermodynamic data are collected in Table 2.

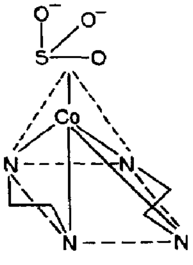
## C. REACTIONS OF OTHER AMINE COMPLEXES OF COBALT(III) CONTAINING LESS THAN TWO AQUA LIGANDS

Attention is now focused on cobalt(III) complexes where a non-replaceable group may facilitate or retard the rate of replacement of the leaving group, depending on the electron donating or accepting property of the former. The rates and activation parameters [31–35] for substitution of the aqua ligand in *trans*-$Co(en)_2(SO_3)(OH_2)^+$ and *trans*-$Co(en)_2(SO_3)(OH)$ provide a quantitative illustration of the dramatic *trans* labilizing effect of the coordinated sulphite ligand. The anation of $Co(en)_2(SO_3)(OH_2)^+$ with several nucleophiles, e.g. $S_2O_3^{2-}$, $NCS^-$, $NO_2^-$, $N_3^-$, $Fe(CN)_6^{3-}$, $HN_3$, $NH_3$, imidazole and $SO_3^{2-}$ has been reported by Yandell and coworkers [31,32]. Except for the reaction with $SO_3^{2-}$, where the $Co(en)_2(SO_3)_2^-$ formation mechanism involves the generation of a five-coordinate intermediate (D mechanism), an $I_d$ mechanism has been put forward for all other reactions. The researchers have substantiated their arguments in favour of an $I_d$ mechanism by noting that (i) the observed second-order rate constants correlate with the charge on the ligands, as expected for such a mechanism, and (ii) deviations from second-order behaviour at high concentrations of the charged ligands are consistent with saturation of the outer-sphere pre-equilibrium and yield outer-sphere formation constants which, although in most cases not well defined, are comparable with values reported for similar complexes and ligands. The rate constants for outer-sphere–inner-sphere interchange are calculated. Assuming this value to be independent of the incoming ligand, the outer-sphere equilibrium constants for different ligands are calculated and these values are found to be reasonable for a different degree of interaction of the differently charged as well as neutral ligands with the complex. However, the researchers [32] have found an unusual reciprocal dependence of the rate of substitution by $SO_3^{2-}$ of the neutral species *trans*-Co(en)$_2$(SO$_3$)(OH) on hydroxide ion concentration. Hence they reasonably conclude that a reversible limiting "D" mechanism is the only plausible mechanism compatible with the rate law. The rate data for substitution of *trans*-$Co(en)_2(SO_3)(OH_2)^+$ by $SO_3^{2-}$ are consistent with the following D mechanism:

$$trans\text{-}Co(en)_2(SO_3)(OH_2)^+ \underset{k_w}{\overset{k_{-w}}{\rightleftharpoons}} Co(en)_2(SO_3)^+ + H_2O \tag{9}$$

$$Co(en)_2(SO_3)^+ + SO_3^{2-} \underset{k_{-s}}{\overset{k_s}{\rightleftharpoons}} trans\text{-}Co(en)_2(SO_3)_2^- \tag{10}$$

The D mechanism requires that, at a high nucleophile concentration, a limiting rate equivalent to $k_{-w}$ should be attained. This is observed within experimental error for $SO_3^{2-}$, $HSO_3^-$ and $N_3^-$. The rapid exchange of the aqua ligand in *trans*-$Co(en)_2(SO_3)(OH_2)^+$ with the solvent $H_2{}^{18}O$ is in accord with this mechanism [32]. Also, the very high value required for the ion-pair stability constant for $Co(en)_2(SO_3)(OH_2)^+, SO_3^{2-}$ ($(1.5 \pm 0.5) \times 10^2$) compels the researchers to reject an $I_d$ mechanism for this reaction. In an identical study on the water substitution reactions of *trans*-Co(en/tn)$_2$(SO$_3$)(OH$_2$/OH)$^{+/0}$ with $Cl^-$, $Br^-$, $CH_3COO^-$, $N_3^-$, $NO_2^-$, $NCS^-$, $CN^-$ and $SO_3^{2-}$, Ito et al. [36] have stressed the operation of a reversible D mechanism. The labilizing effect of the sulphite ligand in these complexes is derived almost wholly from the relatively low $\Delta H^{\neq}$ values for dissociative release of the ligands *trans* to sulphito. The origin of the low $\Delta H^{\neq}$ values lies in differences in bond energy terms between the ground state and the transition state leading to the dissociated intermediate, $Co(en)_2(SO_3)^+$. One unusual characteristic of the sulphito ligand is its potential ability to bond either through sulphur or through oxygen [37]. In the ground state of the *trans* sulphitocobalt(III) complexes the bonding is through sulphur. Dissociation to yield a pseudo-tetragonal intermediate $Co(en)_2(SO_3)^+$ provides the possibility of forming a three-centre $\pi$–$\pi$ bond utilizing the empty $E_g$ Co(III) orbital. This would render considerable stabilization of this inter-



mediate and give relatively low $\Delta H^{\neq}$ values. Stereospecificity would be achieved by entry of the incoming nucleophile below the tetragonal plane as the ethylenediamine ligands revert to their ground state octahedral sites. Studies on the rapid formation of *trans*-$Co(en)_2(SO_3)L^+$ by reaction of its aqua analogue with imidazole and imidazole-containing ligands (L) have recently been reported [34]. The kinetic and equilibrium constants for the imidazole anation have been measured. It has been observed from equilibrium studies that appreciable amounts of the complex form only in the pH range 6.0–9.0. The researchers propose a similar mechanism ($I_d$) to that suggested by Yandell and Tomlines [31]. Formation of $\mu$-cyano complexes from the reaction between *trans*-$Co(en)_2(SO_3)(OH_2)^+$ and $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, $Co(CN)_6^{3-}$, $Fe(CN)_5(NO)^{2-}$ ions has been investigated [35]. The strong *trans* effect of the S-bonded sulphite ion is again apparent, and in the anation with ferrocyanide ion a first-order reaction is observed even at a 1 : 1 ratio of reactants. Although a D mechanism is indicated for this reaction, the limiting rate at high concentrations of $Fe(CN)_6^{4-}$ exceeds the rate of pure dissociative loss of water and this may reflect some contribution from an associative mechanism to the overall rate or to the effect of high negative charge on the ion pair. The researchers have shown that the first-order kinetics obtained under the conditions where $[Fe(CN)_6^{4-}] = [trans\text{-}Co(en)_2(SO_3)(OH_2)^+]$ cannot be due to virtually complete ion pairing of reactants since this would require a very high formation constant (greater than $10^5$ $M^{-1}$). Another example of a kinetic *trans* effect (KTE) phenomenon shown by an S-bonded ligand ($S_2O_3^{2-}$) has been cited by Cooper et al. [38] while studying the chemistry and reactivity of *trans*-$Co(en)_2(S_2O_3)(OH_2)^+$. The rate law governing the anation by L ($L = NCS^-$, $NO_2^-$) to yield the characterized complexes, *trans*-$Co(en)_2L(S_2O_3)$ is

$$\text{rate} = k[Co(en)_2(S_2O_3)(OH_2)^+][L^-] \tag{11}$$

As observed for similar anation reactions at *trans*-labilized Co(III) centres [31], the researchers have anticipated a more complex dependence of $k_{obs}$ on $[L^-]$:

$$k_{obs} = \frac{a + bc[L^-]}{1 + c[L^-]} \tag{12}$$

Since both the D and $I_d$ mechanisms satisfy this rate law, in order to ascertain the actual reaction path, the researchers have further studied the reactions in the presence of $SO_4^{2-}$ ions and have noticed a decrease in rate. This inhibitory effect of the $SO_4^{2-}$ ion clearly indicates a prior association mechanism as outlined below:

$$M{-}OH_2^+ + SO_4^{2-} \rightleftharpoons M{-}OH_2^+,SO_4^{2-} \qquad K_{OS,S} \tag{13}$$

$$M{-}OH_2^+ + L^- \rightleftharpoons M{-}OH_2^+,L^- \qquad K_{OS,L} \tag{14}$$

$$M{-}OH_2^+,L^- \rightarrow M{-}L + H_2O \qquad k_L \tag{15}$$

This scheme leads to the following rate expression:

$$k_{\text{obs}} = \frac{k_L K_{\text{OS,L}}[\text{L}^-]}{1 + K_{\text{OS,L}}[\text{L}^-] + K_{\text{OS,S}}[\text{SO}_4^{2-}]}$$

The $I_d$ mechanism is further supported by the excellent agreement of the rate data calculated assuming the $I_d$ mechanism with those obtained from experiments. Comparing these results with literature data it is seen that (i) S-bonded $S_2O_3^{2-}$ is a relatively efficient *trans* labilizing group (substitution *trans* to $S_2O_3^{2-}$ occurs about $2 \times 10^4$ times faster than the substitution *trans* to $NH_3$), (ii) the kinetic *trans* effect induced by S-bonded $SO_3^{2-}$ on $H_2O$ is about $5 \times 10^3$ times larger than that induced by S-bonded $S_2O_3^{2-}$, and (iii) the kinetic *trans* effect series for ligands S-bonded to Co(III) is $SO_3^{2-} > RSO_2^- > S_2O_3^{2-}$ which corresponds exactly to the structural *trans* effect (STE) series determined for these ligands. From this speculation the researchers have concluded that the lability of the ligand situated *trans* to sulphur (KTE) is highly correlated with the length of the *trans* Co–L bond (STE).

The kinetics of formation of $\text{Co(en)}_2(\text{GlyO})^{2+}$ from *trans*-$\text{Co(en)}_2(\text{GlyO/H})(\text{OH}_2/\text{OH})^{3+/2+}$ have recently been studied [39]. A process involving the synergic displacement of coordinated water or hydroxide ion by the *trans* carboxylic acid or carboxylate anion, as shown below, has been suggested. The acid form of the complex for the *cis* species has interestingly been found [40] to be about 10 times more reactive than its conjugate base, whereas the reverse is true for the *trans* complex [39]. Recently a study on the cyclization of monodentate oxalate in *trans*-$\text{Co(en)}_2(\text{C}_2\text{O}_4\text{H})(\text{OH}_2)^{2+}$ and *trans*-$\text{Co(en)}_2(\text{C}_2\text{O}_4)(\text{OH}_2)^+$ has been reported [41]. For the latter ion, chelation is found to proceed quantitatively via *cis*-$\text{Co(en)}_2(\text{C}_2\text{O}_4)(\text{OH}_2)^+$. Cyclization of oxalate predominates at pH < 7. The researchers have suggested the presence of two consecutive processes from the spectral data. From a knowledge of the spectral characteristics of the *cis* monodentate complex, they have suggested that the reaction proceeds via the *cis* species. For the reaction of *cis*-$\text{Co(en)}_2(\text{NH}_3)(\text{OH}_2)^{3+}$ with salicylate ion ($\text{HL}^-$) the kinetic results have been found to be consistent with a mechanism involving

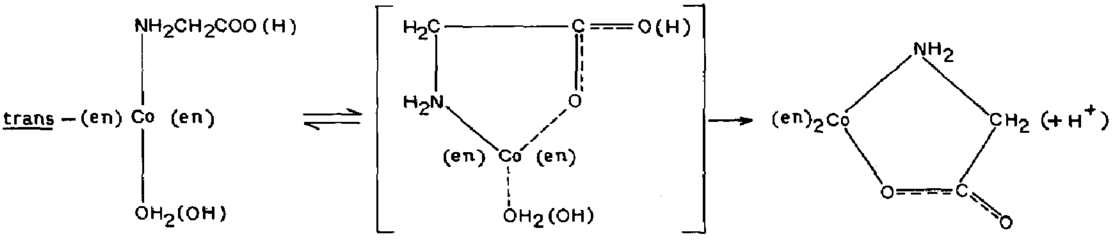


TABLE 3

Kinetic and thermodynamic parameters for the anation of other cobalt(III) ammine complexes containing less than two aqua ligands

| Complex | Ligand | $T$ (°C) | $I$ (M) | $k$ ($M^{-1}\ s^{-1}$) | $k_i$ ($s^{-1}$) | $Q$ ($M^{-1}$) | $\Delta H^{\neq}$ (kcal $M^{-1}$) | $\Delta S^{\neq}$ (e.u.) | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| *Trans*-$Co(en)_2(SO_3)(OH_2)^+$ | $H_2O^{18}$ | 25 | | 13.2 $s^{-1}$ | | | 15.90 | 0.20 | 32 |
| | $S_2O_3^{2-}$ | 25 | 1.0 | 1270 | ~ 420 | 3.00 | 10.87 | | 31 |
| | $NCS^-$ | 25 | 1.0 | 275 | ~ 420 | 0.65 | | | 31 |
| | $NO_2^-$ | 25 | 1.0 | 206 | ~ 420 | 0.50 | | | 31 |
| | $HN_3$ | 25 | 1.0 | 14 | ~ 420 | 0.033 | | | 31 |
| | $N_3^-$ | 25 | 1.0 | 240 | ~ 420 | 0.55 | | | 31 |
| | $Fe(CN)_6^{3-}$ | 25 | 1.0 | 1720 | ~ 420 | 4.00 | | | 31 |
| | $NH_3$ | 25 | 1.0 | 6.70 | ~ 420 | 0.016 | | | 31 |
| | Imidazole | 25 | 1.0 | 5.20 | ~ 420 | 0.012 | | | 31 |
| | | | | 5.90 | | | 22.00 | | 34 |
| *Trans*-$Co(en)_2(SO_3)(OH)$ | $N_3^-$ | 25 | 1.0 | 3.62 | | | | | 33 |
| | $NO_2^-$ | 25 | 1.0 | 1.34 | | | | | 33 |
| | $NCS^-$ | 25 | 1.0 | 2.53 | | | | | 33 |
| | $CN^-$ | 25 | 1.0 | 1.33 | | | | | 33 |
| | $SO_3^{2-}$ | 25 | 1.0 | 4.09 | | | | | 33 |
| | Imidazole | 25 | 1.0 | 4.00 | | | ~ 7.00 | | 34 |
| *Trans*-$Co(tn)_2(SO_3)(OH)$ | $N_3^-$ | 25 | 1.0 | 45.50 | | | | | 33 |
| | $NO_2^-$ | 25 | 1.0 | 25.10 | | | | | 33 |
| | $NCS^-$ | 25 | 1.0 | 28.90 | | | | | 33 |
| | $CN^-$ | 25 | 1.0 | 44.80 | | | | | 33 |
| | $SO_3^{2-}$ | 25 | 1.0 | 33.10 | | | | | 33 |
| *Trans*-$Co(en)_2(S_2O_3)(OH_2)^+$ | $NCS^-$ | 26.4 | 1.0 | 0.04 | | | 14.40 | −17.00 | 38 |
| | $NO_2^-$ | 26.4 | 1.0 | 0.046 | 0.17 | 0.34 | 13.80 | −19.00 | 38 |
| *Cis*-$Co(en)_2(NH_3)(OH_2)^{3+}$ | $H_2C_2O_4$ | 60 | 1.0 | $5.24\times10^{-5}$ | | | 22.94 | 9.32 | 43 |
| | $HC_2O_4^-$ | 60 | 1.0 | $2.31\times10^{-4}$ | | 1.50 | 26.05 | 2.62 | 43 |
| | $C_2O_4^{2-}$ | 60 | 1.0 | $1.96\times10^{-4}$ | | 5.80 | 25.81 | 1.19 | 43 |
| | $Hsal^-$ | 60 | 1.0 | | $6.53\times10^{-5}$ | 2.30 | 24.47 | −4.30 | 42 |

outer-sphere association between the cobalt(III) complex and $HL^-$ followed by its transformation into the product, *cis*-$Co(en)_2(NH_3)(HL)^{2+}$, by an essentially dissociative process in which rupture of the Co(III)–$OH_2$ bond is of primary importance in the transition state [42]. The interchange rate constant is very close to the solvent exchange rate constant and the reaction is stereoretentive. The water substitution reactions of *cis*-$Co(en)_2(NH_3)(OH_2)^{3+}$ by all the molecular and anionic forms of oxalic acid have also been investigated [43]. Association of the complex cation with $H_2C_2O_4$ has not been identified. The temperature-independent association constants of the $Co(en)_2(NH_3)(OH_2)^{3+},HC_2O_4^-$ and $Co(en)_2(NH_3)(OH_2)^{3+},C_2O_4^{2-}$ ion pairs have values 1.5 M and 5.8 M (50–60 °C) respectively. The interchange reactions of the ion pairs to yield inner-sphere complexes, *cis*-$Co(en)_2(NH_3)(HC_2O_4)^{2+}$ or its base form, are believed to occur through an $I_d$ path. The mechanism of the anation of the aqua cation with $H_2C_2O_4$ may be $I_d$ but the possibility of the rate-limiting addition of oxalic acid to the Co–O bond has not been ruled out. Table 3 includes the related kinetic data.

## D. REACTIONS OF CYANOCOBALT(III) COMPLEXES

The pentacyanocobaltate(III) family of complexes has been supposed to form an ideal group for the demonstration of a D-type mechanism. The choice of the cyanide system lies in the fact that a strongly $\pi$-acid high field ligand such as this might be expected to promote a limiting dissociative path by selectively weakening the Co(III)–$OH_2$ bond *trans* to it and stabilizing the five-coordinate intermediate formed [44,45]. The rate of formation of equilibrium amounts of $Co(CN)_5L^{3-}$ has been followed using excess concentrations of nucleophile, L, so as to maintain the pseudo-first-order condition. The results conform to the following reaction scheme:

$$Co(CN)_5OH_2^{2-} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Co(CN)_5^{2-} + H_2O \tag{16}$$

$$Co(CN)_5^{2-} + L^- \underset{k_4}{\overset{k_3}{\rightleftharpoons}} Co(CN)_5L^{3-} \tag{17}$$

The assumption of a steady state condition for the concentration of $Co(CN)_5^{2-}$ leads to eqn. (18), a relationship between the pseudo-first-order rate constant and the other kinetic parameters:

$$k = \frac{k_1[L^-] + k_2k_4/k_3}{(k_2/k_3) + [L^-]} \tag{18}$$

Plots of $1/(k-k_4)$ vs. $1/[L^-]$ for several nucleophiles, e.g. $N_3^-$, $NCS^-$, $I^-$, $Br^-$, give a common intercept, showing that $k_1 \gg k_4$. A numerical value of

$k_1 = (1.47 \pm 0.1) \times 10^{-3}$ s$^{-1}$ (obtained through least-squares treatment of both $N_3^-$ and NCS$^-$ data) is adopted to treat the kinetic data of various nucleophiles [46]. The following decreasing order of nucleophilic reactivity for the pentacoordinate species, $Co(CN)_5^{2-}$, has been found: $OH^- > I_3^- > HN_3 > N_3^- > NCS^- >$ thiourea $> I^- > NH_3 > Br^- > S_2O_3^{2-} > NCO^- > H_2O$ [47]. An elegant test for the proposed D mechanism is that $k_a$ should equal the rate constant for the water exchange reaction. Using water labelled with $^{18}O$, a direct measurement of the exchange rate was made. The value lies in the range $(1.0–1.3) \times 10^{-3}$ s$^{-1}$ at 40 °C, in reasonably good agreement with the value of $k_1$ deduced from the anation studies of $Co(CN)_5OH_2^{2-}$. Displacement of the aqua ligand in $Co(CN)_5OH_2^{2-}$ by py, $NH_3$, $N_2H_4$, $N_2H_5^+$ has also been studied [48]. The kinetic data are consistent with a D mechanism, with the possible exception in the case of py, even though no independent support has been provided. The deviation of the py results may be due to the activity coefficients in the py–$H_2O$ system being far from ideal and to the inappropriate approximation made in the rate equation. Other evidence from solvent effects [49] on the substitution of $Co(CN)_5OH_2^{2-}$ by $N_3^-$, and activation volume ($\Delta V^{\neq}$) measurements on the anation reactions of $Co(CN)_5OH_2^{2-}$ by Palmer and Kelm [50] also suggest a D mechanism. The activation volumes for the anation of $Co(CN)_5OH_2^{2-}$ with $Br^-$, $I^-$ and NCS$^-$ (at 40 °C and ionic strength of $I = 1.0$ M) are $+8.4 \pm 1.0$, $+9.4 \pm 1.6$ and $+8.2 \pm 0.9$ cm$^3$ mol$^{-1}$ and are entirely in accord with the extreme D mechanism which infers that the volume of the cobalt(III) complex in its transition state should be independent of the leaving and entering groups. This study provides sound evidence in favour of the D mechanism originally proposed by Haim et al. [51] by a more traditional kinetic approach.

The substitution of $Co(CN)_5OH^{3-}$ by azide ion [52] has been found to occur by the reaction of $N_3^-$ with $Co(CN)_5OH_2^{2-}$ in equilibrium with the hydroxo complex:

$$Co(CN)_5OH_2^{2-} + OH^- \overset{K_2}{\rightleftharpoons} Co(CN)_5OH^{3-} + H_2O \tag{19}$$

$$Co(CN)_5OH_2^{2-} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} Co(CN)_5^{2-} + H_2O \tag{20}$$

$$Co(CN)_5OH^{3-} \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} Co(CN)_5^{2-} + OH^- \tag{21}$$

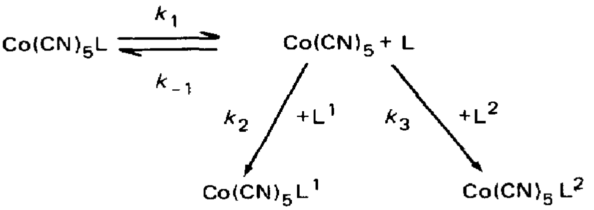
$$Co(CN)_5^{2-} + N_3^- \xrightarrow{k_7} Co(CN)_5N_3^{3-} \tag{22}$$

The second-order rate constant $k_e$ is given by

$$k_e = \frac{k_5 + k_6K_2[OH^-]}{\{(k_{-5}[H_2O]/k_7) + (k_{-6}[OH^-]/k_7) + [N_3^-]\}(1 + K_2[OH^-])} \tag{23}$$

Deviations from simple second-order rate laws for the substitution of $N_3^-$, $NCS^-$ and $CN^-$ into $Co(CN)_5OH_2^{2-}$ at $I = 1.0$ M and 40 °C are small and can be attributed to variations in ionic activities. Though the researchers have commented on the original assignment of a D mechanism to be less clear cut, the most trivial deviations from simple kinetics cannot be upheld as convincing evidence for the D path. In 1982 Haim [53] reinvestigated the $Co(CN)_5OH_2^{2-}$–$N_3^-$ reaction and observed a clear first-order dependence of rate on $[N_3^-]$. This is contrary to his earlier observations but at par with that of Burnett and Gilfillan [52]. The deviations from first-order dependence on azide are believed to be caused by the presence of polymeric pentacyanocobaltate(III) species in the reacting solutions. The polymerization occurs during preparation of $Co(CN)_5OH_2^{2-}$ by the acid aquation of $Co_2O_2(CN)_{10}^{6-}$. Thus the switch-over of the functional dependence as shown by eqn. (18) to a simple first-order dependence on $[N_3^-]$ seems to destabilize the unambiguous approach to a true D mechanism. However, in view of the supporting studies, the assignment of the D mechanism is still upheld but a question now hangs over the true nature of a long-lived intermediate.

The pentacyanocobaltate(III) chemistry has been taken further by Abou-El-Wafe and Burnett [54]. They used an improved monitoring system, and computer modelling of the various kinetic parameters based on the simple D scheme:



In this scheme the charges have been omitted for brevity, and $L = Cl^-$, $OH_2$ and $L^1/L^2 = NCS^-$, $N_3^-$, $N_3H$ or DMSO.

Although the kinetic data are consistent with the requirements of a D mechanism in that the rate of hydrolysis of $Co(CN)_5Cl^{3-}$ and $Co(CN)_5(N_3H)^{2-}$ are both unaffected by added nucleophiles, the efficiency of nucleophiles ($N_3^-$, $NCS^-$ and DMSO) in combining with the intermediate $Co(CN)_5^{2-}$ largely depends on the ion from which the intermediate is formed, $Co(CN)_5OH_2^{2-}$, $Co(CN)_5Cl^{3-}$ or $Co(CN)_5N_3H^{2-}$. This behaviour is more compatible with an $I_d$ rather than a D path. On the basis of the observations of Abou-El-Wafe and Burnett, it is worth probing into the "nucleophilic efficiency factor" by computer modelling of the kinetic data derived from some other nucleophiles.

Substitution of coordinated water in *trans*-$Co(CN)_4(SO_3)OH_2^{3-}$ by a wide range of neutral, monoanionic and bianionic nucleophiles has been undertaken in detail [55,56]. Assuming medium (water) effects are negligible, the relative reactivity order of the nucleophiles towards the five-coordinate intermediate $Co(CN)_4(SO_3)^{3-}$ is $I^- >$ py $>$ 4-methylpy $\approx$ 4-acetylpy $>$ $NCS^- > NH_3 > N_3^- > CH_3NH_2 > NO_2^- > CN^- > HSO_3^- > S_2O_3^{2-} > SO_3^{2-} > H_2O$. The observed reactivity pattern matches with neither the basicity nor the polarizability order of the nucleophiles. The major factor influencing the reactivity pattern is the presence of coulombic repulsion between the incoming nucleophile and the negatively charged intermediate. The suggested mechanism (D) may be corroborated by further studies, e.g. solvation effects, activation volume measurement and water exchange rate of *trans*-$Co(CN)_4(SO_3)OH_2^{3-}$. The existing kinetic data have been summarized [55,56].

## E. REACTIONS OF COBALOXIMES AND AQUACOBALAMINS

Cobaloximes and other cobalt(III) complexes of dioximato ligands are considered to be the models for cobalamins, which may account for the recent growth of work [57] related to studies of cobalamins and vitamin-$B_{12}$. A review of the kinetics and mechanism of substitution reactions of *trans*-$CoL_2XY^{n+}$ (L = dioxime; X and Y = unidentate ligands) complexes has been published by Samus and Ablov [58]. A series of papers illustrating the kinetics of formation of *trans*-$Co(dmgH)_2XY^{n+}$ and other dioximato complexes of cobalt(III) (X and Y are unidentate ligands, e.g. $NCS^-$, $CN^-$, $Cl^-$, $Br^-$, $NH_3$, $SO_3^{2-}$, tu, py etc.) has recently been published [59]. Most of these reactions have been assigned to a D mechanism without any reasonable argument regarding its applicability. Results obtained from kinetic studies on the water substitution reactions of some alkylaquacobaloximes, $RCo(dmgH)_2(OH_2)_2$ ($R = CH_3$, $CH_2Cl$, $CF_3CH_2$) by several nucleophiles, e.g. $NH_3$, $NCS^-$, imidazole and morpholine in aqueous media suggest a mechanism involving the direct replacement of coordinated water [60]. At high nucleophile concentration, pre-equilibrium association of the cobalt(III) substrate with $NH_3$, morpholine and imidazole is also evident according to the following scheme:

$$RCo(DH)_2(OH_2) + L \overset{K}{\rightleftharpoons} RCo(DH)_2(OH_2)L \tag{24}$$

$$RCo(DH)_2(OH_2) + L \xrightarrow{k_1} RCo(DH)_2L + H_2O \tag{25}$$

$$RCo(DH)_2(OH_2)L \xrightarrow{k_2} RCo(DH)_2L + H_2O \tag{26}$$

An alternative D scheme of the type

$$\mathrm{RCo(DH)_2(OH_2)} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{RCo(DH)_2 + H_2O} \tag{27}$$

$$\mathrm{RCo(DH)_2 + L} \xrightarrow{k_4} \mathrm{RCo(DH)_2L} \tag{28}$$

is considered untenable as the $k_3$ values are strongly dependent on the nature of L, contrary to the expectation of a purely dissociative process. The degree of association follows the order imidazole > morpholine ⩾ $NH_3$. No such prior association has been observed for $NCS^-$. This suggests that the interaction between the substrate and the nucleophile cannot be caused by electrostatic or polarization forces since the charged ligand does not associate with the neutral complex. A possible mode of interaction is a hydrogen bond between the planar chelate ring and nucleophile. In such a case the distance of the interaction site from the coordination position would lead us to think that the associated form would be quite unreactive and that eqn. (25) would be the main reaction pathway. The same group of workers [61] has proposed a conjugate base mechanism for the axial water substitution of some organocobaloximes, $\mathrm{RCo(dmgH)_2(OH_2)}$ ($R = CH_3$, $CH_2Cl$ and $C_2H_5$), in aqueous solution by $NH_3$. The behaviour of these complexes in an alkaline medium has been interpreted as the result of two counterbalancing effects: a decrease in reactivity owing to the formation of an inert hydroxo complex and an enhancement in the reactivity owing to the formation of the conjugate base, identified as the species deprotonated at the equatorial ligand system. The possible existence of any thermodynamically distinct pentacoordinate species of alkylcobaloxime in solution has not been taken into consideration. The kinetics, equilibria and thermodynamics of the axial ligation of a series of substituted alkylcobaloximes by pyridine and dimethoxyethylamine (DEA) have been measured in aqueous solution by Brown and Awtrey [62]. Free-energy correlations of the equilibrium constants for DEA ligation, equilibrium constants for $OH^-$ ligation and the enthalpy and entropy of DEA ligation with the Taft polar substituent constant $\delta^*$ for the cobalt-bound alkyl groups are all distinctly non-linear. These results have been interpreted in terms of a mechanism for axial ligand substitution involving a pre-equilibrium dissociation of axial water to form a five-coordinate alkylcobaloxime, followed by addition of the incoming ligand to this pentacoordinate species (D mechanism). The earlier work [63] of these researchers presents three convincing lines of evidence for the occurrence of some type of thermodynamically distinct pentacoordinate species of alkylcobaloxime in aqueous solution: (1) the spectral characteristics of the alkylcobaloxime series; (2) temperature dependence of the spectra for the alkylcobaloxime series; (3) non-linear free-energy relationships. It has proved extremely difficult prior to this study to detect and measure this type of equilibrium and this study should be considered as well-documented literature on this aspect.

Espenson and Russel [64] have studied the reaction of *trans*-$C_2H_5Co(dmgH)(OH_2)$ with $M(CN)_6^{n-}$ ($M = Fe(II), Fe(III), Co(III)$ and $Cr(III)$). The product in each case (1 : 1) corresponds simply to the displacement of water, $C_2H_5Co(dmgH)_2CNM(CN)_5^{n-}$, except that a slower secondary process is noted for $Cr(CN)_6^{3-}$. To fit the reactions with $M(CN)_6^{n-}$ ($= L$) to a D mechanism, the kinetic equations would assume the following forms:

$$R(Co)OH_2 \rightleftharpoons [R(Co)] + H_2O \quad k_1, k_{-1} \tag{29}$$

$$[R(Co)] + L \rightleftharpoons R(Co)L \quad k_2, k_{-2} \tag{30}$$

$$k_{obs} = \frac{(k_1k_2/k_{-1})[L] + k_{-2}}{1 + (k_2/k_{-1})[L]} \tag{31}$$

To fit the reactions to an $I_d$ mechanism the following sequence must be assumed:

$$R(Co)OH_2 + L \rightleftharpoons [R(Co)OH_2 \cdots L] \quad K_{OS} \tag{32}$$

$$[R(Co)OH_2 \cdots L] \rightleftharpoons R(Co)L + H_2O \quad k_3, k_{-3} \tag{33}$$

$$k_{obs} = \frac{(k_3 + k_{-3})K_{OS}[L] + k_{-3}}{1 + K_{OS}[L]} \tag{34}$$

The experimental kinetic data for the equilibrium take the simple form of the rate equation:

$$k_{obs} = k_f[L] + k_r \tag{35}$$

which may result from the D scheme with $(k_2/k_{-1})[L] \ll 1$ or from the $I_d$ scheme with $K_{OS}[L] \ll 1$. The computed values for $k_2/k_{-1}$ at 25 °C are 64 $M^{-1}$, 66 $M^{-1}$ and 110 $M^{-1}$ for $Co(CN)_6^{3-}$, $Fe(CN)_6^{3-}$ and $Cr(CN)_6^{3-}$ respectively, and are inconsistent with the requisite inequality as in the D scheme; the rather approximate constancy of the quantity $k_f (= (k_3 + k_{-3})K_{OS})$ for $M(CN)_6^{3-}$ reactions indicates a common $I_d$ mechanism to be operative. That $k_3$ for $M(CN)_6^{3-}$ is tenfold greater than $k_3$ for $Fe(CN)_6^{4-}$ has been explained by the greater difficulty in the dissociation of the water molecule owing to additional hydrogen bonding to the entering ferrocyanide. However, no experimental evidence has been presented for such an effect.

The kinetics of axial ligation by ammonia of a series of complexes of the type *trans*-$\{RCo[(DO)(DOH)pn]OH_2\}^+$ ($R = CH_3$, $C_2H_5$ and $C_6H_5$; (DO)(DOH)pn = diacetylmonoxime diacetylmonoximato propane-1,3-diyldiimino) have been measured [65] in aqueous solution as a function of $[\mathrm{OH}^-]$. The kinetic data indicate that a conjugate base mechanism of the type shown below is operative:

$$\begin{array}{ll}
 & \{\mathrm{RCo[(DO)_2pn]OH}\}^- \\
 & \qquad\qquad \uparrow\downarrow\ +2\,\mathrm{OH}^-, K_3 \\
\{\mathrm{RCo[(DO)(DOH)pn]OH}\} \rightleftharpoons & \{\mathrm{RCo[(DO)(DOH)pn]OH_2}\}^+ \\
 & \xrightleftharpoons{+\mathrm{OH}^-, K_2} \quad \{\mathrm{RCo[(DO)_2pn]OH_2}\} \\
 & +\mathrm{H_2O}, K_{-\mathrm{a}}\ \uparrow\downarrow\ +\mathrm{NH_3}, K_\mathrm{a} \\
 & \{\mathrm{RCo[(DO)(DOH)pn]NH_3}\} \\
 & \xrightleftharpoons{+\mathrm{OH}^-, K_\mathrm{cb}} \quad \{\mathrm{RCo[(DO)_2pn]NH_3}\}
\end{array}$$

The kinetic *trans* effect increases in the sequence $\mathrm{R} = \mathrm{C_6H_5} < \mathrm{CH_3} < \mathrm{C_2H_5}$ which can be attributed to an increasing donor character of the R group. This sequence suggests dissociative-type character. The thermodynamic *trans* influence also follows the same sequence and is reflected by the equilibrium constants for ammonia ligand binding and by the $\mathrm{p}K_\mathrm{a}$ values of the aqua complexes. It would have been interesting to extend the work to other aqua systems having planar chelate rings containing a potentially acidic function to verify the present scheme. The same group has measured [66] the activation parameters for the axial water substitution reactions in $\{\mathrm{RCo(DH)_2OH_2}\}$ $(\mathrm{R} = \mathrm{CH_3})$ and $\{\mathrm{RCo[(DO)(DOH)pn]OH_2}\}^+$ by $\mathrm{NCS}^-$, $\mathrm{NH_3}$ and tu. Comparing their results with the activation parameters of the corresponding reactions of aquacobalamin [67], the researchers have emphasized that the lability of the biological complexes arises mainly from entropy effects. The same conclusion has also been reached by Thusius [68] from a detailed study on the rates of formation and dissociation of a number of cobalamins CBM–L ($\mathrm{L} = \mathrm{SCN}^-$, $\mathrm{SO_3^{2-}}$, $\mathrm{S_2O_3^{2-}}$, $\mathrm{NCO}^-$, $\mathrm{N_3^-}$, $\mathrm{I}^-$ and $\mathrm{Br}^-$). The possible effects of the bulkiness of the axial group ($\mathrm{CH_3}$ and $\mathrm{C_2H_5}$) or the steric strain of the equatorial ligand are based on relatively scanty data, although such effects are quite reasonable.

Rate and equilibrium constants for the interaction of L-cysteine with vitamin $\mathrm{B_{12a}}$, bzm–Co–$\mathrm{OH_2}$ (bzm = benzimidazole), have been determined by Nome and Fendler [69] in aqueous solutions both in the absence and presence of air as functions of pH, buffer concentration and temperature. It is of interest to note that the L-cysteinate is 4–5 times more reactive than the neutral L-cysteine towards both the aqua and hydroxo forms of vitamin $\mathrm{B_{12a}}$. Similarly aquacobalamin is 8–9 times more reactive than hydroxocobalamin with both L-cysteine and L-cysteinate ions. Activation parameters for the anation are calculated from the temperature dependence of apparent rate constants at pH 5.0 and 5.5. The values obtained ($\Delta H^{\neq} = 14.9 \pm 0.3$ kcal $mol^{-1}$ and $\Delta S^{\neq} = -3.6 \pm 2.0$ cal $K^{-1}$ $mol^{-1}$) closely resemble those determined for a variety of ligands with vitamin $B_{12a}$, consistent with a D-type mechanism which involves the dissociation of water in the rate-determining step, or with outer-sphere complex formation in which a fast exchange occurs. No attempt has been made to delineate the two mechanisms. The substitution kinetics of vitamin $B_{12a}$ with 8-azaguanine and 6-mercaptopurine have been investigated [70] in aqueous media at 25 °C and ionic strength 0.1 M. The complex pH dependence is interpreted in terms of reactions of the "base on" aquacobalamin with protonated and deprotonated forms of the ligands. Rate constants are consistent with an $I_d$ mechanism. The addition of cyanide to cyanocobalamin proceeds through addition of $CN^-$ above pH 9 and a threefold slower addition of HCN between pH 6 and 8. Below pH 6, there is a change in the rate-limiting step that is attributed to a slow rotation of bound $CN^-$ [71]. The rate of cyanide addition to aquacobalamin shows a positive deviation in hydrochloric acid (up to threefold in 1 M HCl) that reflects an unusual H-acidity function for the ionization of HCN. The researchers have offered a very useful comparison in terms of Gibbs energy diagrams to illustrate how the choice of an $I_d$ or a D mechanism depends on the lifetime of the pentacoordinate intermediate, and finally all the different kinetic patterns have been singly accommodated to an $I_d$ mechanism.

In a series of papers [72–77] on the reactivity of vitamin $B_{12}$ and model compounds, Balt and coworkers have attempted to obtain insight into the factors that determine the solvent dependence of the kinetic parameters by separating the solvent effects in initial state and transition state contributions by combining kinetic data with solubilities of reactants. It has been shown that the influence of solvent composition on the axial ligand substitution reactions of vitamin $B_{12}$ is rather small. The reactions of these complexes with thiourea and the thiocyanate ion in dioxane–water and acetonitrile–water mixtures have been examined. The solubilities provide interesting information on solvation effects. From these studies it can be concluded that vitamin $B_{12}$ essentially creates a fairly constant chemical microenvironment resulting in solvent effects on activation parameters, whereas the ground state parameters vary much more. To compare these effects with the properties of model compounds such as the cobaloximes, a study has been performed on the reactivity of vitamin $B_{12}$ and aquamethylcobaloxime towards several neutral sulphur-coordinating ligands [74]. From this study it has been suggested that the solvent effects on this model compound are comparable with those on vitamin $B_{12}$ but the kinetic parameters are more influenced by steric factors and hydrogen bonding in the case of vitamin $B_{12}$. In both water and 50 vol.% dioxane–50 vol.% water mixture, a linear free-energy relationship with unit slope has been noticed for the two complexes, indicating a dissociative mode of activation. A very recent paper [78] by Balt et al. describes solvent effects on the axial ligand substitution reaction of the model compound aquanitrocobaloxime, $[Co(dmg)_2(NO_2)(OH_2)]$, with thiourea in terms of transfer Gibbs energies, enthalpies and volumes of activation. The activation enthalpy and entropy have been shown to vary with solvent composition. This is in contrast with the variations found for vitamin $B_{12}$. Another difference is that the rate constants with vitamin $B_{12}$ increase strongly with more than 50 vol.% dioxane in the dioxane–water mixtures. An explanation put forward for this different behaviour is that the reaction gradually changes from $I_a$ to $I_d$ when the medium becomes apolar, in accord with the gradual change of the activation entropy from negative to positive. The volumes of activation (both in water and in 20 vol.% dioxane–80 vol.% water) are small and positive in accordance with a dissociative or dissociative interchange mechanism. The dissociation path is supported by earlier observations of Hasinoff [79] who obtained a small positive activation volume in the binding of iodide to vitamin $B_{12}$ in aqueous medium from a high pressure laser T-jump study. Studies of the axial ligand binding of other donors (both N or O) in solvent mixtures may lend additional support to the present state of knowledge.

A study [80] on the kinetics and thermodynamics of the reactions of *trans*-$[Co(PnAO{-}H)(NO_2)(OH_2)]^+$ with $N_3^-$ and $NO_2^-$ showed that the reactions are abnormally fast. An unexpected dependence on the hydroxide ion concentration is observed for anation of the aqua complex and for isotopic exchange studies, but not for water exchange in the aqua complex. This has been attributed to unidentified conjugate base formation. No evidence for any nitrito intermediate has been obtained during nitrite anation. The reactions reach a limiting rate at high anion concentrations, in agreement with the proposed D mechanism:

$$[R(NO_2)(OH_2)]^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [R(NO_2)]^+ + H_2O \tag{36}$$

$$[R(NO_2)]^+ + X^- \xrightarrow{k_3} [R(NO_2)X] \tag{37}$$

where $R = Co(PnAO{-}H)$.

For $X^- = N_3^-$, $10^2 k_1 = 1.17\ s^{-1}$ and for $X^- = NO_2^-$, $10^2 k_1 = 1.21\ s^{-1}$ at pH 7.5, $I = 0.55$ M and a temperature of 25 °C. Values of the respective discriminating factors $k_2/k_3$ are 0.023 $M^{-1}$ and 0.112 $M^{-1}$ under identical conditions. The value of $k_1$ is comparable with the solvent exchange rate but unfortunately this has to be determined under different conditions. At 0 °C, pH 7.8 and $I = 0.24$ M, the water exchange rate is $4.65 \times 10^{-4}\ s^{-1}$. The abnormally high rate and unusual $[OH^-]$ dependence of the reactions seem justified owing to the ground state distortion of the octahedron around cobalt(III) as has been indicated from its solid state X-ray crystal structure [81].

## F. REACTIONS OF COBALT(III) COMPLEXES CONTAINING MORE THAN ONE AQUA LIGAND

The anation reactions of *cis*-diaquacobalt(III) complexes, e.g. $Co(NH_3)_4(OH_2)_2^{3+}$, $Co(en)_2(OH_2)_2^{3+}$, $Co(trien)(OH_2)_2^{3+}$ etc. with oxalic acid have been the subject of several papers [82–89]. In all these studies the researchers have put forward a mechanism in which the anation of diaquacobalt(III) cation by both oxalic acid ($H_2C_2O_4$) and bioxalate ion ($HC_2O_4^-$) involves outer-sphere ion-association equilibria between the reacting species followed by a rate-determining outer-sphere to inner-sphere interconversion process by an $I_d$ path. The final product is formed very rapidly by subsequent chelation. The general reaction scheme and the rate law of such reactions may be described as follows:

$$\mathrm{CoL(OH_2)_2^{3+}}\left\{\begin{array}{lcl} +\,\mathrm{H_2C_2O_4} & \overset{Q_1}{\rightleftharpoons} & \mathrm{CoL(OH_2)_2^{3+},\ H_2C_2O_4} \\ K_1 \downarrow\uparrow & & K_2 \downarrow\uparrow \\ +\,\mathrm{HC_2O_4^-} & \overset{Q_2}{\rightleftharpoons} & \mathrm{CoL(OH_2)_2^{3+},\ HC_2O_4^-} \end{array}\right\} \xrightarrow{k_0} \begin{array}{l}\mathrm{CoL(C_2O_4)OH_2^+} \\ +\,\mathrm{H_2O + H^+}\end{array}$$

$$\mathrm{CoL(C_2O_4)OH_2^+} \xrightarrow{\text{fast}} \mathrm{CoL(C_2O_4)^+ + H_2O}$$

$$k_{\text{obs}} = \frac{k_0 Q_1 (K_2 + [\mathrm{H^+}])[\mathrm{H_2C_2O_4}]_T}{Q_1(K_2 + [\mathrm{H^+}])[\mathrm{H_2C_2O_4}]_T + K_1 + [\mathrm{H^+}]} \tag{38}$$

where L = trien or $(en)_2$ or $(NH_3)_4$.

A hydrogen-bonding interaction has been attributed in the association of oxalic acid with *cis*-$Co(en)_2(OH_2)_2^{3+}$ [90].

An $I_d$ mechanism has been proposed [91] for the anation reaction of *cis*-$Co(NH_3)_4(OH)(OH_2)^{2+}$ by $NCS^-$ leading to the formation of *cis*-$Co(NH_3)_4(OH)(NCS)^+$. An extraordinary lability of the aquahydroxo complex relative to its diaqua or dihydroxo analogue has been encountered. This is also evident from the *cis–trans* isomerization [92] and ammonia substitution [93] reaction of *cis*-$Co(NH_3)_4(OH)(OH_2)^+$. Recent studies by Banerjee and coworkers [94–96] on the anation reactions of *cis*-$Co(NH_3)_4(OH_2)_2^{3+}$ with $NO_2^-$, $N_3^-$ and $NCS^-$ have shown that all these reactions are biphasic, corresponding to the replacement of two coordinated aqua ligands. The lability of the hydroxoaqua complex over its diaqua analogue is of the order of $3 \times 10^3$ and 16 for the first aqua ligand substitution reactions by $NCS^-$

and $N_3^-$ respectively. However, the reactivity of *cis*-$Co(NH_3)_4(OH_2)_2^{3+}$ and its conjugate base is the same for nitrite anation and for the second water substitution reactions by all three ligands. An $I_d$ mechanism has been put forward for all these reactions. A series of papers [96–99] by the same group has reported the anation reactions of this complex with a number of organic acids, e.g. salicylic, phthalic, iminodiacetic, acetic and succinic acids over wide pH ranges. The reactions with phthalic, iminodiacetic and succinic acids proceed in a single-step process owing to very fast ring closure. However, with acetic and salicylic acids consecutive reactions have been noticed. An $I_d$ mechanism has been suggested for all these reaction systems.

Anation reactions of $Co(en)_2(OH)(OH_2)^{2+}$ with a series of dicarboxylate anions of the general formula $C_nH_{2n}(COO)_2^{2-}$ ($n = 0$–$8$) have been reported [100]. Pal and De [101] have emphasized that both dissociative and associative mechanisms are operative in the water substitution reaction of *cis*-$Co(en)_2(OH_2)_2^{3+}$ with *o*-phenanthroline in aqueous ethanolic medium. In a recent report [102] on the formation of *trans*-$Co(en)_2(S_2O_3)_2^-$ from *cis*-$Co(en)_2(OH_2)_2^{3+}$ and $S_2O_3^{2-}$ in neutral aqueous medium, it has been proposed that, although the diaqua complex exists in solution in various isomeric hydroxoaqua and dihydroxo forms, only the *cis* diaqua form is reactive. *Trans*-$Co(en)_2(S_2O_3)_2^-$ is the final product, with probable formation of the intermediate *cis*-$Co(en)_2(S_2O_3)(OH_2)^+$. The reaction proceeds through ion pair formation ($I_d$) in both stages of the reaction. Activation parameters for the first stage of the reaction are in conformity with those obtained in other reactions involving the replacement of an aqua ligand from a $Co(en)_2^{3+}$ complex, but those of the second stage are low by cobalt(III) standards and indicate a high *trans* labilization due to substitution of the first $S_2O_3^{2-}$ on the complex. This also explains the *trans* structure of the final product. An $I_d$ path has also been suggested for the water substitution reaction of the same complex by picolinic acid in a water–ethanol medium [103]. The chloride anation of *cis*-$Co(NH_3)_2(OH_2)_4^{3+}$ and $Co(en)(OH_2)_4^{3+}$ has been found [104,105] to follow a conjugate base mechanism.

Two recent reports [106,107] have shown that in the biphasic anation of *cis*-$\beta$-$Co(trien)(OH_2)_2^{3+}$, the hydroxoaqua species is about $3.5 \times 10^3$ and $6 \times 10^2$ times more reactive than its diaqua analogue with thiocyanate and thiourea respectively. Krishnamurthy et al. [108] have studied the kinetics of aqua ligand substitution of $Co(tren)(OH_2)_2^{3+}$ by adenine and have observed that the reaction is controlled by the loss of water molecule followed by rapid ring closure. Recently the anation reactions of $Co(salen)(OH_2)_2^+$ with various nucleophiles, e.g. pyridine, thiourea, imidazole, morpholine, aniline, $NCO^-$, $HSO_3^-$ and $S_2O_3^{2-}$ have been studied [109] in aqueous solution. The monosubstitution reactions have been found to be very fast with second-order rate constants nearly independent of the nature of the incoming ligand. Taking into account the X-ray structural results for some similar Co(salen) complexes the researchers have proposed that conformational changes of the chelate ring probably occur during the substitution process, resulting in a large distortion of the transition state which, in turn, facilitates the rupture of the Co–OH$_2$ bond. A *cis* labilization effect of the coordinated hydroxo group has been observed in the anation reactions of *cis*-Co(BigH)$_2$(OH$_2$)$_2^{3+}$ with biguanide [110] and phenylbiguanide [111] where no ion pair formation takes place. The researchers have demonstrated that multiple hydrogen bonding is responsible for the association of the reactants. Thacker and Higginson [112] have proposed a limiting dissociative (D) mechanism for the substitution reactions of *cis*-Co(nta)(OH$_2$)$_2$ with NCS$^-$ and NO$_2^-$. Ghosh and Banerjee have studied the reaction of the same complex with imidazole and benzimidazole [113]. Both reactions produce a bisubstituted product but the entry of the first ligand is rate determining in each case. The pH dependence of the rate shows that the neutral ligand reacts with both the acid and base forms of the complex, the reactivity of the base form being slightly higher in each case. The water exchange rate constant $k_{ex}$ of Co(nta)(OH$_2$)$_2$ is not available at present. However, it is not likely to be widely different from that of *cis*-Co(en)$_2$(OH$_2$)$_2^{3+}$ having $k_{ex} = 7.7 \times 10^{-5}$ s$^{-1}$ at 40 °C or that of the aquapentaamminecobalt(III) ion having $k_{ex} = 1 \times 10^{-4}$ s$^{-1}$ at 45 °C ($I = 0.6$ M) [45]. The validity of the dissociative mechanism has been upheld by the observation that the rate constant $k_a$ for loss of coordinated water ($2.7 \times 10^{-5}$ s$^{-1}$ for imidazole and $3.7 \times 10^{-5}$ s$^{-1}$ for benzimidazole reactions at 40 °C and $I = 0.1$ M) agrees more or less

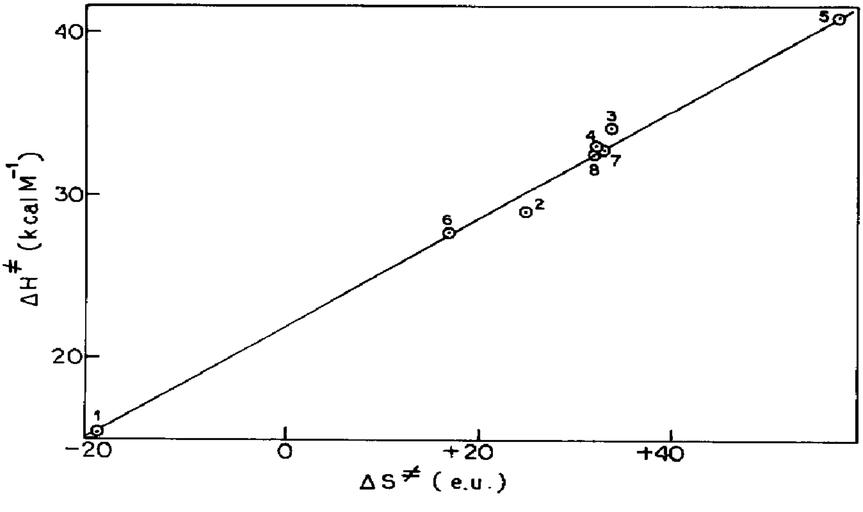


Fig. 2. Isokinetic plot for the water substitution reactions of *cis*-Co(NH$_3$)$_4$(OH$_2$)$_2^{3+}$ with 1, NO$_2^-$; 2, N$_3^-$; 3, NCS$^-$; 4, Hsal$^-$; 5, Hida$^-$; 6, Hph$^-$; 7, OAc$^-$; 8, Hsucc$^-$.

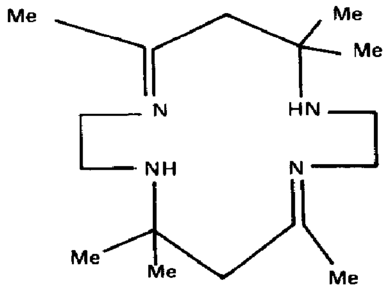
TABLE 4

Summary of rate and activation parameters for the anation reactions of cobalt(III) complexes containing more than one aqua ligand (proceeding through pre-equilibrium ion-pair formation)

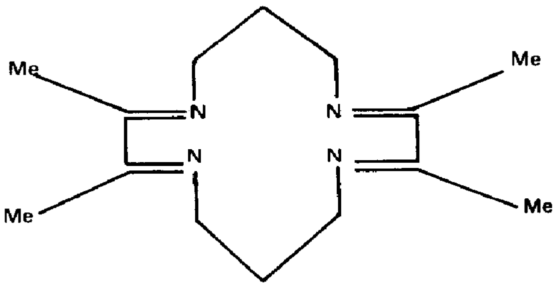
| Complex | Ligand | $T$ (°C) | $I$ (M) | $10^4k$ ($s^{-1}$) | $Q$ ($M^{-1}$) | $\Delta H^{\neq}$ (kcal $M^{-1}$) | $\Delta S^{\neq}$ (e.u.) | Ref. |
|---|---|---|---|---|---|---|---|---|
| *cis*-$Co(NH_3)_4(OH_2)_2^{3+}$ | $NO_2^-$ | 40 | 0.50 | 60.40 | 4.27 | 15.53 | −19.59 | 96 |
| | $N_3^-$ | 40 | 0.50 | 16.90 | 1.69 | 28.92 | 24.62 | 96 |
| | $NCS^-$ | 40 | 0.51 | 21.50 | 0.22 | 34.18 | 33.69 | 95 |
| | $Hsal^-$ | 39.8 | 0.50 | 7.50 | 2.68 | 32.98 | 32.26 | 96 |
| | $Hida^-$ | 40 | 0.50 | 5.60 | 1.00 | 40.63 | 57.12 | 98 |
| | $Hph^-$ | 40 | 0.50 | 10.00 | 1.20 | 27.72 | 16.73 | 97, 99 |
| | $ph^{2-}$ | 40 | 0.50 | 3.60 | 15.00 | | | 99 |
| | $OAc^-$ | 40 | 0.50 | 15.40 | 5.72 | 32.74 | 32.74 | 99 |
| | $Hsucc^-$ | 40 | 0.50 | 23.80 | 1.02 | 32.26 | 32.50 | 99 |
| | $succ^{2-}$ | 40 | 0.50 | 37.50 | 13.00 | | | 99 |
| | $H_2C_2O_4$ | 62.5 | 1.00 | 4.20 | 0.52 | | | 86 |
| | $HC_2O_4^-$ | 62.5 | 1.00 | 4.20 | 5.30 | | | 86 |
| | $C_2O_4^{2-}$ | 60 | 0.40 | 114.00 | 6.60 | | | 87 |
| *cis*-$Co(en)_2(OH_2)_2^{3+}$ | $H_2C_2O_4$ | 50 | 1.00 | 0.59 | 1.00 | 27.40 | 6.70 | 85 |
| | $HC_2O_4^-$ | 50 | 1.00 | 0.58 | 4.40 | 27.00 | 5.50 | 85 |
| | $pic^-$ | 45 | 0.10 | 6.20 | 2.30 | 25.60 | 7.00 | 103 |
| *cis*-β-$Co(trien)(OH_2)_2^{3+}$ | $H_2C_2O_4$ | 40 | 1.00 | 0.67 | 6.80 | 24.50 | 0.80 | 88 |
| | $HC_2O_4^-$ | 40 | 1.00 | 0.67 | | | | 88 |
| | $C_2O_4^{2-}$ | 40 | 1.00 | 70.00 | | 28.90 | 24.00 | 88 |
| | $NCS^-$ | 40 | 0.55 | 3.68 | 4.25 | 28.92 | 19.36 | 106 |
| | tu | 40 | 0.55 | 22.80 | 1.00 | | | 107 |
| *cis*-$Co(tn)_2(OH_2)_2^{3+}$ | $H_2C_2O_4$ | 40 | 1.00 | 10.73 | 1.70 | 29.30 | 21.39 | 89 |
| | $HC_2O_4^-$ | 40 | 1.00 | 11.00 | 11.50 | 24.81 | 7.00 | 89 |
| α-*cis*-$Co(EDDA)(OH_2)_2^+$ | $HC_2O_4^-$ | 38 | 0.50 | 0.12 | 41.00 | 27.60 | 1.60 | 82 |
| | $C_2O_4^{2-}$ | 38 | 0.50 | 0.12 | 72.00 | 27.60 | 1.60 | 82 |
| | $H_2C_2O_4$ | 62 | 0.50 | 1.77 | 4.90 | | | 83 |

with the above exchange rate parameters. The computed $K_{IP}$ (IP = ion pair) values for the imidazole substitution ($4.46 \times 10^4$ $M^{-1}$, $1.88 \times 10^4$ $M^{-1}$ and $2.15 \times 10^4$ $M^{-1}$ at 40 °C, 50 °C and 60 °C respectively at pH 6.10) are very large if we consider a 0,0 (for the diaqua species) or −1,0 (for the aquahydroxo species) interaction. These seem unreasonable for justifying an $I_d$ path. A pure D mechanism has been suggested. In a recent investigation [114] of the reaction of *cis*-$Co(NH_3)_4(OH_2)_2^{3+}$ with $Pd(CN)_4^{2-}$ it has been noticed that the reaction is fast when the complex species exists in hydroxoaqua form.

The kinetics of anation of *trans*-$Co(N_4)(OH)(OH_2)^{2+}$ complexes with acetate ion has been studied [115] in the pH range 3.6–5.2; $N_4$ represents the series of macrocyclic ligand cyclams, C-*meso*-$Me_6$[14]ane $N_4$, C-*rac*-$Me_6$[14]ane $N_4$, $Me_6$[14]4,11-diene $N_4$ (**1**) and $Me_4$[14]tetraene $N_4$ (**2**).



(1)



(2)

The reaction is considered to proceed by a D mechanism. Steric acceleration by the ring methyl substituents is observed. The anation of the cyclam complex with $Cl^-$ and $Br^-$ in an acetate buffer has also been studied. The relative effectiveness of entering ligands for the pentacoordinate intermediate follows the order $H_2O < OAc^- < Cl^- < Br^-$. The corresponding kinetic and thermodynamic data are presented in Table 4. Excellent linearity in the isokinetic plot for the anation of $Co(NH_3)_4(OH_2)_2^{3+}$ with various ligands shows that the reactions obey a common ($I_d$) mechanism (Fig. 2).

### G. REACTIONS OF COBALT(III) PORPHYRIN COMPLEXES

The substitution reactions of cobalt(III) porphyrins have been the subject of continuing interest [116–125]. The most dramatic kinetic manifestation of the porphyrin ligand is its influence on the rates of axial substitution. This marked *cis* effect may be the result of extensive mixing of metal ion *d* orbitals with $\pi$ orbitals of the porphyrin moiety (resulting from stabilization of the five-coordinate complex, presumed to form products en route, relative to the ground state of the complex). The substitution reactions of CoTMpyP with thiocyanate [116,117] and pyridine [118] are very much more rapid than the analogous processes for most cobalt(III) complexes, for example

$$\mathrm{CoP(H_2O)_2^{5+} + SCN^- \xrightarrow{2.1\ M^{-1}\ s^{-1}} CoP(H_2O)(SCN)^{4+} + H_2O} \qquad (39)$$

$$\mathrm{Co(NH_3)_5(H_2O)^{3+} + SCN^- \xrightarrow{1.3\times 10^{-6}\ M^{-1}\ s^{-1}} Co(NH_3)_5NCS^{2+} + H_2O} \qquad (40)$$

where P = TMpyP. Available evidence suggests that both the above reactions proceed by a dissociative mechanism in which the rate-determining step involves the breaking of a Co(III)–$OH_2$ bond. The rate constant for this step has been estimated as 2.5 $s^{-1}$ for the porphyrin complex and $7 \times 10^{-6}$ $s^{-1}$ for the ammine complex. A dissociative mechanism is also operative for the anation of $Co^{III}$TMpyP with $N_3^-$ and tmtu [119]. Pathways involving the diaqua and the aquahydroxo forms of the complex are detected but $[Co^{III}TMpyP(OH)_2]$ is unreactive, the order of metalloporphyrin reactivity being $CoP(H_2O)(tmtu)^{5+} \approx CoP(H_2O)(SCN)^{4+} \gg CoP(H_2O)(N_3)^{4+} > CoP(H_2O)(OH)^{4+} \gg CoP(H_2O)(py)^{5+} > CoP(H_2O)_2^{5+}$. The remarkable similarity between the *trans*-labilizing influence of tmtu and $SCN^-$ is consistent with the suggestion that $SCN^-$ (like tmtu) bonds to the metal site through a sulphur atom. The reactions have been assigned to proceed through either a D or an $I_d$ path. Other nitrogenous bases, both aromatic and non-aromatic, will have to be investigated to delineate these kinetic patterns. Ashley et al. [120] have studied the anation of $CoP(OH_2)_2^{5+}$ with $NCS^-$, $Br^-$, $I^-$ and $Cl^-$. From a comparison of the first stability constants and the rate constants for the reaction between the anating ligand and $CoP(OH_2)_2^{5+}$ at 25 °C, it was observed that the former parameter varies by a factor of 80000, whereas the latter varies by only a factor of 32. This is clearly indicative of a dissociative activation. Since there is kinetic evidence for an intermediate in the reaction with $NCS^-$, a D mechanism has been suggested for this reaction. The higher rates of anation of $CoTPPS_4(OH_2)_2^{3-}$ with $NCS^-$ and $I^-$ [121] compared with those of a previous report [120] have been ascribed to the increased availability of electron density on the cobalt(III) in the latter compared with that in the former. The reaction proceeds through an $I_d$ path. The reaction of $CoTPPS_4(OH_2)^{3-}$ with py [122] in the pH range 2–13 and that of $Co(TMpyP)(OH_2)_2^{5+}$ with $Co(CN)_6^{3-}$, $Fe(CN)_6^{3-}$, $Mo(CN)_8^{3-}$ and $W(CN)_8^{3-}$ [123] have also been reported. In general the results suggest a dissociative activation. The addition of a second py according to the reactions

$$\mathrm{CoTPPS_4pyOH_2^{3-} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} CoTPPS_4py^{3-} + H_2O} \qquad (41)$$

$$\mathrm{CoTPPS_4py^{3-} + py \overset{k_3}{\rightleftharpoons} CoTPPS_4(py)_2^{3-}} \qquad (42)$$

TABLE 5

Kinetic and thermodynamic parameters for the anation of cobalt(III) porphyrin complexes

| Complex | Ligand | $T$ (°C) | $I$ (M) | $k$ ($M^{-1}\,s^{-1}$) | $\Delta H^{\neq}$ (kcal $M^{-1}$) | $\Delta S^{\neq}$ (e.u.) | Ref. |
|---|---|---|---|---|---|---|---|
| Co(TMpyP)-$(OH_2)_2^{5+}$ | $NCS^-$ | 25 | 0.5 | 2.10 | 19.00 | 7.00 | 119, 120 |
| | py | 25 | 0.5 | 0.70 | | | 119 |
| | tmtu | 25 | 0.5 | 1.10 | | | 119 |
| | $N_3^-$ | 25 | 0.5 | 1.70 | | | 119 |
| | $HN_3$ | 25 | 0.5 | 0.30 | | | 119 |
| | $Cl^-$ | 25 | 0.5 | 0.09 | | | 120 |
| | $Br^-$ | 25 | 0.5 | 0.25 | | | 120 |
| | $I^-$ | 25 | 0.5 | 1.62 | 20.30 | 10.40 | 120 |
| | $Co(CN)_6^{3-}$ | 25 | 1.0 | 0.35 | 17.49 | −1.98 | 123 |
| | $Fe(CN)_6^{3-}$ | 25 | 1.0 | 0.54 | 15.77 | −6.69 | 123 |
| | $Mo(CN)_8^{3-}$ | 25 | 1.0 | 2.54 | 17.20 | 1.19 | 123 |
| | $W(CN)_8^{3-}$ | 25 | 1.0 | 3.73 | 15.53 | −3.82 | 123 |
| Co($TPPS_4$)-$(OH_2)_2^{3-}$ | py | 25 | 1.0 | 956.0 | 17.60 | 14.40 | 122 |
| | $NCS^-$ | 25 | 1.0 | 324.0 | 18.40 | 14.40 | 122 |
| | $I^-$ | 25 | 1.0 | 118.0 | 20.80 | 20.70 | 122 |

has been interpreted to generate a five-coordinate intermediate. None of the mechanistic assignments in this area has been backed up by comparison with the solvent (water) exchange rates. While investigating the complexation of $NCS^-$ by synthetic water-soluble cobalt(III) porphyrins both in the presence and absence of a neutral detergent, Williams and Hambright [124] observed that the neutral detergents increase the equilibrium formation constants and the rates of thiocyanate anation of cobalt(III) porphyrins by a factor of less than two. Funahashi et al. [126] have performed a high pressure study on the thiocyanate anation of diaqua[*meso*-tetrakis(*N*-methyl-4-pyridyl)porphinato]cobalt(III) ion. This work seems to be the first high pressure study of substitution with a metalloporphyrin. It has been concluded that the reaction proceeds through a dissociative mechanism. Negative pressure effects on the reaction makes an associative scheme untenable. The mechanism conforms to that of similar reactions [118,120] studied under ordinary conditions for which a rate-limiting Co(III)–$OH_2$ bond breaking has been suggested. The existing data are shown in Table 5.

## H. ANATION REACTIONS OF COBALT(III) COMPLEXES CATALYSED BY NITRATE ION

Nitrate-ion-induced anation reactions of some diaquacobalt(III) complexes with oxalate species ($H_2C_2O_4/HC_2O_4^-$) have recently been demonstrated by various workers [127–129]. It has been suggested [127] that the anation proceeds via the formation of a five-coordinate intermediate, facilitated by the nitrate ion which pulls off an aqua ligand. This effect results in an abnormally high ion pair formation constant in the nitrate medium [128]. The most reasonable reaction scheme suggested by van Eldik and Harris [127] for the nitrate-promoted anation of *cis*-$Co(en)_2(OH_2)_2^{3+}$ by oxalic acid is delineated as follows:

$$\textit{cis}\text{-}Co(en)_2(OH_2)_2^{3+} + H_2C_2O_4 \overset{Q_1}{\rightleftharpoons} \textit{cis}\text{-}Co(en)_2(OH_2)_2^{3+},H_2C_2O_4$$

$$\downarrow k_1$$

$$\textit{cis}\text{-}Co(en)_2C_2O_4^+ + 2\ H_3O^+ \tag{43}$$

$$\textit{cis}\text{-}Co(en)_2(OH_2)_2^{3+} + NO_3^- \xrightarrow{k_2} Co(en)_2(OH_2)^{3+} + NO_3^- + H_2O \tag{44}$$

$$Co(en)_2(OH_2)^{3+} + NO_3^- \xrightarrow{k_3} \textit{cis}\text{-}Co(en)_2(OH_2)(NO_3)^{2+} \tag{45}$$

$$Co(en)_2(OH_2)^{3+} + H_2C_2O_4 \xrightarrow{k_4} \textit{cis}\text{-}Co(en)_2(OH_2)(HC_2O_4)^{2+} + H^+ \tag{46}$$

$$\textit{cis}\text{-}Co(en)_2(OH_2)(NO_3)^{2+} + H_2O \xrightarrow{\text{fast}} \textit{cis}\text{-}Co(en)_2(OH_2)_2^{3+} + NO_3^- \tag{47}$$

$$\textit{cis}\text{-}Co(en)_2(OH_2)(HC_2O_4)^{2+} \xrightarrow[\text{ring closure}]{\text{fast}} Co(en)_2C_2O_4^+ + H_3O^+ \tag{48}$$

The overall rate law is given by eqn. (49):

$$k_{\text{obs}} = \frac{k_1Q_1[H_2C_2O_4]}{1 + Q_1[H_2C_2O_4]} + \frac{k_2k_4[NO_3^-][H_2C_2O_4]}{k_3[NO_3^-] + k_4[H_2C_2O_4]} \tag{49}$$

Although studies by a high pressure technique of water exchange between the bulk solvent and the *trans*-$Co(en)_2(OH_2)_2^{3+}$ ion show a dissociative interchange mechanism involving a tetragonal-pyramidal intermediate [130], the formation of a five-coordinate intermediate has been strongly supported by the volume of activation obtained [131] for the nitrate-promoted oxalate anation of *cis*-$Co(en)_2(OH_2)_2^{3+}$ which has been shown to follow a limiting dissociative (D) path. It has also been emphasized that the nitrate-ion-promoted process is not observed in the anation reactions of $Co(NH_3)_5(OH_2)^{3+}$ with a range of carboxylate ions and that this phenomenon arises from the interaction of two aqua ligands in *cis* positions. However, a recent study by Ghosh and Banerjee [132] has shown that in the stepwise anation reactions of *cis*-$Co(NH_3)_4(OH_2)_2^{3+}$ with $X^-$ ($X^- = NCS^-$ and $N_3^-$) a reasonable rate acceleration in nitrate medium occurs also for the second step, i.e. for the anation of *cis*-$Co(NH_3)_4X(OH_2)^{2+}$. Davies and Lethbridge [129] have observed a pH-dependent rate acceleration by nitrate ion while pursuing the anation reactions of *cis*-$Co(NH_3)_4(OH_2)_2^{3+}$ with oxalate. They have proposed a mechanism similar to that suggested earlier by van Eldik [128].

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