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METAL-ION CATALYSED AQUATION OF TRANSITION METAL COMPLEXES

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CONTENTS

A. INTRODUCTION

Removal of certain coordinated ligands from their complexes is considerably enhanced by the addition of some labile metal ions. Thus, solvolysis reaction rates of various transition metal complexes are found to be accelerated to various degrees by different metal ions of 'hard', 'intermediate' and 'soft' types. The leaving groups/atoms include halides, pseudohalides, alkyl groups, carboxylates, biguanides, etc. Removal of some of these ligands,

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particularly when they are the 'hard' type (F^- for example), is also acid catalysed. In other cases, particularly with Cl^-, Br^-, I^- and other 'soft' ligands, acid catalysis is not noticeable.

Most studies of such 'assisted' aquations have been devoted to Co(III) complexes, with considerable attention to Cr(III) and stray reports on Rh(III), Ru(III), Re(IV), Fe(II), Pd(II) (see text). Only scanty data are available on such reactions of Pt(II) [1a], Pt(IV) [1b], Ni(II) [1c], etc., complexes.

Such metal-ion effects had been known even at the time of Werner [2] and these metal-ion 'assisted' reactions have been studied to gain insight into the effect of solvent [3], ionic strength [4] and polyelectrolytes [5] on reaction rate and equilibrium; to provide evidence for intermediates of reduced coordination number and hence for dissociative mechanism [6]; to probe indirectly into the mechanism of 'unassisted' aquation [7] and Cr(II)-reduction reactions [8]; to synthesise products not obtainable by conventional paths [9]; and to estimate trace quantities of metal ions [10].

(i) Terminology and scope

Technically, these processes may not always be termed as catalysis, since the initial and the final states of the added metal ions may be different. The term 'assisted' has, therefore, been coined. However, this aspect is rarely checked and whether the investigated reaction is a truly catalysed one or an assisted process is not always certain. Hence, here the two terms will be used interchangeably without any prejudice to the mechanism.

Under the conditions and during the course of a catalysed solvolysis reaction, the catalysing metal ion may find itself distributed in various forms. Thus, for example, during the course of Hg^{2+}-catalysed aquation of a chloro complex (R–Cl) in nitrate media, Hg^{2+}, $HgCl^+$, $HgCl(NO_3)$, $R{-}ClHg^{2+}$, $R{-}ClHgCl^+$, etc. all might be present. Hydrolysed species such as $Hg(OH)^+$ are absent in most cases since, generally, the media pH are much lower than pK_h (K_h [11] is the hydrolysis constant of the metal ion). Some of these species might remarkably affect the rate, stereochemistry and product distribution of the reaction. Such effects will therefore, be considered, although discussion on the catalysing effects of simple solvated labile metal ions on the solvolysis of transition metal complexes is the primary concern.

Only non-redox catalysis will be dealt with, and rate enhancements due to primary salt effects is not discussed in general. Reactions in which hydrolytic activity of a ligand is enhanced by coordination to nonlabile metal centres are also not covered.

The literature up to December 1984 has been consulted.

B. RATE LAW

(i) Metal-ion dependence

Rates of these metal-ion catalysed solvolysis reactions exhibit dependence on the metal ion concentration in either of the following two general forms

$$k_{\text{obs}} = k\,[\text{M}] \tag{1}$$

(k_{obs} vs. [M] plot is linear)

$$k_{\text{obs}} = \text{A}[\text{M}]/(1 + \text{B}[\text{M}]) \tag{2}$$

($1/k_{\text{obs}}$ vs. 1/[M] is linear)
Dependence of type (1) might arise from a one-step attack by the metal ion, M, at a suitable site on the leaving ligand, L, in the complex RL, i.e. $\text{S}_\text{E}2$ attack at M (eqn. 3).

$$\text{RL} + \text{M} \xrightarrow{k} [\text{Activated complex}]^{\ddagger} \xrightarrow{\text{fast}} \text{Products} \tag{3}$$

Dependence of type (2) might originate from a rapid pre-equilibrium adduct (R–L–M) formation, whose decomposition is rate determining (eqn. 4a), or from a situation where R–L–M is formed but is not the kinetically active species (eqn. 4b)

$$\text{RL} + \text{M} \overset{K_{\text{RLM}}}{\rightleftharpoons} \text{R–L–M} \xrightarrow{k_{\text{RLM}}} [\text{Activated complex}]^{\ddagger} \xrightarrow{\text{fast}} \text{Products} \tag{4a}$$

$$\text{RL} + \text{M} \overset{K_{\text{RLM}}}{\rightleftharpoons} \text{R–L–M}$$

$$\text{RL} + \text{M} \xrightarrow{k_2} [\text{Activated complex}]^{\ddagger} \xrightarrow{\text{fast}} \text{Products} \tag{4b}$$

For both the schemes,

$$B = K_{\text{RLM}} \tag{5}$$

Whereas, for scheme (4a),

$$A = k_{\text{M}} = K_{\text{RLM}} \cdot k_{\text{RLM}} \tag{6}$$

and for scheme (4b),

$$A = k_2 \tag{7}$$

(ii) Rate law ambiguity

In the limiting case of $K_{\text{RLM}}[\text{M}] \ll 1$, eqn. (2) reduces to

$$k_{\text{obs}} = A[\text{M}] \tag{8}$$

and paths (3), (4a) and (4b) becomes kinetically indistinguishable.

At the other extreme, where $K_{RLM}[M] \gg 1$, the rate might become independent of [M], indicating that at sufficiently high [M], all the substrate complex is converted to adduct, when

$$k_{obs} = A/B \tag{9}$$

In principle, it is possible to distinguish between paths (3) and (4) by a sufficient increase in [M] [12] or by using less polar solvents to increase K_{RLM} [3,13]. Experimental difficulties, however, do not permit this in certain cases [14]. A technically much more difficult method of distinguishing between (3) and (4) involves an isotopic fractionation experiment which has established path (4) for $Co(NH_3)_5Cl^{2+}/Hg^{2+}$ aquation [15]. Parallelism of k_M with K_{RLM} also suggests path (4).

Path (3) has been proposed [16] for both of the consecutive steps of Hg^{2+}-catalysed aquation of $Co(dmgH)_2(NCS)_2^-$ ion into $Co(dmgH)_2(NCS)(H_2O)$ and then into $Co(dmgH)_2(H_2O)_2^+$. Because of the possibility of soft–soft interaction and favourable electrostatic interaction between anionic RL and cationic M in forming RLM in this case, one might expect very high K_{RLM} and hence a rate law of the form (2) or (9). The observed linearity of k_{obs} vs. $[Hg^{2+}]$ is thus indicative of path (3).

Although it might sometimes be possible to eliminate scheme (3) in favour of (4) or in fewer cases (4) in favour of (3), it is not easy to discriminate between (4a) and (4b). Worrell [17] from indirect evidence has shown that the double bridged $Co(eee)Cl_2Hg^{3+}$ (eee is 1,8-diamino-3,6-dithiooctane) intermediate is too stable to be a kinetically active species and hence proposed path (4b). In cases where such ambiguity cannot be resolved, two sets of rate constants are reported [18].

(iii) Acid dependence

If the conjugate base form of the complex exists under the reaction conditions and if this too interacts with M, metal-ion catalysed base hydrolysis path might be observable, when inverse acid dependence in the metal ion catalysed path appears. Thus, for Hg^{2+}-catalysed aquation of $Cr(H_2O)_5X^{2+}$ ($X = Cl^-$, Br^- [19], N_3^- [20])

$$k_{obs} = \left(k_0 + k_1[H^+]^{-1}\right)[Hg^{2+}] \tag{10}$$

indicative of the acid/base equilibrium

$$Cr(H_2O)_5X^{2+} \rightleftharpoons Cr(H_2O)_4(OH)X^+ + H^+ \tag{11}$$

Similar acid dependence is observed in *trans*-$Cr(H_2O)_4Cl_2^+/Hg^{2+}$ aquation [21].

Since coordinated amine protons are in general much less acidic, the

Hg^{2+}-catalysed aquation paths of $Cr(NH_3)_5Cl^{2+}$ [18] and $Cr(NH_3)_5N_3^{2+}$ [20] exhibit no acid dependence provided in the media $[H^+] \geqslant 10\,[Hg^{2+}]$ to check hydrolysis of Hg^{2+}. This also indirectly indicates that under the experimental conditions, acid dependence of type (10) originates from equilibria like (11) and not from hydrolysis of Hg^{2+}

$$Hg^{2+} + H_2O \overset{K_h}{\rightleftharpoons} Hg(OH)^{+} + H^{+} \tag{12}$$

Unlike $Cr(NH_3)_5X^{2+}$, some chloroamine complexes of Co(III) have recently been shown to have sufficiently acidic amine protons, so that the conjugate base forms of these complexes are kinetically important even at $pH < 3$. Thus effects of unhydrolysed Hg^{2+} on the conjugate base form, i.e. on the base hydrolysis path, might be tested. Such experiments on the complexes *cis*-$Co(en)_2(RNH_2)Cl^{2+}$ ($R = Ph$ or m-, or p-MeC_6H_4) led to the rate law [22]

$$\text{Rate} = (A + B[OH^-])[\text{Complex}][Hg^{2+}] \tag{13}$$

Equation (13) readily transforms to

$$k_{obs} = \left(A + BK_w[H^+]^{-1}\right)[Hg^{2+}]$$

a form similar to eqn. (10).

Cases are known where only the conjugate base form is kinetically active due to lack of a suitable M binding site in the complex itself. Thus, $Co(NH_3)_5(LH)^{2+}$ complexes (LH = unicoordinated carboxylates—Hox^- for example [23]) bind M ($M = Fe^{3+}$, Al^{3+}, Ga^{3+}, In^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+}) through the following equilibrium

$$Co(NH_3)_5(LH)^{2+} + M \overset{K_{RLM}}{\rightleftharpoons} Co(NH_3)_5LM^{2+} + H^{+} \tag{14}$$

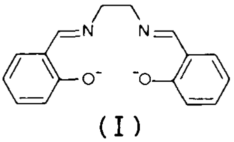
For an M catalysed path in these systems

$$k_{obs} = (K_{RLM} \cdot k_{RLM}[M]/[H^+])/(1 + K_{RLM}[M]/[H^+]) \tag{15}$$

Equation (15) applies when H^+ and M both compete for the conjugate base form of the complex. A slightly different type of rate law might arise when H^+ and M compete for the substrate complex itself, to form the conjugate acid and the binuclear adduct, respectively. Thus [24],

$$k_{obs} = K_{RLM} \cdot k_{RLM}[Hg^{2+}]/\left(1 + K_{RLM}[H^+] + K_{RLM}[Hg^{2+}]\right) \tag{16}$$

for Hg^{2+}-catalysed dealkylation of $RCo(salen)(OH_2)$ ($R = Me$ or Et, salen = (**I**)).



(I)

(iv) Formation of multiple adducts

In suitable situations, formation of more than one type of adduct is possible. In the Ag^+-catalysed aquation of $Rh(NH_3)_5I^{2+}$, for example, upto three Ag^+ have been claimed to bind at $Rh(NH_3)_5I^{2+}$ (RI^{2+}) in a stepwise fashion [12b].

$$RI^{2+} + Ag^+ \overset{K_1}{\rightleftharpoons} RIAg^{3+}$$

$$RIAg^{3+} + Ag^+ \overset{K_2}{\rightleftharpoons} RIAg_2^{4+} \tag{17}$$

$$RIAg_2^{4+} + Ag^+ \overset{K_3}{\rightleftharpoons} RIAg_3^{5+}$$

All the adducts are kinetically active, aquating at different rates (k''_{RLM}) in the presence of 1 M Ag^+ ion, so that

$$k_{obs} = \frac{k_{aq} + \sum\limits_1^3 k^n_{RLM} \cdot \beta_n [Ag^+]^n}{1 + \sum\limits_1^3 \beta_n [Ag^+]^n} \tag{18}$$

Similarly, for *cis*-$Cr(H_2O)_4Cl_2^+/Hg^{2+}$ solvolysis [21],

$$k_{obs} = \left(k_0 + k_{-1}[H^+]^{-1}\right)[Hg^{2+}]^2/\left(1 + K_1[Hg^{2+}] + K_1K_2[Hg^{2+}]^2\right) \tag{19}$$

(cf. eqn. (10); difference between *cis*- and *trans*-complex). This equation is consistent with the formation of two adducts, $Cr(H_2O)_4Cl_2Hg^{3+}$ and $Cr(H_2O)_4Cl_2Hg_2^{5+}$. Formation of an even higher adduct with Hg^{2+} is indicated for $Cr(H_2O)_5I^{2+}/Hg^{2+}$ aquation, for which [19],

$$k_{obs} = a[Hg^{2+}] + b[Hg^{2+}]^2 + c[Hg^{2+}]^3 \tag{20}$$

Binding of more than one molecule of substrate complex (here acting as a ligand) to the catalyst metal ion is also known to be possible. The complex $Cr(CN)(H_2O)_4(NO)^+$ (L say) with Ag^+ and Hg^{2+} forms both ML and ML_2 ($M = Ag^+$ or Hg^{2+}) species through cyanide bridge [25]. Hg^{2+}-catalysed aquation of this complex is, however, independent of $[Hg^{2+}]$. This has been accounted for as arising from high K_{RLM} (cf. eqn. (9)) and assuming nearly equal reactivity of HgL^{3+} and HgL_2^{4+} in spite of their different charges.

(v) Dependence of released or added anions

(a) Dependence on halides

In the Hg^{2+}-catalysed hydrolysis of $Co(NH_3)_5Cl^{2+}$ addition of Cl^- ions caused a rate increase of ca. 8% and this was attributed to $HgCl^+$ catalysis

[26]. Similarly, an 11% increase was observed in the $Cr(NH_3)_5Cl^{2+}$ system [8]. Thus, it has been suggested [27] that rate expression for the catalysed path of these reactions should be written as

$$\text{Rate} = \sum_{n=0}^{n=4} k_{HgCl_n^{2-n}}[HgCl_n^{2-n}][\text{Complex}] \tag{21}$$

Similar situations can arise with Tl(III) as catalyst [27b, 28]. Here, n might have values between 0 to 6.

In presence of added halide, Hg(II)-catalysed aquation of $Co(CN)_5Br^{3-}$ follows [29] rate law of the type (21)

$$k_{obs} = k_{aq} + k_1[HgX^+] + k_2[HgX_2](X = Cl^-, Br^-) \tag{22}$$

Even when no halide is added from outside, Cl^- released from the complex itself during the course of aquation is sufficient to give, in the case of $Cr(NH_3)_5Cl^{2+}/Hg^{2+}$ aquation, a rate law [8]

$$k_{obs} = k_0[Hg^{2+}] + k_1[HgCl^+] \tag{23}$$

In absence of added halide, however, X^- is usually low, since the complex, now the only source of X^-, is generally kept low to maintain pseudo-first-order conditions. Hence, terms of eqn. (21) with $n > 1$ are rarely appreciable under such conditions and even HgX^+, because of its low concentration, normally plays only a minor role. Effects of $HgCl_2$ and $HgCl_3^-$ have been shown to be comparable to media effect in catalysing the aquation of $Cr(H_2O)_5Cl^{2+}$ [30].

(b) Dependence on other anions

While considerable attention has been paid to the possibility and effect of the formation of HgX_n^{2-n} from X^- present or released in the medium, nitrate and (to a greater extent) perchlorate are generally assumed to be 'innocent'. Often, therefore, constant ionic strength media are maintained by addition of rather high (0.2–3.0 M) concentrations of NO_3^- or ClO_4^-, or both, in the form of acid and/or salts during kinetic investigations. However, it has been pointed out that [30,31] although for reactions between ions of unlike sign, the salt effect is governed by the principle of ionic strength, i.e., some form of the Debye–Hückel equation, for reactions between ions of like sign, such a relation does not appear to be obeyed. In these cases, the rate is determined by the concentration of the supporting ion of opposite sign and specific salt effects are often apparent. Thus, for example, constancy of total perchlorate concentration is more important than constant ionic strength to keep the Hg^{2+}-catalysed aquation rate of $Cr(NH_3)_5Cl^{2+}$ constant under otherwise similar conditions. Perchlorate and nitrate show different types of positive salt effects, whereas the CF_3COO^- and SO_4^{2-} are more in line with a neutral molecule. At high ionic strength, ion-pairing with substrate complex or complexation with the catalyst may arise. Thus, interpretation of product ratios from competition studies for catalysed aquations in the presence of competing anions, might be controversial unless the possibility of reactive ion-pairs of the reactants with supporting electrolyte is taken into account [6,32]. This effect in favourable cases might appear in the rate law as anion-dependent terms. Reynold and Alton [33] showed that for $Co(NH_3)_5Cl^{2+}/Hg^{2+}$ aquation in $(NO_3^- + ClO_4^-)$ media,

$$k_{obs} = (k'_0 + k'_1[NO_3^-])[Hg^{2+}] \tag{24}$$

where the overall reaction is

$$Co(NH_3)_5Cl^{2+} + Hg^{2+} \xrightarrow{H_2O/NO_3^-} Co(NH_3)_5NO_3^{2+} + Co(NH_3)_5(H_2O)^{3+} + HgCl^+ \tag{25}$$

and importance of $HgNO_3^+$ as electrophile has been established.

In sulphate media, this aquation obeys [34]

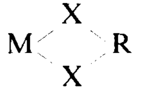
$$k_{obs} = (k'_0 + k'_1[SO_4^{2-}] + k'_2[SO_4^{2-}]^2)[Hg^{2+}] \tag{26}$$

Analogous situations arise in the Mg^{2+} ion catalysed *trans* → *cis* isomerisation of the $Cr(ox)_2(H_2O)_2^-$ ion. Here, in the presence of added SO_4^{2-}, an additional kinetic path involving $MgSO_4$ as catalyst appears and $k_{obs}/[Mg^{2+}]$ vs. $[SO_4^{2-}]$ is linear but k_{obs} vs. $[Mg^{2+}]$ is not [35].

Now, since most of the earlier kinetic data were collected in the presence of background electrolytes of varied strength and types, they are possibly not strictly comparable and mechanistic conclusions drawn from such comparison are subject to controversy. House [31] has developed a set of experimental relationships to convert such data to those expected for a standard medium (1 M $HClO_4$).

C. ADDUCT

(i) Stability

Polyvalent cationic complexes do not commonly associate strongly with cationic catalysing metal ions. Not only do their like charges destabilize the interaction, but also the coordination strength of a polar solvent which is capable of dissolving the parent compound outweighs the stability of an RLM species. When, however, two halogen or pseudohalogen atoms *cis* to one another are present in the substrate complex RX_2,  $M\overset{X}{\underset{X}{\langle\rangle}}R$ type bridge formation strongly increases the magnitude of K_{RLM}. If the spectral characteristics of such an intermediate are sufficiently different its formation can thus be confirmed. Some adducts of high K_{RLM} (30–1300 M^{-1}) are thus formed during the Hg^{2+}-catalysed aquation of *cis*-$Co(en)_2(N_3)_2^{+}$ [36], *cis*-$Co(en)_2Cl_2^+$ [7], *cis*-$Co(eee)Cl_2^+$ [17,18a], *cis*-$Co(en)_2(CN)Cl^+$ [37], *cis*-$Cr(H_2O)_4Cl_2^+$ [21], *mer*- and *fac*-$Rh(H_2O)_3Cl_3$ [38]. With none of the corresponding *trans*-isomers or their mono-aquated products are such high K_{RLM} values observed. Moreover, in spite of its lower charge, $HgCl^+$ forms weaker adduct than Hg^{2+} with *cis*-$Cr(H_2O)_4Cl_2^+$ [39]. Since $K_3 \ll K_2 \approx K_1$ for Hg(II)–halide complex, it is reasonable that a binuclear complex would not be formed in this system to any appreciable extent if such a binuclear complex would necessarily involve double bridging.

A somewhat similar situation arises when a single coordinated ligand alone offers suitable sites for chelation of the catalysing metal ion. Formation of some very highly stable adducts occurs under such situations, e.g. between $Co(NH_3)_5(L)^{n+}$ ($L = nta^{3-}$ [40], ox^{2-} [23,41], mal^{2-} [42], salicylate [43]) and bivalent, trivalent metal ions [44].

Yet another condition that strongly favours stable association is when the binding centre of the complex and the catalyst metal ion are both soft. Thus, K_{RLM} values for isothiocyanato complexes such as $M'(NH_3)_5NCS^{2+}$ (M' = Co(III) [45], Cr(III) [46]), $Cr(H_2O)_5NCS^{2+}$ [45], *trans*-$Co(en)_2(Cl)(NCS)^+$ [45], *trans*-$Co(en)_2(H_2O)NCS^{2+}$ [45], *cis*-$Co(en)_2(NO_2)NCS^+$ [45] and isocyano complexes like $Cr(H_2O)_5NC^{2+}$ [47], $Cr(H_2O)_4(NO)(NC)^+$ [25,48] or $Co(NC)_5H^{3-}$ [49] with Hg^{2+} and/or Ag^+ are very much higher than the stability of the adduct formed by the corresponding cyano, thiocyanato-, and azido-complexes [50].

Among the halides, iodide is the softest. Iodo complexes, therefore, often form stable adducts with soft metal ions such as Hg^{2+} and Ag^+. Thus, in the Hg(II)-catalysed aquation of $Rh(NH_3)_5X^{2+}$, simple second order kinetics, at least when $[Hg^{2+}]$ is relatively low, are observed with $X = Cl^-$, Br^- [51]. However, when $X = I^-$, a limiting rate is approached at higher Hg^{2+} concentration. The K_{RLM} value for the intermediate adduct $Rh(NH_3)_5IHg^{4+}$ has been evaluated to be 200 M^{-1} at 25°C [52]. High K_{RLM} values (100–10,000 M^{-1}) are observed also when Hg^{2+} interacts with σ-bonded alkylcobalt(III) complexes [24].

Ionic strength [53] and solvent [54] have a marked effect on K_{RLM} values. Kinetic evidence for the formation of RLM (linear $1/k_{obs}$ vs. $1/[M]$, but nonlinear k_{obs} vs. [M] plot) might be thus obtained in non-aqueous media when such evidence are lacking in aqueous solution.

(ii) Nature of bonding

The L–M bond in RLM is often suggested to involve distinct covalent interaction. The following facts are advanced in support:

(a) K_{RLM} values are often too high to be accounted for by simple ion-pair formation, particularly when the complex and catalyst are both cationic.

(b) The large difference in K_{RLM} values for the adduct of two geometrical or linkage isomers of a complex with the same catalyst [38,45].

(c) Fe^{3+}, although it bears a higher charge, is a better catalyst than H^+ or M^{2+} ions in catalysing the aquation of even a cationic complex such as $Cr(ox)(H_2O)_4^+$ [55] or $Co(NH_3)_5(Hox)^{2+}$ [23], indicating the importance of specific binding of M with RL. In line with this, K_{RLM} for anionic $Co(edtaH)Cl^-$ with Pb^{2+} and K_{RLM} for cationic $Co(en)_2(glycine)Cl^+$ with Pb^{2+} seems to be similar [56].

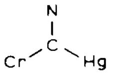
(d) In aqueous solution, substitutionally inert metal ions and complexes such as Cr^{3+} or $Co(NH_3)_5^{3+}$ are catalytically ineffective [56], although labile metal ions of the same charge (Fe^{3+} for example) exhibit a strong catalytic effect.

(e) Spectroscopic changes associated with such adduct formation often extend through the visible spectrum and only affect the longest wavelength band of the complex spectrum. This suggests the formation of a new species rather than a charge-transfer effect expected for simple ion-pair formation [38].

(iii) Structure

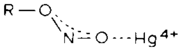
Ambiguity as to the site of attack of M to RL to form RLM might arise if L is a polyatomic group such as N_3^-, SCN^-, $SeCN^-$, CN^-, NO_2^-, etc. Thus, Hg(II) might add to $Pd(MeEt_4dien)YCN^+$ and $Pd(Et_4dien)YCN^+$ (Y = S or Se) [57] or $Co(NH_3)_5SCN^{2+}$ [45] either through terminal N or through coordinated S/Se. With the R–NCY isomer, attachment of Hg(II) through nitrogen not only involves an unfavourable hard–soft interaction but the electronic and steric situations are also unfavourable for stable adduct formation. Such thermodynamically unstable adducts, if formed, however, might be more active kinetically.

In the aquation of $Cr(H_2O)_5CN^{2+}$, there is a major reaction path through formation of $Cr(CN)Hg^{4+}$. In this, Hg(II) possibly binds through coordinated carbon forming a structure (**II**) comparable to bridged carbonyls. This structure is more consistent than is $Cr–C–N–Hg^{4+}$ with the observed facile rearrangement of (**II**) into $Cr–N–C–Hg^{4+}$ [ref. 47, also cf. ref. 48].



(II)

The suggested [54] intermediate adduct in the Hg^{2+}-catalysed linkage isomerisation of $Co(NH_3)_5(ONO)^{2+}$ might have any one of the following modes of binding (**III–VI**).



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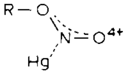

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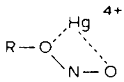

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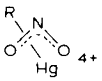
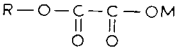


(VI)

With unicoordinated dicarboxylates (Hox^- for example) also, M might bind as in (**VII**) and (**VIII**). The chelated structure (**VIII**) is favoured since K_{RLM} is high [44,58].



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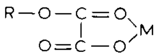

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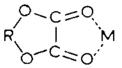
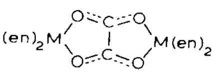


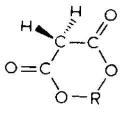
(IX)

Association of M to a bicoordinated dicarboxylate moiety might occur through the formation of a structure of the type (**IX**) (for oxalate) [55,59] or of type (**VII**) or (**VIII**) after one-ended dissociation of the dicarboxylate ligand [60, cf. 61].

Structure (**IX**) gains support from the synthesis and X-ray structure characterisation [62] of compounds of type (**X**) (M = Ni^{II} [62a], Cu^{II} [62b]). For malonate, however, an intermediate of type (**IX**) is unlikely [cf. 61] since the two carbonyl oxygen atoms, being separated by the $-CH_2-$ group, are too far apart to make a proper bite on M (**XI**).



(X)



(XI)

D. CATALYTIC EFFICIENCY

The catalytic efficiency of a particular metal ion is a complicated function of several factors. Of these factors, the ability of M to bind at a suitable substrate site, is distinctly recognisable. It is reflected in a fairly close correlation of rate of catalysed aquation with factors related to the complexing ability of M and RL, e.g., the relative hardness and softness of the various reactants [63]. Indeed, metal ion catalysis falls into two broad categories. Class (a) or hard metal ions such as Be^{2+}, Al^{3+}, Sc^{3+}, Th^{4+}, etc. They, along with H^+, readily remove hard ligands such as fluoride. Class (b) or soft metal ions, for example Hg^{2+} and Ag^+ are most effective as aquation catalysts when the leaving group is a soft ligand (Cl^-, Br^-, I^-, etc.).

The importance of catalyst binding to RL is reflected in a similar correlation. The catalytic efficiency of a series of closely related metal ions in aquating a metal complex RL parallels K_{RLM} values or any other related parameters (e.g., K_{LM}, the first formation constant of the complex between the M and L). Thus, in the aquation of several carboxylate complexes of Cr(III) and Co(III), the order of catalytic effectiveness of added metal ions parallels the stability constants of the monocarboxylato complexes: Mn(II) < Co(II) < Ni(II) < Cu(II) > Zn(II) (the Irving–William sequence); In(III) < Al(III) < Ga(III) < Fe(III); M(III) ions being more efficient than M(II) [42,43,55,64].

Similarly, the catalytic efficiency of Hg(II) in aquating R–X complexes increases [65,66] in the sequence of $X = I^- > Br^- > Cl^-$, which parallels the thermodynamic stability of HgX^+ species. Tl(III) is also a more effective catalyst for removing bromide from Co(III), specifically from *cis*-$Co(en)_2(NH_3)Br^{2+}$, than it is for removing chloride [14].

Further, Cd^{2+} which is isoelectronic with Hg^{2+} and bears the same charge, is a much inferior catalyst than Hg^{2+} because K_{LM} for Cd^{2+} is much lower. Similarly, $TlCl^{2+}$ and $HgCl_2$ also exhibit only feeble catalysis.

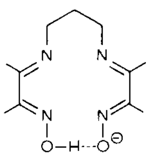
More quantitatively, with a series of closely related metal ions, log k_{RLM} or log k_M is linearly related [42,43,55,64,70,75] to factors that reflect the complexing ability of M with RL, e.g., log K_{RLM}, log K_{LM}, χ_M (the Alred–Rochow electronegativity of M), $Z^*/(r_M)^2$ (effective ionic potential; Z^* = effective nuclear charge, r_M = ionic radius of the catalysing metal ion), and adjusted ionic potential, $Z/(r_M + 0.64\ Z)$. All these factors are known to be interrelated [67,68,69]. The catalytic effect of a range of cations in catalysing the displacement of chloride ion from the complex $Co(edtaH)Cl^{-1}$ to give $Co(edta)^-$ containing hexadentate edta, has been correlated with a function incorporating stability constants of the catalyst with both chloride and carboxylate group. This has been interpreted in terms of interaction of the catalysing metal ion with two sites on the substrate, i.e. the unbound carboxylate group and the bound chloride ligand [56]. Similar suggestions have been made for the Cu^{2+}-catalysed chloride elimination in $Co(en)_2(NH_2CH_2COOH)Cl^+$ [71]. Note that quantitative parallelism of log k_M and log K_{LM} is possible even if k_{RLM} is constant and independent of K_{RLM}. Thus, for example in Hg^{2+}-catalysed halide (Cl^-, Br^-, I^-) displacement from some cationic Pd(II) complexes, log $k_{Hg^{2+}}$ vs. log K_{HgX^+} is linear, yet the solvolysis rate constant (k_{RLM}) of the adduct RLM formed, does not vary significantly with the nature of the coordinated halide [66].

Deviation from such correlations, on the other hand, does not, however, necessarily indicate a change in mechanism. For example, log k_M for the aquation of $Cr(ox)_3^{3-}$ into *cis*-$Cr(ox)_2(H_2O)_2^-$ ion is linearly related to log K_{M-ox}, when M = Cu(II), Ni(II), Co(II), Mn(II) or Zn(II), but Fe^{3+} and

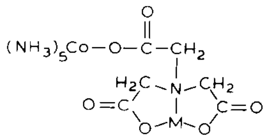
Pb^{2+} do not fit in, possibly because Fe^{3+} is of different charge type and Pb^{2+} is not a transition element. However, a plot of log k_M vs. $-\Delta S_{\text{solvation}}$ of these catalysing metal ions is fairly linear inclusive of all M^{2+} and M^{3+} mentioned, indicating similarity of mechanism [72].

Lack of correlation between k_{RLM} (or k_M) and K_{RLM} (or K_{LM}) may also result from the stabilization of the ground state as opposed to that of the transition state of RL as a result of the formation of RLM. This may arise from (a) too strong binding of the metal ion (M) to the substrate (RL) in an intermediate step or (b) involvement of the catalyst in binding at substrate sites other than required for a desired reaction. In the Hg^{2+}-catalysed dealkylation of *trans*-$RCo(L)(H_2O)$ ($L^- =$ (**XII**); $L^{2-} =$ salen (**I**)) formation of highly stable adducts (log K_{RLM} ranging from 3.5 to 7.5 for different L and R) has been demonstrated, but no apparent correlation of k_{RLM} with K_{RLM} exists [34].

Formation of very highly stable adducts (log K_{RLM} ranges from 4.4 for Ca^{2+} to 11.4 for Fe^{3+}) by $Co(NH_3)_5$(O-nta) ion with various bi- and tri-positive metal ions has been reported [40]. However, such adduct formation, presumably in the following fashion (**XIII**), very strongly stabilizes the ground state of the complex and aquation of the adducts is extremely slow.



(XII)



(XIII)

Analogously, formation of the $Co(en)_2(gly)^{2+}$ ion from $Co(en)_2Cl(NH_2CH_2COOH)^{2+}$, which possibly takes place directly without prior formation of the aquated product, proceeds with inhibition by coordination of Cu^{2+} at the unbound carboxylate group [71].

When two catalysts have comparable K_{LM} values, then the charge borne by the catalysts might play a dominant role. Thus, although Hg^{2+} and Tl^{3+} are isoelectronic and $K_{HgCl} \approx K_{TlCl^{2+}}$, yet at least for cationic complexes, Hg^{2+} is always a superior catalyst because of its lower charge. Tl^{3+} predictably exhibits particularly weak catalysis in eliminating Cl^- from the cationic $[(NH_3)_4Co\text{-}\mu\text{-}(NH_2,Cl)\text{-}Co(NH_3)_4]^{4+}$ [73]. On the other hand, in the aquation of some anionic and neutral complexes catalytic superiority of Tl^{3+} over Hg^{2+} has been demonstrated, as expected [56b,74].

Similarly, although $HgCl^+$ and Hg^{2+} are almost equally effective in binding to Cl^- ($K_{HgCl_2} \approx K_{HgCl^+}$), because of its lower charge, $HgCl^+$ in several cases is almost twice as effective as Hg^{2+} in catalysing aquation of cationic chloro-complexes.

On electrostatic grounds, it is possible to explain the higher catalytic activity of Hg^{2+} on the conjugate base form than on the original complex [8,20,21,22]. However, besides K_{LM} and the charge borne by the catalyst, the size of the catalyst might also play some role in determining the catalytic efficiency.

Hg^{2+} is more effective on R–YCN than on R–NCY (Y = S, R = $Co(NH_3)_5$ [45] or $Cr(NH_3)_5$ [46]; Y = S/Se, R = $Pd^{II}(Et_4$ dien) or Pd^{II} $(MeEt_4$dien) [57]). Possibly, Hg^{2+} attacks on the coordinated Y of R–YCN in these complexes and this very effectively weakens the R–Y bond through the inductive effect.

Hg^{2+} is more effective in aquating the Re^{IV}–Cl bond than the Co^{III}–Cl, Rh^{III}–Cl or Cr^{III}–Cl bonds [75]. Among Ru(III), Rh(III) and Co(III), catalytic efficiency of Hg(II) increases in the order mentioned [76].

The rate of HgX_2 catalysed demethylation of methylcobalamines decreases in the order $X = OAc^- \geqslant Cl^- \geqslant SCN^- \geqslant Br^- \geqslant CN^-$, a sequence which correlates with the stability of the Hg–X bond. The HgX^+ ion acts as the more reactive electrophile in each case; $HgCl_4^-$ is somewhat less reactive than $HgCl_2$ and HgCl(CN) is very inactive [77].

Formation of a polynuclear adduct enhances catalytic activity. In $Rh(NH_3)_5I^{2+}/Ag^+$ aquation, $Rh(NH_3)_5IAg_n$ (n = 1,2,3) are formed; k_{RLM} increases with increase of n [12b] (β_n increases).

The catalytic efficiency often increases remarkably on the addition of synthetic polyelectrolytes [5]. The observed acceleration might have some bearing on the dehydration of the metal ions brought about by the polyelectrolytes. In their presence even an 'ineffective' metal ion such as Cr^{3+} becomes an active aquation catalyst. In aqueous solution their inactivity is attributed to relatively strong hydration and hence inability to bind at a suitable substrate site. In line with the dehydration hypothesis, it has been observed that the trend of k_M for Hg^{2+}-catalysed nitro → nitrito isomerisation [54] of $Co(NH_3)_5(ONO)^{2+}$ in different solvents is $k_{Hg}(Me_2SO) < k_{Hg}(H_2O) < k_{Hg}(Me_2CO)$ while the degree of solvation of Hg^{2+} follows the order $Me_2SO > H_2O > Me_2CO$. The observed linear correlation of $\log k_M$ with $-\Delta S_{\text{solvation}}$ [72] in $M^{n+}/Cr(ox)_3^{3-}$ aquation also points to the importance of desolvation of the catalyst in forming the transition state. Desolvation of the catalyst, however, may take place either in forming the intermediate RLM or in supplying the aquating aqua ligand to the substrate.

E. NATURE OF THE ACTIVATED COMPLEX

Whereas the assignment of mechanism to spontaneous thermal aquation may at times be uncertain, the mechanism of metal ion catalysed aquation of halide complexes of cobalt(III), chromium(III) and similar cations is unlikely to be other than dissociative as far as the metal(III) center is concerned [78]. This is expected since in assisted aquation good leaving groups with large volume (7-coordination disfavoured) and positive charge are formed. However, large size also makes the departing group slower moving than other nucleophiles present in the medium. Its effect on mechanistic behaviour will be discussed later.

Hg^{2+}-catalysed aquation of $Cr(OH_2)_5X^{2+}$ ($X = Cl^-, Br^-, I^-$) [19], whose spontaneous aquation counterpart is so well known for its associative nature, has been proposed to proceed through a dissociative pathway, since a LFER ($\Delta G^{\ddagger}$ vs. ΔG^0) correlation has a slope of 0.90 instead of the 0.56 observed in spontaneous aquation.

Unlike Cr(III) complexes, even the spontaneous aquations of $Co(N_5)X^{n+}$ complexes are more or less well established to be dissociative. When assisted by a metal ion, logically such reactions are even more likely to take a dissociative course. However, this has been a point of considerable controversy over the years. For example, a plot of log k_{Hg} vs. log k_{aq} for a limited number of $Co(en)_2LX^{n+}$ complexes had been shown to be linear with a slope (0.6) much less than expected (1.0) if similar five-coordinate species are produced in the k_{Hg} as well as the k_{aq} path. Later, House [31], using a larger number of data points and using k_{Hg} values corrected for media effects, showed the slope to be 0.96.

Involvement of similar activated intermediate demands stereochanges (where possible) for the two reaction paths also to be similar. Again, however, until recently, stereochemical changes were mostly known to be different for the spontaneous and assisted paths [79,80]. It was a general doctrine that whereas, in general, spontaneous aquation involves stereochange, assisted aquation mostly proceeds with retention [9]. Structural assignments had also been made on the basis of this belief [81]. Recent careful measurements by better techniques now very strongly suggest that the previous results and views might have been grossly incorrect. Actually, the immediate stereochemical product ratio, at least for the aquation of $Co(en)_2XY^{n+}$ complexes, are independent of the nature of the leaving group [82] (i.e., whether X^- (spontaneous aquation) or HgX^+ (Hg^{2+}-assisted aquation) or $N_2 + N_2O$ (NO^+-induced aquation of azido complexes). The steric course is determined largely by the nature of the non-replaceable ligand, Y. OH^- and CN^- are the prototypes of stereomobility and stereoretention inducing ligands, while the behaviour of the other non-replaceable ligands is intermediate [63,83,84].

Formation of similar five-coordinate intermediates also requires that if the aquation of $Co(N_5)X^{n+}$ is carried out in the presence of water enriched with $^{18}OH_2$, then this will be incorporated in the aquation product and the $^{18}OH_2/^{16}OH_2$ ratio in the product will be the same irrespective of whether the leaving group is X^-, MX^{n+} ($X = Cl$, Br, I) or $N_2 + N_2O$. This ratio was actually found [15] to be constant (1.001 ± 0.001) when $M = Hg(II)$. However for $M = Ag^+$ or Tl^{3+} different isotopic ratios were reported [15]. Later investigation showed the ratio to be the same even for Ag^+ and Tl^{3+} within the precision limit (±0.001) attainable [85]. It might be pointed out here that these 'constant' fractionation factors may suggest, but can never prove, that a common intermediate is involved; any difference in the fractionation factor that emerges from the mechanistic differences may well be beyond the reach of precision limits presently available. However, the fact that these factors are so nearly alike, suggests that the Co(III)-leaving group separation is large when the bond to the incoming group is formed.

Attempts to detect the possible five-coordinate intermediate might involve trapping it with nucleophilic competition reactions in the presence of nucleophiles (including co-solvent) other than water. However, the interpretation of results is often complicated and made controversial by the question of ion-pairing [6,31–34] and even a subtle difference brought thus or otherwise (by a difference of media temperature, for example) in the stability, structure and life-time of the intermediate, might make a difference in competition ratio [86].

If $Co(NH_3)_5^{3+}$ exists sufficiently long to meet and react with nucleophiles not originally present in its solvation shell, the mechanism of ligand exchange is 'D'. If the life span of the intermediate is too small to survive change of composition of the solvation shell, then it must react with a component in its solvation shell and the mechanism of ligand exchange is I_d. Yet another situation is where the departing group, due to its heaviness and/or large size, is much slower moving than other nucleophiles present in the media. Here the dissociated leaving ligand could be retained in the solvation shell to influence the product ratio while other nucleophiles are diffusing in. In this case the reaction would be borderline between D and I_d and would appear to be I_d because of the influence of the leaving ligand on the product ratio. The actual reason of a difference or similarity in product ratio is therefore not easy to discern.

The I_d path has been suggested for $Co(Metren)(NH_3)X^{n+}/Hg^{2+}$, Ag^+, NO^+ ($X = Cl$, Br, N_3) aquation [87] (Metren is 1-methyltriethylenetetramine) and $Co(NH_3)_5Cl^{2+}/Hg^{2+}$ aquation in $ClO_4^- + NO_3^-$ media [33].

Since aquation at Co(III) is more or less accepted to be dissociative, similar '*m*' values for the Grunwald–Winstein plots for the Hg^{2+}-catalysed aquation of $Co(NH_3)_5Cl^{2+}$ (0.35) [88], $Rh(NH_3)_5Cl^{2+}$ (0.25) [88], and $Ru(NH_3)_5Cl^{2+}$ (0.24) [89], are often advanced as proof of a similar dissociative mechanism for all these reactions. Lower '*m*' values for M(III) complexes compared to that for t-butyl chloride (1.0) are attributed to the more polar nature of the M(III)–Cl bond. However, with the same logic, second row Ru(III) and Rh(III), which are more covalent than Co(III), should claim higher 'm' values than Co(III). Hence the 'm' values noted above cannot exclude associative path for Ru(III) and Rh(III). 'm' values are quite low also for Hg^{2+}-assisted aquation of $Cr(NH_3)_5Cl^{2+}$ ($m = -0.4$) and $Cr(NH_3)_4(H_2O)Cl^{2+}$ ($m = -0.1$) [3]. Such small values suggest unexpectedly high associative character for these assisted aquation reactions. Further, the remarkable difference in 'm' values for the two apparently similar Cr(III) complexes is also surprising. On the other hand, 'm' = 1.7 [18b] for $ReCl_6^{2-}/Hg^{2+}$ aquation could stand for 'more than dissociative' reaction. Moreover, a Grunwald–Winstein plot for the Hg(II)-catalysed aquation of the *trans*-$Co(en)_2Cl_2^+$ cation shows markedly less correlation than for $Co(NH_3)_5Cl^{2+}$ and $ReCl_6^{2-}$ [18b] indicating considerable associative nature for $Co(en)_2Cl_2^+$ but dissociative activation in the case of $Co(NH_3)_5Cl^{2+}$. Such anomalies might be partly attributed to the fact that the rate constants used in such correlations are often composite constants ($k_M = k_{RLM} \cdot K_{RLM}$). But even when k_{RLM} values are available, it is often noted that k_{RLM} is rather insensitive to solvent composition and only poorly correlated [13,90] to 'Y', the Grunwald–Winstein solvent parameter. This could indicate associative activation for these assisted aquation processes.

However, it has now been pointed out that these slope values may not be diagnostic of the mechanism [91]. The Grunwald–Winstein analysis just concerns reaction rates and this includes both initial and transition state solvation contributions. To understand the nature of the activated complex from solvent effects on rate, one needs to establish solvent effects on the initial states and on reactivity and thence by arithmetic, obtain the transition state contributions. The importance of such dissections of solvent effects on reactivity trends for reactions of transition metal complexes has recently been emphasized [90,92,93] and such analysis suggests a dissociative activation for the assisted aquation path.

The similarity of mechanism for metal ion catalysed aquation reactions at cobalt(III) and chromium(III) centers is further indicated from a linear plot of log $k_M(Co^{III})$ vs. log $k_M(Cr^{III})$ for the Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+} and Zn^{2+} catalysed aquation of $M(biguanide)_3^{3+}$ ($M = Co^{III}, Cr^{III}$) complexes. Parallels in the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were also observed [70].

Rudakov and Kozhenikov [94] found a linear correlation between log k_M and log K_{MX} for metal ion catalysed aquation of halogeno-cobalt(III), -chromium(III), and -rhodium(III) complexes. The equation for this line and that for catalysis of t-butyl halide (for which the dissociative mechanism is known to be operative) are very similar and a dissociative mechanism has been suggested for all these reactions.

Dissociative activation has been suggested from the measurements of activation parameters. $\Delta V^{\ddagger}$ values for the Hg^{2+}-catalysed aquation of

$Co(NH_3)_5X^{2+}$ (X = Cl, Br), $Cr(NH_3)_5Cl^{2+}$, and $Rh(NH_3)_5Cl^{2+}$ in aqueous media [95a] lie between -2 and $+1$ and that for the Pb(II)-catalysed aquation of $Co(NH_3)_5Br^{2+}$ in aqueous polyelectrolyte media [5b], is $+2.5$. This similarity suggests a common dissociative mechanism with preequilibrium formation of RLM. Again, one should recall that the rate constants used are composite constants and more than one factor [95a] contribute to the absolute value of $\Delta V^{\ddagger}$. For the *mer*-$Rh(H_2O)_3Cl_3/Hg^{2+}$ system in acidic aqueous solution, k_{RLM} values could be evaluated. Here $\Delta V^{\ddagger}$ for the k_{RLM} path is $+8.1$ cm^3 mol^{-1} [38]. $\Delta V^{\ddagger}$ also has been determined for racemization of $Cr(ox)_3^{3-}$ as catalysed by Cu^{2+}. In 0.05 M Cu^{2+} solution $\Delta V^{\ddagger} = +2$ [95b].

In Hg^{2+}-assisted aquation of $Rh(NH_3)_5X^{2+}$ [52,96], $\Delta H^{\ddagger}$ values decrease in the sequence: $Cl^- > Br^- > I^-$, as might be expected for a dissociative transition state, whereas for the unassisted aquation $Cl^- < Br^-$, suggestive of an associative pathway [96].

A constant $\Delta H^{\ddagger}$ value for the HgX^+-catalysed aquation of $Cr(H_2O)_4Cl_2^+$ suggests that the energy involved in breaking the Cr–Cl bond is considerably more important than Hg–Cl bond making [39] in reaching the transition state.

The effect of variation of the non-labile group on rate has been studied, to explore the reaction mechanism of catalysed aquation of transition metal complexes [97]. In the Hg(II)-assisted aquation of *cis*-$Co(en)_2(RNH_2)Cl^{2+}$ (R = H, Me, Et, Pr^n and Pr^i [98]; R = n-, iso- and sec-Bu [99]) it has been found that the rate increases and activation enthalpy decreases as the size of R increases. This is consistent with the formation of a binuclear intermediate which aquates dissociatively. Kinetic parameters on assisted aquation of $Co(en)_2AX^{n+}$ type complexes have been compiled by House [100].

Reaction rate of Hg^{2+} with *cis*-$Co(en)_2LX^{2+}$ is faster when L = N-bonded $NH_2CH_2CH_2OH$ than when L = N-bonded $NH_2CH_2CH_2OCOMe$. The OH group of the 2-aminoethanol stabilizes the five coordinated intermediate [101].

F. APPLICATION IN ANALYSIS

Based on these catalysed aquation reactions, various kinetic and equilibrium methods have been developed for trace analysis of catalyst/s either singly or in mixture [102]. The advantages and analytical potential of such reactions are being recognized and utilised [10]. However, as early as 1954, Asperger and Murati [103] developed a method for determining small amounts of mercury in the atmosphere by making use of its catalytic effect on the aquation of potassium ferrocyanide. The reaction progress was monitored by the color developed on addition of nitrosobenzene, which quickly develops an intense violet color with the aquation product. When the nitrosobenzene concentration is $> 1.4 \times 10^{-3}$ M, the rate of color development becomes independent of this (non-limiting) species and the color intensity at a fixed reaction time is a direct measure of the $[Hg^{2+}]$ in the solution. Concentrations of Hg^{2+} as low as 5×10^{-7} M were analyzed. 2,2′-Dipyridyl and *o*-phenanthroline have also been used [104] instead of nitrosobenzene for color development. Further, $Fe(CN)_5(NH_3)^{3-}$ may be used instead of $Fe(CN)_6^{4-}$ [105].

ACKNOWLEDGMENT

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Note added in proof. An important study [106] in the field of metal-ion catalysis has been the structural characterisation of the binuclear complex *cis*-$[Rh(en)_2Cl_2]Cl \cdot HgCl_2$, which is formed from the reaction of *cis*-$[Rh(en)_2Cl_2]^+$ with Hg^{2+}. The crystal structure of this complex clearly shows the role of mercury in forming the μ-chloro bridge.

An X-ray investigation of an aqueous solution of $Hg(NO_3)_2$ has also been done and shows that Hg^{2+} forms hexahydrated species, $Hg(H_2O)_6^{2+}$, in aqueous solution [107].

Formation of binuclear adducts, RLM, through the aqua ligand displacement at the substitutionally labile M by RL, is a fast process. If at the same time the R–L bond is substitutionally inert, then RLM formation is treated as a fast preequilibrium step in the overall process of the aquation of RL as catalysed by M. Kinetics of such preequilibria have now been determined by the stopped-flow technique for the Fe(III)-catalysed aquation of $Co(NH_3)_5(Hox)^{2+}$ [108] and some (salicylato)pentaaminecobalt(III) ions [109], also for the Al(III)-catalysed aquation of $Co(NH_3)_5(HL)^{2+}$, H_2L being salicylic and substituted salicylic acids [110].

Based on the parallelism of k_M and K_{M-mal} values, Basak and Chatterjee [111] have claimed that M^{2+} ions (M = Cu, Ni, Co, Zn, and Mn) catalyse the aquation of $Cr(mal)_3^{3-}$ ion into *cis*-$Cr(mal)_2(H_2O)_2^-$ ion through the formation of a binuclear intermediate. However, they failed to recognise the danger of basing mechanistic conclusions on rates determined within a narrow temperature range [112] and the fact that although according to their data the catalytic efficiency of the M^{2+} ions parallels the sequence of K_{M-mal} ($Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+} > Mn^{2+}$) up to 40°C, beyond this temperature such parallelism breaks down. For example, at 50°C the sequence of k_M is: $Ni^{2+} > Cu^{2+} \approx Mn^{2+} > Co^{2+} > Zn^{2+}$, which at 60°C further changes to $Mn^{2+} > Ni^{2+} > Cu^{2+} > Zn^{2+} > Co^{2+}$. Such sequences have no apparent correlation with K_{M-mal} and there are reasons to believe that the rather insignificant catalysis observed in this system is actually a medium effect.

Kinetic influence of various added simple organic sulfonate anions on the Hg^{2+}-ion assisted aquation of chlorocobalt(III) complexes shows unusual deviations from the expected primary salt effects in the reactions of the complexes containing bipyridyl or phenanthroline [113]. Such specific effects were attributed to the hydrophobic interactions between the complex cations and the sulfonate anions (cf. ref. 114) and demand further precautions while choosing 'innocent' background electrolytes for kinetic investigations.

Although, Hg(II) is a well-known catalyst for aquation reactions, Hg(I) has been much less investigated. It is an effective catalyst for the aquation of $Co(en)(dien)X^{2+}$ (X = Cl, Br) and $Co(en)(dipropylenetriamine)Cl^{2+}$ complexes in binary mixed solvents [115].

Fe^{3+}-ion catalysed aquation of some salicylatopentaamine cobalt(III) ions has been investigated very recently [116].

While reviewing the recent works on the Group IIB elements, Constable [117,118] has referred to various recent investigations on the Hg^{2+}-catalysed aquation reactions.

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