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STEREOCHEMISTRY AND REACTION RATES OF ANIONOPENTAAMINE COMPLEXES OF COBALT(III) AND CHROMIUM(III)

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CONTENTS

A. INTRODUCTION

Complexes of the $MCl(NH_3)_5^{2+}$ type have played an important role in the development of coordination chemistry. Such systems exist in only one geometric form (except where ^{14}N is replaced by one or more ^{15}N) but replacement of the coordinated NH_3 by a flexible quinquidentate polyamine ligand (such as tetren) will give the possibility of 15 isomers including all enantiomeric forms (Scheme 6). The isolation of these isomers would provide a

series of coordination compounds with constant central atom, charge and ligand, differing only in geometry. Substitution rates of the coordinated chloro ligand by water or hydroxide in such systems provide useful information as to the role of structure in the mechanism of the substitution.

In this review we will be concerned with the synthesis, structure, kinetics and mechanism and optical activity of $MX(N_5)^{n+}$ complexes (M = Co, Cr; X = aniono ligand or water; N = primary, secondary or tertiary amine donor). Because of the large amount of information available, certain aspects of the pentaammine complexes will not be covered in detail. The reader's attention is drawn to a recent review [1] which summarises the rates of ligand substitution for $MX(NH_3)_5^{n+}$ complexes.

Chemical Abstracts and most of the leading chemical journals have been searched through August 1976.

(i) Nomenclature

The nomenclature used is that recommended by the Commission on the Nomenclature of Inorganic Chemistry, Pure Appl. Chem., 28 (1971) 1. The prefixed lower case letters refer to the positions of the donor atoms in the octahedron (*a* and *f* in the axial positions) in the order in which they are written in the cation formula. The convention adopted here is that the polyamine ligands are coordinated stepwise from one end and in the order of the alphabetical letters. According to the above nomenclature system, chloro and aqua cations with the same geometric configuration should have different lettering systems due to the different alphabetical ordering of the donor atoms, e.g. *a, bc, def*-$CoCl(en)(dien)^{2+}$ and *ab, cdf, e*-$Co(en)(dien)(OH_2)^{3+}$ both have configuration I (Scheme 26). We believe that this can cause undue confusion and the lettering system used for the chloro complex will be retained in the aqua or hydroxo if the geometry is unchanged. The recommended nomenclature system does not distinguish between the alternative positions for the NH proton of the secondary amine group in a symmetric tridentate polyamine ligand coordinated meridionally. The system adopted here is to use (H↑) or (H↓) for this proton if it is adjacent to, or remote from the coordinated aniono or aqua ligand.

The term, ammine is used when ammonia is the coordinated amine; other nitrogen donor ligands, which may be regarded as organic derivatives of ammonia, are referred to in general as amines.

(ii) Abreviations and units

Abbreviations used in this work are listed in the Appendix. SI units have been used throughout, but mole $litre^{-1}$ (M) has been retained for the unit of concentration and Angstrom (Å), (1 Å = 10^{-10} m) for bond lengths. The symbols and values for the Fundamental Constants are those used by G.H. Aylward and T.J.V. Findlay, SI Chemical Data, John Wiley and Sons, Australasia Pty. Ltd., 1971.

(iii) Syntheses and kinetics

Many of the complexes considered in this review have been prepared for reaction rate studies and the synthetic procedure will be outlined if the method appears to be of general applicability. Most rate studies have been made in aqueous solution although there is a growing body of kinetic information on reactions in mixed and non-aqueous solvents.

Reactions involving replacement of one ligand by another, or one metal by another are called substitution reactions. Mechanistically, they can be quite complicated and many isomerisation or racemisation reactions are special cases of substitution reactions. The substitution reactions illustrated by eqn. (1) are known as aquation or acid hydrolysis reactions because

$$MCl(N_5)^{2+} + H_2O \rightarrow M(N_5)OH_2^{3+} + Cl^- \quad (1)$$

they are normally carried out in acidic solution. In such cases, the rate law can be expressed by eqn. (2) where k_{aq} is

$$\text{Rate} = k_{aq}[\text{complex}] \quad (2)$$

independent of the acidity (Table 1) but slightly dependent on ionic strength (μ). Exceptions to this occur when the leaving group is a basic ligand e.g. NO_2^-, N_3^-, F^- etc. where the rate increases with increasing acidity in a sometimes complicated manner (Table 2). Indeed, it is difficult to systematise this type of reaction because of the wide variety of experimental parameters that can be varied. Also, it would be unjustified to assume that even the reaction products from the hydrolysis of say $Co(NO_2)(NH_3)_5^{2+}$ could be compared, when the reaction medium is varied from NH_4^+/NH_3 buffers [2] to 15 M H_2SO_4 [3], let alone the rate parameters.

Probably, most "well behaved" acid catalysed hydrolysis reactions can be expressed in terms of the following reactions

$$CoX(NH_3)_5^{(3-n)+} + H_2O \overset{k_1}{\rightarrow} Co(NH_3)_5(OH_2)^{3+} + X^{n-} \quad (3)$$

$$CoX(NH_3)_5^{(3-n)+} + H^+ \overset{K_1}{\rightleftharpoons} CoXH(NH_3)_5^{(4-n)+} \quad (4)$$

$$CoXH(NH_3)_5^{(4-n)+} + H_2O \overset{k_2}{\rightarrow} Co(NH_3)_5(OH_2)^{3+} + HX^{(n+1)-} \quad (5)$$

$$CoXH(NH_3)_5^{(4-n)+} + H^+ \overset{K_2}{\rightleftharpoons} CoXH_2(NH_3)_5^{(5-n)+} \quad (6)$$

$$CoXH_2(NH_3)_5^{(5-n)+} + H_2O \overset{k_3}{\rightarrow} Co(NH_3)_5(OH_2)^{3+} + XH_2^{(n+2)-} \quad (7)$$

etc., where X^{n-} is a polyprotic anionic ligand.

Thus, (ionic charges omitted)

$$k_{obs}[\text{complex}]_{total} = k_1[CoX(NH_3)_5] + k_2[CoXH(NH_3)_5] + \ldots \quad (8)$$

$$k_{obs}\{[CoX(NH_3)_5] + [CoXH(NH_3)_5] + \ldots\}$$
$$= k_1[CoX(NH_3)_5] + k_1K_1[CoX(NH_3)_5][H^+] + \ldots \quad (9)$$

where K_1, K_2, ... are given by eqns. (4), (6) etc. Hence,

$$k_{obs}\{[CoX(NH_3)_5]\}\{[1 + K_1[H^+] + K_1K_2[H^+]^2 + ...\}$$
$$= \{[CoX(NH_3)_5]\}\{k_1 + k_2K_1[H^+] + k_3K_1K_2[H^+]^2 + ...\} \quad (10)$$

and

$$k_{obs} = \frac{k_1 + k_2K_1[H^+] + k_3K_1K_2[H^+]^2 + ...}{1 + K_1[H^+] + K_1K_2[H^+]^2 + ...} \quad (11)$$

By appropriate choice of acidity, particular values of k_n can be made to dominate the reaction and in favourable situations [4], all k_n and K_{n+1} can be evaluated.

Most studies, however, present data in the simplified form

$$k_{obs} = k_1 + k_2[H^+] \quad (12)$$

where k_2 is now the product of the rate and equilibrium constants in eqns. (4) and (5), e.g. for $X = N_3$ [5] or $X = F$ [6].

When k_3 becomes large, every act of protonation results in an hydrolysis step and eqns. (6) and (7) can be combined. Thus for $X = C_2O_4$ [7,8] or $X = CO_3$ [9], the rate law becomes

$$k_{obs} = \frac{k_1 + k_2K_1[H^+] + k_3K_1[H^+]^2}{1 + K_1[H^+]} \quad (13)$$

$$= \frac{k_1K_1'[H^+]^{-1} + k_2 + k_3[H^+]}{1 + K_1'[H^+]^{-1}} \quad (14)$$

where $K_1' = (K_1)^{-1}$ (15)

For halogeno complexes, the rate of aquation is considerably enhanced by the addition of halide abstractors, e.g. Hg^{2+}, Tl^{3+} or Ag^+ to the acidic solution. These are technically not catalysts, as the initial and final states of the added reagent are different, but the term has crept into the literature. For Hg^{2+}, the rate law should probably be written as

$$-d[complex]/dt = k_{aq}[complex] + \sum_{x=0}^{x=4} k_{HgCl_x^{2-x}}\{[HgCl_x^{2-x}][complex]\} \quad (16)$$

as both Hg^{2+} and HgX^+ participate, the latter being about twice as effective [10,11].

Other reagents have also been used to assist the removal of a particular aniono ligand, e.g. HNO_2 (as NO^+) [12,13] reacts rapidly with the coordinated azido ligand to produce the aqua complex and MnO_4^- reacts similarly with coordinated DMSO [14]. Coordinated bromide reacts rapidly with HOCl or Cl_2 to give the analogous chloro complex [15].

As the acidity of the reaction medium drops, competition between (1) and

(17) (base hydrolysis) begins to occur, and at high pH, (17) becomes predominant.

$$MCl(N_5)^{2+} + OH^- \rightarrow M(OH)(N_5)^{2+} + Cl^- \quad (17)$$

Unfortunately, a number of the systems described in this review have been studied only in aqeous solution with no added acid to prevent the often significant base hydrolysis contribution. The hydroxide ion generally reacts several orders of magnitude faster than H_2O (especially for Co(III), Table 9) and aquation rate constants and activation parameters reported for water will probably be composite.

For reaction (17), the rate law is usually of the form

$$\text{Rate} = k_{OH}[\text{complex}][OH^-] \quad (18)$$

and many base hydrolysis studies have been made under pseudo-first-order conditions with the $[OH^-]$ being maintained with buffers or a pH-stat. Considerable care is needed to ensure that the buffer system used does not take part in the reaction. An additional complication (also inherent in the pH-stat method) is that the acidity of the aqua ligand is appreciable both for Co(III) and Cr(III), and the reaction

$$M(OH)(N_5)^{2+} + H_2O \rightarrow M(N_5)OH_2^{3+} + OH^- \quad (19)$$

can become kinetically important at pH values near the pK_a for the coordinated water (Table 21). This is especially true for reactions where k_{OH} is greater than 10^4 M^{-1} s^{-1} [16].

Base hydrolysis reactions are rather more sensitive to changes in ionic strength than aquation reactions and a number of investigators have reported data extrapolated to zero ionic strength. However, for *cis*-$CoCl(en)_2(amine)^{2+}$ complexes (Table 18), μ = 0.1 M appears to be the preferred medium.

Inspection of the Tables presenting base hydrolysis kinetic parameters (especially Table 8) allows some generalisations. The order of lability of the coordinated donor atom bound to Co(III) (as judged by the value of k_{OH} (298)) is: O (univalent oxo ligand) > I > Br > Cl > S > F ~ O (univalent carboxylate) > N and, as expected, increasing the negative charge on the leaving group causes a decrease in reaction rate cf. NO_3^-, ReO_4^- and SO_4^{2-}, CO_3^{2-}, PO_4^{3-} or (less spectacularly) $CH_3CO_2^-$, HCO_2^- and $C_2O_4^{2-}$, $CH_2(CO_2^-)_2$.

Rate laws rather similar to those for acid catalysed aquation are observed for the anation of $M(N_5)(OH_2)^{3+}$ by aniono ligands (i.e., the reverse of eqn. (1)). Thus

$$k_{obs} = \frac{k_0[H_2X] + k_1Q_1[HX^-] + k_2Q_2[X^{2-}]}{1 + Q_1[HX^-] + Q_2[X^{2-}]} \quad (20)$$

for a dibasic anion, where the Q_i terms correspond to ion-pair formation constants such as

$$M(NH_3)_5(OH_2)^{3+} + HX^- \overset{Q_1}{\rightleftharpoons} [M(NH_3)_5OH_2 \cdot HX]^{2+} \quad (21)$$

Again, by suitable choice of conditions, one or other of the anating species can usually be made to predominate and the individual k_i, Q_i determined [17]. If the values for the rates of the forward and backward reactions of eqn. (1) are known, an equilibrium quotient, Q_E can be calculated.

$$Q_E = \frac{k_{\text{anation}}}{k_{\text{aquation}}} \tag{22}$$

It has been shown that plots of log k_{aq} [18—20] or log k_{OH} [21] vs. $-\log Q_E$ are linear with slopes = 1.0 (for M = Co(III)). It follows that there must also be a linear relationship of unit slope between log k_{aq} and log k_{OH}. Table 9 presents the "best available" data and Fig. 1 shows the log k_{aq} vs. log k_{OH} plot, together with a line of unit slope. The correlation is not ideal, but some of the aquation rate constants may be in error (e.g. the value plotted for NO_2 is for NH_3 loss, not NO_2^- loss [2]), especially for the more inert leaving groups. Also, it is important that only reactions involving Co—X bond rupture be compared, rather than hydrolysis of the coordinated ligand, and this may not always be the case for the systems plotted. A similar plot of log k_{aq} vs. log k_{OH} for $CrX(NH_3)_5^{2+}$ systems [22] shows even more scatter, but a slope of 0.71 ± 0.22 is obtained.

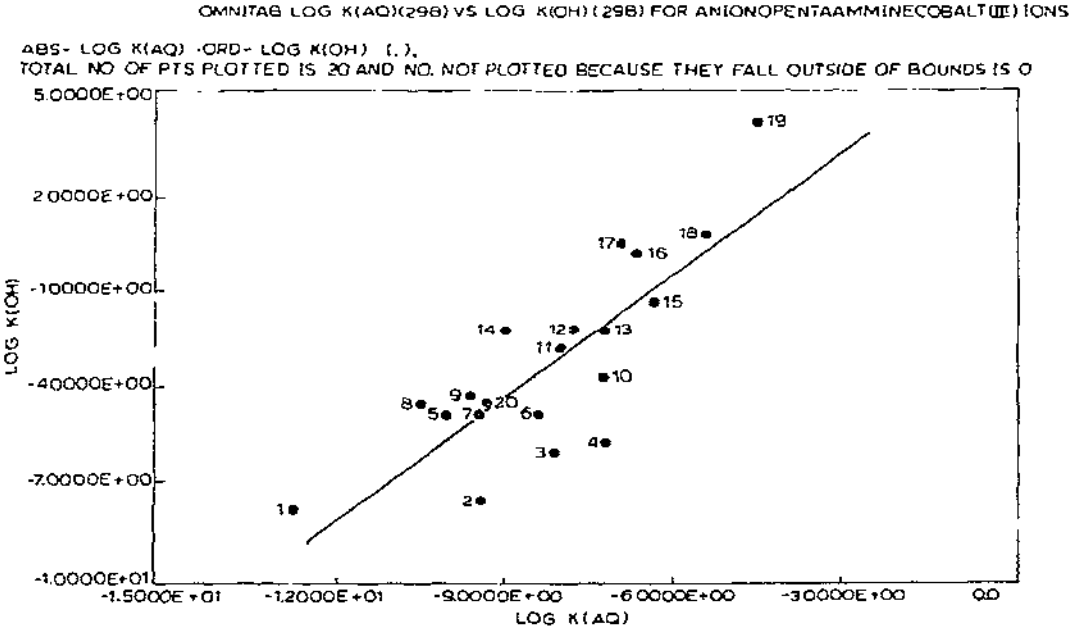


Fig. 1. A plot of log k_{aq} vs. log k_{OH} (298 K) for some $CoX(NH_3)_5^{n+}$ complexes. The line of best fit can be represented by the equation log k_{OH} = (1.29 ± 0.22) log k_{aq} + (7.35 ± 1.86). The numbers refer to the systems listed in Table 9.

The kinetic data obtained for rates of reduction of $MX(NH_3)_5^{n+}$ complexes by a variety of reducing agents (especially V^{2+}, Cr^{2+}, Eu^{2+} and Fe^{2+}) are nicely summarised in refs. 23—26 and the information will not be reproduced here. Interest centres in distinguishing between inner sphere and outer sphere electron transfer processes, and, if inner sphere, whether the attack is "adjacent" or "remote". The use of log—log rate plots appears to have considerable application, e.g., the data from 17 $CoX(NH_3)_5^{n+}$ systems for V^{2+} and Cr^{2+} outer sphere reductions gives the relationship [26]

$$\log k_V = 1.02 \log k_{Cr} + 1.73$$

Such equations should be useful in testing mechanistic proposals in the early literature [27,27a].

(iv) Reaction mechanisms

General aspects of inorganic reaction mechanisms are well covered in ref. 28 and only concepts that concern $MX(N_5)^{n+}$ systems will be discussed here.

Until recently, it was generally considered that aquation reactions proceeded via a dissociative mechanism (D). However, a recent review by Swaddle [29] has highlighted the accumulating evidence that it is probably only Co(III) complexes that aquate without some dissociative interchange (I_d). Kinetic parameters determined for some isomorphous $MCl(AA)(dien)^{2+}$ (M = Co, Cr) complexes appear to support this suggestion [30,31]. The nature of the 5-coordinate transition state in the aquation of $CoX(N_5)^{2+}$ systems remains speculative as most stereochemical changes have been established for dianionobis(ethylenediamine)cobalt(III) complexes. Tobe [32] has postulated that extensive stereochemical change, and consequently a trigonal bipyramid transition state, is associated with a large positive activation entropy, but only one $CoX(N_5)^{n+}$ complex was included in the systems considered. Tobe's postulation appears to be valid for the more limited Cr(III) data [33], but here no $CrX(N_5)^{n+}$ complexes were included.

Inspection of Tables 4, 5 and 17 shows that while most $CoX(NH_3)_5^{2+}$ and *cis*-$CoX(en)_2(A)^{2+}$ (A = amine) complexes aquate with retention of configuration and with negative values for the entropy of activation (thus via a tetragonal pyramid transition state by Tobe's theory), there is a disturbing trend to positive entropies of activation for bromo complexes. It would be surprising if the substitution of Br for Cl resulted in a change in transition state and we feel that the case for aquation via a tetragonal pyramid is not proven. If isomerisation were observed, a trigonal bipyramid transition state would be strongly implied, but the fact that no isomerisation or racemisation takes place during aquation does not exclude this intermediate [28, p. 250]. Indeed, we will discuss later situations where the rate data are more easily accounted for on the basis of a trigonal bipyramid intermediate for $CoCl(N_5)^{2+}$ systems.

As with aquation, there are also current controversies with regard to the mechanism of base hydrolysis [400]. An SN_1CB conjugate base mechanism [34,35] is probably the closest approach to the truth and the base hydrolysis

data from many $CoX(N_5)^{n+}$ systems have been analysed in terms of this mechanism. An essential feature of the mechanism is the availability of a potentially acidic proton on the metal complex. Such a feature is satisfied by all the complexes under the scope of this review. Indeed, there is usually the problem of deciding which of the many protons potentially available is the one involved in the major pathway. Proton exchange rates (Table 3), best measured by ^1H NMR techniques, are one means of deciding which is the most labile proton but it has been pointed out that the deprotonated species producing the lowest energy transition state may not necessarily be formed from the most labile site [36]. The observation that the rate of proton exchange is usually much faster than base hydrolysis is in keeping with the SN_1CB mechanism but does not constitute proof. Of more interest, are systems where the rates are comparable or where k_{OH} is greater than k_{exch} [37, 389,393]. In these cases, $k_{OH} > 10^4$ M^{-1} s^{-1} and every act of deprotonation leads to base hydrolysis

Although only limited data are available for the base hydrolysis of $CrX(N_5)^{2+}$ complexes, these present some problems for the conjugate base mechanism, as the rates are about 100 times slower than for the analogous Co(III) complexes (Tables 2 and 8) while the proton exchange rates for $MCl(NH_3)_5^{2+}$ are apparently similar (Table 3). To explain the rate decrease, either the conjugate base formed by the Cr(III) systems must be less labile or the reaction occurs via a more associative mechanism. The general arguments against an SN_1CB base hydrolysis mechanism for $CrX(N_5)^{2+}$ systems have been presented previously [33] but a convincing alternative has yet to be formulated.

(v) Data presentation

Most of the kinetic parameters cited in the following Tables have been recalculated (IBM 360/44) using OMNITAB II, N.B.S., Washington, D.C. (1971) from the k_{obs} vs. T data reported in the original literature. This was necessary as it was not always clear if the $\Delta H^{\neq}$ reported was actually $\Delta H_{298}{}^{\neq}$ or the calculated activation energy (E_a). The slopes (= E_a/19.148 kJ mol^{-1}) and intercepts (= log PZ) of plots of log k_{obs} (k_{obs} in s^{-1} or M^{-1} s^{-1}) vs. 1000 K^{-1} were calculated and $\Delta S_{298}{}^{\neq}$ was obtained using eqns. (23) and (24).

$$\Delta H_{298}{}^{\neq} = E_a - 2.49 \text{ (kJ mol}^{-1}\text{)} \tag{23}$$

$$k_{298} = (298.18\ k/h)\ e^{\Delta S_{298}{}^{\neq}/R} \cdot e^{-\Delta H_{298}{}^{\neq}/298.18\ R} \tag{24}$$

This treatment assumes that the medium used is defined as the standard state [38].

In concluding this section, we thoroughly recommend that the chapter on Errors, Precision and Accuracy in the review by Edwards et al. [1], be required reading for all who are interested in the measurement of reaction rates.

B. UNIDENTATE AMINE COMPLEXES

This group is dominated by the pentaammine series with an extensive chemistry of $MX(NH_3)_5^{n+}$ complexes [39]. The five ammonia groups give rise to only one geometric isomer, but the geometric isomers formed by replacement of one $^{14}NH_3$ by $^{15}NH_3$ have been characterised for Co(III) [36,40], (Scheme 1) and Cr(III) [42].

$$[Co(SO_3)(NH_3)_5]Cl\ [43] \xrightarrow{LiOH/EtOH} \textit{trans}\text{-}Co(OH)(SO_3)(NH_3)_4$$

$$\textit{trans}\text{-}Co(OH)(SO_3)(NH_3)_4 \xrightarrow{amine\,HCl/LiOH} \textit{trans}\text{-}[Co(SO_3)(NH_3)_4(A)]Cl$$

$$\textit{trans}\text{-}[Co(SO_3)(NH_3)_4(A)]Cl \xrightarrow{HCl/LiCl} \textit{trans}\text{-}[CoCl(NH_3)_4(A)]Cl_2$$

SCHEME 1. Synthetic sequence for *trans*-$CoCl(NH_3)_4(A)^{2+}$ (A = $^{15}NH_3$, $MeNH_2$) [40,44]. The lability of the starting material is apparently due to the effect of the S-bonded sulphite [41,45].

Apart from *trans*-$CoCl(NH_3)_4(MeNH_2)^{2+}$ [40] successive replacement of ammonia by other unidentate amines has not yet been reported and the other major class in this series is the pentakis(alkylamine) complexes. If the "arms" of the alkylamine in the MN_4 plane are arranged in a "handed" manner (clockwise or anticlockwise), it may be possible to separate complexes of this type into their chiral forms. The published structural details [46] of $[CoCl(MeNH_2)_5](NO_3)_2$ are not sufficient to establish this possibility rigorously, but they do not exclude it.

Tables 1–8 list the complexes synthesised and the kinetic parameters obtained for aquation, base hydrolysis and proton exchange. Of particular inter-

TABLE 1

Kinetic parameters for the aquation of some $MCl(RNH_2)_5^{2+}$ complexes

M	R	$10^6\ k_{aq}(298)$ (s^{-1})	log *PZ*	E_a (kJ mol^{-1})	$\Delta S_{298}^{\neq}$ (J K^{-1} mol^{-1})	Ref.
Co	H	1.77	11.19	96.7	−39.0	[a]
Cr	H	9.50	10.62	89.3	−50.0	[b]
Co	Me	36.7	11.65	91.8	−30.2	85,401
Cr	Me	0.248	13.15	112.8	−1.4	81,82
		0.252	12.11	106.7	−21.4	81
Cr	Et	0.493	11.89	103.9	−25.6	81,82
		0.491	12.41	106.9	−15.6	81
Cr	*n*Pr	1.16	12.83	107.1	−7.5	81
Cr	*n*Bu	2.03	13.05	107.0	−3.4	81
Co	*i*Bu	180				86
Cr	Allyl	0.253	13.25	113	+0.5	81

[a] Data from refs. 55–72a.

[b] Data from refs. 73–82a and 437. See also refs. 83–84a.

TABLE 2

Kinetic parameters for the base hydrolysis of some $MCl(RNH_2)_5^{2+}$ complexes

M	R	$k_{OH}(298)$ (M^{-1} s^{-1})	log PZ	E_a (kJ mol^{-1})	$\Delta S_{298}^{\neq}$ (J K^{-1} mol^{-1})	Ref.
Co	H	1.58	20.54	116	+140	a
Cr	H	1.85×10^{-3}	16.20	108.1	+57	81
Co	Me	3.4×10^{3}				85
		0.8×10^{3}		77.7	+71.5	94
Cr	Me	4.2×10^{-1}	17.66	102.9	+85	81
Co	Et	1.1×10^{3}		77.7	+74.8	94
Cr	Et	1.50	18.86	106.6	+108	81
Co	nPr	1.1×10^{4}				85
		0.56×10^{4}		73.6	+67.7	94
Cr	nPr	3.29	19.40	107.7	+118	81
Co	nBu	3.6×10^{3}		74.0	+71.5	94
Cr	nBu	9.24	19.62	106.5	+123	81
Co	iBu	1.5×10^{5}				85

[a] Data from refs. 55,87–93a at μ = 0.0 M.

est is the fact that $CoCl(MeNH_2)_5^{2+}$ aquates about 19 times faster than $CoCl(NH_3)_5^{2+}$, whereas $CrCl(MeNH_2)_5^{2+}$ aquates 38 times more slowly than $CrCl(NH_3)_5^{2+}$. This change in reactivity pattern has been interpreted as evidence for a change in mechanism (I_d for Co(III), I_a for Cr(III)) [29], but isomorphism between the alkylamine complexes has not been established.

TABLE 3

Proton exchange rates for some $MX(N_5)^{2+}$ complexes

Complex	T (K)	Proton	k_{exch} (M^{-1} s^{-1})	Ref.
$CoCl(ND_3)_5^{2+}$	298.2	*cis* [a]	5×10^{4}	86
	298.2	*trans* [a]	3×10^{6}	86
$CrCl(NH_3)_5^{2+}$	298.2	all (?)	9.5×10^{5}	80
$CoCl(MeNH_2)_5^{2+}$	298.2	*cis* [a]	3×10^{5}	86
	332.2	*trans* [b]	3×10^{7}	86
	298.2	*trans* [b,c]	1.4×10^{7}	86
trans-$CoCl(en)_2(NH_3)^{2+}$	?	*trans*	300 × *cis*	95
cis-$CoCl(en)_2(NH_3)^{2+}$	?	*trans*	200 × *cis*	95
sym-$CoCl(trenen)^{2+}$	307	*trans* [d]	5.6×10^{9}	95
sym-$CoN_3(trenen)^{2+}$	307	*trans*	1.3×10^{9}	95
p-$CoCl(tren)(NH_3)^{2+}$	298.2	*trans*	3.5×10^{7}	96
	298.2	NH_3	1×10^{5}	96
t-$CoCl(tren)(NH_3)^{2+}$	298.2	NH_3	3.2×10^{5}	96

[a] At μ = 0.2 M; [b] at μ = 0.8 M. [c] Estimated using E_a = 117 kJ mol^{-1}; [d] E_a = 117 kJ mol^{-1} (see ref. 97).

TABLE 4

Kinetic parameters for the aquation of some $MX(NH_3)_5^{n+}$ complexes I. Not acid catalysed

M	X	$k_{aq}(298)$ (s^{-1})	log PZ	E_a (kJ mol^{-1})	$\Delta S_{298}^{\neq}$ (J K^{-1} mol^{-1})	Ref.
Co	Cl	1.77×10^{-6}	11.19	96.7	−39	a
				98.0	−34.7	98
				97.8	−28	72
Cr	Cl	9.50×10^{-6}	10.62	89.3	−50	a
Co	Br	5.97×10^{-6}	12.20	99.5	−19.6	b
				97.7	−25	98
Cr	Br	1.13×10^{-4}	11.82	89.9	−26	80
		9.5×10^{-5}	10.06	80.4	−61	c
Co	I	8.3×10^{-6}		110	+49	112—113a
				100	−14	114
Cr	I	1.04×10^{-3}	12.70	89.4	−8	80,437
Co	NO_3	2.41×10^{-5}	13.40	102.8	+3.3	d
Cr	NO_3	7.0×10^{-4}		90.3	−12	115
		2.4×10^{-3} [f]	12.74	87.7	−9.4	116
Co	S_2O_3	1.6×10^{-7}		80.6	−104	117
Co	NCS	2.3×10^{-9}	13	108	−35	118
		3.6×10^{-10}		126	−3	119
Cr	NCS	9.4×10^{-8}		104	−33	73,118,119
Co	SCN → NCS	8×10^{-7}				120
	Cat. by Hg^{2+}					121
Co	ClO_4	8.1×10^{-2}				47
Co	CF_3SO_3	2.7×10^{-2}				47
Co	DMSO	2.0×10^{-5}	13.09	102	−2.6	111, 122—125
Co	DMF	4.2×10^{-6}		111	+16	127
Co	$OP(OMe)_3$	2.4×10^{-4}				128
Co	$OP(OBu)_3$	1.38×10^{-4}				128
Co	H_2O	6.1×10^{-6}	14.25	111	+19.7	129,130
Cr	H_2O	7.8×10^{-5}	11.11	86.9	−40.5	73
Co	NH_3 [e]	5.8×10^{-12}		153	+44.7	49
Cr	NH_3 [e]	4.3×10^{-11}	9.868	115.3	−65	50
		1.8×10^{-7}	11.641	105	−30	399

[a] See Table 1, footnotes [a] and [b].
[b] Data from refs. 55,64,67,99—105.
[c] Data from refs. 9,76,79,106—108a.
[d] Data from refs. 21,64,109—111a.
[e] At μ = 1.0 M.
[f] Evidence for NH_3 loss.

Tables 4—9 summarise the considerable body of kinetic data accummulated for $MX(NH_3)_5^{n+}$ complexes. Two important features should be noted. Firstly, there is the observation that perchlorate coordination can compete with water in rapidly aquating systems that are 1 M in ClO_4^- (Scheme 2) [47].

TABLE 5

Kinetic parameters for the aquation of some $MX(NH_3)_5^{n+}$ complexes
II. Acid catalysed. (For additional entries see Note added in proof)

M	X	Rate law	T (K)	k_1 [a]	k_2 [a]	E_a (kJ mol^{-1})	$\Delta S_{298}^{\#}$ (J K^{-1} mol^{-1})	Ref.
Co	F	$k_{obs} = k_1 + k_2[H^+]$	298.2	0.87×10^{-7}		105	−37	114
		Data at $\mu = 0.12$ M	308.2	3.30×10^{-7}				
		($LiClO_4$), pH =	318.2	12.2×10^{-7}				
		4.3–5.8. NH_3 loss	328.2	44.5×10^{-7}				
		evident after 8%	338.2	127×10^{-7}				
		react.	348.2	365×10^{-7}				
Co	F	$k_{obs} = k_1 + k_2[H^+]$	298.2	0.86×10^{-7}		89	−90	6
		Aq. soln. for k_1	308.2	2.44×10^{-7}				
		$[H^+] = 0.02$–0.10 M for	318.2	7.50×10^{-7}				
		k_2, $\mu = 0.112$ M	298.2		1.07×10^{-4}	126	+55	6
			308.2		5.2×10^{-4}			
			318.2		25.0×10^{-4}			
Cr	F	k_1 path only	300.2	1.2×10^{-5}				79
		$[H^+] = 1.0$ M $= \mu$	306.9	3.2×10^{-5}				
			314.2	9.8×10^{-5}				
			298.2	0.7×10^{-5}		117	+2	79
Cr	F	$k_{obs} = k_1 + k_2[H^+]$	318.2	0.35×10^{-5}	k_{obs} inc. from			106
		at pH ≤ 1	328.2	1.14×10^{-5}	(1.42–4.80) $\times 10^{-5}$			
		$[H^+] = 0.1$ M $= \mu$	333.2	2.45×10^{-5}	at 338.2 as $[H^+]$			
		k_2 not calcd.	338.2	3.78×10^{-5}	inc. from 0.1–1.0 M			
		Rate inc. by addn.	345.6	8.2×10^{-5}	at $\mu = 1.0$ M			
		of SO_4^{2-} or $P_2O_7^{2-}$	353.2	18.2×10^{-5}				
		Evidence for NH_3 loss	298.2	3.5×10^{-6}		104	−19	106
Cr	F	$k_{obs} = k_1 + k_2[OH^-]$	328.1	0.6×10^{-5}	1.03×10^{-4}			132
		Rate not inc. by inc.	332.7	1.03×10^{-5}	1.83×10^{-4}			
		$[H^+]$, $\mu = 0.1$ M	338.7	2.17×10^{-5}	3.33×10^{-4}			
		For react. in D_2O,	343.3	3.67×10^{-5}	5.33×10^{-4}			
		see ref. 131	298.2	9.4×10^{-8}		113	−10	
			298.2		2.6×10^{-6}	101	−22	

Co	N_3	$k_{obs} = k_1 + k_2[H^+]$	342.8	3.617×10^{-6}				5,133
		$[H^+] = 0.0$—0.2 M	352.8	14.13×10^{-6}				
		Rate indep. of μ	362.8	55.4×10^{-6}				
			298.2	2.1×10^{-9}		141	+53	133
			298.2		7.4×10^{-11}	200	+220	
		Estimated	298.2	2.24×10^{-8}		138	+63	114
Co	N_3	For rate data in H_2SO_4 (2—12 M) see ref. 134						
		The order of reactivity is Cr > Co > Rh						134
Co	N_3	Rate inc. by addn. of HNO_2. $\mu = 0.5$ M	298.2		1.6×10^3			135
		$k_{obs} = k_2[H^+][HNO_2]$						
		Further acc. by anions						
Cr	N_3	$k_{obs} = k_1 + k_2[H^+]$	333.2	4.42×10^{-6}	7.62×10^{-5}			136
		$\mu = 0.2$ M	338.2	7.66×10^{-6}	1.3×10^{-4}			
		$[H^+] = 0.01$—0.05 M	343.2	1.43×10^{-5}	2.25×10^{-4}			
		k_1 indep. of μ. k_2	298.2	3.9×10^{-8}		112	−21	
		inc. with inc. μ	298.2		9.7×10^{-7}	103	−23	
Co	NO_2	$k_{obs} = k_1 + k_2[H^+]$	343.29	0.96×10^{-5}				5
		$[H^+] = 0.02$—0.1 M	353.17	3.15×10^{-5}				
			363.17	10.7×10^{-5}				
			370.28	25.0×10^{-5}				
			298.2	1.15×10^{-8}		126	+17	5
		$\mu = 0.12$ M ($HClO_4$)	298.2	1.42×10^{-8}		124	+19	2
			298.2		4.04×10^{-9}	162	+129	5
Co	NO_2	Complex rate law in	336.1	0.270×10^{-5}				2
		NH_3/NH_4^+ soln. and	342.4	0.535×10^{-5}				
		NH_3 loss is the	348.5	1.56×10^{-5}				
		major aquation step	353.2	2.87×10^{-5}				
			298.2	1.34×10^{-8}		135.7	+51	2
Co	NO_2	$k_{obs} = k_1 + k_2[H^+]$	348.2	0.53×10^{-5}				137
		At $\mu = 1.0$ M, in	353.2	1.18×10^{-5}				
		HAc/NaAc buffers,	358.2	2.22×10^{-5}				
		decompn. to Co(II)	363.2	3.60×10^{-5}				
		is the major	368.4	7.00×10^{-5}				
		reaction	298.2	4.96×10^{-9}		131	+27	137

TABLE 5 (continued)

M	X	Rate law	T (K)	k_1 [a]	k_2 [a]	E_a (kJ mol^{-1})	$\Delta S_{298}^{\#}$ (J K^{-1} mol^{-1})	Ref.
Co	NO_2	$k_{obs} = k_1 + k_2[H^+]$	343.2	2.16×10^{-5}	1.75×10^{-4}			137
		$[H^+] = 0.05$—0.2 M.	353.2	6.42×10^{-5}	3.83×10^{-4}			
		$\mu = 1.0$ M (KNO_3)	363.2	17.8×10^{-5}	8.33×10^{-4}			
		with added urea	298.2	6.7×10^{-8}		109	−24	
			298.2		2.4×10^{-6}	80	−90	
Co	NO_2	$H_2SO_4 = 15.23$ M	For rate data in H_2SO_4 (14—17 M) (T = 293—333 K) see refs. 3,138,139.			75.2	−56	3
Rh	NO_2	$H_2SO_4 = 17.71$ M				68.5	−79	3
Co	ONO	$H_2SO_4 = 0.4$ M	For rate data in H_2SO_4 (0.1—0.7 M) (T = 278—293 K) see ref. 3.			66.4	−75	3
Rh	ONO	$H_2SO_4 = 0.4$ M				65.6	−65	3
Ir	ONO	$H_2SO_4 = 0.4$ M				68.1	−56	3
Co	ONO	Isomerises to $-NO_2$ in dil. H^+ [69,140,141]. As $[H^+]$ inc. prodn. of $Co(NH_3)_5(OH_2)^{3+}$ inc.	298.2	$k_{isom} = 6.2 \times 10^{-5}$ (μ = 1.0, $LiClO_4$)				140
			298.2	$k_{isom} = 8.2 \times 10^{-5}$ (μ = 1.0, LiCl)				140
Co	ONO	$k_{obs} = k_{isom} + k_1[H^+] + k_2[H^+]^2$	298.2	1.32×10^{-3}	1.37×10^{-3}			140
		Aqun. react. also cat. by Cl^-, Br^-, I^-, NCS^- $k'_{obs} = k_{obs} + k_1[H^+][X^-] + k_2[H^+]^2[X^-]$						
		X = Cl^-	298.2	8.47×10^{-2}	2.6×10^{-2}			140
		X = Br^-	298.2	1.04×10^{-2}	3.1×10^{-3}			
		X = I^-	298.2	15.8×10^{-2}				
		X = NCS^-	298.2	6.53×10^{-2}				
Cr	ONO	Rate indep. of $[H^+]$ for 0.005—0.5 M H^+						142
Cr	ONO	$\mu = 0.1$ M K_2SO_4	298.2	1.9×10^{-4}				77
Cr	ONO	$k_{obs} = k_1 + k_2[H^+]$	278.2		2.02×10^{-2}			108,143
		$k_1 \sim 0$ for $HClO_4$ =	283.2		5.35×10^{-2}			
		0.01—0.1 M at μ =	290.2		12.9×10^{-2}			
		1.0 M ($NaClO_4$)	298.2		3.7×10^{-3}	88.6	+46	108,143

Cr	ONO	$k_{obs} = k_1[H^+] + k_2[H^+]^2$	283.2	4.32×10^{-2}	5.54×10^{-2}			143
		for $HClO_4$ = 0.1—1.0 M	283.2		6.89×10^{-2}			144
		at μ = 1.0 M ($NaClO_4$)						
Cr	ONO	React. cat. by Cl^-, Br^-	283.2	3.12 (X^- = Cl^-)				144
		$k_{obs} = k_1[H^+][X^-]$	283.2	27.9 (X^- = Br^-)				
Cr	ONO	Dilute NaOH	283.2	3.0×10^{-4}				145
		Rate indep. of $[OH^-]$	288.6	6.0×10^{-4}				
			293.2	14.2×10^{-4}				
			298.2	20.9×10^{-4}		95	+13	
Cr	ONO	HAc/NaAc buffers	298.2	3.2×10^{-5}		146	+148	145
		$k_{obs} = k_1 + k_2[H^+]$	298.2		5.1×10^{-2}	56	—90	
		$+ k_3[Ac^-]$ at	303.2	7.5×10^{-5}	7.5×10^{-2}			
		μ = 1.0 M (KNO_3)	308.2	21.5×10^{-5}	10.6×10^{-2}			
Co	NH_2SO_3	N- to O-bonded isom.	294.4	$k_{isom} = 0.694 \times 10^{-3}$				146
		(indep. of $[H^+]$) obs.	297.8	1.07×10^{-3}				
		at 293—303 K (μ = 1.0 M	302.4	2.18×10^{-3}				
		$LiClO_4$)	298.2	1.18×10^{-3}		106	+47.5	
		$k_{obs} = k_1 + k_2[H^+]$	298.2	2.63×10^{-5}		101	+6	146
		Only values of k_{obs}	298.2		2.97×10^{-5}	86	—44	146
		reported for 300—333 K						
Co	SO_4	$k_{obs} = k_1 + k_2[H^+]$	328.5	0.334×10^{-4}				147
		μ = 1.0 M ($NaClO_4$)	338.3	0.994×10^{-4}	0.327×10^{-3}			
		$[H^+]$ = 0.005—1.0 M	347.5	2.36×10^{-4}	1.03×10^{-3}			
		Also Rh analog.	356.8	5.86×10^{-4}	3.06×10^{-3}			
		k_1 dec. with inc. μ	298.2	8.9×10^{-7}		95	—42	147
			298.2		9.5×10^{-7}	119	+38.5	147
Co	SO_4		298.2	12×10^{-7}		78	—100	135,148
Co	SO_4	Rate law as above	298.2			91.22	+52.67	103
		μ = 0.1 M = $HClO_4$		E_a, $\Delta S_{298}^{\#}$ and $\Delta C_p^{\#}$ depend on				
		T = 278.45—343.26 K		temp. interval taken.				103
		Data corr. for k_2 at high T using ref. 147						103
Co	SO_4	Na_2SO_4	303.2	8.56×10^{-5}				149
			343.2	1.58×10^{-2}		113		149
Cr	SO_4	NH_3 loss						150

TABLE 5 (continued)

M	X	Rate law	T (K)	k_1 [a]	k_2 [a]	E_a (kJ mol^{-1})	ΔS_{298}# (J K^{-1} mol^{-1})	Ref.
Co	CO_3	$k_{obs} = k_1[OH^-]^{-1} + k_2[OH^-]$	318.2	0.19 x 10^{-5}	8.1 x 10^{-5}			151,152
			323.2	0.44 x 10^{-5}	16.1 x 10^{-5}			
			328.2	0.82 x 10^{-5}	35.2 x 10^{-5}			
		Hydrolysis is via C—O bond rupture	298.2	7.8 x 10^{-8}		127	+37	
		μ = 1.0 M ($NaNO_3$)	298.2		3.1 x 10^{-6}	128	+69	
		Rate dec. then inc. with inc. [OH^-]						
Co	CO_3	k_{obs} indep. of [H^+] for pH ≤ 5. k_{obs} dec. for pH 5—7. Data for k_{obs} at pH = 3, μ = 0.5 M.	298.2	1.25		71.1	−2.1	153
			308.2	3.1				
			317.7	7.5				
Co	CO_3	HCl = 0.286 mM	273.2	3.88 x 10^{-4}				18a,154
		= 0.715 mM	273.2	8.58 x 10^{-4}				
		= 2.86 mM	273.2	38 x 10^{-4}				
Co	C_2O_4	k_0 in ref. [7]	298.2	1.52 x 10^{-8}		109	−21	7
		μ = 1.0 M Co—O bond rupture	318.2	2.36 x 10^{-7}				
			343.2	5.5 x 10^{-6}				
Co	C_2O_4	k_0 in ref. 8	323.2	0.23 x 10^{-6}				8
		μ = 0.3 M	328.2	0.78 x 10^{-6}				
			333.2	1.26 x 10^{-6}				
			339.2	2.67 x 10^{-6}				
			298.2	4.2 x 10^{-9}		134	+40	
Co	C_2O_4	See also refs. 17,155,156						
Cr	C_2O_4	No evidence for $Cr(NH_3)_5(C_2O_4)^+$ [157] See, however, refs. 150,158.						
Co	C_2O_4H	$k_{obs} = k_1 + k_2[H^+]$	298.2	2.20 x 10^{-8}		123	+14	7
		$HClO_4$ = 0.00—1.0 M	298.2		19.5 x 10^{-8}	94	−67	7
		μ = 1.0 M Co—O bond rupture for k_1 path and C—O bond rupture for the k_2 path [159]	318.2	5.8 x 10^{-7}	22 x 10^{-7}			
			343.2	15.1 x 10^{-6}	27.8 x 10^{-6}			

Co	C_2O_4H	$k_{obs} = k_1 + k_2[H^+]$	323.2	2.04	$\times 10^{-6}$	3.7	$\times 10^{-6}$		8
		$[H^+] = 0.002$—0.3 M	328.2	4.16	$\times 10^{-6}$	7.5	$\times 10^{-6}$		
		$\mu = 0.3$ M	333.2	7.86	$\times 10^{-6}$	9.7	$\times 10^{-6}$		
		See also ref. 160	339.2	13.8	$\times 10^{-6}$	23.2	$\times 10^{-6}$		
			298.2	7.1	$\times 10^{-8}$			109 —24	
			298.2			1.7	$\times 10^{-7}$	100 —49	
Co	PO_4	Evidence for NH_3 loss	393.2	2	$\times 10^{-5}$				4
		at high pH. React.	298.2	3.3	$\times 10^{-9}$			166 +141	4
		via Co—O bond rupture							
Co	PO_4H	$\mu = 1.0$ M. See	393.2	1.05	$\times 10^{-5}$				
		also refs. 162—165	298.2	1.4	$\times 10^{-8}$			112 —28	4
			295	3.1	$\times 10^{-9}$				161
Co	PO_4H_2		393.2	15.7	$\times 10^{-5}$				
			298.2	2.18	$\times 10^{-7}$			97.4 —49	4
			295	1.2	$\times 10^{-7}$				161
Co	PO_4H_3		393.2	150	$\times 10^{-5}$				4
			298.2	2.74	$\times 10^{-6}$			107 —1	4
Co	ReO_4	$k_{obs} = k_1 + k_2[H^+]$	298.2	3.12	$\times 10^{-4}$	1.22			166,167
		$\mu = 0.004$—0.12 M							
		React. via O—Re bond rupture and is cat. by Ac^-							166
Co	NCO	Gives $Co(NH_3)_6^{3+}$	278.2			2.9	$\times 10^{-2}$		168
		as product in H^+	288.2			7.8	$\times 10^{-2}$		
		(0.02—0.2 M)	298.2			1.62	$\times 10^{-1}$	55 —75	168
		$\mu = 1.0$ M							
		$k_{obs} = k_1[H^+]$	See also refs. 169,170						
Co	AsO_4H	$\mu = 1.0$ M. React. via	295	2.90	$\times 10^{-5}$				161
		As—O bond rupture							
Co	AsO_4H_2	Hyd. 100 x faster	295	4.08	$\times 10^{-4}$	6.7	$\times 10^{-2}$		161
		than PO_4 systems							

[a] Units of k_1 and k_2 depend on the form of the rate law. Time is in seconds.

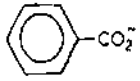
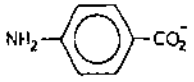
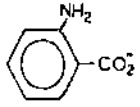
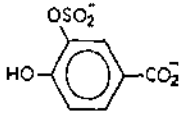
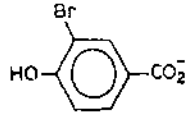
TABLE 6

Kinetic parameters for the acid catalysed aquation of some M(carboxylato)$(NH_3)_5^{n+}$ complexes [a]
A. Monocarboxylates

M	Carboxylato	$[H^+]$ (M)	μ (M)	T (K)	k_1 (s^{-1})	k_2 ($M^{-1}\,s^{-1}$)	E_a (kJ mol^{-1})	$\Delta S_{298}^{\neq}$ (J K^{-1} mol^{-1})	Ref.
Co	HCO_2^-								52
Co	$CH_3CO_2^-$	0.01—0.05	0.1	328.2	1.4×10^{-6}	1.7×10^{-4}			171
	See also ref. 51			343.1	8.0×10^{-6}	9.3×10^{-4}			
				352.0	2.0×10^{-5}	2.5×10^{-3}			
				298.2	2.7×10^{-8}		108	−37	
						3.1×10^{-6} [c]	108	+4	
		0.008	0.01	343.2	8.16×10^{-6}				172
							110		173
Cr	$CH_3CO_2^-$	0.01—0.1	0.13	298.2	2.3×10^{-5}		80		174
	React. due to NH_3 loss,			313.2	1.15×10^{-4}				
	indep. of $[H^+]$			343.2	2×10^{-2}				174
Co	$CH_2ClCO_2^-$	0.008	0.01	343.2	5.7×10^{-6}				172
				298.2	3.9×10^{-7}		110	−7	173
			0.1	328.2	3.7×10^{-5}	2.8×10^{-5}			175
				338.2	1.8×10^{-4}	3.2×10^{-5}			
				348.2	6.2×10^{-4}	1.3×10^{-4}			
				298.2	2.8×10^{-7}		134	+70	
				298.2		1.6×10^{-6}	72	−121	
Co	$CH_2(OH)CO_2^-$		0.1	328.2	5.8×10^{-5}	4.5×10^{-5}			175
				338.2	1.6×10^{-4}	1.5×10^{-4}			
				348.2	8.0×10^{-4}	4.4×10^{-4}			
				298.2	5.3×10^{-7}		124	+43	
				298.2		8.4×10^{-7}	108	−6	
Cr	$CH_2ClCO_2^-$	0.01—0.1	0.13	298.2	2.3×10^{-6}		106	+20	174
	React. due to NH_3			313.2	1.5×10^{-5}				
	loss, indep. of $[H^+]$			328.2	1.25×10^{-4}				
				343.2	5.9×10^{-2}				174

Co	$CHCl_2CO_2^-$	0.008	0.01	343.2	1.6	$\times 10^{-5}$					172
				298.2	1.5	$\times 10^{-7}$			110	−15	173
Cr	$CHCl_2CO_2^-$	0.01−0.1	0.13	298.2	7.5	$\times 10^{-6}$			103	+4	174
	React. due to NH_3			313.2	5.0	$\times 10^{-5}$					
	loss, indep. of $[H^+]$			328.2	3.75	$\times 10^{-4}$					
				343.2	1.7	$\times 10^{-3}$					174
Co	$CCl_3CO_2^-$	0.008	0.01	343.2	5.3	$\times 10^{-5}$					172
				298.2	5.8	$\times 10^{-7}$			107.4	−12.5	173
Cr	$CCl_3CO_2^-$	0.1	0.13	298.2	4.15	$\times 10^{-6}$					174
				313.2	2.9	$\times 10^{-5}$					
				328.2	1.55	$\times 10^{-4}$					
				342.2	5.1	$\times 10^{-4}$					
		0.01−0.1	0.13	313.2	2.12	$\times 10^{-5}$	7.8	$\times 10^{-5}$			174
				343.2	4.9	$\times 10^{-4}$	2.0	$\times 10^{-3}$			
				298.2	1.0	$\times 10^{-5}$			90	−47	174
Co	$CF_3CO_2^-$	0.01−0.05	0.1	333.2	1.8	$\times 10^{-5}$					171
				343.2	5.7	$\times 10^{-5}$	3	$\times 10^{-5}$			
				352.1	1.5	$\times 10^{-4}$	1	$\times 10^{-4}$			
				298.2	1.7	$\times 10^{-7}$			109	−16	171
		0.008	0.01	343.2	5.5	$\times 10^{-5}$					172
Cr	$CF_3CO_2^-$	0.001−0.1	0.1	330.7	2.77	$\times 10^{-4}$					176
	Only k_1 path obs.			340.7	6.79	$\times 10^{-4}$					
				349.7	1.532	$\times 10^{-3}$					
				298.2	8.9	$\times 10^{-6}$			86	−60	176
Co	$CH_3CH_2CO_2^-$	0.008	0.01	343.2	3.2	$\times 10^{-6}$					172
	See also ref. 54										
Co	$(CH_3)_2CHCO_2^-$	0.008	0.01	343.2	2.6	$\times 10^{-6}$					172
Co	$(CH_3)_3CCO_2^-$	0.008	0.01	343.2	4.3	$\times 10^{-6}$					172
		0.01−0.05	0.1	344.1	5.2	$\times 10^{-6}$	2.5	$\times 10^{-4}$			171
				351.8	2.1	$\times 10^{-5}$	5.8	$\times 10^{-4}$			
				361.5	7.7	$\times 10^{-5}$	1.6	$\times 10^{-3}$			
				298.2	1.0	$\times 10^{-9}$			160	+109	
				298.2			6.6	$\times 10^{-7}$	110	−2	

TABLE 6 (continued)

M	Carboxylato	$[H^+]$ (M)	μ (M)	T (K)	k_1 (s^{-1})	k_2 ($M^{-1}\ s^{-1}$)	E_a (kJ mol^{-1})	$\Delta S_{298}^{\#}$ ($J\ K^{-1}\ mol^{-1}$)	Ref.
Co			1.0	328.2	1.0×10^{-6}	2.8×10^{-5}			175
Co			1.0	328.2	1.4×10^{-6}	1.5×10^{-5}			175
Co			1.0	328.2	5×10^{-8}	3.0×10^{-6}			175
Co		0.05—0.6	0.6	333.2	0.63×10^{-6}	1.03×10^{-5}			177
By titration				338.2	2.01×10^{-6}	1.82×10^{-5}			
				343.2	4.64×10^{-6}	3.26×10^{-5}			
				298.2	2×10^{-10}		190	+190	
				298.2		6.4×10^{-8}	119	+10	
By spectrophotometry				333.2	0.86×10^{-6}	1.21×10^{-5}			177
				338.2	2.56×10^{-6}	2.14×10^{-5}			
				343.2	5.49×10^{-6}	4.02×10^{-5}			
				298.2	5×10^{-10}		176	+160	
				298.2		1×10^{-7}	114	—5	
Co			1.0	343.2	2.29×10^{-6}	1.55×10^{-5}			
				298.2	9.1×10^{-8}		86	—100	178
				298.2		5.3×10^{-8}	124	+24	178
Co		0.05—1.0	1.0	338.2	1.3×10^{-6}	1.11×10^{-5}			178

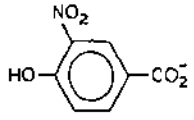
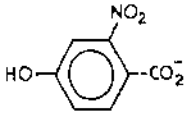
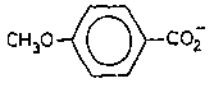
				343.2	3.1 x 10^{-6}	1.84 x 10^{-5}			
				348.2	8.49 x 10^{-6}	5.24 x 10^{-5}			
				298.2	2.5 x 10^{-8}		107	−40	178
				298.2		1.1 x 10^{-8}	161	+134	178
Co		0.05—1.0	1.0	343.2	5.45 x 10^{-6}	1.05 x 10^{-5}			178
				348.2	1.26 x 10^{-5}	1.82 x 10^{-5}			
				353.2	2.04 x 10^{-5}	2.55 x 10^{-5}			
				298.2	1.9 x 10^{-8}		125	+18	178
				298.2		4.4 x 10^{-7}	82	−100	178
Co		0.05—1.0	1.0	343.2	5.43 x 10^{-6}	2.03 x 10^{-5}			178
				348.2	1.18 x 10^{-5}	3.16 x 10^{-5}			
				353.2	2.58 x 10^{-5}	4.57 x 10^{-5}			
				298.2	1.3 x 10^{-9}		153	+101	178
				298.2		2.7 x 10^{-7}	79	−105	178
Co		0.01—0.3	0.3	328.2	1.02 x 10^{-6}	8.54 x 10^{-5}			160
				333.2	2.16 x 10^{-6}	15.6 x 10^{-5}			
				338.2	4.24 x 10^{-6}	27.0 x 10^{-5}			
				343.2	8.9 x 10^{-6}	45.8 x 10^{-5}			
				298.2	7.2 x 10^{-9}		134	+41	
				298.2		1.8 x 10^{-6}	104	−12	
B. Dicarboxylates									
Co	$(CO_2)_2^{2-}$ See also Table 5	0.005—0.3	0.3	323.2	2.04 x 10^{-6}	0.37 x 10^{-5}			8,160
				328.2	4.16 x 10^{-6}	0.75 x 10^{-5}			
				333.2	7.86 x 10^{-6}	0.97 x 10^{-5}			
				339.3	13.8 x 10^{-6}	2.32 x 10^{-5}			
				343.2	26.7 x 10^{-6}	3.4 x 10^{-5}			
				298.2	6.0 x 10^{-8}		114	−9	
				298.2		1.6 x 10^{-7}	100	−45	
Co	$CH_2(CO_2)_2^{2-}$ See also refs. 53,387	0.005—0.3	0.3	333.2	0.96 x 10^{-6}	4.25 x 10^{-5}			160
				338.2	2.01 x 10^{-6}	7.31 x 10^{-5}			
				343.2	4.03 x 10^{-6}	13.5 x 10^{-5}			
				298.2	3.0 x 10^{-9}		136	+41	
				298.2		4.0 x 10^{-7}	110	−7	

TABLE 6 (continued)

M	Carboxylato	$[H^+]$ (M)	μ (M)	T (K)	k_1 (s^{-1})	k_2 ($M^{-1}\ s^{-1}$)	E_a (kJ mol^{-1})	$\Delta S_{298}^{\#}$ (J K^{-1} mol^{-1})	Ref.
Co	$(CH_2)_2(CO_2)_2^{2-}$	0.005—0.3	0.3	333.2	1.94×10^{-6}	10.6×10^{-5}			160
				338.2	3.68×10^{-6}	18.5×10^{-5}			
				343.2	7.40×10^{-6}	34.0×10^{-5}			
				298.2	8.7×10^{-9}		127	+19	
				298.2		9.6×10^{-7}	110	+3	
Co		0.005—0.3	0.3	333.2	1.29×10^{-6}	1.70×10^{-5}			160
				338.2	2.49×10^{-6}	2.82×10^{-5}			
				343.2	4.84×10^{-6}	4.86×10^{-5}			
				298.2	6.1×10^{-9}		126	+12	
				298.2		2.5×10^{-7}	100	—45	
C. Aminoacid complexes									
Co	gly		0.1	328.2	0.57×10^{-6}				178a
				338.2	1.8×10^{-6}				
				348.2	7.6×10^{-6}				
				298.2	5.8×10^{-9}		123	+1	
			1.0	328.2	0.4×10^{-6}	2.0×10^{-6}			178a
				338.2	1.1×10^{-6}	7.4×10^{-6}			
				348.2	1.9×10^{-6}	27×10^{-6}			
				298.2	2.8×10^{-8}		74	—149	
				298.2		2.1×10^{-8}	124	+14	
Cr	gly [b]		1.0	313.2	0.44×10^{-4}		101	—5.3	160
				318.2	0.83×10^{-4}				
				323.2	1.45×10^{-4}				
				328.2	2.79×10^{-4}				
				333.2	4.87×10^{-4}				
				298.2	5.8×10^{-6}		104	—3	
Co	sarc		1.0	328.2	0.25×10^{-6}	1.8×10^{-6}			178a
Co	bet		1.0	328.2	0.44×10^{-6}	1.0×10^{-6}			178a
Co	al		0.1	328.2	0.3×10^{-6}	8.6×10^{-6}			178a
			1.0	328.2	0.2×10^{-6}	26×10^{-6}			178a

Co	γ-aminobut	0.1	328.2	2	$\times 10^{-7}$	3.2	$\times 10^{-5}$	175
		1.0	328.2	3	$\times 10^{-6}$	7.6	$\times 10^{-5}$	
Co	ϵ-aminocap	0.1	328.2	2	$\times 10^{-7}$	6.6	$\times 10^{-5}$	175
		1.0	328.2	4	$\times 10^{-6}$	1.4	$\times 10^{-4}$	
Co	pro	1.0	328.2	2.8	$\times 10^{-7}$	1.5	$\times 10^{-6}$	175
Co	α-amino-i-but	1.0	328.2	1.8	$\times 10^{-7}$	1.3	$\times 10^{-6}$	175
Co	Ornithine	0.1	328.2	5	$\times 10^{-7}$			175
		1.0	328.2	1.6	$\times 10^{-7}$	1.1	$\times 10^{-6}$	
Co	$NTAH_2$	1.0	352.2	2.1	$\times 10^{-5}$	1.8	$\times 10^{-5}$	179

[a] Rate law is $k_{obs} = k_1 + k_2[H^+]$.
[b] Rate data for NH_3 loss independent of $[H^+]$ [150].

TABLE 7

Kinetic parameters for the anation reactions $M(NH_3)_5(OH_2)^{3+} + X^{n-}$. (For additional entries see Note added in proof)

M	X	μ [a] (M)	T (K)	k_1 [b] (s^{-1})	Q_1 [c] (M^{-1})	k_1Q_1 [d] ($M^{-1}\ s^{-1}$)	E_a (kJ mol^{-1})	$\Delta S_{298}^{\#}$ (J $K^{-1}\ s^{-1}$)	Ref.
Co	Cl	1.0	318.2	3.48×10^{-5}	1.21	4.2×10^{-5}			180
		1.0	318.2	2.1×10^{-5}	3.1	6.5×10^{-5}			65
		1.0	318.2	2.05×10^{-5}	31.3				181
Cr	Cl	0.106	309.9			0.46×10^{-3}			73
			313.29			1.9×10^{-3}			
			318.2			3.8×10^{-3}			
			333.36			30×10^{-3}			
			298.2		3	8.4×10^{-5}	141	+142	
Cr	Cl	1.71	303.2			0.16×10^{-3}			73
			318.2			1.3×10^{-3}			
			333.72			8.3×10^{-3}			
			298.2			7.9×10^{-5}	109	+34	
Co	Br	1.0	298.2		0.295	1.32×10^{-6}			104
Co	N_3	0.51	338.2			41.5×10^{-6}			20
			333.2			22.4×10^{-6}			
			328.2			12.0×10^{-6}			
			323.2			6.1×10^{-6}			
			313.2			1.6×10^{-6}			
			298.2			1.74×10^{-6}	114.6	+22	20
Co	N_3	2.0	318.2	1.01×10^{-4}	0.26	2.6×10^{-5}			20
Cr	N_3	1.0	313.2			7.83×10^{-5}			182
			323.2			2.63×10^{-4}			
			333.2			1.00×10^{-3}			
			298.2			9.0×10^{-6}	110	+20	
Co	NCS	1.0	318.2	1.6×10^{-5}	0.43	6.8×10^{-6}			65
Co	NCS		298.2	2.9×10^{-7}	4.5	1.3×10^{-6}			28

Cr	NCS	0.106	303.1			2.9×10^{-3}			73
			318.2			20×10^{-3}			
			334.1			130×10^{-3}			
			298.2		10	1.5×10^{-3}	103	+38	
Cr	NCS	1.71	303.2			1.2×10^{-3}			73
			318.2			7.0×10^{-3}			
			333.2			32×10^{-3}			
			298.2			6.6×10^{-4}	92	−6	
Co	SO_4		298.2	1.3×10^{-6}	11.2	1.5×10^{-5}			148,183
			304.3	2.0×10^{-6}	357				184
Co	NO_3	1.0	343.2	0.36×10^{-5}					51
Cr	IO_3H	1.0	298.2		0.3	0.58×10^{-4}			150,185
Co	H_2PO_4		298.2	7.7×10^{-7}	2.75	2.0×10^{-6}			126
Co	ClO_4	1.0	318.2		29.4				181
Co	HCO_2H	1.0	333.2			0.42×10^{-4}			52
			343.2			1.08×10^{-4}			
			353.2			2.83×10^{-4}			
			298.2			8.0×10^{-7}	93	−57	
Co	HCO_2	1.0	333.2	3.0×10^{-4}	0.5	1.6×10^{-4}			17,52
			343.2	5.6×10^{-4}	1.0	5.9×10^{-4}			
			353.2	14.7×10^{-4}	1.4	21.2×10^{-4}			
			298.2	1.1×10^{-5}			77.5	−88	
			298.2			2.5×10^{-6}	123	+52	17,52
Co	CH_3CO_2H	1.0	333.2			1.7×10^{-5}			51
			343.2			5.3×10^{-5}			
			353.2			12.5×10^{-5}			
			298.2			2.8×10^{-7}	98	−51	
Co	CH_3CO_2	1.0	333.2	0.5×10^{-4}					51
			343.2	1.5×10^{-4}	5.9	8.6×10^{-4}			
			353.2	3.9×10^{-4}					
			298.2	2.5×10^{-6}			95.3	−41	51
			298.2			3.6×10^{-5}			51

TABLE 7 (continued)

M	X	μ [a] (M)	T (K)	k_1 [b] (s^{-1})	Q_1 [c] (M^{-1})	k_1Q_1 [d] ($M^{-1}\ s^{-1}$)	E_a (kJ mol^{-1})	$\Delta S_{298}^{\neq}$ (J $K^{-1}\ s^{-1}$)	Ref.
Co	AsO_4H	1.0	295			1.1×10^{-1}			161
Co	AsO_4H_2	1.0	295			1.2×10^{-2}			161
Cr	CH_3CO_2H	1.0	313.2	5.8×10^{-5}					186
			318.2	8.3×10^{-5}					
			323.2	1.5×10^{-4}					
			328.2	2.1×10^{-4}					
			298.2	1.3×10^{-5}			76	−91	
Cr	CH_3CO_2	1.0	313.2			1.0×10^{-4}			186
			318.2			1.5×10^{-4}			
			323.2			3.3×10^{-4}			
			328.2			6.7×10^{-4}			
			298.2			1.0×10^{-5}	110	+23	
							74	−84	186
Co	$CH_3CH_2CO_2H$	1.0	333.2			1.08×10^{-5}			54
			343.2			3.3×10^{-5}			
			353.2			10.0×10^{-5}			
			298.2			1.1×10^{-7}	109	−22	
Co	$CH_3CH_2CO_2$	1.0	333.2	0.6×10^{-4}	5.0	3.1×10^{-4}			17,54
			343.2	2.5×10^{-4}	3.4	8.6×10^{-4}			
			353.2	5.8×10^{-4}	3.4	31.8×10^{-4}			
			298.2	5.9×10^{-7}			111	+0.5	17,54
			298.2			2.3×10^{-6}	113	+20	17,54
Co	$C_2O_4H_2$	1.0	323.2			0.35×10^{-4}			17,155
			333.2			0.66×10^{-4}			
			343.2			1.50×10^{-4}			
			353.2			2.30×10^{-4}			
			298.2			1.35×10^{-5}	59.8	−146	17,155
Co	C_2O_4H	1.0	353.2	13×10^{-4}	1.8				155
			343.2	4.9×10^{-4}	1.8	8.82×10^{-4}			

			333.2	1.8×10^{-4}	1.8					
			323.2	0.61×10^{-4}	1.8					
			298.2	9.05×10^{-6}				93.6	−36	17,155
			298.2			1.63×10^{-5}				17,155
Co	C_2O_4	1.0	353.2	11.5×10^{-4}	9.2					17,155
			343.2	4.0×10^{-4}	9.2					
			333.2	1.25×10^{-4}	9.2					
			323.2	0.40×10^{-4}	9.2					
			298.2	3.5×10^{-6}				104	−9	17,155
			298.2			3.2×10^{-5}				17,155
Cr	C_2O_4 [c]	1.0	313.2	1.68×10^{-4}	4.7			110	+33	157
			323.2	6.46×10^{-4}	4.5					
			333.2	2.24×10^{-3}	4.17					
			298.2	1.9×10^{-5}				112	+33	
			303.2	4.5×10^{-5}						157
Cr	C_2O_4H [c]	1.0	313.2	1.55×10^{-4}	1.4			112	+39	157
			323.2	5.86×10^{-4}	1.16					
			333.2	2.22×10^{-3}	0.92					
			298.2	1.6×10^{-5}				115	+42	
			303.2	3.5×10^{-5}						157
Co	$CH_2(CO_2H)_2$	1.0	333.2			2.8×10^{-5}				53
			343.2			8.0×10^{-5}				
			353.2			22×10^{-5}				
			298.2			3.9×10^{-7}		101	−38	53
Co	$CH_2(CO_2H)CO_2$	1.0	333.2	1.49×10^{-4}	1.9	2.8×10^{-4}				53
			343.2	5.3×10^{-4}	1.3	6.9×10^{-4}				
			353.2	20.4×10^{-4}	1.2	25.5×10^{-4}				
			298.2	5.4×10^{-7}				131	+66	53
			298.2			2.7×10^{-6}		108	+1.7	53
Co	$CH_2(CO_2)_2$	1.0	333.2	2.3×10^{-4}	5.9	1.38×10^{-3}				53
			343.2	7.3×10^{-4}	5.4	4.0×10^{-3}				
			353.2	22.9×10^{-4}	5.6	1.29×10^{-2}				
			298.2	1.9×10^{-6}				112	+14	53
			298.2			1.3×10^{-5}		109	+20	53

TABLE 7 (continued)

M	X	μ [a] (M)	T (K)	k_1 [b] (s^{-1})	Q_1 [c] (M^{-1})	k_1Q_1 [d] ($M^{-1}\ s^{-1}$)	E_a (kJ mol^{-1})	ΔS_{298}# (J $K^{-1}\ s^{-1}$)	Ref.
Co	$NH_2CH_2CO_2H$	1.0	322.2			2.46×10^{-5}			188
			333.2			9.65×10^{-5}			
			343.2			3.21×10^{-4}			
			298.2			6.2×10^{-7}	118	+25	
Co	$NH_2CH_2CO_2H$	0.1	328.2			7×10^{-5}			175
			338.5			2.5×10^{-4}			
			348.2			9.2×10^{-4}			
			298.2			7.6×10^{-7}	122	+40	
Co	$NH_2CH(CH_3)CO_2H$	0.1	328.2			8.5×10^{-5}			175
Co	ϵ-aminocaproic acid	0.1	328.2			1.6×10^{-4}			175

[a] pH usually less than 5.5 to avoid the formation of $M(OH)(NH_3)_5^{2+}$. See, however, ref. 187 for the uptake of CO_2 by $Co(OH)(NH_3)_5^{2+}$, ref. 140 for the O-nitrosation of this ion by NO^+ and ref. 182 for the reaction of $Cr(OH)(NH_3)_5^{2+}$ with N_3^-.

[b] k_1 (s^{-1}) = rate constant for the interchange reaction, i.e. the reverse of eqn. (1).

[c] Q_1 (M^{-1}) = ion-pair formation constant, eqn. (21).

[d] k_1Q_1 ($M^{-1}\ s^{-1}$) = obs. or calcd. second order rate constant for the anation by the appropriate anion.

[e] Anation followed by NH_3 loss and cyclisation with k_{cy} (318) = $3.47 \times 10^{-3}\ s^{-1}$ (μ = 1.0 M) [150]. All four *cis* NH_3 ligands appear to have an equal chance of being lost [42].

TABLE 8

Kinetic parameters for the base hydrolysis of some $MX(NH_3)_5^{n+}$ complexes

M	X	μ (M)	$k_{OH}(298)$ (M^{-1} s^{-1})	E_a (kJ mol^{-1})	$\Delta S_{298}^{\neq}$ (J K^{-1} mol^{-1})	Ref.
Co	Cl	0	1.58	116	+140	[a]
Co	Cl	1.1	0.23			120
Cr	Cl		1.85×10^{-3}	109	+69	81
Co	Br	0	7.71	126	+187	[b]
Co	Br	1.1	1.4			120
Cr	Br		7.1×10^{-2}	107	+94	81
Co	I	0	18.2	114	+152	[c]
Co	I	1.1	3.2			120
Cr	I		3.7	109.5	+112	81
Co	NO_3	0	39.6	120	+180	21,191
Co	NO_3	1.1	5.5			120
Cr	NO_3	1.0	1.1×10^{-2}	107	+69	116
Co	ReO_4	0.1	2.89×10^{4}			166
Co	SO_4	1.0	4.9×10^{-2}	110	+103	193
Co	NO_2	0	1.4×10^{-5}	156	+177	194
Co	NO_2	1.0	1.6×10^{-6}	153	+149	2,195
Co	NO_2 [d]	1.0	1.73×10^{-6}	158.7	+168.6	2
Co	NCS	0	8.1×10^{-6}	149	+149	119,145
Cr	NCS	0	5.0×10^{-4}	144.8	+169	119,196
Co	SCN	1.1	0.16			120
Co	S_3O_3	1.0	6×10^{-5}	115	+60	117
Co	S_2O_3	0	11×10^{-5}	129.6	+107	197
Co	N_3	0	3.0×10^{-4}	136	+145	133
Cr	N_3 [e]	0.2	2.1×10^{-4}	98	+6	136
Co	F	0	1.3×10^{-2}	109	+85	90
Co	F [f]	0.11	2.1×10^{-2}	111	+95	198
Co	F [g]	0.11	1.0×10^{-2}	110	+87	198
Cr	F	0.1	2.7×10^{-6}	97	−26	132
Cr	F	0.1	3.2×10^{-6}	135	+86	106
Cr	F [f]	0.11	6.3×10^{-6}	107	+13	198
Co	PO_4	1.0	5.0×10^{-7}	154	+150	4
Co	CO_3	1.0	3.3×10^{-6}	125.4	+75	151
Co	C_2O_4 [h]	1.0	2.5×10^{-4}	132	+135	199
Co	mal [h]	1.0	2.8×10^{-5}	117	+60	199
Co	fum [h]	1.0	8.0×10^{-5}	119	+77	199
Co	form	1.0	5.8×10^{-4}			21
Co	CH_3CO_2	0	9.65×10^{-4}			59
Co	$CHCl_2CO_2$ [h]	1.0	5.80×10^{-3}	121	+120	172,200
Co	CCl_3CO_2 [h]	1.0	2.22×10^{-2}	97.4	+52	172,200
Co	CF_3CO_2 [h]	1.0	2.1×10^{-2}	95	+42	172,201,202
Co	NH_2SO_4	1.0	1.0×10^{-2}	134	+242	146
Co	$NHSO_4$	1.0	2.5×10^{-7}	172	+207	146
Co	OSO_3NH_2	1.0	20			146,193
Co	NH_3	1.4	7.14×10^{-7}	146.3	+114	203

TABLE 8 (continued)

M	X	μ (M)	$k_{OH}(298)$ (M^{-1} s^{-1})	E_a (kJ mol^{-1})	$\Delta S_{298}^{\#}$ (J K^{-1} mol^{-1})	Ref.
Co	OH		Very slow exchange, if any			127,204
Cr	OH		Rate inc. with inc. pH in the range pH = 2.2—4.0			73

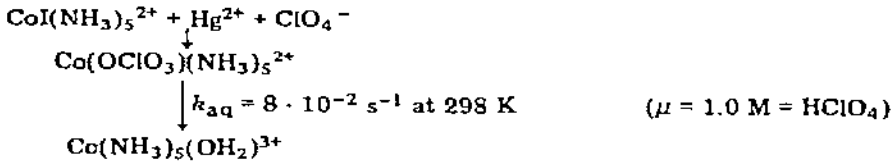
[a] Data from refs. 55,87,88,90—93,189.
[b] Data from refs. 90,93,99,108a,190.
[c] Data from refs. 90,93,191,192.
[d] NH_4^+/NH_3 buffers.
[e] Evidence for NH_3 loss.
[f] EtOH : H_2O = 1 : 4.5.
[g] MeOH : H_2O = 1 : 4.5.
[h] $k_{obs} = k_1[OH^-] + k_2[OH^-]^2$, data cited here are for the k_1 path. The k_2 path involves C—O bond rupture [199,201].

TABLE 9

Aquation, anation and base hydrolysis rate constants (298 K) for some $CoX(NH_3)_5^{n+}$ complexes. (For additional entries see Note added in proof)

Plot No. [a]	X	k_{OH} (M^{-1} s^{-1})	μ (M)	Ref.	k_{aq} (s^{-1})
1	NH_3	7.14×10^{-7}	1.4	203	5.8×10^{-12}
2	PO_4	5.0×10^{-7}	1.0	4	3.3×10^{-9}
3	NO_2	1.6×10^{-6}	1.0	2,195	6.7×10^{-8}
4	S_2O_3	6×10^{-5}	1.0	117	1.6×10^{-7}
5	mal	1.0×10^{-5}	1.0	199	9.8×10^{-9}
6	Ac	9.56×10^{-4}	0	59	2.7×10^{-8}
7	form	5.8×10^{-4}	1.0	21	2.6×10^{-9}
8	NCS	5.0×10^{-4}	0	196,119	3.7×10^{-10}
9	C_2O_4	2.5×10^{-4}	1.0	199	4.2×10^{-9}
10	$CHCl_2CO_2$	5.8×10^{-3}	1.0	172,200	1.5×10^{-7}
11	SO_4	4.9×10^{-2}	1.0	193	8.9×10^{-7}
12	CCl_3CO_2	2.22×10^{-2}	1.0	172,200	5.8×10^{-7}
13	CF_3CO_2	2.2×10^{-2}	1.0	172,201,202	1.7×10^{-7}
14	F	1.3×10^{-2}	0	90	8.6×10^{-8}
15	Cl	2.3×10^{-1}	1.1	120	1.8×10^{-6}
16	Br	1.4	1.1	120	3.9×10^{-6}
17	I	3.2	1.1	120	8.3×10^{-6}
18	NO_3	5.5	1.1	120	2.41×10^{-5}
19	ReO_4	2.9×10^{4}	0.1	166	3.12×10^{-4}
20	N_3	3.0×10^{-4}	0	133	2.1×10^{-9}

[a] Numbers in this column refer to the points in the plot of log k_{OH} vs. log k_{aq} (Fig. 1).
[b] See eqn. (22).
[c] The plot of log k_{OH} vs. log k_{aq} (Fig. 1) has a slope of 1.29 ± 0.22 and an intercept of 7.35 ± 1.86. This column gives the standardized residuals for each point. That is, the deviations from the predicted values divided by their standard deviation.



SCHEME 2. Production and aquation of the perchloratopentaammine cobalt(III) ion [47].

Secondly, while there have been hints in the literature [40] (Table 5) that ammine loss can be an important pathway in the acid hydrolysis of $CoX(NH_3)_5^{2+}$ complexes, especially with labilising aniono ligands (e.g. NO_2 or SO_3 (Scheme 1)), it is only recently that this has received some systematic study [2,48]. The competitive $Cr—NH_3$ bond rupture is perhaps better recognised [33], but "aquation" studies with reported activation energies close to that of

$$M(NH_3)_6^{3+} + H_2O = \text{products}$$

should be regarded with caution. (E_a = 153 kJ mol^{-1} for M = Co(III) [49] and 115 kJ mol^{-1} for M = Cr(III) [50,238]).

μ (M)	Ref.	k_{an} (M^{-1} s^{-1})	μ (M)	Ref.	Q_E [b] (M)	Std. Res.[c]
1.0	49					+0.87
1.0	4					−1.54
1.0	137					−1.66
1.0	117					−2.14
0.3	160	4.0×10^{-4}	1.0	53	4.0×10^{4}	+0.32
0.1	171	3.6×10^{-5}	1.0	51	1.3×10^{3}	−0.75
1.0	21	2.5×10^{-6}	1.0	9,52	9.7×10^{2}	+0.03
0.5	119	1.3×10^{-6}		205	3.5×10^{3}	+0.94
0.3	8	3.5×10^{-6}	1.0	17,155	9.8×10^{2}	+0.34
	173					−1.03
1.0	147	1.5×10^{-5}	1.0	183,148	1.7×10	+0.13
	173					+0.19
0.1	171					−0.18
0.1	6,114		0.1	21	1×10^{2}	+1.16
1.0	Table 5	2.0×10^{-6}	1.0	12	1.11	−0.35
1.0	104	1.32×10^{-6}	1.0	104	3.4×10^{-1}	+0.75
1.0	113	1.0×10^{-6}	1.0	113	1.2×10^{-1}	+1.20
var	Table 5	2.2×10^{-6}	1.0	12	9×10^{-2}	+0.20
0.1	166					+1.82
0.5	133	1.74×10^{-6}	0.5	20	8.3×10^{3}	+0.12

Mention should also be made ot the excellent data being produced by the South African Research Unit for Chemical Kinetics especially for the anation of $Co(NH_3)_5(OH_2)^{3+}$ with various carboxylate ligands [17,51—54].

(i) Dinuclear pentaammine complexes

μ-Hydroxo bridged complexes of the type $(NH_3)_5M(OH)M(NH_3)_5^{5+}$ are known for both Cr(III) and Co(III). The Co(III) complexes have only recently been described [206] and are isolated from the reaction between $(NH_3)_3Co(OH)_3Co(NH_3)_3^{3+}$ and liquid ammonia. The Cr(III) analogs (the rhodochromium salts) have been known for almost a century and have been extensively investigated [33,207]. The latter are obtained by air oxidation of highly buffered (NH_4^+/NH_3) solutions of Cr(II) [33].

In acid solution, the hydroxo bridge is cleaved, and $M(NH_3)_5(OH_2)^{3+}$ ions are generated. The Co(III) complex reacts some 300 times faster than the Cr(III) analog (k_{aq}(288)(Co(III)) = 6.4×10^{-4} s^{-1}, μ = 0.2 M vs. k_{aq}(289)-(Cr(III)) = 2×10^{-6} s^{-1}) [206], apparently independent of $[H^+]$ in the range 5×10^{-4}—5×10^{-2} M. More recent investigations [126,208] show that for Co(III) this range was too limited and a rate law represented by eqn. (12) is observed for $[H^+] = 10^{-4}$—2.0 M (μ = 2.0 M, $LiClO_4$). The acid independence for the Cr(III) analog has been confirmed [209] in the range $[H^+]$ = 0.1—1.0 M (μ = 1.0 M, $NaClO_4$). Kinetic parameters (298.2 K) for the Co(III) complex (eqn. (12)) are 10^3 k_1 (s^{-1}) (μ = 2.0 M, $LiClO_4$) = 7.58 E_a (kJ mol^{-1}) = 86, $\Delta S_{298}^{\neq}$ (J K^{-1} mol^{-1}) = —5; 10^3 k_2 ($M^{-1}s^{-1}$) (μ = 2.0 M $LiClO_4$) = 5.37, E_a = 52, $\Delta S_{298}^{\neq}$ = —121; and for the Cr(III) analog 10^5 k_1 (μ = 1.0 M, $NaClO_4$) = 1.04, E_a = 116, $\Delta S_{298}^{\neq}$ = +41.

(ii) μ-Peroxo and μ-superoxopentaaminecobalt(III) complexes

Air or molecular oxygen oxidation of cobalt(II) solutions in the presence of ligands (or ligand mixtures) containing five nitrogen donor atoms, very often produces binuclear μ-peroxo bridged complexes [210], $(N_5)CoO_2Co(N_5)^{4+}$.

Further oxidation of the brown diamagnetic μ-peroxo complexes with Cl_2, Br_2, HNO_3 or Ce^{4+} can give the green paramagnetic μ-superoxo complexes $(N_5)CoO_2Co(N_5)^{5+}$ with a characteristic 13-line ESR spectrum even in aqueous solution [211]. The general chemistry of these compounds has been reviewed [210] and the data for complexes pertinent to this review are summarised in Table 10.

These μ-peroxo complexes are important precursors to the mononuclear anionopentaaminecobalt(III) complexes containing polyamine ligands [212, 213] as the μ-peroxo bridge is cleaved in strong acid to give first aqua and then aniono complexes, if the anion is a good nucleophile (Scheme 3).

$$(N_5)CoO_2Co(N_5)^{4+} + HX \xrightarrow{H_2O} 2\ Co(N_5)(OH_2)^{3+} + \text{decomposition products}$$

$$Co(N_5)OH_2^{3+} + X^- \rightarrow CoXN_5^{2+} + H_2O$$

SCHEME 3. Decomposition of μ-peroxocobalt(III) complexes in acidic solution.

TABLE 10

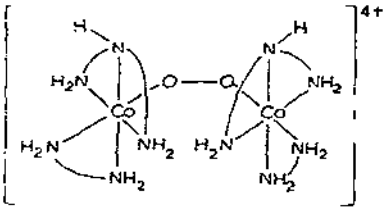
Characteristics of some μ-peroxo and μ-superoxopentaamminecobalt(III) complexes

N_5	μ-Peroxo [a]			μ-Superoxo				
	λ_{max}(nm)	(ϵ(M^{-1} cm^{-1})) [b]	Ref.	λ_{max}(nm)	(ϵ(M^{-1} cm^{-1})) [b]	μ_{eff}(B.M.)	g [c]	Ref.
tetren	310(12,580)	416sh(714)	221	468(560)	704(1330)	1.86	2.0313	211
	312(12,250) [d]		219	465(602)	709(1412)			221
		437sh(619)	211					
trien(NH_3)	Unstable		221	469(447)	706(1190)	1.89	2.0303	211
		562sh(230)	211	469(457)	709(1288)			221
tren(NH_3)	303(9120)	500sh(302)	222	473(363)	716(912)			222
dien(NH_3)$_2$		537sh(272)	211	469(365)	707(1170)	1.97	2.0297	211
dien(en) [e]	300(9550)	416sh(602)	221	472(385)	706(1210)	1.89	2.0304	211
		420sh(557)	211	476	706			223
	305	356	223					
dien[(−)-pn]	301(10,000)	416sh(537)	221	467(616)	714(1549)			221
dien[(+)-pn]			212					
dien(tmd)			212	Unstable				211,213
dpt(en)			212	Unstable				211,213
dpt(tmd)			212	Unstable				211,213
(en)$_2$(NH_3)	Unstable		221	476(302)	709(1122)			221
		550sh(247)	211		693(1240)			211
			224	471(350)				224
[(−)-pn)$_2$(NH_3)	Unstable		221					
(tmd)$_2$(NH_3)								211,213
(NH_3)$_5$ [a, f]				471(275)	670(842)	1.74	2.0249	210,225,226

[a] In water; [b] in 0.1 M H^+; [c] Zeeman splitting factor (accuracy ±0.0003); [d] α-isomer (see Scheme 5); [e] for crystal structure see Ref. 217; [f] for crystal structure see Ref. 227.

When $N_5 = 5\ NH_3$, the yield of mononuclear Co(III) complexes is low with strong mineral acids [210] but quite good using aqueous NH_4Cl solutions [214]. As the degree of chelation increases the amount of decomposition to Co(II) decreases and yields of 50—75% of the chloropentaamine can be obtained from the μ-peroxo using 6 M HCl [215,216].

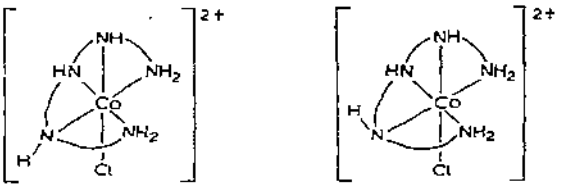
Also, as the degree of chelation increases, the number of potential isomers to the μ-peroxo rapidly increases. It has been reported [217], without detail, that several $Co_2(en)_2(dien)_2O_2^{4+}$ isomers have been prepared. The crystal structure of one of these has the symmetrical configuration shown in Scheme 4 [217].



SCHEME 4. Sketch of the geometric configuration adopted by $[Co_2(en)_2(dien)_2(O_2)](ClO_4)_4$ [217].

The configuration of the polyamines is the same as that found for the κ-$CoCl(en)(dien)^{2+}$ isomer, one of the two forms isolated from the HCl decomposition of the μ-peroxo [215,218] (see Scheme 26).

Zehnder and Fallab [219] have isolated two forms of $Co_2(tetren)_2O_2^{4+}$. Oxygenation of Co(II) plus tetren in 60% aqueous ethanol at 35°C gives the μ-peroxo isomer which on decomposition produces α-$CoCl(tetren)^{2+}$ (Scheme 5).



α-$CoCl(tetren)^{2+}$ β-$CoCl(tetren)^{2+}$

SCHEME 5. Geometric configurations adopted by the α- and β-$CoCl(tetren)^{2+}$ ions [220].

Lower oxygenation temperatures (0°C) favour the μ-peroxo which gives β-$CoCl(tetren)^{2+}$ on decomposition. Thus we suggest that the low temperature tetren μ-peroxo has the same configuration as the above $Co_2(en)_2(dien)_2O_2^{4+}$ isomer, apart from an added chelate ring.

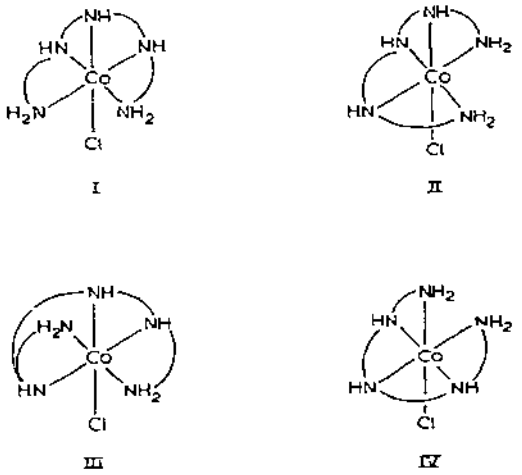
Unfortunately, the isolation of an isomeric mixture of mononuclear chloropentaaminecobalt(III) complexes from a particular μ-peroxo complex does not mean that the parent is a mixture, as it is known that the mononuclear aqua complexes can isomerise [11]. The relative proportion of isomers will thus depend on the anation rate relative to the isomerisation rate.

We note here, that analogues of these μ-peroxo cobalt(III) complexes have not yet been reported for chromium(III).

C. QUINQUIDENTATE POLYAMINE LIGANDS

An excellent introduction to this field is the article by Lions [228]. Among the ligands decribed in this section are tetren [68,229] and trenen and their N or C substituted analogues.

The modes of coordination of tetren are depicted in Scheme 6 (I, II, III, IV). I has a plane of symmetry but II, III and IV are asymmetric. In addition to the stereochemistry resulting from the arrangement of the chelate rings, there is the possibility of diasteroisomeric forms resulting from alternative configurations about the sec-N atoms which fuse chelate rings in the same plane. From this source II could exist in two forms and IV in four forms. The alternative forms in III are identical as seen by rotation about the N—Co—X axis.



SCHEME 6. Possible geometric configurations for $MCl(tetren)^{2+}$.

Using the commercially available (but impure) ligand, House and Garner [230,231] isolated two $CoCl(tetren)^{2+}$ isomers (α and β) and Marzilli and Sargeson a third ($\alpha\alpha$). Only the β isomer was resolved by House and Garner, but optically active forms of both α and β isomers were obtained by Marzilli. Single crystal X-ray structures by Snow [220,232—234] have established the $\alpha\alpha$ form as I and the α and β isomers as II with enantiomeric arrangements about the sec-N center joining the coplanar chelate rings (Scheme 5).

The α form is converted to the β form by replacement of the chloro by nitro in acid solution and the reverse transformation ($\beta \rightarrow \alpha$) is achieved by base hydrolysis [230,231].

Strain energy minimum calculations have been performed by Snow [220]

and the strain energies relative to α as zero, are 10.9 kJ mole^{-1} for β and 2.1 kJ mole^{-1} for αα. The chromium(III) complexes α-CrX(tetren)$^{n+}$ (X = Cl, NCS, OH_2) have also been prepared [230,231, 235—237] and the rates of the stepwise "unwrapping" of the quinquidentate ligand from the metal center have been measured in acid solution [236,237] (Scheme 7).

$$Cr(tetren)(OH_2)^{3+} \underset{-36}{\overset{550}{-86.5\rightarrow}} Cr(Htetren)(OH_2)_2^{4+} \underset{+4}{\overset{2100}{-96.6\rightarrow}}$$

$$a,\ b,\ c\text{-}Cr(H_2tetren)(OH_2)_3^{5+} \underset{-8}{\overset{24}{-105\rightarrow}} Cr(H_3tetren)(OH_2)_4^{6+} \underset{-24}{\overset{1}{-108\rightarrow}}$$

$$Cr(H_4tetren)(OH_2)_5^{7+} \underset{-16}{\overset{0.173}{-116\rightarrow}} Cr(OH_2)_6^{3+} + H_5tetren^{5+}$$

SCHEME 7. Stepwise unwrapping of Cr(tetren)$(OH_2)^{3+}$. Numbers on the arrows (reading downwards) are 10^5 k (s^{-1}) in 4 M $HClO_4$ at 333.2 K; E_a (kJ mol^{-1}); ΔS_{298}= (J K^{-1} mol^{-1}).

Similar unwrapping schemes have also been established for less chelated Cr(III) amine systems [50,237,238].

The most thoroughly investigated Co(III) tetren complexes are α and β-CoX(tetren)$^{2+}$ with X = Cl [239], NCS [240,241] and N_3 [242]. These complexes are thought to have an unusually acidic N—H proton (believed to be the sec-NH proton common to the two coplanar rings, Scheme 6, configuration II) [240—242]. This is reflected in an estimated $k_{OH}(298) = 3.5 \times 10^4$ M^{-1} s^{-1} for α-CoCl(tetren)$^{2+}$ [239] (cf. $k_{OH}(298)$ $CoCl(NH_3)_5^{2+} = 0.86$ M^{-1} s^{-1}) so that even in 0.1 M H^+ there is a considerable contribution to the release of the X groups via the base hydrolysis path [241,242]. The α → β isomerism of Co(NCS)(tetren)$^{2+}$ in the pH range 2.2—2.7 is also believed [240] to proceed via direct base catalysed proton inversion at this site. At 343.2 K and μ = 1.0 M the α-CoCl(tetren)$^{2+}$ isomer aquates 1.7 times and base hydrolyses 3.4 times as fast as the β isomer, whereas for CoNCS-(tetren)$^{2+}$ the β form base hydrolyses about 1.2 times faster than the α (μ = 1.0 M, T = 288—298). Kinetic data are summarised in Tables 11 and 12.

Recently, the tetren and trenen ligands (and some C-substituted analogues) have been synthesised by condensation of coordinated amino aldehydes or ketones to coordinated trien or tren (Schemes 8,9) [243,244].

Alternatively, trenen and sec-N-Metrenen can be synthesised by conventional organic techniques [246] and the Co(III) complexes have been prepared. Unfortunately, the isolated complexes have different geometric configurations as established by single crystal X-ray analysis [95,243] (Scheme 10).

Quinquidentate ligand complexes have also been obtained from the poten-

TABLE 11

Second-order rate constants for the base hydrolysis of some CoX(quinquidentate polyamine)$^{2+}$ complexes

N_5	X	Isomer	T (K)	k_{OH} ($M^{-1}\ s^{-1}$)	E_a (kJ mol^{-1})	$\Delta S_{298}^{\neq}$ (J K^{-1} mol^{-1})	Ref.
tetren	Cl	α	298.2	3.5×10^4	100	+171	239
			343.2	5.7×10^6			
	Cl	β	343.2	1.7×10^6			239
	NCS	α	288.2	51.5			242
			293.2	66.5			
			298.2	88.5	39	−86	242
	NCS	β	288.2	60.0			242
			293.2	83.0			
			298.2	108.0	42	−73	242
	N_3	α	298.2	3.2×10^2	111	+173	240
trenen	Cl	sym	298.2	518			95,243
Metrenen	Cl	unsym	298.2	29			243

TABLE 12

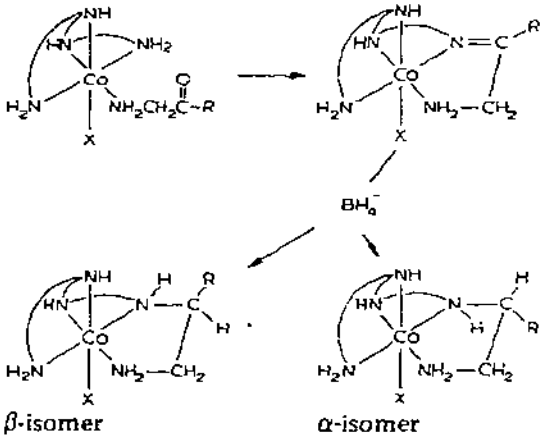
Kinetic parameters for the aquation of α- and β-CoX(tetren)$^{n+}$ complexes

Isomer	X	H^+ (M)	μ (M)	T (K)	k_{obs} (s^{-1})	k_1 (s^{-1})	k_2 ($M^{-1}\ s^{-1}$)	E_a (kJ mol^{-1})	$\Delta S_{298}^{\neq}$ (J K^{-1} mol^{-1})
α [a]	Cl	1.0	1.0	323.08	1.91×10^{-6}				
		0.02	1.0	323.08	3.50×10^{-6}				
		0.01	1.0	323.08	5.18×10^{-6}				
		0.1	0.1	323.08	3.22×10^{-6}				
		0.01	0.1	323.08	9.57×10^{-6}				
		0.001	0.1	323.08	48×10^{-6}				
		0.1	0.1	298.2	3.6×10^{-8}			113	−17
		0.1	1.0	298.2		0.4×10^{-6}		113	−29
		0.1	1.0	323.08		1.9×10^{-6}			
		0.1	1.0	337.98		12.2×10^{-6}			
		0.1	1.0	343.2		22×10^{-6}			
β [a]	Cl	0.1	1.0	343.2		13×10^{-6}			
		0.1	0.1	298.2	9.7×10^{-8}			123	−28
		0.1	0.1	323.08	4.43×10^{-6}				
		0.1	0.1	337.98	38.6×10^{-6}				
		0.1	0.1	343.2	62.8×10^{-6}				

α [b]	N_3	0.1—0.5	1.0	353.2	1.05×10^{-6}	1.68×10^{-5}		
				363.2	3.7×10^{-6}	5.9×10^{-5}		
				371.2	11.5×10^{-6}	19.7×10^{-5}		
				298.2	1.1×10^{-10}		142	+42
				298.2		1.5×10^{-9}	146	+71
α [c]	NCS		1.0	363.2	4.5×10^{-8}			
				368.2	10.2×10^{-8}			
				373.1	19.5×10^{-8}			
				298.2	2.7×10^{-13}		167	+66
				Isomerisation reactions				
α → β [d]	NCS		1.4	323.2	1.71×10^{-6}	0.42×10^{-6}		
				328.2	13.6×10^{-6}	3.84×10^{-6}		
				343.2	25.7×10^{-6}	9.00×10^{-6}		
				298.2	3.0×10^{-8}		129	+25
				298.2		4.6×10^{-9}	144	+67

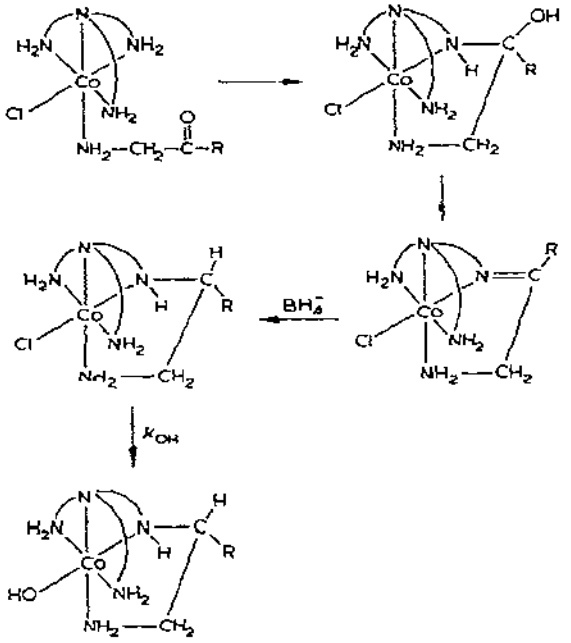
[a] Ref. 239, see also refs. 68,229. Rate law: $k_{obs} = k_1 + k_{OH}K_w[H^+]^{-1}$.
[b] Ref. 240. Rate law: $k_{obs} = k_1 + k_2[H^+]$.
[c] Ref. 242. Complex rate law at low $[H^+]$.
[d] Ref. 241. Rate law: $k_{obs} = k_1 + k_2[NCS]$.

tially hexadentate ligand, penten [247], a polyamine EDTA analogue, where one end has failed to coordinate (Scheme 11).



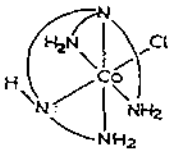
X = Cl, R = CH_3: β = 80%, α = 20%
X = Cl, R = H : β = 7%, α = 93%
X = NO_3, R = H: β = 35%, α = 65%

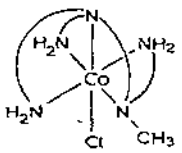
SCHEME 8. Synthesis of tetren via reactions of coordinated ligands.



R = H: $k_{OH}(298)$ = 518 M^{-1} s^{-1} [243]
R = CH_3: $k_{OH}(298)$ ~ 520 M^{-1} s^{-1} [244]
R = Ph: $k_{OH}(298)$ ~ 3700 M^{-1} s^{-1} [244]

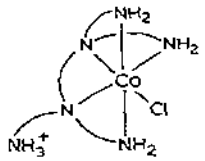
SCHEME 9. Synthesis of trenen via reactions of coordinated ligands.





trenen: $k_{OH}(298) = 518\ M^{-1}\ s^{-1}$ [95,243]
Metrenen: $k_{OH}(298) = 29\ M^{-1}\ s^{-1}$ [243]

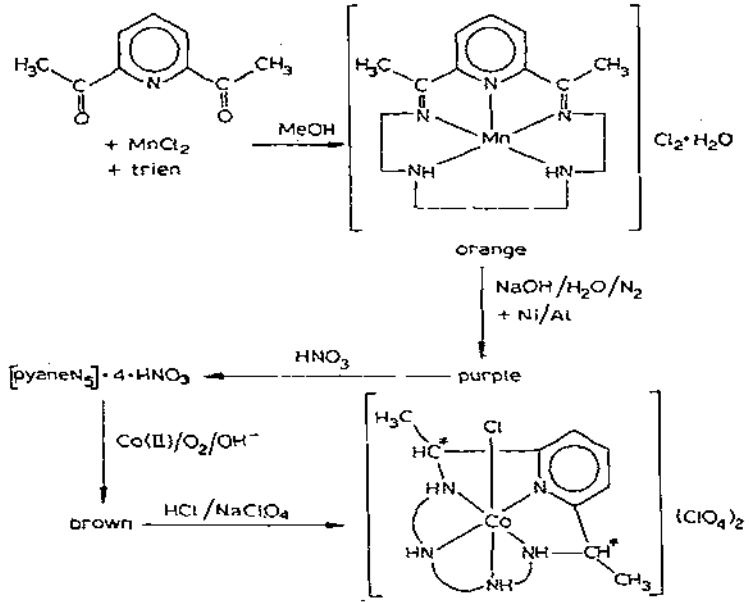
SCHEME 10. Geometric configurations adopted by *sym*-CoCl(trenen)$^{2+}$ and CoCl(Metrenen)$^{2+}$.



SCHEME 11. A possible isomer of CoCl(Hpenten)$^{3+}$.

Various equilibria between Co(penten)$^{3+}$, Co(penten)OH^{2+}, Co(Hpenten)-(OH)$^{3+}$ and Co(Hpenten)OH$_2^{4+}$ have been measured as well as the rates of ring opening and ring closure [247]. The hexamine has been resolved with active Co(ox)$_3^{3-}$ and the ORD spectra of Λ-Co(Hpenten)X^{3+} (X = OH, Br) have been recorded [247].

Cobalt(III) complexes of the macrocyclic pentaamine, pyaneN$_5$ [248] (Scheme 12) have been isolated in apparently one isomeric form and their physical properties suggest that all five nitrogen donor groups are coordinated.



SCHEME 12. Synthesis of pyaneN$_5$ and one possible form of the chloropentaaminecobalt(III) complex. Carbon atoms marked (*) are potential asymmetric centers [248, 249].

D. QUADRIDENTATE–UNIDENTATE SYSTEMS

Polyamines represented in this class include linear $CoX(trien)(NH_3)^{2+}$, "tripod" $CoCl(tren)NH_3^{2+}$ and macrocyclic tetraamines, $CoCl(cyclam)(NH_3)^{2+}$. The unidentate ligand is almost exclusively ammonia. The exception is found in the recently described crystal structure of *trans*-chloro-α, β, γ, δ-tetraphenylporphinatopyridinecobalt(III) [250]. Chromium(III) complexes are not yet represented although both the *cis*-α-$CrXY(trien)^{n+}$ [251] and $CrXY(tren)^{n+}$ [252] systems are well characterised.

The $CoX(trien)NH_3^{n+}$ system is again one of considerable isomeric complexity (Scheme 13).

Independent investigators [213,253] have characterised three $CoCl(trien)(NH_3)^{2+}$ isomers, but it is not known if these are identical. A single crystal X-ray analysis of the isomer which has the slowest rate of base hydrolysis

TABLE 13

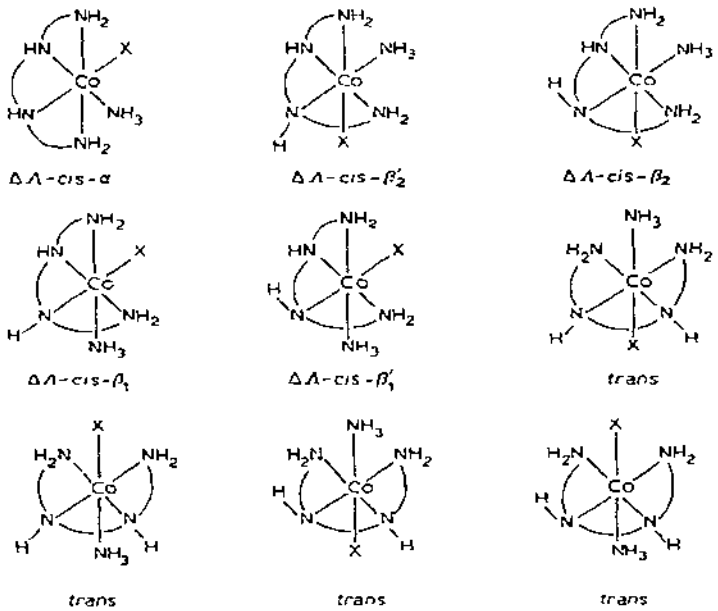
Kinetic parameters for the aquation and base hydrolysis of some aniono(quadridentate polyamine)(ammine)cobalt(III) complexes

Complex	μ (M)	T (K)	k_{OH} (M^{-1} s^{-1})	Ref.
Base hydrolysis				
cis-α-$CoCl(trien)(NH_3)^{2+}$	1.0	298.2	10.6	253
cis-β_2-$CoCl(trien)(NH_3)^{2+}$	1.0	298.2	4.8×10^4	253
cis-β_2'-$CoCl(trien)(NH_3)^{2+}$	1.0	298.2	2.3×10^5	253
Red-$CoCl(tren)(NH_3)^{2+}$ [a]	1.0	298.2	380	96
Purple-$CoCl(tren)(NH_3)^{2+}$ [b]	1.0	298.2	2.0×10^{-2}	96
trans-$CoCl(cyclam)(NH_3)^{2+}$	0.21	298.2 [c]	1.4×10^4	
→ Cl^-	0.21	297.2	1.2×10^4	259
	0.21	273.2	4.0×10^2	259
trans-$CoCl(cyclam)(NH_3)^{2+}$ → NH_3	0.51	273.2	1.7	259
Complex	H^+ (M)	T (K)	k_{aq} (s^{-1})	Ref.
Aquation				
Red-$CoCl(tren)(NH_3)^{2+}$	0.1	299	15×10^{-5}	255
Purple-$CoCl(tren)(NH_3)^{2+}$	0.1	299	7.4×10^{-5}	255
trans-$CoCl(cyclam)(NH_3)^{2+}$ [d] → Cl^-	0.51	298.2	7.3×10^{-8}	259
trans-$CoCl(cyclam)(NH_3)^{2+}$ [e] → NH_3	0.51	298.2	4.2×10^{-11}	259

[a] 100% retention [96,258].
[b] 15% retention [96,258].
[c] E_a = 95.5 kJ mol^{-1}, $\Delta S_{298}^{\neq}$ = −146 J K^{-1} mol^{-1} [259].
[d] E_a = 122 kJ mol^{-1}, $\Delta S_{298}^{\#}$ = +19 J K^{-1} mol^{-1} [259], μ = 0.51 M.
[e] μ = 0.51 M.

(k_{OH} = 10.7 M^{-1} s^{-1}, 298 K, μ = 1.0) [253] shows this to be the $\Delta\Lambda$-*cis*-α form [254] (Scheme 13). The other two isomers isolated by Dwyer base hydrolyse much more rapidly (Table 13) and are believed [253] to have the β_2 and β_2' configurations. A complex analysing correctly for $[CoCl(trien)(NH_3)]Cl_2$ was also isolated by Pearson et al. [68] but this may be an isomeric mixture as the base hydrolysis rate (k_{OH} = 160 M^{-1} s^{-1}, 298 K, μ = ?) [256] does not agree with that obtained for the pure *cis*-α form. Another possibility is that the isolated complex is mainly the red form of $CoCl(tren)(NH_3)^{2+}$ as, at that time, the commercially available "triethylenetetramine" contained considerable quantities of tren [257].

Although only two geometric isomers (Scheme 14) are possible for $CoCl(tren)(NH_3)^{2+}$, and two (red and purple) have been isolated [96,222,255,258] there is controversy with regard to the assignment [96,255].



SCHEME 13. The 14 possible $CoX(trien)(NH_3)^{2+}$ isomers. Nomenclature is that of Dwyer [253,254].

p-red [96]
α [255]

t-purple [96]
β [255]

SCHEME 14. Geometric isomers possible for $CoCl(tren)(NH_3)^{2+}$. The assignment of the red and purple forms is from reference [96]. *

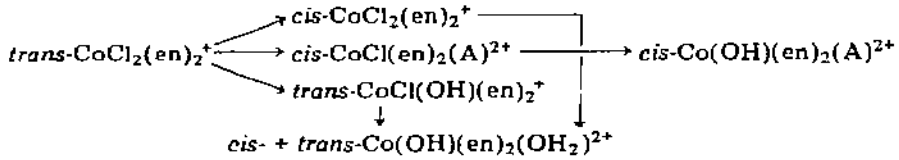
* Note that the isomer assignments in Table IV of ref. 96 are incorrect and should be reversed.

Base hydrolysis studies show that the red form reacts about 10^4 times faster than the purple form. This is explained in terms of *trans* activation by the coordinated chloride as the red form has two rapidly exchangeable protons. ($k_{ex} = 3.2 \times 10^7\ M^{-1}\ s^{-1}$, 298 K, μ = 1.0 M, for the two most readily exchanged protons in the red form: k_{ex} (max) = $7 \times 10^5\ M^{-1}\ s^{-1}$, 298 K, μ = 1.0 M, for the purple form). The additional reactivity is thought to come from the difference in the ease of distortion to a five-coordinate intermediate as the geometry assigned to the red form (Scheme 14) shows that this is nicely poised for such an event, despite almost equal strain energy in both isomers [96].

Of the macrocyclic complexes [260,261] only *trans*-CoCl(cyclam)$(NH_3)^{2+}$ has been studied in any detail [259]. One unusual feature of this complex is that NH_3 loss competes with chloride release in acid solution, a situation not often encountered in Co(III) amine chemistry but more characteristic of the Cr(III) analogues. This ready loss of unidentate amine may be a relatively unrecognised feature of cobalt(III) macrocyclic complexes as Co(tet)$(NH_3)_2^{3+}$ (tet = 5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetrazacyclotetradeca-4,11-diene) produces Co(tet)$(NH_3)(OH_2)^{3+}$ in hot water—methanol in 10 min [262].

E..BIS(DIAMINE)—UNIDENTATE SYSTEMS

This section is dominated by complexes of the type $CoX(en)_2(A)^{n+}$, where A is a unidentate aliphatic or aromatic heterocyclic amine. These were first investigated by Meisenheimer and his students and the results were published in a rather neglected "classic" paper in Annalen [263]. The general synthetic method developed by Meisenheimer and used essentially unchanged by subsequent investigators [264—267] is to stir an aqueous slurry of *trans*$[CoCl_2(en)_2]Cl$ with slightly more than the calculated amount of the amine, which is dissolved in ethanol if it is not soluble in water. Reaction time varies from a few seconds ($MeNH_2$) [264] to several days (isoquinoline) [267]. Despite much qualitative study, the influence of the nature of the amine on the products of the reaction remains speculative (Scheme 15).



SCHEME 15. Reaction products identified from *trans*-$[CoCl_2(en)_2]Cl$ plus amine.

A number of investigators have tried to correlate the basicity of the amine with reactivity but the general conclusion is "the marked influence of basicity on complex formation may sometimes be overshadowed by the effect of other factors which cannot be strictly defined at present" [266]. It is obvious that a more quantitative study of this interesting reaction is desirable.

For a number of amines, the stereochemistry of the chloropentaamine product has been unambiguously established as *cis* by resolution of the race-

mic mixture. (A *trans* configuration would be achiral.) Table 14 lists the complexes that have been resolved and it can be reasonably assumed that a *trans* → *cis* stereochemical change from parent to product is characteristic of this reaction. The *cis*-configuration for racemic $[CoCl(en)_2py](NO_3)_2$ has been confirmed by an X-ray crystal structure [439].

Perhaps a simpler method of geometric assignment can be made on the basis of the C-13 NMR spectra where resonances due to the ethylenediamine carbon atoms are apparently diagnostic of the stereochemistry. It has been shown for several *cis*- and *trans*-$CoXY(en)_2^{n+}$ pairs that only one en-C resonance is observed in *trans* complexes but two or more are observed for the racemic *cis* [277,279]. However, this method has not been tested with *trans*-$CoX(en)_2(A)^{n+}$ systems and would not be applicable to Cr(III) complexes. In fact, $CoX(en)_2(NH_3)^{n+}$ is the only Co(III) system of this type where both *cis* and *trans* forms have been characterised. This latter complex is made by oxidation of the coordinated thiocyanate in *trans*-$CoCl(NCS)(en)_2^+$ [280].

TABLE 14

Sign of rotation at the Na_D line and absolute configuration of the less soluble diastereoisomeride of some *cis*-$CoCl(en)_2(A)^{2+}$ salts [a]

Resolving agent [b]	Λ	Ref.	Δ	Ref.
NH_4(+)BCS	(+)-NH_3	268	(−)-aniline	270
	(+)-NH_3 [c]	269	(−)-benzylamine	270
			(−)-cyclohexylamine	273
			? (−)-az	274
			? (−)-$NH_2(CH_2)_2Br$	274
			? (−)-$NH_2CH_2CONH_2$	275
K(+)SbOT	(+)-benzylamine	270	(−)-NH_3	276
	(−)-pyridine	270		
	(+)-$MeNH_2$	271		
Na(+)SbOT	(+)-$MeNH_2$	267	(+)-pyridine	267
	(+)-$EtNH_2$	267	(+)-imidazole	267
	(−)-benzimidazole	267		
	(−)-4-benzylpyridine	272		
Na(+)AsOT	(+)-benzylamine	267	(−)-nButylamine	267
	(−)-isoquinoline	267	(+)-4-methylpyridine	273
			(+)-N-methylimidazole	273
			(+)-3,4-dimethylpyridine	277
			(+)-3,5-dimethylpyridine	277
			(−)-2-aminoethanol	214
			(+)-3,5-dimethylpyridine [d]	272

[a] For a description of the Λ and Δ arrangements of the chelate rings in *cis*-$M(en)_2XY^{n+}$ complexes see Fig. 3 in ref. 278.

[b] See appendix for the abbreviations used.

[c] For *cis*-$CoBr(en)_2(NH_3)^{2+}$.

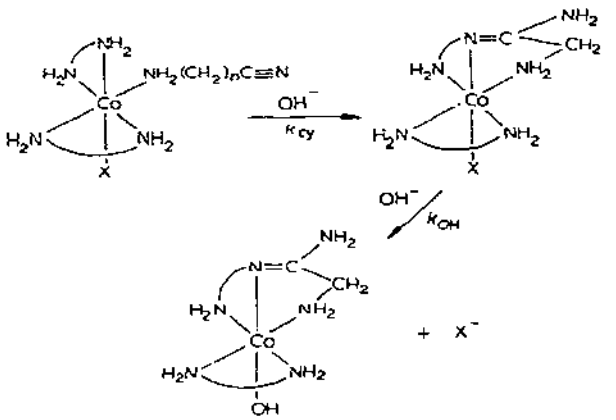
[d] For *cis*-$CoBr(en)_2$(3,5-dimethylpyridine)$^{2+}$.

The *cis*- and *trans*-$CrX(en)_2(NH_3)^{n+}$ analogues have recently been prepared [84,281,282] by the reaction of liquid ammonia on suitable chloro or bromo bis(ethylenediamine) complexes. Table 15 lists the visible absorption spectral parameters for the $MX(en)_2(NH_3)^{n+}$ isomers. No other $CrX(en)_2A^{n+}$ complexes appear to have been characterised.

The "Meisenheimer" reaction is not confined to monoamines and bridged dinuclear complexes of the type $[CoCl(en)_2NH_2(CH_2)_xNH_2(en)_2ClCo]X_4$ can be obtained [290,291]. Careful control of the conditions can also yield unidentate diamine complexes such as *cis*-$[CoCl(en)_2(enH)]X_3$ [284,292—294]. These latter complexes, as well as those containing other potentially bidentate ligands e.g. $NH_2(CH_2)_xCO_2R$ [275,295,296], $NH_2(CH_2)_xCN$ [297—299] or $NH_2(CH_2)_xX$ (X = Cl, Br) [274,300] are of particular interest because of the possibility of chelation, either at a nitrogen or the Co(III) centre, during a subsequent reaction. Such possibilities have been realised and are illustrated in Schemes 16—22.

An interesting extension of the Meisenheimer reaction is the synthesis of a water soluble inorganic polymer by reacting *trans*-$[CoCl_2(en)_2]Cl$ with polyvinylpyridine (PVP) to give $[CoCl(en)_2(PVP)]Cl_2 \cdot 2\,H_2O$ [312,313]. Polymers with up to 108 repeating units (and up to 50 Co(III) atoms) have been characterised (Scheme 23).

Pentaamine complexes with other diamine ligands have not been extensively investigated. *Trans*-$CoCl(chn)_2(NH_3)^{2+}$ salts with both the racemic and



n = 1, X = Cl: $k_{cy} = 2.57 \times 10^4\ M^{-1}\ s^{-1}$
$k_{OH} = 2.43\ M^{-1}\ s^{-1}$
n = 1, X = Cl: $k_{cy} = 1.2 \times 10^{-3}\ s^{-1}$ in water [298]
n = 1, X = Br: $k_{cy} = 4.5 \times 10^4\ M^{-1}\ s^{-1}$
$k_{OH} = 11.8\ M^{-1}\ s^{-1}$
n = 2, X = Cl: $k_{cy} \sim 0$ [301]

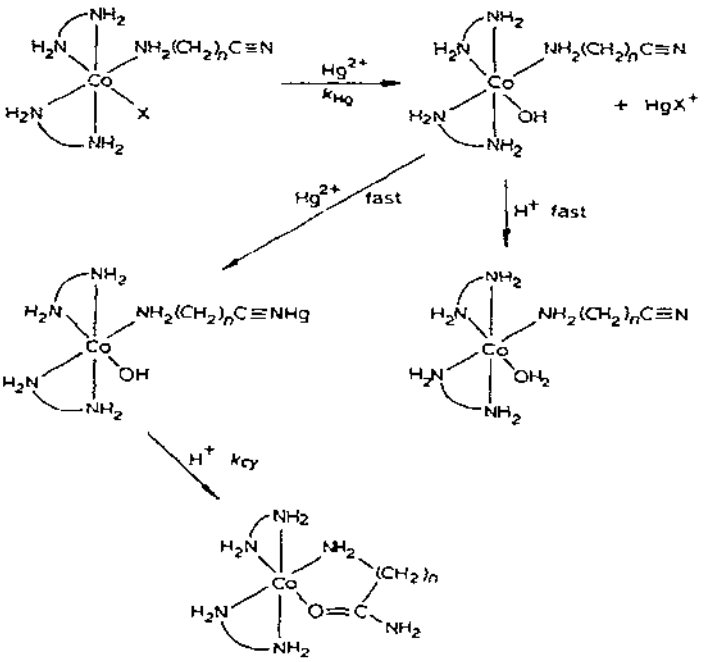
SCHEME 16. Cyclisation and base hydrolysis of *cis*-$CoX(en)_2(NH_2(CH_2)_nCN)^{2+}$ [297—299,301] at 298 K (μ = 0.1 M) [299]. Note that the configuration of the isolated Co(en)(tri)$^{2+}$ isomer [297], strongly supports the hypothesis that NH protons *trans* to the aniono group are the most labile [96].

TABLE 15

Visible absorption spectral parameters for some *cis*- and *trans*-$MX(en)_2(NH_3)^{n+}$ complexes [a,b]

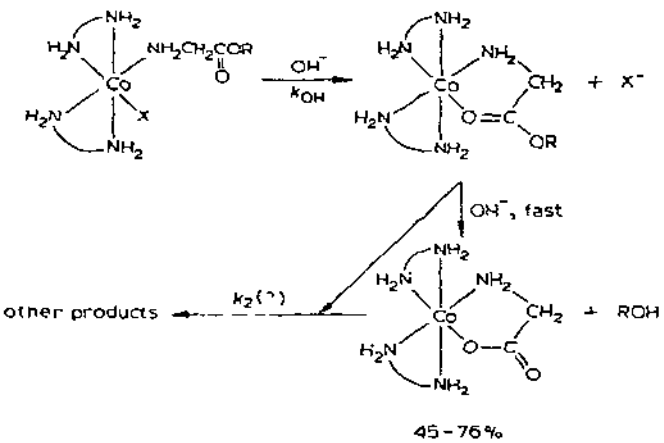
Config.	M	X	λ_{max}	λ_{min}	λ_{max}	Ref.
cis	Co	Cl	525 (73)	420 (16)	367 (77)	280,283—286
cis	Cr	Cl	506 (54.0)	424 (18.2)	374 (58.9)	84
trans	Co	Cl	525 (47)	415 (14)	365 (52)	280,283,285
trans	Cr	Cl [c]	504 (39.9)	417 (17.5)	371 (45.0)	84
cis	Co	OH_2	480 (65)	400 (15)	340 (60)	280,284—286
cis	Cr	OH_2	473 (59.2)	406 (16.8)	359 (46.6)	84
trans	Co	OH_2	480 (48)	400 (15)	340 (54)	280,285
trans	Cr	OH_2	466 (40.2)	400 (14)	354 (35.7)	84
cis	Co	Br	549 (71)		317 (775)	286
cis	Cr	Br	517 (60.1)	472 (22.1)	377 (66.2)	84
trans	Co	Br	550 (50)		300 (960)	287
cis	Cr	F	494 (64.9)	417 (16.6)	360 (34.4)	84
trans	Cr	F	490 (45.7)	409 (12.8)	356 (24.1)	84
cis	Co	NCS	490 (220)			285,286,288
cis	Cr	NCS	476 (120)			281
trans	Co	NCS	490 (168)		303 (1660)	285,288
trans	Cr	NCS	476 (80)			281
cis	Co	NO_2	458 (109)			286,289
trans	Co	NO_2				287,289
cis	Co	N_3	508 (347)			285
trans	Co	N_3	512 (277)			285

[a] In 0.1 M H^+ for Cr(III) complexes.
[b] Numbers in parenthesis are the molar extinction coefficient (M^{-1} cm^{-1}).
[c] A shoulder at ca. 470 nm is evident in the published figure [84].



$n = 1$, X = Cl: $k_{Hg} = 8.99 \times 10^{-4}$ M^{-1} s^{-1} ($\mu \sim 2$ M) [299]
$n = 1$, X = Br: $k_{Hg} = 1.58 \times 10^{-1}$ M^{-1} s^{-1} ($\mu \sim 2$ M) [299]
$= 1.4 \times 10^{-4}$ M^{-1} s^{-1} ($\mu \sim 1.4$ M) [302]
$n = 1$, X = Cl, Br: k_{cy} = rapid [299,302]
k_{Hg} indep. of $[H^+]$ in the range 0.09—0.89 M [302]
$n = 2$, X = Br: k_{Hg} = rapid [302]
$t_{1/2}$ (cyclisation) ~ 108 min, $[Hg^{2+}] = 0.1$ M, $[H^+] = 0.1$ M
k_{cy} dependent on $[H^+]^{-1}$ and $[Hg^{2+}]$ [302].

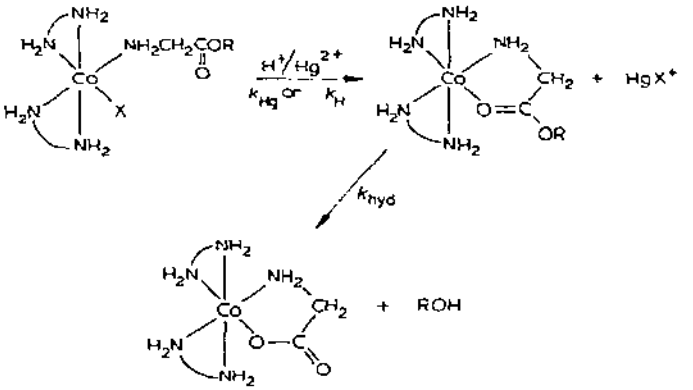
SCHEME 17. Hg^{2+} assisted hydration of a coordinated nitrile to a chelated amine [299, 302] at 298 K.



45 - 76%

	X = Cl	X = Br	
$k_{OH}(M^{-1} s^{-1})$	200	820	independent of R
$k_2 (M^{-1} s^{-1})$	~60	~100	dependent on R

SCHEME 18. Proposed reaction path for the formation of $Co(en)_2(gly)^{2+}$ from the base hydrolysis of *cis*-$CoX(en)_2(NH_2CH_2CO_2R)^{2+}$ [275,295] at 298 K ($\mu = 0.3$ M) [275].



X = Cl, R = Me:	$k_{Hg}(298) = 1.76 \times 10^{-2}$ M^{-1} s^{-1}	μ = 0.66 M [303]
X = Cl, R = Et:	$k_{Hg}(298) = 1.73 \times 10^{-2}$ M^{-1} s^{-1}	μ = 0.66 M [303]
X = Cl, R = iPr:	$k_{Hg}(298) = 1.76 \times 10^{-2}$ M^{-1} s^{-1}	μ = 0.66 M [303]
X = Br, R = as above:	$k_{Hg}(298) > 0.8$ M^{-1} s^{-1}	
R = Me:	$k_{hyd}(298) = 2.6 \times 10^{-2}$ s^{-1}	μ = 0.66 M [303]
R = Et:	$k_{hyd}(298) = 7.1 \times 10^{-3}$ s^{-1}	μ = 0.66 M [303]
	$k_{hyd}(305) = 3.0 \times 10^{-3}$ s^{-1}	μ = 4.0 M [304]
	k_{hyd} dec. with inc. μ,	see also ref. 305
R = iPr:	$k_{hyd}(298) = 1.1 \times 10^{-3}$ s^{-1}	μ = 0.66 M [303]
	$k_{hyd}(298) = 1.18 \times 10^{-3}$ s^{-1}	μ = 1.0 M [306]
X = Cl, R = H:	$k_H(313) = 9.0 \times 10^{-6}$ s^{-1}	μ = 1.0 M [307]
X = Cl, R absent	$k_{cy}(313) = 1.98 \times 10^{-5}$ s^{-1}	μ = 1.0 M [307]
	k_H cat. by Pb^{2+} [307]	

SCHEME 19. Proposed reaction paths for the cyclisation and hydrolysis of some *cis*-$CoX(en)_2(NH_2CH_2CO_2R)^{2+}$ complexes [303—307,441].

active ligand have been prepared by the action of liquid ammonia on the dichloro complex [314,315]. Kinetic parameters for the aquation and base hydrolysis of some *trans*-$CoX(AA)_2(NH_3)^{2+}$ complexes are listed in Table 16.

Reaction of *trans*-$Co(OH)(tmd)_2(OH_2)^+$ with aqueous ammonia, highly buffered with Na_2HAsO_4, slowly yields *trans*-$Co(tmd)_2(NH_3)_2^{3+}$ [320], but *trans*-$Co(tmd)_2Cl_2^+$ reacts with aqueous amines to form $Co(OH)_2(tmd)_2^+$ or $Co(OH)(tmd)_2(OH_2)^{2+}$. However, *trans*-$[CoCl_2(tmd)_2]ClO_4$, dissolved in DMA, readily forms *cis*-$CoCl(tmd)_2(A)^{2+}$ (A = NH_3, $MeNH_2$, benzylamine). The reaction with heterocyclic aromatic bases such as pyridine, is much slower. The *cis* stereochemistry of the resulting pentaamine has been confirmed by resolution [214].

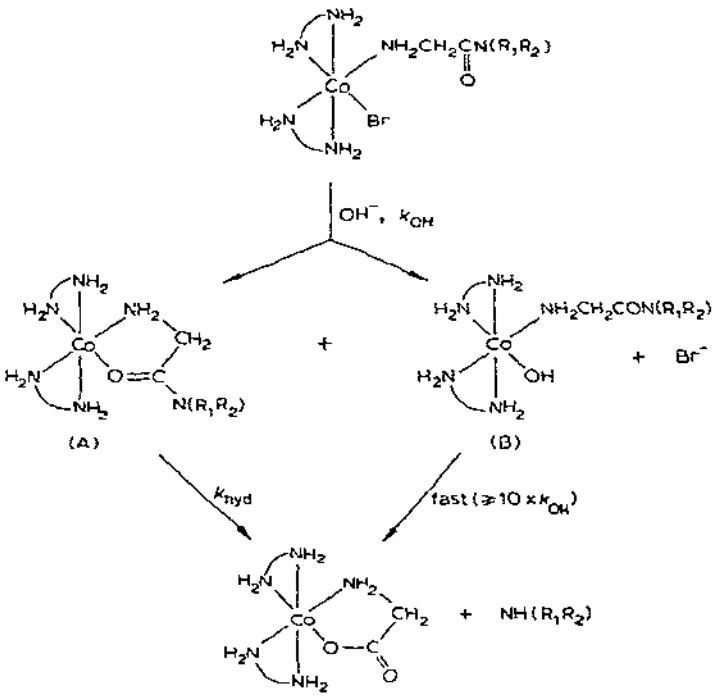
The *cis*-$CoX(AA)_2(A)^{2+}$ (X = Cl, Br) complexes are potentially useful precursers for the synthesis of hexaamines, $Co(AA)_2(A)(NH_3)^{3+}$, via displacement of the coordinated halide by liquid ammonia. (See ref. 321 for a kinetic study of this reaction.) Such syntheses have been achieved with AA = en and A = NH_3, py, 3,4-Me_2-py and 3,5-Me_2-py. In all cases, the *cis* geometric configuration is substantially retained, but while for A = NH_3, there is

TABLE 16

Kinetic parameters for the aquation and base hydrolysis of some $CoX(AA)_2(NH_3)^{2+}$ complexes

X	Config.	AA	T (K)	k_{aq} (s^{-1})	k_{OH} ($M^{-1}\ s^{-1}$)	E_a (kJ mol^{-1})	$\Delta S_{298}^{\neq}$ (J K^{-1} mol^{-1})	Ref.
Cl	*trans*	en	273.2		1.25			280
NO_2	*trans*	en	298.2		7.6×10^{-5}	138	+143	289,391
NO_3	*trans*	en	298.2		1.6×10^{3}			316
NCS	*trans*	en	298.2		5.9×10^{-3}	133	+159	288
SCN	*trans*	en	298.2		1.4×10^{2}			316
Cl	*trans*	(+)chn	273.2		0.38			314
Cl	*trans*	en	298.2	3.7×10^{-7}		96	−45	280
			298.2	2.9×10^{-7}		96	−47	287
			298.2	6×10^{-9}		99	−71	317
Cl [a]	*trans* [a]	en [a]	295.2	$<6 \times 10^{-6}$				282
Br	*trans*	en	298.2	1.2×10^{-6}		100	−21	287
NO_3	*trans*	en	298.2	6.9×10^{-6}		104	+6	287
H_3PO_4	*trans*	en	298.2	3.6×10^{-7}		113	−11	318
Cl	*trans*	(±)chn	298.2	5.5×10^{-7}		107	−8	314
Cl	[b]	(en)(phen)	298.2	6.5×10^{-6}		115	+77	319
Br	[b]	(en)(phen)	298.2	1.5×10^{-5}		121	+104	319
Cl	[b]	(en)(bipy)	298.2	4.5×10^{-6}		117	+84	319
Br	[b]	(en)(bipy)	298.2	2.2×10^{-5}		119	+99	319

[a] *trans*-$CrCl(en)_2(NH_3)^{2+}$ [282], chloride release path only.
[b] Probably one of the two possible *cis* configurations [319].



$R_1 = R_2 = H$:	$k_{OH} = 260\ M^{-1}\ s^{-1}$,	46% A
$R_1 = H$, $R_2 = Me$:	$k_{OH} = 280\ M^{-1}\ s^{-1}$,	66% A
$R_1 = R_2 = Me$:	$k_{OH} = 240\ M^{-1}\ s^{-1}$,	82% A

SCHEME 20. Proposed reaction paths for the hydrolysis of *cis*-$CoBr(en)_2(NH_2CH_2CON(R_1R_2))^{2+}$ at 298 K (μ = 1.0 M) [274,309]. For k_{hyd} data see ref. 308.

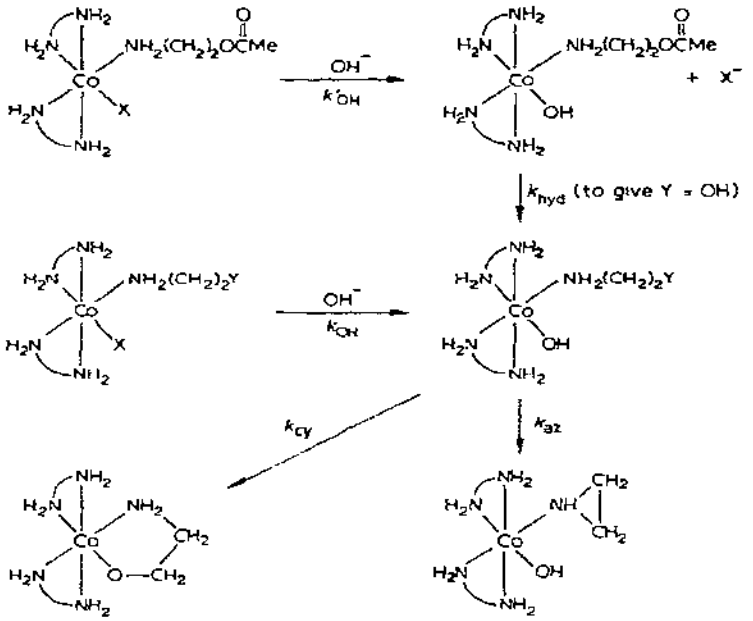
considerable optical retention [322,323], for the heterocyclic amines, the chiral chloro yields mainly the racemic hexaamine [277].

An extensive series of $Co(N_4)(aminoalcohol)^{3+}$ complexes (Scheme 21) (containing the $CoON_5$ chromophore) have been prepared with N_4 = 4 NH_3, 2en or 2R-chn [324]. Also in this class are the $M(N_4)(aminoacid)^{2+}$ chelates [325–327,438], of which the 2-carboxylpyridine and 2-carboxylhyrazine chelates (Scheme 24) are members [328].

(i) Reaction rates

Complexes described in this section have provided a fruitful source of systems for aquation, base hydrolysis and halide assisted reaction rate studies (Tables 17–19). The kinetic parameters for many of these reactions have been reviewed in 1974 (literature cited to 1972) [1] and not all the data have been reproduced here.

The aquation and halide assisted aquation reactions appear to proceed with full retention of stereochemistry, but base hydrolysis reactions usually result in some isomerisation. The steric course taken during the base hydrol-

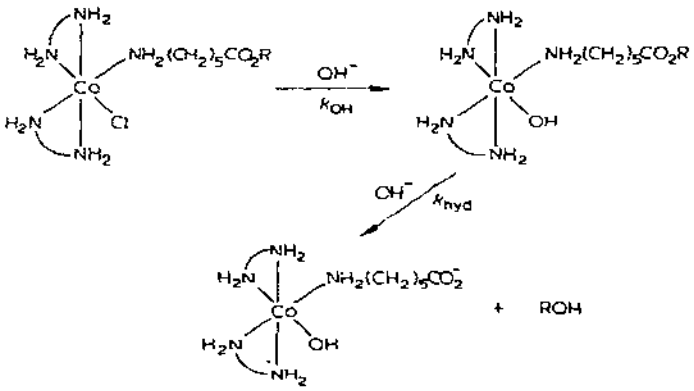


Y = Br:	77% az produced at $[OH^-]$ = 1.0 M [274]	
	21% az produced at $[OH^-]$ = 0.05 M [274]	
X = Cl:	$k'_{OH}(298) = 23\ M^{-1}\ s^{-1}$,	μ = 0.1 M [310]
	$k_{hyd}(298) = 2.4\ M^{-1}\ s^{-1}$,	μ = 0.1 M [310]
X = Y = Br:	$k_{OH}(298) = 180\ M^{-1}\ s^{-1}$	μ = 1.0 M [274]
	$k_{cy}(298) = 3.3 \times 10^{-3}\ s^{-1}$	μ = 1.0 M [274]
	$k_{az}(298) = 1.1 \times 10^{-2}\ s^{-1}$	μ = 1.0 M [274]
X = OH, Y = Cl:	$k_{cy}(298) = 1.1 \times 10^{-4}\ s^{-1}$	μ = 1.0 M [274]
X = Cl, Y = OH:	$k_{OH}(298) = 20.6\ M^{-1}\ s^{-1}$	μ = 0.1 M [310]
X = Br, Y = OH:	$k_{OH}(298) = 167\ M^{-1}\ s^{-1}$	μ = 0.1 M [310]
	$k_{OH}(298) = 190\ M^{-1}\ s^{-1}$	μ = 1.0 M [274]
$X = OH_2$, Y = OH:	$k_{cy}(298) = 1.53 \times 10^{-5}\ s^{-1}$	μ = 0.03 M [311]
	(E_a = 109 kJ mol^{-1}, $\Delta S_{298}^{\neq}$ = +21 J K^{-1} mol^{-1}) [311].	

SCHEME 21. Hydrolysis, chelation and cyclisation rates of some *cis*-$CoX(en)_2(NH_2(CH_2)_2Y)^{n+}$ complexes [274,300,310,311].

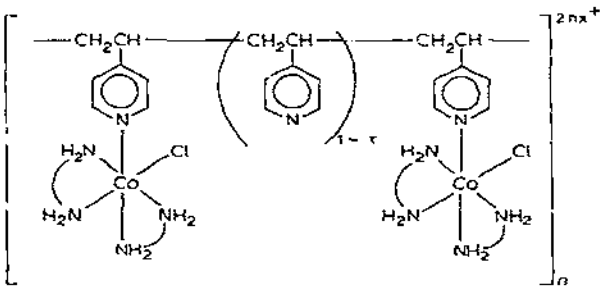
ysis of a reasonable series of optically active *cis*-$CoX(en)_2(A)^{2+}$ (X = Cl, Br) complexes has recently been determined [272]. Unfortunately, the visible absorption spectral parameters for the *trans*-$Co(en)_2(A)(OH_2)^{3+}$ complexes are unknown and the amount of *trans*-$Co(OH)(en)_2(A)^{2+}$ produced has had to be established indirectly. Nevertheless, these data (Table 18) provide a significant advance on the information available on the stereochemistry of this reaction.

Despite a considerable interest in redox reactions in Co(III) chemistry, the easily prepared *cis*-$CoX(en)_2(A)^{n+}$ systems have been almost neglected apart from the use of Fe(II) as a reductant (Table 20). A study of the Fe^{2+} + $CoCl(en)_2(NH_2(CH_2)_2OH)^{2+}$ reaction in acidic aqueous solution, and

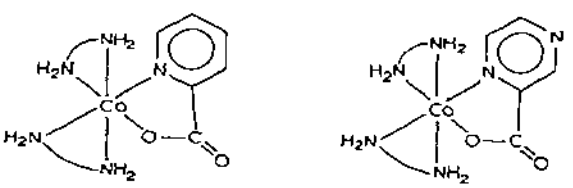


X = Cl, R = Me: $k_{OH} = 12.8\ M^{-1}\ s^{-1}$
$k_{hyd} = 0.22\ M^{-1}\ s^{-1}$
X = Cl, R = H: $k_{OH} = 9.3\ M^{-1}\ s^{-1}$
Uncoordinated ester: $k_{hyd} = 0.148\ M^{-1}\ s^{-1}$.

SCHEME 22. Consecutive hydrolysis steps for *cis*-$CoCl(en)_2(NH_2(CH_2)_5CO_2R)^{2+}$ at 298 K (μ = 0.1 M) [296].



SCHEME 23. $[CoCl(en)_2(PVP)]Cl_2$ [312,313] (x = 0.2—0.6, n = 19—108). The chirality of the chelate rings is speculative.



SCHEME 24. Bis(ethylenediamine)(picolinato)cobalt(III) and bis(ethylenediamine)-(2-carboxylatopyrazine)cobalt(III) complexes [328].

TABLE 17

Kinetic parameters for the aquation of some *cis*-$CoX(en)_2(A)^{n+}$ complexes

X	A	Solvent or H^+ (M)	T (K)	k_{aq} (s^{-1})	E_a (kJ mol^{-1})	$\Delta S_{298}^{\#}$ (J K^{-1} mol^{-1})	Ref.
Cl	NH_3	0.17 $HClO_4$	335.8	4×10^{-5}			280
		0.1 HNO_3	303.2	1.42×10^{-6}			68
		H_2O	298.2	5.5×10^{-7}	104	−18	60
		H^+/mixed solvents	298.2	2.1×10^{-8}	97	−75	317
		H_2O/H^+ all data	298.2	4.2×10^{-7}	100	−39	
		See also refs. 329,330					
Br	NH_3	0.17 $HClO_4$	298.2	1.6×10^{-6}	94	−40	280
C_2O_4H	NH_3 [a]	0.3–1.0 H^+	343.2	1.8×10^{-5}			331
			298.2	4.4×10^{-8}	112	−19	331
Cl	NH_2CH_3	H_2O	298.2	1.8×10^{-7}	110	−12	332,333
		0.1 HNO_3	298.2	3.5×10^{-7}	103	−33	283
		H_2O/H^+ all data	298.2	1.6×10^{-7}	114	0	
		See also refs. 329,334,346					
Br	NH_2CH_3	H_2O	298.2	4.7×10^{-7}	112	+3	334
		H_2O	298.2	1.4×10^{-6}	103	−19	335
		0.1 HNO_3	298.2	1.5×10^{-6}	103	−20	336
Cl	NH_2OH	0.5 $HClO_4$	298.2	4.95×10^{-6}	86	−68	337
		See also refs. 329,334					
Br	NH_2OH	0.5 $HClO_4$	298.2	2.13×10^{-5}	85	−59	334
Cl	$NH_2NH_2CH_3$	0.5 H^+	298.2	6.4×10^{-7}	90	−69	338
Cl	$NH_2CH_2CH_3$	H_2O	298.2	1.5×10^{-7}	107	−9	332
		H_2O	298.2	4.1×10^{-7}	90	−73	339
		H_2O/H^+ all data	298.2	2.1×10^{-7}	109	−14	
		See also refs. 329,330,333,334,340,341					
Br	$NH_2CH_2CH_3$	H_2O	298.2	3×10^{-7}	117	+15	334
		H_2O	298.2	1.4×10^{-6}	104	−16	335
Cl	$NH_2CH_2CH{=}CH_2$	H_2O/H^+ all data	298.2	2.0×10^{-7}	109	−17	283,399
		See also ref. 334					
Br	$NH_2CH_2CH{=}CH_2$	H_2O	298.2	5.6×10^{-6}	115	+12	334
		0.1 HNO_3	298.2	7.0×10^{-7}	107	−12	336

Cl	$NH_2CH_2C{\equiv}CH$	H_2O	298.2	1.3×10^{-7}	108	−23	334,399
Br	$NH_2CH_2C{\equiv}CH$	H_2O	298.2	2.9×10^{-7}	116	+9	334
Cl	$NH_2CH_2C{\equiv}N$	H^+	343.2	4.81×10^{-5}	125	+38	298
			298.2	5.4×10^{-8}	129	+39	
Cl	$NH_2CH_2CONH_2$	H^+	343.2	2.2×10^{-4}	87	−63	298
			298.2	1.9×10^{-6}	89	−63	
Cl	$NH_2CH(CH_3)_2$	H_2O	298.2	1.23×10^{-6}	104	−18	343,344
		See also refs. 329,334					
Br	$NH_2CH(CH_3)_2$	H_2O	298.2	7.4×10^{-6}	98	−22	334
Cl	$NH_2(CH_2)_2CH_3$	H_2O	298.2	3.1×10^{-7}	106	−23	343,344
		H_2O	333.4	2.91×10^{-5}	102	−25	345
		H_2O	343.2	8.5×10^{-5}	102	−25	343
Br	$NH_2(CH_2)_2CH_3$	H_2O	298.2	2.05×10^{-6}	96	−41	334
Cl	$NH_2(CH_2)_2Cl$	0.1 $HClO_4$	298.2	8.1×10^{-8}	106	−21	300,346
Br	$NH_2(CH_2)_2Cl$	0.1 $HClO_4$	298.2	4.2×10^{-7}	106	−9	346
Cl	$NH_2(CH_2)_2Br$	0.1 $HClO_4$	298.2	7.3×10^{-7}	107	−2	300,346
Cl	$NH_2(CH_2)_2OH$	H_2O	298.2	1.7×10^{-6}	91	−49	329,347–349
Br	$NH_2(CH_2)_2OH$	0.1 HNO_3	298.2	6.0×10^{-6}	97	−28	336
Cl	$NH_2(CH_2)_2OCH_3$	H_2O	298.2	5.6×10^{-7}	94	−49	350
Cl	$NH_2(CH_2)_2NH(CH_3)_2$	0.1 HNO_3	348.2	0.49×10^{-4}	120	+15	293
		0.1 HNO_3	298.2	3.8×10^{-8}	123	+16	
Cl	$NH_2(CH_2)_2C{\equiv}N$	H^+	298.2	2.4×10^{-7}	113	−1	301
Cl	$NH_2(CH_2)_3CH_3$	H_2O	343.2	9.3×10^{-5}	96	−46	343
		H_2O	333.4	3.2×10^{-5}	96	−45	345
		0.1 HNO_3	348.2	1.48×10^{-4}	96	−46	293
		H_2O/H^+ all data	298.2	4.7×10^{-7}	100	−40	
Br	$NH_2(CH_2)_3CH_3$	H_2O	298.2	1.7×10^{-5}	101	−24	335
		0.1 HNO_3	298.2	1.7×10^{-5}	101	−24	336
Cl	$NH_2(CH_2)_3NH_3$	0.1 HNO_3	348.2	0.64×10^{-4}	99	−43	293
		0.1 HNO_3	298.2	1.9×10^{-7}	100	−47	
Cl	$NH_2(CH_2)_3Cl$	0.1 $HClO_4$	298.2	1.3×10^{-7}	108	−15	300,346
Cl	$NH_2(CH_2)_3OH$	H_2O	298.2	3.8×10^{-7}	99	−43	329,347,348
Cl	$NH_2(CH_2)_3OCH_3$	H_2O	298.2	6.5×10^{-7}	93	−52	350
Cl	$NH_2CH_2CH(Cl)CH_3$	0.1 $HClO_4$	298.2	9.8×10^{-8}	110	−20	346
Cl	$NH_2CH_2CH(OH)CH_3$	H_2O/H^+	298.2	1.3×10^{-6}	93	−46	300,329,348
Cl	$NH_2CH_2CH(CH_3)_2$	H_2O	343.2	9.7×10^{-5}	98	−38	343
		H_2O	298.2	4.5×10^{-7}	101	−36	

TABLE 17 (continued)

X	A	Solvent or H^+ (M)	T (K)	k_{aq} (s^{-1})	E_a (kJ mol^{-1})	$\Delta S_{298}^{\#}$ (J K^{-1} mol^{-1})	Ref.
Cl	$NH_2CH(CH_3)CH_2CH_3$	H_2O	343.2	4.85×10^{-4}	87	−54	343
			298.2	4.1×10^{-6}	90	−53	
Cl	$NH_2(CH_2)_4CH_3$	H_2O	333.4	3.07×10^{-5}	85	−77	345
			298.2	2.1×10^{-6}			
Cl	$NH_2(CH_2)_4OH$	H_2O	298.2	3.4×10^{-7}	102	−40	347
Cl	$NH_2(CH_2)_5CH_3$	H_2O	333.4	3.07×10^{-5}	86	−73	345
			298.2	2.3×10^{-6}			
Cl	$NH_2(CH_2)_5OH$	H_2O	298.2	4.3×10^{-7}	101	−37	347
Cl	$NH_2(CH_2)_6CH_3$	H_2O	333.4	3.12×10^{-5}	86	−72	345
			298.2	2.6×10^{-6}			
Cl	$NH_2(CH_2)_6OH$	H_2O	298.2	4.2×10^{-7}	101	−35	347
Cl	$NH_2(CH_2)_6NH_3$	0.1 HNO_3	348.2	0.91×10^{-4}	98	−42	293
		0.1 HNO_3	298.2	2.6×10^{-7}	101	−41	
Cl	$NH_2(CH_2)_7CH_3$	H_2O	333.4	3.18×10^{-5}	86	−74	345
			298.2	2.0×10^{-6}			
Cl	$NH_2(CH_2)_7NH_3$	0.1 HNO_3	348.2	0.94×10^{-4}	98	−41	293
		0.1 HNO_3	298.2	2.7×10^{-7}	101	−40	
Cl	$NH_2(CH_2)_8CH_3$	H_2O	333.4	3.21×10^{-5}	86	−74	345
			298.2	2.0×10^{-6}			
Cl	$NH_2(CH_2)_8NH_3$	0.1 HNO_3	348.2	0.97×10^{-4}	98	−42	293
		0.1 HNO_3	298.2	2.8×10^{-7}	101	−40	
Cl	$NH_2(CH_2)_9CH_3$	H_2O	333.4	3.26×10^{-5}	86	−74	345
			298.2	2.0×10^{-6}			
Cl	$NH_2(CH_2)_{10}CH_3$	H_2O	333.4	3.44×10^{-5}	86	−74	345
			298.2	2.0×10^{-6}			
Cl	$NH_2(CH_2)_{10}NH_3$	0.1 HNO_3	348.2	1.06×10^{-4}	98	−40	293
		0.1 HNO_3	298.2	3×10^{-7}	101	−38	
Cl	$NH_2(CH_2)_{11}CH_3$	H_2O	333.4	3.81×10^{-5}	86	−71	345
		H_2O	298.2	8.4×10^{-7}	90	−69	
Cl	Aziridine	H_2O	298.2	6.9×10^{-8}	108	−28	351
Cl	2-Me-aziridine	H_2O	298.2	5.4×10^{-8}	116	−5	351

Cl	Cyclopropylamine	H_2O	323.7	2.18×10^{-5}			352
Cl	Cyclobutylamine	H_2O	323.7	2.42×10^{-5}			352
Cl	Cyclopentylamine	H_2O	323.7	3.06×10^{-5}			352
Cl	Cyclohexylamine	H_2O	323.7	5.1×10^{-5}			352
		H^+	298.2	3.4×10^{-6}	92	−45	353
Br	Cyclohexylamine	H^+	298.2	1.5×10^{-5}	92	−38	353
Cl	Cyclopentylamine	H_2O	323.7	9.6×10^{-5}			352
Cl	Cyclooctylamine	H_2O	323.7	11.4×10^{-5}			352
Cl	an	H^+ 0.005	338.2	2.5×10^{-4}			354
		H^+ 0.005	334.0	1.0×10^{-4}	113		355
		H^+ 0.005	323.2	1.87×10^{-5}			
		H^+ 0.005	313.7	5.9×10^{-6}			
		H^+ 0.005	298.2	3.6×10^{-7}	133	+70	
an	an	H^+ 0.005	338.2	1.89×10^{-4}			354
		See also refs. 357–9					
Br	an	H^+ 0.05	298.2	9.1×10^{-7}	120	+34	356
Cl	3-Me-an	H^+ 0.005	338.2	2.06×10^{-4}			354
		H^+ 0.005	334.0	7.98×10^{-5}	125		355
		H^+ 0.005	323.2	1.68×10^{-5}			
		H^+ 0.005	313.7	4.37×10^{-6}			
		H^+ 0.005	298.2	2.7×10^{-7}	135	+74	
3-Me-an	3-Me-an	H^+ 0.005	338.2	1.22×10^{-4}			354
		See also refs. 360					
Cl	4-Me-an	H^+ 0.005	338.2	4.65×10^{-4}			354
		H^+ 0.005	334.0	1.75×10^{-4}	133		355
		H^+ 0.005	323.2	3.08×10^{-5}			
		H^+ 0.005	313.7	4.85×10^{-6}			
		H^+ 0.005	298.2	2×10^{-7}	160	+154	
4-Me-an	4-Me-an	H^+ 0.005	338.2	1.03×10^{-4}			354
Cl	3,4-Me_2-an	H^+ 0.005	338.2	6.4×10^{-4}			354
3,4-Me_2-an	3,4-Me_2-an	H^+ 0.005	338.2	1.93×10^{-4}			354
Cl	2-MeO-an	H^+ 0.005	338.2	3.26×10^{-4}			361
2-MeO-an	2-MeO-an	H^+ 0.005	338.2	1.64×10^{-4}			361
Cl	3-MeO-an	H^+ 0.005	338.2	2.44×10^{-4}			361
3-MeO-an	3-MeO-an	H^+ 0.005	338.2	3.42×10^{-4}			361
Cl	Benzylamine	H_2O	353.2	15.4×10^{-5}			362

TABLE 17 (continued)

X	A	Solvent or H^+ (M)	T (K)	k_{aq} (s^{-1})	E_a (kJ mol^{-1})	$\Delta S_{298}^{\#}$ (J K^{-1} mol^{-1})	Ref.
		H_2O	343.2	5.5×10^{-5}			
		H_2O	333.2	1.7×10^{-5}	108	−20	362
		H^+ 0.005	333.2	1.55×10^{-5}			
		H^+ 0.005	328.2	8.75×10^{-6}			
		H^+ 0.005	323.2	4.52×10^{-6}	110	−14	362
		H_2O/H^+ all data	298.2	1.4×10^{-7}	112	−9	362
Cl	Benzylamine	0.1 HNO_3	298.2	1.8×10^{-7}	102	−63	283
		See also refs. 263,402					
Br	Benzylamine	H^+ 0.005	333.2	6.77×10^{-5}			362
		H^+ 0.005	328.0	3.32×10^{-5}			
		H^+ 0.005	323.2	1.79×10^{-5}	113	+8	362
		H^+ 0.005	298.2	4.3×10^{-7}	119	+24	
Cl	4-Me-bz	H_2O	343.2	6.6×10^{-5}			263
Cl	4-MeO-bz	H_2O	343.2	7.4×10^{-5}			263
Cl	2-Cl-bz	H_2O	343.2	5.1×10^{-5}			263
Cl	4-Cl-bz	H_2O	343.2	7.0×10^{-5}			263
Cl	2,4-Cl_2-bz	H_2O	343.2	6.4×10^{-5}			263

Cl	3,4-Cl_2-bz	H_2O	343.2	6.9×10^{-5}			263
Cl	$Ph(CH_2)_2NH_2$	H_2O	343.2	6.3×10^{-5}			263
Cl	4-Cl-$Ph(CH_2)_2NH_2$	H_2O	343.2	6.3×10^{-5}			263
Cl	Pyridine	H^+ 0.1	298.2	2.6×10^{-7}	106	−50	283
		H^+ 0.1	298.2	6.2×10^{-7}	100	−21	364
		See also refs. 365,366					
Br	Pyridine	H^+ 0.1	298.2	1.7×10^{-6}	100	−21	364,367
		H^+ 0.001	298.2	1.4×10^{-6}	110	+6	356
Cl	4-Me-py	H^+ 0.1	298.2	2.4×10^{-6}	97	−28	365,368,369
Cl	3-Me-py	H^+ 0.1	298.2	1.6×10^{-6}	102	−21	365,368,369
Br	3-Me-py		298.2	4.9×10^{-6}	99	−23	368
Br	4-Me-py		298.2	7.7×10^{-6}	97	−26	368
Cl	3-Et-py	H_2O	323.0	1.63×10^{-5}			370
Cl	4-Et-py	H_2O	323.0	1.78×10^{-5}			370
Cl	4-MeO-py	H_2O	323.2	1.5×10^{-5}			365
Cl	3,4-Me_2-py	H_2O	323.0	2.43×10^{-5}			370
Cl	3,5-Me_2-py	H_2O	323.0	1.82×10^{-5}			370
		1.0 HNO_3	298.2	7.44×10^{-7}	103	−26	273
Cl	Imidazole	1.0 HNO_3	298.2	5.7×10^{-7}	101	−32	273
Cl	Benzimidazole	1.0 HNO_3	298.2	9.67×10^{-7}	112	+7	273

[a] Rate law in eqn. (14) is assumed but k_1 found to be ~ 0. This gives a rate law corresponding to eqn. (12).

TABLE 18

Kinetic parameters for the base hydrolysis of some *cis*-$CoX(en)_2(A)^{n+}$ complexes

X	A	μ (M)	T (K)	k_{OH} (M^{-1} s^{-1})	E_a (kJ mol^{-1})	$\Delta S^{\#}_{298}$ (J K^{-1} mol^{-1})	Stereochemistry		Ref.
							% *trans*	% ret.	
Cl	NH_3	0.1	273.2	0.23					342,394,395
		0.1	273.2				16	35	280
		0.1	298.2				22	48	285
		0.1	298.2	8.1					16
Br	NH_3	0.1	273.2	3.3					394,395
		0.1	298.2	66					274,275
		1.0	298.2				23	44	285
		var.	298.2				17	47	272
NCS	NH_3	var.	288.2	5.3×10^{-4}					288
		var.	298.2	2.87×10^{-3}	130	+134	10		288
		var.	308.2	1.86×10^{-2}					288
NO_2	NH_3	var.	298.2	5×10^{-5}	139	+140			289
C_2O_4	NH_3	1.0	303.2	2.75×10^{-3}					331
		1.0	298.2	1.1×10^{-3}	127	+117			331
Cl	NH_2CH_3	0.1	273.2	0.17					342
		0.1	298.2	7.3	98	+100			334
		0.1	298.2	13			0		16
		0.02	298.2				20	32	272
Br	NH_2CH_3	0.1	298.2	50	99	+120			334
Cl	NH_2OH	0.1	298.2	7.0	98	+99			334
Br	NH_2OH	0.1	298.2	48	99	+120			334
Cl	$NH_2CH_2CH_3$	0.1	273.2	0.16					342
		0.1	298.2	6.5	98	+120			334
		0.1	298.2	12	106	+133			340
		0.1	298.2	13			0		16
Br	$NH_2CH_2CH_3$	0.1	298.2	47	99	+119			334
Cl	NH_2NHCH_3	0.1	273.2	0.2					338
		0.1	298.2	8.6	102	+107			338

Cl	$NH_2CH_2CH=CH_2$	0.1	273.2	0.16				342
		0.1	298.2	6.4	98	+99		334
		0.1	298.2	20			0	16
Br	$NH_2CH_2CH=CH_2$	0.1	298.2	120	99	+129		334
		0.1	298.2	180				274
Cl	$NH_2CH_2C\equiv CH$	0.1	273.2	0.08				342
		0.1	298.2	3.3	98	+93		334
Br	$NH_2CH_2C\equiv CH$	0.1	298.2	57	99	+121		334
Br	$NH_2CH_2CONH_2$	1.0	298.2	260				309
Br	$NH_2CH_2CON(CH_3)_2$	1.0	298.2	247				309
Br	$NH_2CH_2CONH(CH_3)$	1.0	298.2	280				309
Br	$NH_2CH_2CO_2CH(CH_3)_2$	1.0	298.2	280				309
Cl	$NH_2CH(CH_3)_2$	0.1	273.2	0.41				342
		0.1	298.2	17	98	+107		334
		0.1	298.2	52			0	16
Br	$NH_2CH(CH_3)_2$	0.1	298.2	420	99	+138		334
Cl	$NH_2(CH_2)_2CH_3$	0.1	273.2	0.273				314,343
		0.1	298.2	11	98	+104		334
		0.1	298.2	13			0	16
Br	$NH_2(CH_2)_2CH_3$	0.1	298.2	270	99	+134		334
Cl	$NH_2(CH_2)_2NH_2$	0.1	298.2	6.3				292
Br	$NH_2(CH_2)_2NH_2$	0.1	298.2	41				292
Cl	$NH_2(CH_2)_2Cl$	0.1	273.2	0.173				300,346
Br	$NH_2(CH_2)_2Br$	0.1	298.2	180				274,300
Cl	$NH_2(CH_2)_2OH$	0.1	298.2	20				16
Br	$NH_2(CH_2)_2OH$	0.1	298.2	190				274
Cl	$NH_2(CH_2)_2Ph$	0.1	273.2	0.256				263
Cl	$4\text{-}Cl\text{—}Ph(CH_2)_2NH_2$	0.1	273.2	0.186				263
Cl	$NH_2(CH_2)_2C\equiv N$	0.1	298.2	13.8	102	+109		301
Cl	$NH_2(CH_2)_3CH_3$	0.5	298.2	6.5				371
		0.1	298.2	13			0	16
		0.1	273.2	0.295	98	+104		343
Cl	$NH_2(CH_2)_3Cl$	0.1	273.2	0.302				300,346
Cl	$NH_2(CH_2)_3OH$	0.1	273.2	0.27				347
Cl	$NH_2CH_2CH(Cl)CH_3$	0.1	273.2	0.405				300,346
Br	$NH_2CH_2CH(OH)CH_3$	0.1	298.2	94				274

TABLE 18 (continued)

X	A	μ (M)	T (K)	k_{OH} (M^{-1} s^{-1})	E_a (kJ mol^{-1})	$\Delta S^{\ddagger}_{298}$ (J K^{-1} mol^{-1})	Stereochemistry		Ref.
							% *trans*	% ret.	
Cl	$NH_2CH_2CH(CH_3)_2$	0.1	273.2	0.387	98	+104			343
Cl	$NH_2CH(CH_3)CH_2CH_3$	0.1	273.2	1.55	98	+117			343
Cl	$NH_2(CH_2)_4OH$	0.1	273.2	0.27					347
Cl	$NH_2(CH_2)_5OH$	0.1	273.2	0.25					347
Cl	$NH_2(CH_2)_5CO_2$	0.1	298.2	0.15					296
Cl	$NH_2(CH_2)_5CO_2CH_3$	0.1	298.2	14					296
Cl	Aziridine	0.1	273.2	0.43					351
Br	Aziridine	0.1	298.2	160					274
Cl	2-Me-aziridine	0.1	273.2	0.41					351
Cl	Cyclopropylamine	0.1	273.2	1.20					352
Cl	Cyclobutylamine	0.1	273.2	1.18					352
Cl	Cyclopentylamine	0.1	273.2	1.21					352
Cl	Cyclohexylamine	0.1	273.2	5.1					352
		0.1	273.2	2.5					353
		0.02	298.2				18	30	272
Br	Cyclohexylamine	0.1	273.2	8.9					353
Cl	Cycloheptylamine	0.1	273.2	9.6					352
Cl	Cyclooctylamine	0.1	273.2	11.4					352
Cl	an	0.1	273.2	2.39×10^3					354, 355
		?	298.2	2.6×10^4	100	+167			372
Cl	3-Me-an	0.1	273.2	2.1×10^3					354,355
Cl	4-Me-an	0.1	273.2	3.28×10^3					354,355
		?	298.2	6.6×10^4	99	+171			372
Cl	3,4-Me_2-an	0.1	273.2	5.92×10^3					354
Cl	2-MeO-an	0.1	273.2	2.65×10^3					361
Cl	3-MeO-an	0.1	273.2	2.38×10^3					361
Cl	Benzylamine	0.1	273.2	0.324					363
		0.1	273.2	1.02					362
		0.02	298.2				10	36	272

Br	Benzylamine	0.1	273.2	4.10					362
Cl	4-Me-bz	0.1	273.2	0.315					363
Cl	4-MeO-bz	0.1	273.2	0.278					363
Cl	2-Cl-bz	0.1	273.2	0.198					363
Cl	4-Cl-bz	0.1	273.2	0.341					363
Cl	3,4-Cl_2-bz	0.1	273.2	0.401					363
Cl	Pyridine	0.1	274.0	34					370
			298.2	1.6×10^3					365
		0.1	298.2	332	86.1	+84			214
		0.02	298.2				21	9	272
Cl	3-Me-py	0.1	274.0	29					370
			298.2	1.3×10^3					365
Cl	4-Me-py	0.1	274.0	30					370
		0.1	298.2	279	93.3	+107	5		214
		0.02	298.2				23	11	272
Cl	3-Et-py	0.1	274.0	32					370
Cl	4-Et-py	0.1	274.0	29					370
		0.1	298.2	240	98.3	+122			214
Cl	4-nPr-py	0.1	298.2	244	95.5	+113			214
Cl	4-MeO-py		298.2	1.2×10^3					365
Cl	4-Bz-py	0.1	298.2	240	89.3	+92			214
		0.02	298.2				16	10	272
Cl	3,4-Me_2-py	0.1	274.0	35					370
		0.1	298.2	207	93.5	+104			214
		0.02	298.2				15	11	272
Cl	3,5-Me_2-py	0.1	274.0	33					370
		0.1	298.2	194	85.7	+78		11	214
		0.02	298.2				14	10	272
Br	3,5-Me_2-py	0.02	298.2				20	16	272
Cl	Isoquinoline	0.02	298.2				29	7	272
		0.1	298.2	292	92.7	+105			214
Cl	Imidazole	0.02	298.2				21	23	272
		0.1	298.2	31 [a]					373
Cl	N-Me-imidazole	0.02	298.2				19	23	272
Cl	Benzimidazole	0.02	273.2				10	45	272
		0.02	298.2				6	42	272
		0.02	315.2				14	40	272

[a] Reaction becomes first-order at $[OH^-] > 0.1$ M with $k_{obs}(298) = 0.58\ s^{-1}$ ($\mu = 0.5$ M) [373].

TABLE 19

Kinetic parameters for the M^{n+} assisted aquation of some $CoX(en)_2(A)^{n+}$ complexes

X	A	M^{n+}	μ (M)	T (K)	k (M^{-1} s^{-1})	E_a (kJ mol^{-1})	$\Delta S^{\#}_{298}$ (J K^{-1} mol^{-1})	Ref.
Cl	NH_3 (*cis*)	Hg^{2+}	0.2	298.2	5.66×10^{-3}	82	−21	330,342
	NH_3 (*cis*)	Hg^{2+}	1.0	298.2	1.45×10^{-2}			374
	NH_3 (*trans*)	Hg^{2+}	1.0	298.2	4.64×10^{-2}			374
	NH_3 (*cis*)	Tl^{3+}	1.0	298.2	0.72×10^{-3}	78	−44	375
Br	NH_3 (*cis*)	Hg^{2+}	0.2	283.2	0.49			342
	NH_3 (*cis*)	Tl^{3+}	1.0	298.2	3.5×10^{-2}	62	−63	375
Cl	NH_2CH_3	Hg^{2+}	0.2	298.2	1.46×10^{-2}	79	−25	330,342
Cl	NH_2CH_3	Tl^{3+}	1.0	298.2	3.10×10^{-3}	74	−46	375
Cl	$NH_2CH_2CH_3$	Hg^{2+}	0.2	298.2	8.83×10^{-3}	79	−29	330,342
Cl	$NH_2CH_2CH_3$	Tl^{3+}	1.0	298.2	1.63×10^{-3}	73	−52	375
Cl	$NH_2CH_2C{\equiv}N$	Hg^{2+}	2.037	298.2	8.99×10^{-4}			299
Br	$NH_2CH_2C{\equiv}N$	Hg^{2+}	2.037	298.2	1.58×10^{-1}			299,302
Cl	$NH_2CH(CH_3)_2$	Hg^{2+}	0.2	298.2	5.38×10^{-2}	72	−38	330,342
Cl	$NH_2CH(CH_3)_2$	Tl^{3+}	1.0	298.2	9.30×10^{-3}	67	−58	375
Cl	$NH_2(CH_2)_2CH_3$	Hg^{2+}	0.2	298.2	1.02×10^{-2}	74	33	343
				298.2	1.03×10^{-2}	77	38	330,342
Cl	$NH_2(CH_2)_2CH_3$	Tl^{3+}	1.0	298.2	1.76×10^{-3}	71	−57	375
Cl	$NH_2(CH_2)_2OH$	Hg^{2+}	2.07	298.2	5.9×10^{-2}			310
Br		Hg^{2+}	2.07	298.2	6.6			310
Cl	$NH_2(CH_2)_2O\overset{O}{\overset{\|}{C}}Me$	Hg^{2+}	2.07	298.2	8×10^{-3}			310
Br		Hg^{2+}	2.00	298.2	1.1			310
Cl	$NH_2(CH_2)_2NH_3$	Hg^{2+}	3.94	298.2	5.5×10^{-3}			292
Br	$NH_2(CH_2)_2NH_3$	Hg^{2+}	3.94	298.2	5.0×10^{-3}			292
Cl	$NH_2(CH_2)_2NH(CH_3)_2$	Hg^{2+}	0.2	298.2	2.83×10^{-4}	92	−3	293
Cl	$NH_2(CH_2)_3CH_3$	Hg^{2+}	0.2	298.2	1.20×10^{-2}	69	−50	293,343
		Hg^{2+}	0.66	298.2	1.8×10^{-2}			303
Cl	$NH_2(CH_2)_3NH_3$	Hg^{2+}	0.2	298.2	1.19×10^{-3}	78	−39	293
Cl	$NH_2CH_2CH(CH_3)_2$	Hg^{2+}	0.2	298.2	1.19×10^{-2}	71	−42	343
Cl	$NH_2CH(CH_3)CH_2CH_3$	Hg^{2+}	0.2	298.2	9.5×10^{-2}	63	−50	343

Cl	$NH_2(CH_2)_6NH_3$	Hg^{2+}	0.2	298.2	4.92×10^{-3}	77	−31	293
Cl	$NH_2(CH_2)_7NH_3$	Hg^{2+}	0.2	298.2	5.1×10^{-3}	77	−31	293
Cl	$NH_2(CH_2)_8NH_3$	Hg^{2+}	0.2	298.2	5.4×10^{-3}	77	−31	293
Cl	$NH_2(CH_2)_{10}NH_3$	Hg^{2+}	0.2	298.2	6.0×10^{-3}	78	−24	293
Br	an	Hg^{2+}	0.2 [a]	308.2	1.76×10^{-2}			376
Cl	pyridine	Hg^{2+}	0.2	298.2	0.9×10^{-2}	81	−11	377
		Hg^{2+}	1.0	298.2	1.51×10^{-2}			374
Cl	3-Me-py	Hg^{2+}	0.2	298.2	1.1×10^{-2}	78	−20	377
Cl	4-Me-py	Hg^{2+}	0.2	298.2	1.3×10^{-2}	77	−23	377
Cl	3-Et-py	Hg^{2+}	0.2	298.2	1.3×10^{-2}	76	−26	377
Cl	4-Et-py	Hg^{2+}	0.2	298.2	1.4×10^{-2}	78	−23	377
Cl	3,5-Me_2-py	Hg^{2+}	0.2	298.2	1.8×10^{-2}	70	−44	377
Cl	3,4-Me_2-py	Hg^{2+}	0.2	298.2	2.1×10^{-2}	69	−47	377
		Hg^{2+}	ca. 0	278.2	4.76×10^{-3}			378
		Hg^{2+}	0.01	298.2	5.4×10^{-2}	83	−1	102,396
Cl	$CoCl(NH_3)_5^{2+}$	Hg^{2+}	0.3	298.2	5.7×10^{-2}			183
		Hg^{2+}	1.0	298.2	1.16×10^{-1}			374
		Hg^{2+}	1.0	298.2	1.22×10^{-1}			30
Cl	$CoCl(NH_3)_5^{2+}$	Hg^{2+}	2.0	308.2	0.55			398
Cl	$CoCl(NH_3)_5^{2+}$	Tl^{3+}	1.0	298.2	6.9×10^{-3}			398
		Tl^{3+}	2.0	298.2	1.23×10^{-2}	79	−15	398
Br	$CoBr(NH_3)_5^{2+}$	Hg^{2+}	0.01	298.2	8.67	59	−29	379
		See also refs. 102,108a,380,390,392						
Br	$CoBr(NH_3)_5^{2+}$	Ag^+	?	298.2	8.33×10^{-2}	60	−63	379
Br	$CoBr(NH_3)_5^{2+}$	Tl^{3+}	0.10	298.2	1.63	43	−96	379
I	$CoI(NH_3)_5^{2+}$	Ag^{2+}	0	318.1	0.8			113a
Cl	$CrCl(NH_3)_5^{2+}$	Hg^{2+}	2.0	298.2	8.73×10^{-2}	62	−56	10
		$HgCl^+$	2.0	298.2	2.7×10^{-1}	60	−63	10
Cl	$NH_2(CH_2)_2Co(en)_2Cl$	Hg^{2+}	0.26	298.2	2.1×10^{-3}			290
Cl	$NH_2(CH_2)_3Co(en)_2Cl$	Hg^{2+}	0.26	298.2	4.8×10^{-3}			290
Cl	$NH_2(CH_2)_4Co(en)_2Cl$	Hg^{2+}	0.26	298.2	2.3×10^{-2}			290
Cl	$NH_2(CH_2)_6Co(en)_2Cl$	Hg^{2+}	0.26	298.2	3.2×10^{-2}			290
Cl	$NH_2(CH_2)_2Co(en)_2(OH_2)$	Hg^{2+}	0.26	298.2	4.8×10^{-4}			290
Cl	$NH_2(CH_2)_3Co(en)_2(OH_2)$	Hg^{2+}	0.26	298.2	1.4×10^{-3}			290
Cl	$NH_2(CH_2)_4Co(en)_2(OH_2)$	Hg^{2+}	0.26	298.2	1.2×10^{-2}			290
Cl	$NH_2(CH_2)_6Co(en)_2(OH_2)$	Hg^{2+}	0.26	298.2	1.6×10^{-2}			290

[a] Rate depends on $[H^+]$ [376].

TABLE 20

Kinetic parameters for the reduction of some $CoCl(N_5)^{2+}$ complexes with Fe(II)

N_5	μ (M)	T (K)	k_{Fe} (M^{-1} s^{-1})	E_a (kJ mol^{-1})	$\Delta S_{298}^{\neq}$ (J K^{-1} mol^{-1})	Ref.
$(NH_3)_5$	0.34	299.0	7.1×10^{-4}	63	−96	382
	1.0	298.2	1.35×10^{-3}	52	−125	383
	1.7	298.7	1.60×10^{-3}	61	−96	384
tetren [a]	1.0	298.2	$<10^{-8}$			385
(trien)(NH_3) [a]	1.0	298.2	2.5×10^{-6}			386
(dien)(en) [a]	1.0	298.2	6.0×10^{-6}			385
	1.0	298.2	8.0×10^{-6}			386
(dien)(tmd) [a]	1.0	298.2	1.4×10^{-5}			386
$(en)_2(NH_3)$	1.0	298.2	1.8×10^{-5}			387
$(en)_2(NH_3)$ [b]	1.0	298.2	6.6×10^{-5}			387
$(pn)_2(NH_3)$ [c]	1.0	298.2	2.5×10^{-5}			386
$(en)_2(MeNH_2)$	1.0	298.2	2.72×10^{-5}	58	−137	385
$(en)_2(EtNH_2)$	1.0	298.2	2.70×10^{-5}	58	−138	385
$(en)_2(nPrNH_2)$	1.0	298.2	2.58×10^{-5}	56	−144	385
$(en)_2(nBuNH_2)$	1.0	298.2	2.03×10^{-5}	58	−141	385
$(en)_2(NH_2(CH_2)_2OH)$	1.0	298.2	4.68×10^{-5}	58	−134	385
	0.6	298.2	4.38×10^{-5}	55	−152	381
$(en)_2(NH_2(CH_2)_3OH)$	1.0	298.2	3.11×10^{-5}	61	−127	385
$(en)_2(py)$	1.25 [d]	298.2	4.1×10^{-3}	71	−58	313
	1.25 [e]	298.2	2.92×10^{-3}	67	−67	313
	1.0	298.2	7.88×10^{-4}			440
	0.12	313.2	1.1×10^{-3}			312
$(en)_2$(3-Cl-py)	1.0	298.2	2.1×10^{-3}			440
$(en)_2$(3-Me-py)	1.0	298.2	5.8×10^{-4}			440
$(en)_2$(3,5-Me_2-py)	1.0	298.2	4.62×10^{-4}			440

[a] Geometric configuration unknown; [b] *trans* isomer; [c] *cis*(?) isomer, but configuration of pn rings unknown; [d] H_2SO_4 = 0.5 M; [e] H_2SO_4 = 1.0 M.

with organic solvents, has been reported [381]. The rate of Fe(II) reduction is essentially independent of $[H^+]$ (0.14—0.43 M) and only slightly increases with increasing ionic strength. With increasing concentrations of organic solvents there is an increase in k_2, $\Delta H^{\neq}$ and $\Delta S_{298}^{\neq}$ and a plot of log k_2 vs. [organic solvent] is linear for ethanol and acetone, but markedly curved for DMF and DMSO. For a comparison of related Fe(II) reductions of Co(III) complexes (especially $CoX(NH_3)_5^{n+}$) in aqueous—organic solvent mixtures, the reader is referred to the recent work of Matthews and Watts [382].

(ii) Aqua complexes

Aqua complexes of Co(III) are weak acids and pK_a values for the equilibrium

$$cis\text{-}Co(en)_2(A)(OH_2)^{3+} \rightleftharpoons cis\text{-}Co(OH)(en)_2(A)^{2+} + H^+ \qquad (25)$$

are given in Table 21. The change from aqua to hydroxo causes a marked increase in the propensity for isomerisation and racemisation (Scheme 25). Kinetic parameters for the racemisation of aqua

$$t\text{-Co(en)}_2(NH_3)(OH_2)^{3+} \rightleftharpoons K_t \rightleftharpoons t\text{-Co(OH)(en)}_2(NH_3)^{2+} + H^+$$
$$\downarrow k_1 \qquad\qquad\qquad \downarrow k_2$$
$$c\text{-Co(en)}_2(NH_3)(OH_2)^{3+} \rightleftharpoons K_c \rightleftharpoons c\text{-Co(OH)(en)}_2(NH_3)^{2+} + H^+$$

$k_1(333.2) = 7.5 \times 10^{-6}\ s^{-1}$
$k_2(333.2) = 3 \times 10^{-5}\ s^{-1}$
$K_t(333.2) = 6 \times 10^{-4}$

SCHEME 25. Rate constants for the isomerisation of aqua and hydroxo bis(ethylenediamine)(ammine)cobalt(III) complexes [287,388].

and hydroxo complexes of this type are listed in Tables 22 and 23. The reason for the ca. 10^3 rate increase for the racemisation of the hydroxo relative to the aqua is not well understood. No ^{18}O exchange was observed in the

TABLE 21

pK_a values for some *cis*-$Co(en)_2(A)(OH_2)^{3+}$ complexes. (For additional entries see Note added in proof)

A	μ (M)	T (K)	pK_a	Ref.
NH_3	0.03	298.2	5.83	349
trans-NH_3			5.80	388
$MeNH_2$	0.03	298.2	5.71	349
$MeNH_2$	2.0	323.8	5.50	273
$iPrNH_2$	0.1	273.2	6.44	361
$nBuNH_2$	0.03	298.2	6.16	349
$BzNH_2$	0.03	298.2	5.99	349
$NH_2(CH_2)_2NH_3$	0.1	298.2	5.05	292
$NH_2(CH_2)_2OH$	0.03	298.2	5.48	349
	0.1	298.2	6.12	310
	0.13	298.2	5.50	311
	0.03	298.2	5.40	311
an	0.03	298.2	5.47	349
2-MeO-an	0.1	273.2	6.29	361
py	0.1	273.2	5.00	370
py	0.03	298.2	5.26	349
3,5-Me_2-py	2.0	323.8	5.65	273
Imidazole	2.0	323.8	6.40	273
$Cr(NH_3)_5OH_2^{3+}$	1.0	298.2	5.16	182
		303.2	5.29	
		308.2	5.41	
		313.2 [a]	5.53	
		323.2 [a]	5.76	
		333.2 [a]	5.98	
$Co(NH_3)_5OH_2^{3+}$	1.0	298.2	5.75 [b]	161

[a] Extrapolated values. [b] Also determined in the presence of added electrolytes.

TABLE 22

Kinetic parameters for the racemisation of some *cis*-$Co(en)_2(A)(OH_2)^{3+}$ ions in 0.1 M acid

A	$10^9\ k_{298}\ (s^{-1})$	E_a (kJ mol^{-1})	$\Delta S^{\neq}_{298}$ (J K^{-1} mol^{-1})	Ref.
NH_3	22.5	118	-3	388
NH_3	1.8	150	+82	273
$MeNH_2$	1.7	156	+101	267
$EtNH_2$	2.0	155	+100	267
$BzNH_2$	2.0	157	+109	403
cyclohexNH_2	38.0	135	+57	273
py	4.3	164	+138	403
3,5-Me_2-py	7.7	152	+102	273
Imidazole	2.7	153	+97	267
N-Me-imidazole	1.8	158	+108	273

racemisation of *cis*-$Co(OH)(en)_2(NH_3)^{2+}$ [388] and a twist mechanism may be likely, as these racemisation reactions are characterised by high activation energies. Such a twist mechanism could be facilitated by deprotonation at an NH site in basic solution.

(iii) Chiroptical properties

Although *cis*-$[CoX(en)_2(NH_3)]X_2$ (X = Cl, Br) were some of the first octahedral complexes to be resolved [269,433], the chiral properties of the relatec *cis*-$CoX(en)_2(A)^{2+}$ complexes received little attention until recently [267]. ORD and CD spectral parameters have now been determined (600—300 nm) for most of the complexes listed in Table 14 and the references cited therein should be consulted for further details.

The absolute configuration of the (+)- or (−)-$CoCl(en)_2(A)^{2+}$ ions are based on the assignment of the Λ configuration of the chelate rings [278] to (+)-

TABLE 23

Kinetic parameters for the racemisation of some *cis*-$Co(OH)(en)_2(A)^{2+}$ ions at pH = 8, μ = 2.0 M ($NaClO_4$)

A	$10^6\ k_{298}\ (s^{-1})$	E_a (kJ mol^{-1})	$\Delta S^{\neq}_{298}$ (J K^{-1} mol^{-1})	Ref.
NH_3	2.55	138	+102	273,388
$MeNH_2$	7.2	123	+60	273
3,5-Me_2-py	30	122	+69	273
Imidazole	7.0	128	+76	273

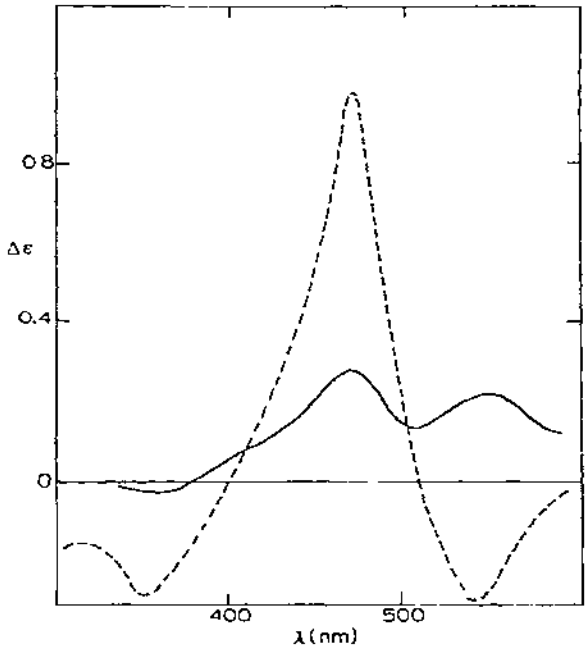


Fig. 2. Typical CD spectra of Λ-*cis*-$CoCl(en)_2$(alkylamine)$^{2+}$ (———) and Λ-*cis*-$CoCl(en)_2$(aromatic tertiary amine)$^{2+}$ (- - - - -) [267, 271—273].

$CoCl(en)_2(NH_3)^{2+}$ [276,286,323] and the complexes with A = alkylamine are related to this by a comparison of the ORD or CD spectra [267,271]. However, the ORD or CD spectra of complexes with A = aromatic tertiary amine are not obviously related to those with A = alkylamine (Fig. 2) and absolute configurational assignments have been made by comparing the CD spectra of the related aqua ions with that of Λ-(+)-$Co(en)_2(OH_2)_2^{3+}$ [267].

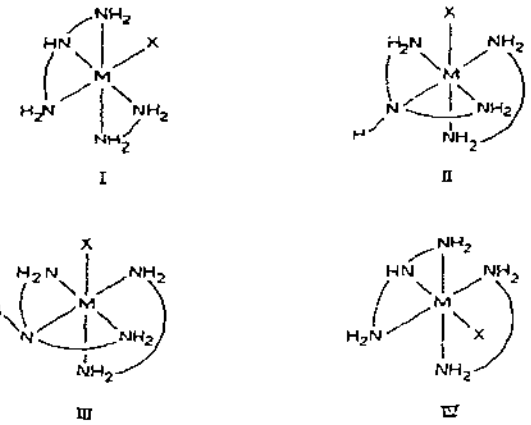
It has been suggested that the difference in chiroptical parameters between the two classes of amines can be related in some way to the bonding effects of the π-system of the heterocyclic ring [267,277].

F. BIDENTATE—TRIDENTATE COMPLEXES

With symmetrical polyamines, there are four geometric isomers possible for this class of complex (Scheme 26). All of these have been characterised by single crystal X-ray studies; however a complete set for a particular amine system has only been indirectly established.

Two isomeric forms for $CrCl(en)(dien)^{2+}$ have been isolated but only those with configuration IV have been reasonably investigated [30,31,214].

In an investigation to determine the influence of chelation on aquation rate, Pearson et al. [68] prepared a number of $CoCl(N_5)^{2+}$ complexes including $CoCl(en)(dien)^{2+}$, and measured the rate of chloride release in acid solu-



SCHEME 26. Possible geometric isomers for bidentate—tridentate complexes.

tion. Unfortunately, the isomeric composition and purity of the complexes prepared was not well established and the rate data obtained cannot be validly used to interpret the influence of chelation [28]. Sadly, similar remarks

TABLE 24

Isomer assignments for some $[CoCl(AA)(ABA0)]X_2$ systems [a—d]

Configuration (Scheme 26)	I	II	III	IV	Ref.
(en) (dien)	$\underline{\pi}$	$\underline{\kappa}$		$\underline{\omega}$	215,218,410
(pn) (dien)	$\underline{A}$, D	$\underline{B}$, G	C	H, I (?)	212
(ibn) (dien)	2	$\underline{2}$	1	2 (?)	212
(N-iPr-ibn) (dien)	3	2			212
(stien) (dien)	2	2			212
(tmd) (dien)	d, e, f	a, b	c	h	412
(N-Me-tmd) (dien)	IV, $\underline{V}$	I', II'	I, II		212, 414
(N-Bu-tmd) (dien)	1			$\underline{1}$	212
(N-hex-tmd) (dien)	2				212
(bn) (dien)	1				212
(2,3-tri) (dien)		1	1		212
(en) (dpt)		$\underline{\beta}$	$\underline{\alpha}$		216, 415, 416
(pn) (dpt)		$\underline{2}$	$\underline{2}$		212
(ibn) (dpt)		2	2		212
(stien) (dpt)		2	2		212
(tmd) (dpt)		k, l	i, j, m, n		412
(ibn) (cytam)	1				404
(en) (tri)				$\underline{1}$	298,299

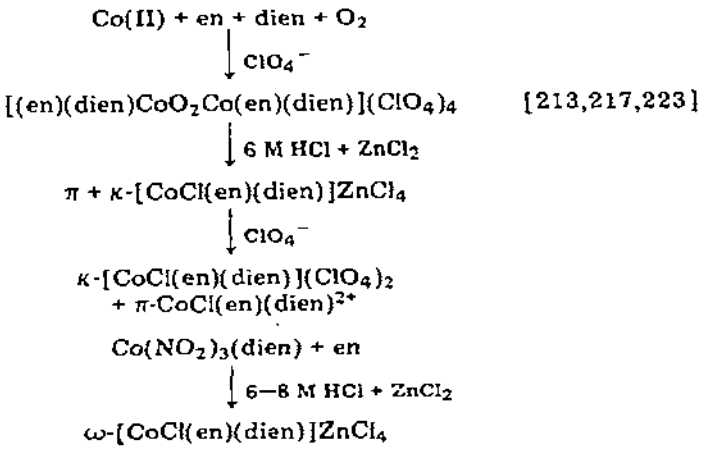
[a] The configuration of the underlined isomers has been established by single crystal X-ray analysis.
[b] Arabic numerals refer to the number of forms assinged to a particular configuration.
[c] As $ZnCl_4^{2-}$ salts, except the last two entries.
[d] See Appendix for ligand abbreviations.

must also be made with regard to a recent study of the influence of chelation on the rates of Fe^{2+} reduction of $CoCl(N_5)^{2+}$ complexes [385,386]. Further investigations of the $CoCl(en)(dien)^{2+}$ system were made by Bosnich and Dwyer [404] who isolated two isomers. The major component (ω) was assigned to configuration IV (Scheme 26) and this was subsequently established by single crystal X-ray analysis [405—407]. The minor component was assigned to either of configurations II and III (Scheme 26). ω-$CoCl(en)(dien)^{2+}$ has also been prepared from the reaction of *trans*-$CoCl_2(dien)(NH_3)^+$ [408, 427] with ethylenediamine [405,408].

In 1968, Gainsford and House reinvestigated the $CoX(en)(dien)^{n+}$ system and isolated isomers (π and κ) corresponding to configurations I and II respectively [218]. Isomer III has not yet been synthesised for this system [409].

Using methods similar to those in Scheme 27, and also the reaction of $CoCl_3(ABA)$ [411,428—432] with diamines, a considerable number of isomers were prepared for various $CoX(AA)(ABA)^{n+}$ systems (Table 24) [212]. The tetrachlorozincate(II) salts proved admirably suitable for isomer separation by fractional crystallisation techniques [412].

For symmetric di- and triamines, only configuration I is potentially chiral and the resolution of d-$CoCl(tmd)(dien)^{2+}$ confirms the assignment of this isomer to this configuration [412,413].

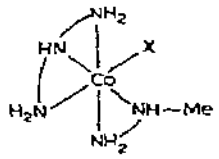


SCHEME 27. Synthetic routes for the production of π, κ and ω-$CoCl(en)(dien)^{2+}$ [215, 218,404,410].

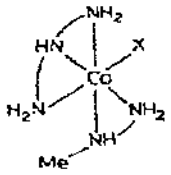
However, the introduction of an asymmetric diamine (e.g. 1,2-diaminopropane or N-methyl-1,3-diaminopropane) almost doubles the number of potential geometric isomers and these seven forms will all be potentially chiral (Scheme 28).

A single crystal X-ray structure of the violet $\{+\}_{520}$—V—$[CoCl(N—Me—tmd)(dien)]ZnCl_4$ * (from the less soluble (+)BCS salt) shows this to have the

* Symbols in the braces give the sign of the CD extrema at the cited wavelength.

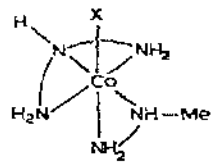


(V)

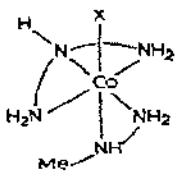


(IV)

Both can be Λ(R), Λ(S), Δ(R) or Δ(S) as well as ΔΛ(R) or ΔΛ(S) and Λ(RS) or Δ(RS).

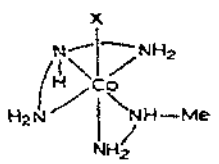


(I)

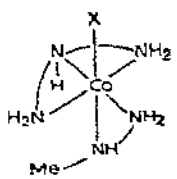


(II)

Both can be (R) or (S)

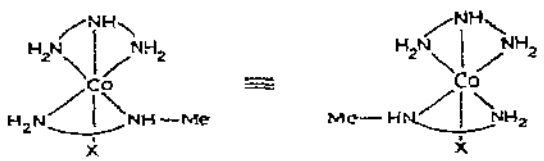


(I')



(II')

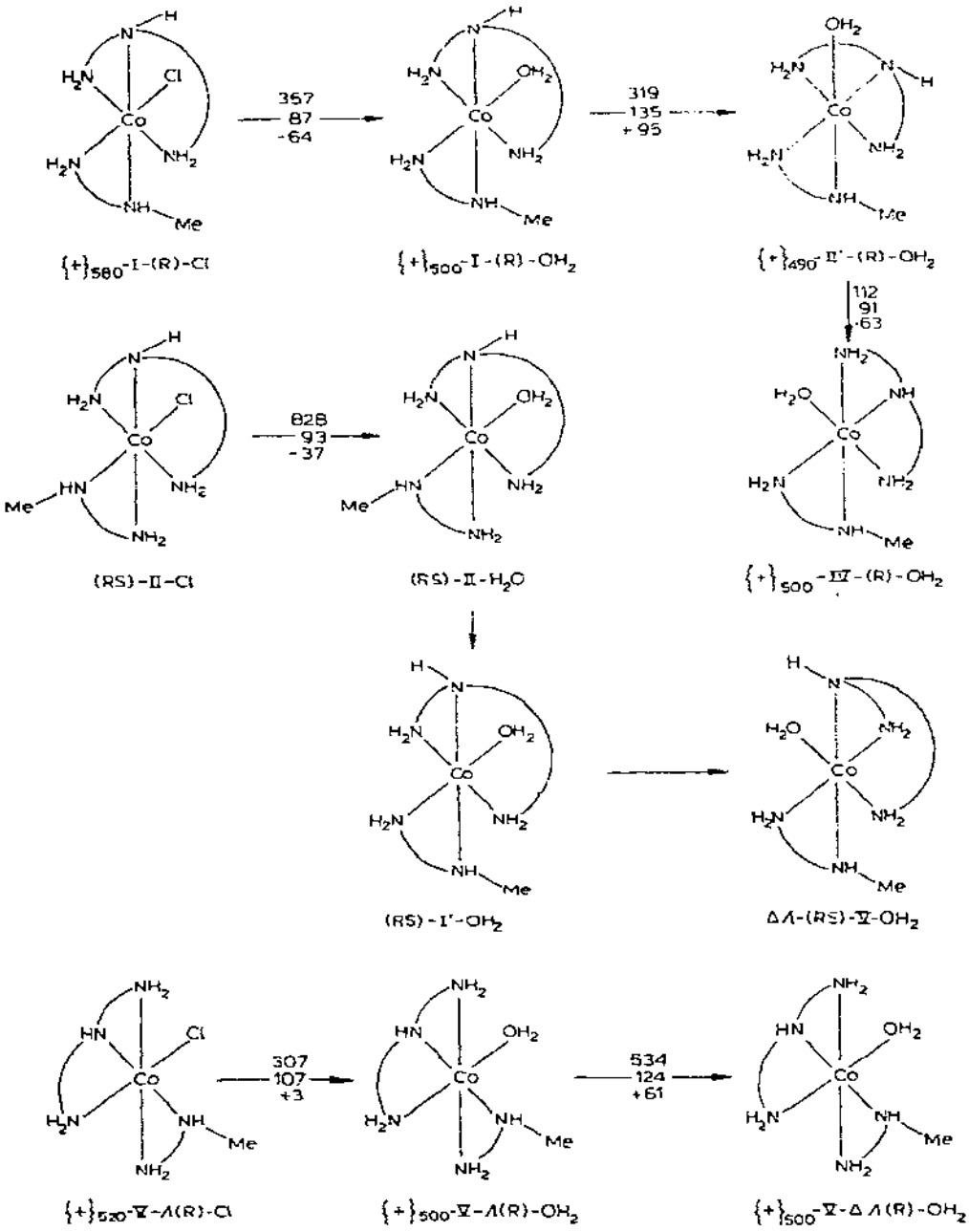
Both can be (R) or (S).



Both can be (R) or (S).

SCHEME 28. Possible optical forms of CoX(N—Me—tmd)(dien)$^{n+}$. The (R), (S) nomenclature refers to the asymmetry of the coordinated sec-NH nitrogen atom and the Λ, Δ refers to the chirality of the chelate rings. Consequently there is a potential total of twenty six optically distinct forms.

Λ(R)-*fac*-dien configuration with the N-Me group *cis* to the Cl and *trans* to the *sec*-NH of the dien (Scheme 29). The $\{-\}_{520}$—V—Δ(*S*) enantiomer was obtained by addition of 2-propanol to the filtrate after removal of the (+)BCS salt [212,244,414]. Subsequent crops obtained by the addition of $HCl/ZnCl_2$ were inactive. Treatment of the $\{+\}_{520}$—V—Λ(R)-chloro isomer with HNO_2 produced $\{+\}_{480}$—I—(R)-*mer*-$Co(NO_2)$(N—Me—tmd)(dien)$^{2+}$ and the $\{+\}_{580}$—



SCHEME 29. Isomeric interconversions for some $CoX(N\text{--}Me\text{—}tmd)(dien)^{n+}$ (X = Cl, OH_2) complexes. Numbers on the arrows (reading downwards) are $10^8\ k_{298}(s^{-1})$, E_a (kJ mol^{-1}) and $\Delta S_{298}^{\neq}$ (J K^{-1} mol^{-1}) in 1.0 M $HClO_4$ [414]. Prefixed signs refer to the sign of the CD maxima at the cited wavelength. See Scheme 35 for the proposed mechanisms for the isomerisation reactions.

I—(R)—*mer*-chloro was obtained from this by decomposition with $HCl/ZnCl_2$.

Changes in the CD spectrum with time for these chloro complexes (and the corresponding aqua isomers produced in situ by Hg^{2+} assisted aquation) have been interpreted in the following scheme (Scheme 29).

A knowledge of the isomerisation rates has permitted a more controlled synthesis of any particular isomer rather than reliance on the method of fractional crystallisation from an isomeric mixture.

A similar situation exists with the $CoX(pn \text{ or } ibn)(dien)^{n+}$ systems and the seven possible geometric isomers have been isolated for both diamines [212]. A single crystal X-ray structure [244] of B-$[CoCl(RSpn)(dien)]ZnCl_4$ shows this isomer to have the configuration illustrated in Scheme 30. The isolated isomers can be grouped into two non-interconvertible series corresponding to the alternative modes of coordination of the diamine and structural assignments have been made by a comparison of these with the $CoCl(en)(dien)^{2+}$ isomers of known configuration.

Chromium(III) complexes of the type $[CrCl(AA)(dien)]ZnCl_4$ have been obtained from $CrCl_3 \cdot 6\ H_2O$ dehydrated in DMSO followed by addition of dien and the diamine (AA = en, pn, tmd). The isolated salts are isomorphous with the ω, H and h-Co(III) isomers respectively and are assigned to configuration IV (Scheme 26) on this basis [31]. This is in agreement with the previous [212] assignment of H-$[CoCl(pn)(dien)]ZnCl_4$ (Scheme 30) to configuration IV (Table 24).

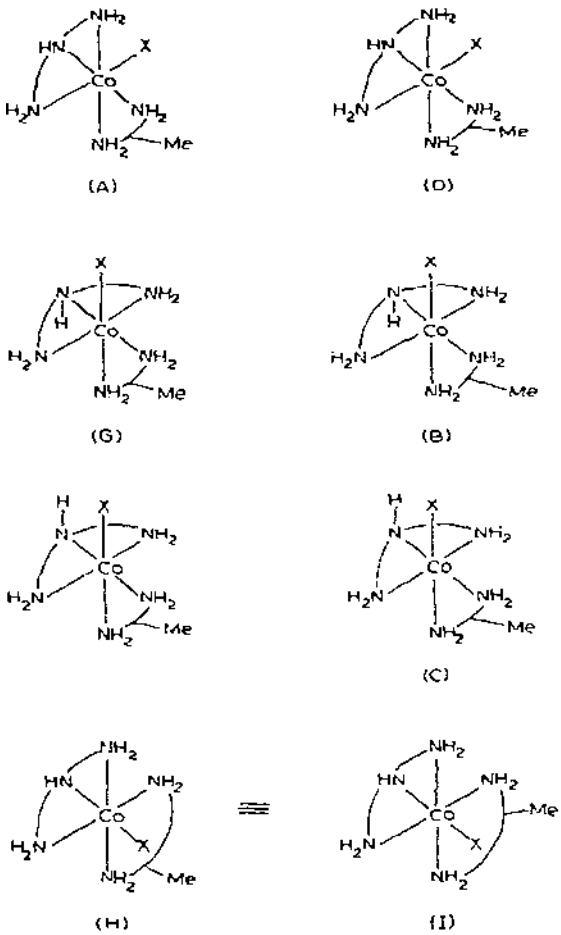
While expansion of the ring size of the diamine appears to have little effect on the number of isomers isolated [412], the use of dpt with two fused six-membered chelate rings appears to restrict the stereochemistry to configurations II and III (Scheme 26, Table 24). Indeed, Co(III) complexes with dpt in a facial configuration do not seem to have been characterised [417].

The structures of α- and β-$CoCl(en)(dpt)^{2+}$ salts [216,415,416] show these to differ only in the configuration of the *sec*-NH proton between the fused six-membered planar chelate rings (cf. α- and β-$CoCl(tetren)^{2+}$, Scheme 5). Strain energy minimisation calculations performed for various ring conformations of the α-(H↑) and β-(H↓) (Scheme 26, III and II) isomers, indicate that the energy difference between the most stable conformers is quite small (1.7 kJ mol^{-1}) and in favour of the α-isomer [415].

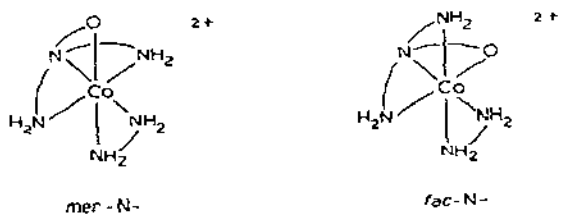
Also included in this section are complexes where the aniono donor is part of the chelate ligand. Thus the preparation [418] of both *mer*-N- and racemic *fac*-N-Co(i-DTMA)$(en)^{2+}$ (Scheme 31) (i-DTMA = diethylenetriaminemonoaceticacid [419]) illustrates the $CoO(N_5)^{2+}$ chromophore in such systems.

(i) Structure—reactivity patterns

In view of the considerable complexity of the $CoX(AA)(ABA)^{n+}$ systems, a number of reaction rate studies have been undertaken to try to establish quantitative structure-reactivity patterns. Tables 25-28 summarise the accumulated kinetic data for aquation, isomerisation, racemisation, Hg^{2+} assisted aquation and base hydrolysis reactions.



SCHEME 30. Possible geometric isomers for $CoX(RSpn)(dien)^{n+}$. Isomers for $CoX(ibn)(dien)^{n+}$ are similar except that two methyl groups are attached to the carbon atom in the diamine ring.



SCHEME 31. Isomers of $Co(i\text{-}DTMA)(en)^{2+}$ [418].

TABLE 25

Aquation rate parameters for some $MX(AA)(ABA)^{2+}$ complexes [a]

M	X	AA	ABA	Isomer (configuration)	$10^7 k_{298}$ (s^{-1})	log PZ (s^{-1})	E_a (kJ mol^{-1})	$\Delta S^{\#}_{298}$ (J K^{-1} mol^{-1})	Ref.
Co	Cl	en	dien	π (I)	2.56	12.78	110	−8	11
Co	Cl	tmd	dien	d (I)	43.0	7.40	73	−111	413
Co	Cl	Me-tmd	dien	V (I)	30.7	13.39	107	+3	414
Co	Cl	Me-tmd	dien	IV (I)	33.4	11.51	97	−33	414
Co	Cl	en	dien	κ (II)	1.78	11.57	104	−31	11
Co	Cl	tmd	dien	a (II)	56.5	11.36	95	−36	413
Co	Cl	Me-tmd	dien	II′ (II)	88.6	12.28	99	−18	414
Co	Cl	en	dpt	β (II)	213	11.88	95	−25	11
Co	Cl	Me-tmd	dien	I (III)	35.7	9.86	87	−64	414
Co	Cl	Me-tmd	dien	II (III)	82.2	11.28	93	−37	414
Co	Cl	en	dpt	α (III)	116	12.68	105	−10	11
Co	Cl	tmd	dpt	i (III)	174	10.51	87	−52	413
Co	Cl	en	dien	ω (IV)	0.94	12.84	113	−7	11,404
Co	Br	en	dien	ω (IV)	5.3		109	−8	404
Co	I	en	dien	ω (IV)	36		121	+29	404
Cr	Cl	en	dien	(IV)	224	10.97	89	−43	30, 31
Co	Cl	tmd	dien	h (IV)	2.16	12.69	110	−10	413
Cr	Cl	tmd	dien	(IV)	218	11.27	91	−37	30, 31
Cr	Cl	pn	dien	(IV)	192	11.70	94	−29	30, 31
Co	Cl	ibn	cytam	(I) or (IV)	1200		100	−2	404
Co	Cl	en	tri	(IV) [b]	30.6	12.61	103	−12	298

[a] In 1.0 M $HClO_4$ except for ref. 404 where 0.01 M $HClO_4$ was used.
[b] Scheme 16 in dil. H^+ [298].

TABLE 26

Base hydrolysis rate parameters for some $MCl(AA)(ABA)^{2+}$ complexes (μ = 1.0 M)

M	AA	ABA	Isomer (configuration)	k_{298} (M^{-1} s^{-1})	E_a (kJ mol^{-1})	$\Delta S_{298}^{\neq}$ (JK^{-1} mol^{-1})	Ref.
Co	en	dien	π (I)	26.6			420
Co	tmd	dien	d (I)	138	91	+94	413
Co	Me-tmd	dien	V (I)	7.57	83	+82	414
Co	en	dien	κ (II) [a]	3×10^4			420
Co	tmd	dien	a (II)	5.0×10^5	83	+135	413
Co	Me-tmd	dien	II' (II)	1.2×10^5	93	+175	414
Co	en	dpt	β (II)	2.2×10^3			420
Co	Me-tmd	dien	II (III)	6.2×10^4	53	+35	414
Co	Me-tmd	dien	I (III)	Very fast			414
Co	en	dpt	α (III)	8.6×10^3			420
Co	tmd	dpt	i (III)	2.8×10^3	102	+175	413
Co	en	dien	ω (IV)	7.26			420
Co	tmd	dien	h (IV)	10.6	123	+179	413
Co	en	tri	(IV) [b]	2.43			298,299
Cr	en	dien	(IV)	7.33×10^{-3}	106	+60	30
Cr	tmd	dien	(IV)	7.67×10^{-3}			30
Cr	pn	dien	(IV)	8.46×10^{-3}			30

[a] For the structurally related *trans*(O, Cl)-$CoCl(gly)(dien)^{2+}$, $k_{OH}(298) = 1.3 \times 10^4$ M^{-1} s^{-1} (μ = 0.1 M) [420]. [b] For the bromo complex, $k_{OH}(298) = 11.8$ M^{-1} s^{-1} (μ = 0.1 M) [299].

TABLE 27

Rate parameters for the Hg^{2+} assisted aquation of some $[MCl(AA)(ABA)]ZnCl_4$ complexes (T = 298 K, μ = 1.0 M)

M	AA	ABA	Isomer (configuration)	$10^3 k_{298}$ (M^{-1} s^{-1})	Ref.
Co	en	dien	π (I)	14.9 [a]	11
Co	en	dien	κ (II)	5.21 [a]	11
Co	en	dien	ω (IV)	4.95 [a]	11
Co	tmd	dien	h (IV)	47.4	30
Co	pn	dien	H (IV)	5.58	30
Co	en	tri	(IV) [b]	528	299
Cr	en	dien	(IV)	23.6	30
Cr	tmd	dien	(IV)	21.6	30
Cr	pn	dien	(IV)	22.6	30

[a] Activation parameters are cited in ref. 11, but these are probably composite as $HgCl^+$ also assists the aquation. [b] For the bromo complex, $10^3 k_{298}$ = 1390 (μ = 2.04 M) [299].

TABLE 28

Rate parameters for the isomerisation and racemisation of some Co(AA)(dien)$(OH_2)^{3+}$ complexes (T = 298 K, μ = 1.0 M)

AA	Reaction [a]	$10^7 k_{298}$ (s^{-1})	E_a (kJ mol^{-1})	$\Delta S_{298}^{\neq}$ (JK^{-1} mol^{-1})	Ref.
en	κ(II) → π(I)	1.2	124	+31	11
tmd	Δ(I) → $\Lambda\Delta$(I)	9.1	130	+68	413
Me-tmd	Λ-(R)-(I) → $\Lambda\Delta$-(R)-(I)	53.4	124	+61	414
Me-tmd	(R)-(III) → (R)-(II)	31.9	135	+95	414
Me-tmd	(R)-(II) → $\Lambda\Delta$-(R)-(I)	11.2	91	−63	414

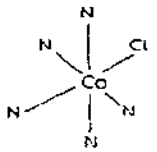
[a] Roman numerals in parentheses refer to the configurations shown in Scheme 26.

These isomeric systems have the advantage that only the stereochemistry within a particular series is influencing the reaction rate, i.e., inductive, conjugative and charge effects and the central metal are constant. On the other hand, when investigating such features as the effect of chelation or ring size on reaction rate, it is necessary to ensure that a common stereochemistry of the reacting species is established. Scheme 32 summarises the available data.

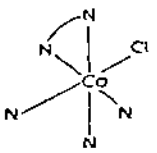
Aquation and Hg^{2+} assisted aquation rates are not particularly sensitive to changes in stereochemistry, although from the limited data configuration IV (Scheme 26) appears to be the most inert. Nor is the "grease effect" [68,237] of the chelated ethylene bridges particularly marked as there is only a decrease of about 20 in the aquation rate in going from $CoCl(NH_3)_5^{2+}$ to ω-CoCl(en)-(dien)$^{2+}$ (Scheme 32) and this reduction in rate may be due to other factors.

In contrast, base hydrolysis rates are markedly dependent on the stereochemistry and rate increases of up to 10^3 are observed (Table 26) for isomers assigned to configurations II and III (Scheme 26). These configurations are characterised by the leaving group *cis* to the *sec*-NH of a planar (meridional) $RNH(CH_2)_xNH(CH_2)_xNHR$ polyamine group. Enhanced rates for base hydrolysis are also observed for more chelated polyamines containing this structural feature (Scheme 32). While no proton exchange rates have been measured in these systems, the enhanced acidity of this type of *sec*-NH proton appears to be well established and will be of considerable help in structural assignments.

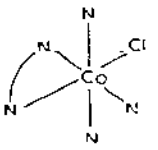
Both the *cis*-$CoCl(en)_2(A)^{2+}$ and $CoCl(AA)(ABA)^{2+}$ systems appear to aquate without isomerisation. However, the resulting aqua ions are geometrically mobile and racemisation (Tables 22, 28) and isomerisation have been observed (Table 28). While the racemisation reactions could proceed via a twist mechanism or a water exchange mechanism (via a trigonal bipyramid, Scheme 33), isomerisation reactions are thought to proceed mainly via the latter. Scheme 34 illustrates the proposed aquation—isomerisation paths for κ-CoCl(en)(dien)$^{2+}$ [11]. While no contribution via the unsymmetrical trigona bipyramid was observed in this case, this intermediate probably participates in the isomerisation paths postulated for Co(N—Me—tmd)(dien)$(OH_2)^{3+}$



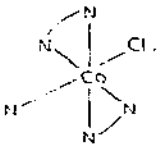
$(NH_3)_5$ 17.6 (0.86)



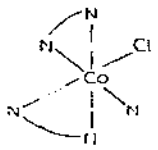
fac-(en)$(NH_3)_3$



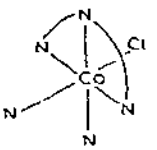
mer-(en)$(NH_3)_3$



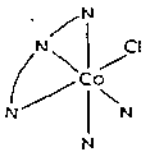
trans-(en)$_2(NH_3)$
2.9 (1.25, 273 K)



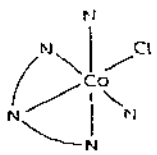
cis-(en)$_2(NH_3)$
4.2 (8.1)



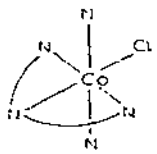
(H↓)-K-(dien)$(NH_3)_2$

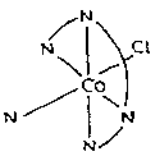


P-(dien)$(NH_3)_2$

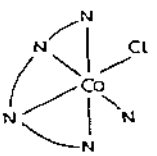


W-(dien)$(NH_3)_2$
−(1.7)

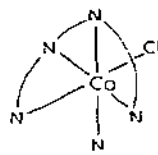




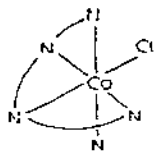
trans-(trien)(NH_3)



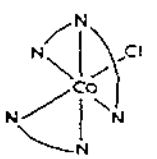
α-(trien)(NH_3)
−(10.7)



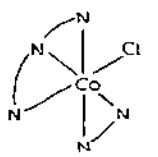
(H↑)-β_2-(trien)(NH_3)
−(4.8×10^4)
(H↓)-β'_2-(trien)(NH_3)
−(2.3×10^5)



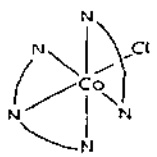
(H↓)-β_1-(trien)(NH_3)
(H↑)-β'_1-(trien)(NH_3)



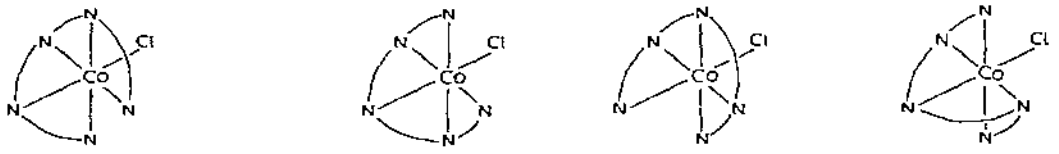
(H↓)-κ-(en)(dien) 1.78 (3.0×10^4)
(H↓)-β-(en)(dpt) 213 (2.2×10^3)
(H↓)-a-(tmd)(dien) 56.5 (5.02×10^5)
(H↓)-II'-(Metmd)(dien) 88.6 (1.2×10^5)
(H↑)-α-(en)(dpt) 116 (8.6×10^3)
(H↑)-I-(Metmd)(dien) 35.7 (v. fast)
(H↑)-II-(Metmd)(dien) 82.2 (6.2×10^4)
(H↑)-i-(tmd)(dpt) 174 (2.8×10^3)



π-(en)(dien) 2.56 (26.6)
d-(tmd)(dien) 43.0 (138)
V-(Metmd)(dien) 30.7 (7.57)
.V-(Metmd)(dien) 33.4 (—)



ω-(en)(dien) 0.94 (7.26)
h-(tmd)(dien) 2.16 (10.6)
(en)(tri) 30.6 (2.43)



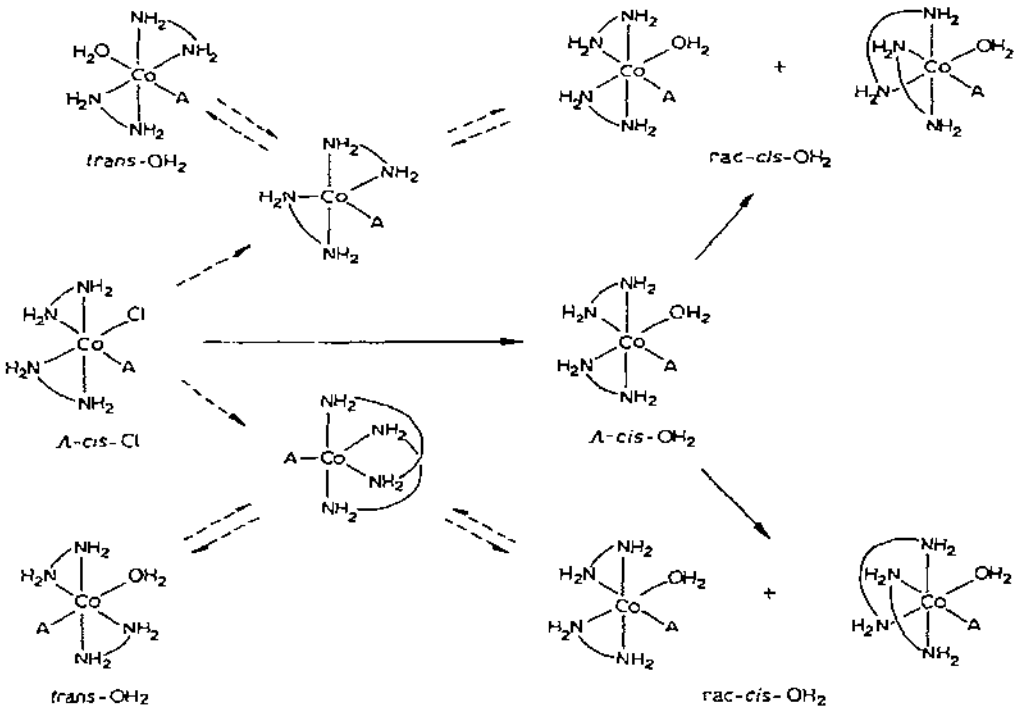
(H↑)-α-(tetren)
0.36 (3.5 × 10^4)
(H↓)-β-(tetren)
0.97 (1.0 × 10^4 est.)

αα-(tetren)

SCHEME 32. Structure—reactivity patterns in some $CoCl(N_5)^{2+}$ systems with increasing chelation. Numbers below the configurations are $10^7\ k_{aq}(298)(s^{-1})$ followed by k_{OH}-(298)($M^{-1}\ s^{-1}$, μ = 0.1 M) in parentheses.

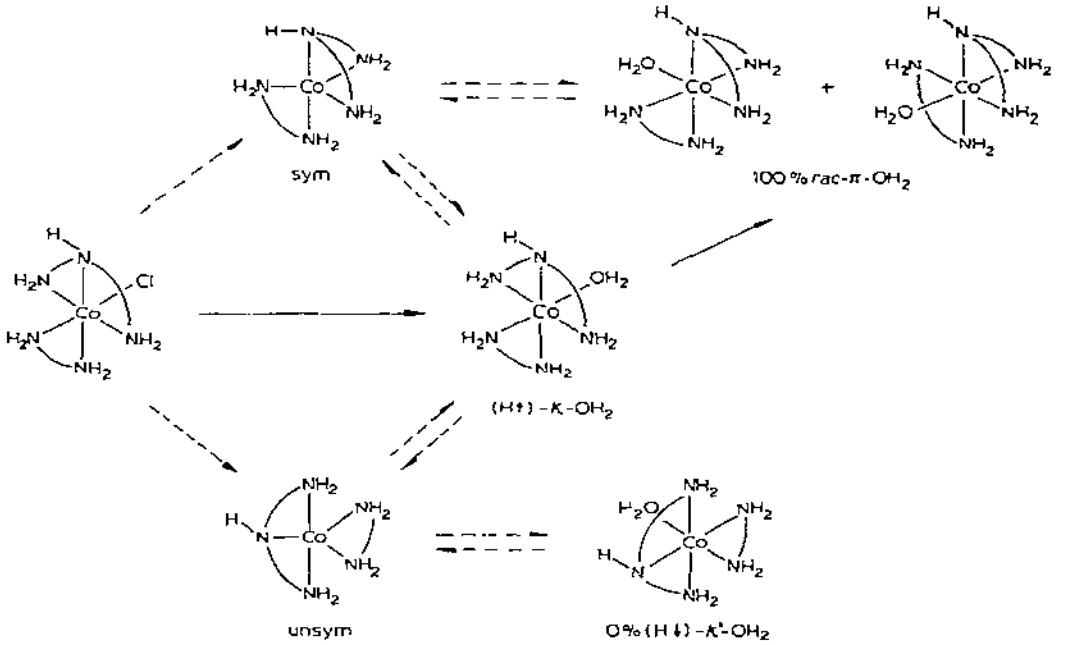
(Scheme 29, $\{+\}_{500}$—I—(R)—OH_2 → $\{+\}_{490}$—II′—(R)—OH_2). The major difference in the two chloro starting materials (κ-Cl and $\{+\}_{580}$—I—(R)—Cl, configurations II and III respectively, Scheme 26) is in the position of the *sec*-NH-*mer*-dien proton and in acid solution, complexes with configuration III cannot fold the NH_2 ends of the dien towards the leaving group, whereas those with configuration II are nicely poised to do so (Schemes 28, 29 and 35).

The simplest interpretation of these data is that the dissociative chloride



SCHEME 33. Racemisation of *cis*-$Co(en)_2(A)(OH_2)^{3+}$ via a trigonal bipyramid intermediate and a water exchange mechanism [28, p. 250].

release path in these Co(III) complexes does not proceed via the trigonal bipyramid intermediate as the kinetics can be accounted for without direct isomerisation [11,239]. Yet there is the observation that the nonreplaced chelate groups can influence the aquation rates of $CoCl(i\text{-}s)^{2+}$ complexes to a considerable extent.



SCHEME 34. proposed mechanism for the isomerisation of $\kappa \rightarrow \pi$-$Co(en)(dien)(OH_2)^{3+}$ in acidic solution [11].

The best documented of these is the "six-membered ring effect" [31,413, 422,423] first noted by Pearson et al. [421], where the replacement of 1,2-diaminoethane by 1,3-diaminopropane as a bidentate chelate caused a dramatic increase in the rate of aquation. On the other hand, no such effect is manifest in the analogous (and in many cases, isomorphous) Cr(III) systems [30,31,424,425].

Three theories as to the origin of this ring size effect have been considered:

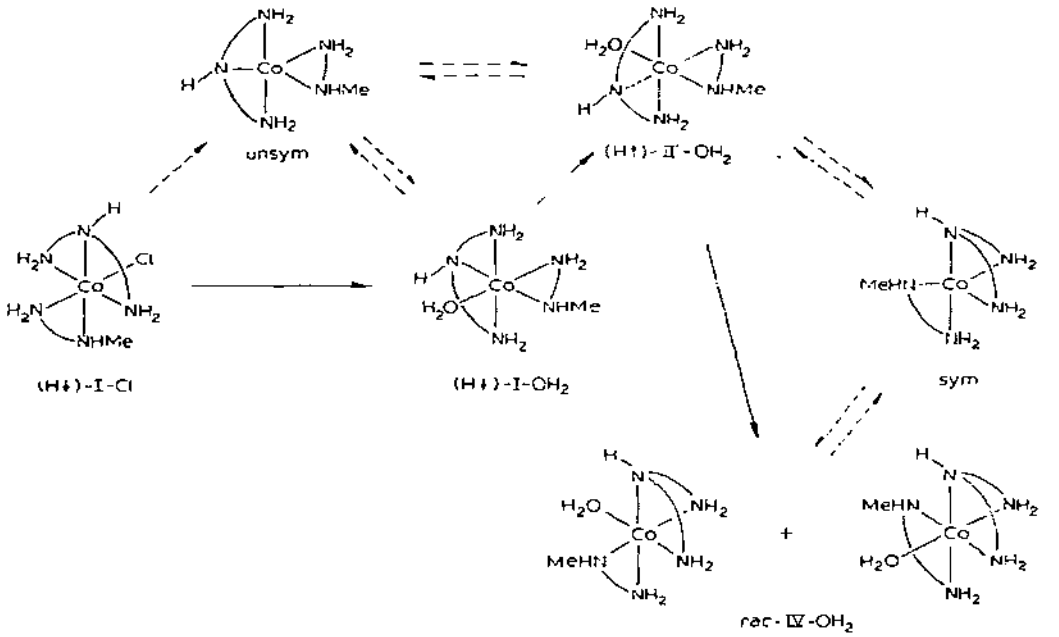
(a) steric strain theory [68,423,428]

(b) steric interaction theory [422,424,425]

(c) distortion theory [413,414].

The increased rate of *trans*-$CoCl_2(tmd)_2^+$ relative to *trans*-$CoCl_2(en)_2^+$ was originally ascribed to release of steric strain (mainly in the "bite" of the chelate ring) in forming a dissociated transition state [28,423]. This hypothesis was rejected on the grounds that the isomorphous *trans*-$CrCl_2(tmd)_2^+$ analog should have similar ring strain and yet no rate increase was observed [422, 424,425].

The demonstrated stereomobility of Co(III) complexes relative to the stereoretentive Cr(III) analogs [33] was invoked to suggest that boat or twist-boat conformations of the six-membered chelate ring in Co(III) complexes were interacting sterically with the leaving group [422,424,425]. However, the isolation of a Co(III) complex with the six-membered ring in such a position that steric interaction with the leaving group was not possible [412], and yet a rate increase relative to the en analog still occurred [413] made this theory untenable (See Scheme 26, (H↓)-*κ*-CoCl(en)(dien)$^{2+}$ and (H↓)-a-CoCl-(tmd)(dien)$^{2+}$).



SCHEME 35. Proposed mechanism for the I → II' → IV-Co(N-Me-tmd)(dien)$(OH_2)^{3+}$ isomerisation in acidic solution [414].

From a low-frequency infrared study, it has been suggested that the rates of *trans*-$CoCl_2(N_4)^+$ aquation can be correlated with an inplane Co—N deformation [426]. Consequently, the driving force for the aquation is interpreted as the tendency to distortion of the octahedral complex to the trigonal bipyramid transition state with the more flexible ligand systems being the most reactive. This distortion theory can be extended to include the *cis*-CoCl-$(en)_2(A)^{2+}$ and $CoCl(AA)(ABA)^{2+}$ systems [413,414] provided that a trigonal bipyramid transition state is acceptable.

Thus, while there seems to be little doubt that trigonal bipyramid intermediates are involved in the isomerisation of $Co(N_5)(OH_2)^{3+}$ complexes, the effects of the non-replaced ligands on the aquation rates strongly support similar intermediates in the acid hydrolysis of $CoCl(N_5)^{2+}$ systems.

The analogous $CrCl(AA)(dien)^{2+}$ complexes aquate with rates (and activa-

tion energies [30]) almost independent of the size of the diamine chelate ring (Table 25). Here an associative interchange mechanism is thought to be operative and the 3 fold rate increase observed for the chelates, relative to $CrCl(NH_3)_5^{2+}$, is attributed to a more open site adjacent to the leaving group [30].

G. TRIDENTATE–BIS(UNIDENTATE) SYSTEMS

Scheme 32 illustrates the five geometric isomers possible for the $CoX(ABA)(A_2)^{2+}$ system. Reaction of *mer*-$CoCl_3$(dien) with aqueous NH_3 produces *trans*-$CoCl_2$(dien)$(NH_3)^+$, $Co(dien)(NH_3)_3^{3+}$ and isomers of $CoCl(dien)(NH_3)_2^{2+}$ [214]. Four forms have been isolated and the K-$CoCl(dien)(NH_3)_2^{2+}$ isomer has been characterised as the (H↓)-*mer*-dien-*cis*-diammine by single crystal X-ray methods [214]. The missing isomer is apparently the *mer*-dien-*trans*-diammine form but more work is required to obtain reproducible synthetic methods.

H. BIDENTATE–TRIS(UNIDENTATE) SYSTEMS

Mer and *fac* isomers are possible in this system (Scheme 32) and both been characterised for $CoX(en)(NH_3)_3^{n+}$ (X = OH, OH_2, N_3, Cl, Br, NO_2) [434,435]. These complexes have been prepared by the reaction of *trans*-$[CoBr_2(en)(NH_3)_2]Br$ with 10% aqueous ammonia [434]. The ^{59}Co NMR spectra of *mer*- and *fac*-$Co(OH)(en)(NH_3)_3^{2+}$ show no change in solution over 90 days at 298 K, suggesting that *mer*- ⇌ *fac*-OH isomerisation does not occur.

Also included in this class is the $Co(gly)(tame)(NH_3)^{2+}$ complex (tame = $CH_3{-}C(CH_2NH_2)_3$) which has been resolved with K-(+)-SbOT [436].

I. SUMMARY AND CONCLUSION

What generalisations can be made as to the present "state of the art" in this area of coordination chemistry?

It should be realised that anionopentaamine complexes are only a small part of the arsenal of compounds available to coordination chemists and many of the difficulties in our interpretation of reactivity associated with these are only part of the wider problems of inorganic reaction mechanisms. Perhaps, at best, we have a clarification of the problems that remain to be solved and the pitfalls that may beset the unwary. One of the latter, that has not thus far been discussed, is a Co(II) catalysed reduction path that can easily be mistaken for aquation [442].

Anionopentaamine complexes will continue to be used to investigate the more subtle nuances of inorganic reaction mechanisms and the pentaammines especially, provide relatively simple systems. However, this very simplicity may restrict the full realisation of stereochemical mobility that is possible in a more complicated system.

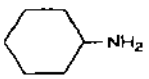
It seems that the most outstanding problem is the one of the stereochemistry of aquation (Sect. F) — the trigonal bipyramid vs. the square pyramid transition state in $CoCl(N_5)^{2+}$ systems and probably associated with this is the problem of the mechanism of racemisation of $Co(N_5)OH_3^{3+}$ systems (Tables 22 and 28).

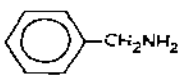
The reviewer believes that more studies involving variation of reactivity and steric course with variation in non replaced ligand will eventually provide a solution to these problems. We are beginning to see useful structure—reactivity patterns emerging but, as with most of chemistry, continual testing and probing of our currently accepted theories is required.

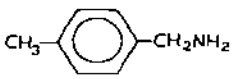
J. APPENDIX

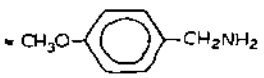
Abbreviations used

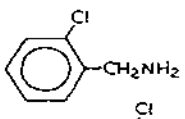
$MeNH_2 = CH_3NH_2$
$EtNH_2 = CH_3CH_2NH_2$
$nPrNH_2 = CH_3(CH_2)_2NH_2$
$iPrNH_2 = (CH_3)_2CHNH_2$
$nBuNH_2 = CH_3(CH_2)_3NH_2$
$iBuNH_2 = (CH_3)_2CHCH_2NH_2$
sec$BuNH_2 = CH_3CH_2CH(NH_2)CH_3$

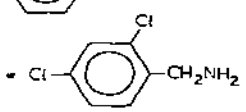
cyclohexNH_2 = 

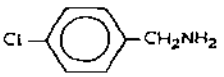
$BzNH_2$ = 

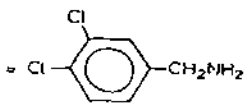
4-Me-bz = 

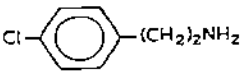
4-MeO-bz = 

2-Cl-bz = 

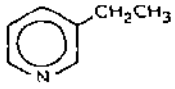
2,4-Cl_2-bz = 

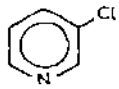
4-Cl-bz = 

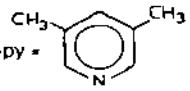
3,4-Cl_2-bz = 

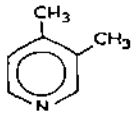
4-Cl-Ph$(CH_2)_2NH_2$ = 

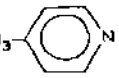
py = 

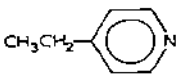
3-Et-py = 

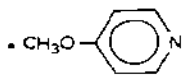
3-Cl-py = 

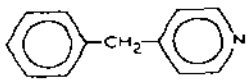
3,5-Me_2-py = 

3,4-Me_2-py = 

4-Me-py = 

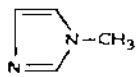
4-Et-py = 

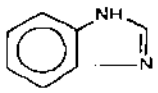
4-MeO-py = 

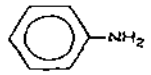
4-Bz-py = 

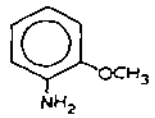
isoquin = 

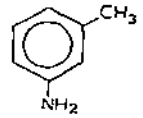
imid = 

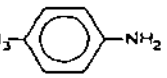
N-Me-imid = 

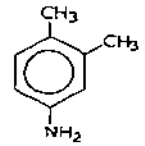
benzimid = 

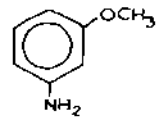
an = 

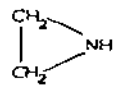
2-MeO-an = 

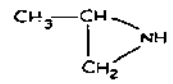
3-Me-an = 

4-Me-an = 

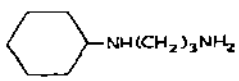
3,4-Me_2-an = 

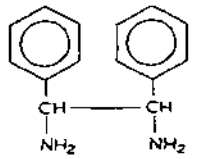
3-MeO-an = 

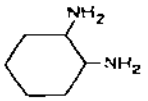
az = 

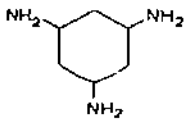
2-Me-az = 

en = $NH_2(CH_2)_2NH_2$
pn = $NH_2CH(CH_3)CH_2NH_2$
tmd = $NH_2(CH_2)_3NH_2$
ibn = $NH_2C(CH_3)_2CH_2NH_2$
sbn = $NH_2CH(CH_3)CH(CH_3)NH_2$
bn = $NH_2(CH_2)_4NH_2$
Me-tmd = $CH_3NH(CH_2)_3NH_2$
N-iPr-ibn = $(CH_3)_2CHNHCH_2CH(CH_3)NH_2$
N-Bu-tmd = $CH_3(CH_2)_3NH(CH_2)_3NH_2$

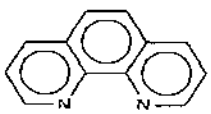
N-hex-tmd = 

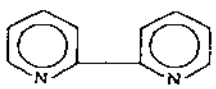
stien = 

chn = 

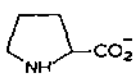
cytam = 

dien = $NH_2(CH_2)_2NH(CH_2)_2NH_2$
dpt = $NH_2(CH_2)_3NH(CH_2)_3NH_2$
2,3-tri = $NH_2(CH_2)_2NH(CH_2)_3NH_2$
tri = $NH_2(CH_2)_2N{=}C(NH_2)CH_2NH_2$
trien = $NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$
tren = $N[(CH_2)_2NH_2]_3$
trenen = $N[(CH_2)_2NH_2]_2(CH_2)_2NH(CH_2)_2NH_2$
Metrenen = $N[(CH_2)_2NH_2]_2(CH_2)_2N(CH_3)(CH_2)_2NH_2$
tetren = $NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$
penten = $[NH_2(CH_2)_2]_2N(CH_2)_2N[(CH_2)_2NH_2]_2$
cyclam = 1,4,8,11-tetraazacyclotetradecane
teta = *meso*-5,7,7,12,14,14-hexamethylcyclam

phen = 

bipy = 

ox = $C_2O_4^{2-}$
Ac = $CH_3CO_2^-$
gly = $NH_2CH_2CO_2^-$
sarc = $CH_3NHCH_2CO_2^-$
bet = $(CH_3)_3\overset{+}{N}CH_2CO_2^-$
al = $CH_3CH(NH_2)CO_2^-$
γ-amine-but = $NH_2(CH_2)_3CO_2^-$
ϵ-amino-cap = $NH_2(CH_2)_4CO_2^-$

pro = 

α-amino-ibut = $(CH_3)_2C(NH_2)CO_2^-$
ornithine = $NH_2(CH_2)_3CH(NH_2)CO_2^-$

$NTAH_2$ = $N[(CH_2)_2CO_2H][(CH_2)_2CO_2^-$
DMF = $(CH_3)_2NCOH$
DMA = $(CH_3)_2NCOCH_3$
DMSO = $(CH_3)_2SO$
NH_4[(+)BCS] = ammonium (+)-α-bromo-camphor-π-sulphonate
K[(+)SbOT] = potassium (+)-tartrato(—2)antimony(III) oxide
Na[(+)AsOT] = sodium (+)-tartrato(—2)arsenic(III) oxide.

NOTE ADDED IN PROOF

The kinetic parameters for the aquation of $CoBr(RNH_2)_5^{2+}$ (R = Me, Et, nPr and nBu) have been reported [443] and are listed in Table 29.

TABLE 29

Kinetic parameters for the hydrolysis of some $CoBr(RNH_2)_5^{2+}$ complexes in 0.05 M HNO_3 at 298 K [a]

R	k (s^{-1})	E_a (kJ mol^{-1})	$\Delta S_{298}^{\neq}$ (J K^{-1} mol^{-1})
H [b]	5.97×10^{-6}	99.5	—19.6
Me	2.86×10^{-4}	88.6	—23.4
Et	8.93×10^{-4}	89.0	—12.5
nPr	10.9×10^{-4}	89.0	—12.1
nBu [c]	14.5×10^{-4}	89.4	—7.1

[a] Data from ref. 443.
[b] Data from Table 4.
[c] Rate estimated by extrapolation of dioxane/HNO_3 data to zero dioxane.

Simple anation and solvent exchange reactions of $Co(NH_3)_5(DMSO)^{3+}$ in DMSO are complicated by reactions in which the conjugate base of this complex undergoes internal redox to Co(II) or relatively rapid substitution. These conjugate base reactions are eliminated by the addition of H^+. The solvent exchange reaction is thought to proceed via a dissociative interchange (I_d) mechanism and is characterised by an activation volume, enthalpy and entropy of +10 cm^3 mol^{-1}, 123 kJ mol^{-1} and +61 J K^{-1} mol^{-1}, respectively [442].

Naik and Nanda [444] have measured the effect of ion-pairing (using maleate and phthalate ions) on the aquation of $CoCl(NH_3)_5^{2+}$ [444]. The results are interpreted in terms of Scheme 36. At 313 K, values of K_{ip} for oxalate, sulphate, malonate, succinate, maleate and phthalate are 33.4, 33.5, 32.2, 28.4, 24.0 and 26.9 with rate enhancement factors (k_1(ip)/k_1) of 1.97, 2.20, 2.25, 2.28, 2.72 and 2.90 respectively (μ = 0.3 M, $NaClO_4$). Values of E_a = 100.3 kJ mol^{-1}, $\Delta S_{298}^{\neq}$ = —28.5 J K^{-1} mol^{-1} and $k_1(298) = 1.47 \times 10^{-6}$ s^{-1} are calculated from the data in the 313—323 K range. These compare favourably with the kinetic parameters for the aquation of $CoCl(NH_3)_5^{2+}$ in Table 4. About 10—15% of the carboxylato product is thought to be formed via the interchange [k_3(ip)] path [444].

TABLE 5

M	X	Rate law	T	k_1	k_2	E_a (kJ mol^{-1})	$\Delta S_{298}^{\neq}$ (J K^{-1} mol^{-1})	Ref.
Co	MoO_4	$k_r = k_a + k_b[H^+] + k_c[MoO_4^{2-}] + k_d[H^+][MoO_4^{2-}]$						
				k_a	k_b			
			298.2	2×10^{-1}	2.3×10^6			445

TABLE 7

M	X	μ	T (K)	k_1 (s^{-1})	Q (M^{-1})	k_1Q_1 (M^{-1} s^{-1})	E_a (kJ mol^{-1})	$\Delta S_{298}^{\neq}$ (J K^{-1} mol^{-1})	Ref.
Co	$HMoO_4^-$	1.0	298.2			3.2×10^5			445
Co	$C_6H_4(CO_2H)CO_2^-$	0.3	323.2	7.38×10^{-5}	3.28	2.42×10^{-4}			
			328.2	15.2×10^{-5}	3.02	4.60×10^{-4}			
			333.2	28.8×10^{-5}	2.92	8.41×10^{-4}			
			298.2	1.7×10^{-6}			121	+43	449
Co	$C_6H_4(CO_2)_2^{2-}$	0.3	323.2	1.15×10^{-4}	22.5	2.58×10^{-3}			
			328.2	2.11×10^{-4}	23.6	4.99×10^{-3}			
			333.2	3.73×10^{-4}	30.0	11.2×10^{-3}			
			298.2	4.3×10^{-6}			45.3	−3	449

TABLE 9

Plot No.	X	k_{OH} (M^{-1} s^{-1})	μ	Ref.	k_{aq} (s^{-1})	μ	Ref.	k_{an} (M^{-1} s^{-1})	μ	Ref.	Q_E (M)	Std. *Res.*
	MoO_4^{2-}				0.2	1.0	445	96	1.0	445	475	

$$CoCl(NH_3)_5^{2+} + H_2O \xrightarrow{k_1} Co(NH_3)_5(OH_2)^{3+} + Cl^-$$

$$CoCl(NH_3)_5^{2+} + L^{2-} \overset{K_{ip}}{\rightleftharpoons} [CoCl(NH_3)_5 \cdot L]$$

$$[CoCl(NH_3)_5 \cdot L] + H_2O \xrightarrow{k_1(ip)} [Co(NH_3)_5(OH_2) \cdot L]^+ + Cl^-$$

$$[CoCl(NH_3)_5 \cdot L] \xrightarrow{k_3(ip)} CoL(NH_3)_5^+ + Cl^-$$

$$[Co(NH_3)_5(OH_2) \cdot L]^+ \xrightarrow{k_2(ip)} CoL(NH_3)_5^+ + H_2O$$

$$Co(NH_3)_5(OH_2)^{3+} + L^{2-} \overset{Q_1}{\rightleftharpoons} [Co(NH_3)_5(OH_2) \cdot L]^+$$

SCHEME 36. Aquation—anation of $CoCl(NH_3)_5^{2+}$ with L^{2-} [57,72,444].

A study of the reaction between $Co(NH_3)_5(OH_2)^{3+}/Co(OH)(NH_3)_5^{2+}/MoO_4^{2-}$ in weakly basic solution [445] allows the additional entries to Tables 5, 7, 9 and 21. Similarly, an anation study of $Co(NH_3)_5(OH_2)^{3+}$ with phthalate ions [449] allows additional entries to Table 7.

Finally, the reader's attention is drawn to a review on acid catalysed aquation reactions [450] which expands part of Section A(iii), and also to the use of the quinquidentate ligand, tpen, N,N,N′-tris[2-(2′-pyridyl)ethyl]ethylenediamine which forms $[Co_2(tpen)_2O_2](ClO_4)_4$ [451].

TABLE 21

A	μ	T	pK_a	Ref.
$Co(NH_3)_5(OH_2)^{3+}$	1.0	298.2	6.39	445
	1.0	298.2	6.55	446
	0.3	298.2	6.22	447
	0.145	298.2	6.24	448

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