

SOLVENTS AND THEIR ROLE IN DETERMINING INORGANIC MECHANISMS

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Abstract - Two aspects of the mechanisms of the reactions of metal complexes in non-aqueous solutions are discussed in this paper. Firstly, the contribution made by studies in non-aqueous solvents, and in particular dipolar aprotic solvents, to the understanding of the mechanisms of substitution reactions at transition metal centres is considered. Secondly, the mechanisms of electron transfer reactions between transition metal centres are discussed with particular reference to recent work on the role of the solvent.

THE SUBSTITUTION REACTIONS OF TRANSITION METAL COMPLEXES

It is helpful to an understanding of these substitution processes to discuss why it is that dipolar aprotic solvents have had a smaller impact on the study of transition metal substitution kinetics than on similar studies in carbon chemistry. The value of the dipolar aprotic solvent to the understanding of the chemistry of carbon has derived from the importance of the bimolecular processes of substitution. In the bimolecular mechanisms the rate of nucleophilic attack by an anionic nucleophile shows a first order dependence on the concentration of the nucleophile, and the rate in any solvent is directly proportional to the activity of the nucleophile in the solvent. Thus anions, which have activities most characteristically dependent on transfer from protic to dipolar aprotic solvents, have rates of nucleophilic attack which can vary dramatically with the nature of the solvent.

The dependence of such rates on solvent characteristics is now well understood and was most elegantly expressed by my Australian colleague, Prof.A.J.Parker in his important review in 1969 (Ref.1). In simple terms, Parker showed that small anions, hard in the Pearson sense (Ref.2), had greatly increased rates of bimolecular nucleophilic attack in dipolar aprotic solvents compared with protic solvents mainly because of the hydrogen bonding contribution to solvation of these anions in the latter solvents. Provided the changes in the solvation of the attacked substrate and the transition state are not important in comparison with these changes in anion solvation, differences in rate of as much as 10^6 fold can be found for bimolecular nucleophilic attack by say chloride ion in dimethylacetamide (DMA) compared with the rate in methanol, being faster in dimethylacetamide. Large polarizable anionic nucleophiles, soft in the Pearson sense (Ref.2), do not show this tendency, indeed their reactions are often slower in dipolar aprotic solvents because these ions are better solvated in these media.

Unimolecular processes in carbon chemistry can also show marked solvent dependence particularly in those cases where considerable charge separation occurs in the transition state and thus the departing anion can manifest a good deal of its separate ion character. In such cases, if the departing ion is for instance the chloride ion, the reaction is significantly faster in a protic solvent compared with an aprotic solvent because of the magnitude of the hydrogen-bonding contribution to the solvation of the chloride ion in the protic medium (ref.1).

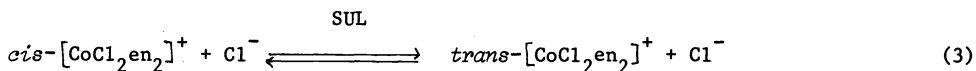
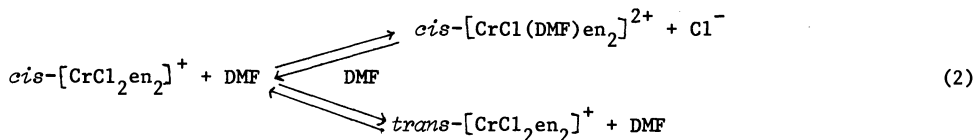
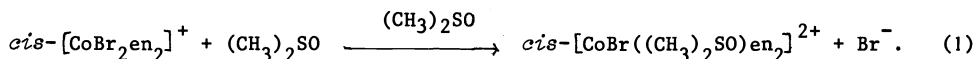
This type of observation has not only led to greater understanding of mechanism and of the description of the transition states but also to advances in organic preparative chemistry where the dependence of rate and yield on the nature of the solvent has been of immeasurable importance to both industry and the preparative chemist.

What is it about the substitution reactions of transition metals that to date has led to a much smaller contribution from the properties of solvent transfer?

The first general feature of substitution kinetics at metal centres which contrasts with organic chemistry is the overwhelming importance of solvolytic reactions. Even in systems where the reaction can be seen as ligand for ligand substitution a solvolytic process is often involved. For example, the isomerization of *cis*-[CrCl₂en₂]⁺ to *trans*-[CrCl₂en₂]⁺ in dimethylformamide (DMF) in the presence of chloride ion is more accurately described as a solvolysis to form *cis*-[CrCl(DMF)en₂]²⁺ followed by chloride ion re-entry (Ref.3).

The rates of these processes are remarkably solvent independent whether they are solvolysis reactions (e.g.(1)), solvolysis controlled substitution processes (e.g.(2)) or substitution

processes in which the role of the solvent cannot be easily determined (e.g.(3)).



(SUL = tetramethylene sulphone)

Whether these reactions for the much studied non-labile systems of cobalt(III) and chromium(III) are associative (S_N2) or dissociative (S_N1) (Ref.4) has been a subject of continuous debate for twenty years and is not my primary concern here. However, the recent work of three groups who are studying these reactions at high pressure is most significant and is likely to resolve these problems in the next few years. I refer here to the outstanding contributions of Professors D.R.Stranks, T.W.Swaddle and H.Kelm and their co-workers (Refs.5-13). Already it is clear that activation volumes will, in general, prove to be easier to interpret in terms of mechanisms than either enthalpies or entropies.

If the reactions above involve bimolecular solvolysis, or if the substitution process is rate determined by bimolecular solvolysis then the rate is a function of the nucleophilicity of the solvent itself. Further, the product or at least the solvent containing intermediate is different in each solvent. Nucleophilicity is a property of a solvent which is uniquely defined for each metal, indeed for each complex and thus conclusions about mechanisms based on generalizations about changes of the rate of a reaction from solvent to solvent are difficult to defend.

If the reaction is dissociative in nature then useful information about the degree of bond breaking in the transition state is potentially available from solvent effects. This is illustrated in a comparison of the solvolysis of $trans-[Co(DH)_2NO_2Br]^-$ in $(CH_3)_2SO$ and water (Ref.14). The solvolytic loss of bromide occurs with first order rate constants of $k_{(CH_3)_2SO} = 6.8 \times 10^{-8} s^{-1}$ and $k_{H_2O} = 1.15 \times 10^{-4} s^{-1}$. For dissociative models of both

reactions we can write:

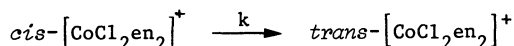
$$\log \left(\frac{k_{(CH_3)_2SO}}{k_{H_2O}} \right) = \log \frac{H_2O}{com^-} \frac{(CH_3)_2SO}{com^-} - \log \frac{H_2O}{TS} \frac{(CH_3)_2SO}{TS}$$

where $com^- \equiv trans-[Co(DH)_2NO_2Br]^-$, $TS \equiv$ the dissociative transition state, $DH =$ dimethylglyoxime and $\frac{H_2O}{com^-} \frac{(CH_3)_2SO}{com^-}$ is a solvent transfer activity coefficient (Ref.1). These results yield a value of $\log \frac{H_2O}{TS} \frac{(CH_3)_2SO}{TS}$ of 4.3, compared with $\log \frac{H_2O}{Br^-} \frac{(CH_3)_2SO}{Br^-}$ of 5.7.

The transition state is clearly not closely related in character to the reactant complex ($\log \frac{H_2O}{com^-} \frac{(CH_3)_2SO}{com^-} = 1.1$) but behaves as one would expect a well developed dissociative transition state consisting of the free Br^- ion and a large neutral complex for which a value of $\log \frac{H_2O}{com^-} \frac{(CH_3)_2SO}{com^-}$ of -1.4 is very reasonable. This particular system is one for which a dissociative mechanism has been established on other grounds and the application of solvent transfer activity coefficients was an interesting exercise but contributed little new knowledge on mechanisms. The characteristic of this reaction, which allowed the successful application of solvent transfer activity coefficients, was the anionic character of the complex which led to a free anion and a residual neutral species on dissociation. In this reaction the change of rate on solvent transfer is dominated by the relatively large change in activity of the dissociated bromide ion because the free energies of the other species are not greatly affected by transfer from $(CH_3)_2SO$ to H_2O .

In the metal system where the greatest contention remains concerning the nature of the rate determining steps, in particular in the chemistry of cobalt(III) and chromium(III) - amine complexes, the complexes are normally cationic. In most cases the transition state and in many cases the products are an anion and a complex residue which is cationic of charge one unit higher than the reactant complex.

In these systems rates are found to be very insensitive to change in the nature of the solvent because to a large extent changes in anion solvation are counteracted by nearly equal changes in the solvation of the cationic residue. This is demonstrated when the rates of reaction



are studied in methanol (M) and tetramethylenesulphone (SUL) (Ref.15). Here $\log M_{CIS}^{SUL} = -4.3$ and $\log(k^M/k^{SUL}) = 2.34$ and thus $\log M_{TS}^{SUL}$ (where TS is the transition state for this isomerization reaction) is -1.9 , that is the transition state is stabilized in SUL compared with methanol. This behaviour is consistent with cationic character, but the stabilization is smaller than such symmetrical cations as $trans-[CoCl_2en_2]^+$ ($\log M_{TS}^{SUL} = -2.9$). If a dissociative transition state is involved, in which the chloride ion ($\log M_{Cl}^{SUL} = 5.8$) has developed appreciable free ion characteristics then the rest of the transition state must be substantially more solvated in SUL ($\log M_{TS}^{SUL}$ very negative). It is clear that the easy interpretation that the slower rate in SUL is a function of the poor solvation of the chloride ion in the transition state is a half true. The transition state energy is relatively insensitive to solvent transfer and the slower rate in SUL is best attributed to the stronger solvation of the reacting cation in SUL.

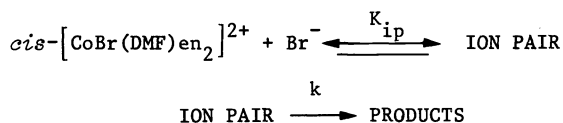
The compensation of changes in the solvation of leaving anion groups by changes in solvation of the cationic residue results in dissociative rates which are relatively solvent independent and thus solvent transfer studies are not an easy answer to mechanistic enquiry. This contrasts with the case of carbon chemistry where the changes in anion solvation often dominate changes in rate. Since transition metal systems are further complicated by the possibility of rate control by bimolecular solvolysis, as emphasized above, rate studies either at one temperature, or a range of temperatures, yielding activation enthalpies and entropies have proven indecisive in the interpretation of mechanisms.

In systems where the primary reaction is solvolysis, it might have been hoped that the transition state could be identified by studying the kinetic features of the reverse anion entry reaction, for example (Ref.16)



The kinetic form of these reactions is not simple because ion association pre-equilibria lead to kinetics of mixed order. In almost all cases the reactions are second order at low bromide ion concentration. On the other hand, concentration independent rates are found at high bromide concentrations where the complex ion is totally ion associated. These ion association pre-equilibria not only affect the kinetic form of these anion entry reactions but also affect the steric course of substitution. These fast pre-associations are a most important feature of the substitution in metal complexes in dipolar aprotic solvents and their study has produced interesting information for the solution chemist. However, these same ion aggregation reactions have often prevented the unambiguous assignment of the mechanisms of the act of substitution.

In the simple case where the complex is involved in only one significant pre-equilibrium the mechanism can be represented by



where k is the rate constant for the interchange of a bromide ion from its position in the first sphere of solvation into the co-ordination sphere. Langford and Gray have described these processes and differentiated between associative (I_a) and dissociative (I_d) acts of interchange (Ref.17). The experimentally determined rate constant (k_{exp}) can be resolved to yield both k and K_{ip} using.

$$\frac{1}{k_{exp}} = \frac{1}{k} + \frac{1}{kK_{ip}}[Br^-]$$

This has been done for a number of systems and the values of K_{ip} compare favourably with those determined by other techniques such as conductivity, and the observation of the charge transfer spectrum of the ion pair (Ref.18). At least it is quite clear that the

kinetically important aggregate is the same species recognised by these other techniques and by pmr measurements made on the nitrogen protons of the ethylenediamine ligands. Although these observations are interesting they tell us very little that is new about ion association phenomena and certainly do little to help resolve the nature of the substitution act. However, I believe that studies of this type will greatly contribute to our understanding of inter-ionic reactions in solution and in particular, to the importance of structural relationships between the co-ordination sphere and the first sphere of solvation. For simple labile metal cations these regions are normally referred to as the first and second spheres of solvation.

The actual site occupied by the bromide ion in the aggregate, although unimportant in the simple observation of rate is of primary importance in determining the steric course of the substitution process. In the reaction described above the steric course of substitution is found to be bromide ion concentration dependent even when the rate has reached its asymptotic limit.

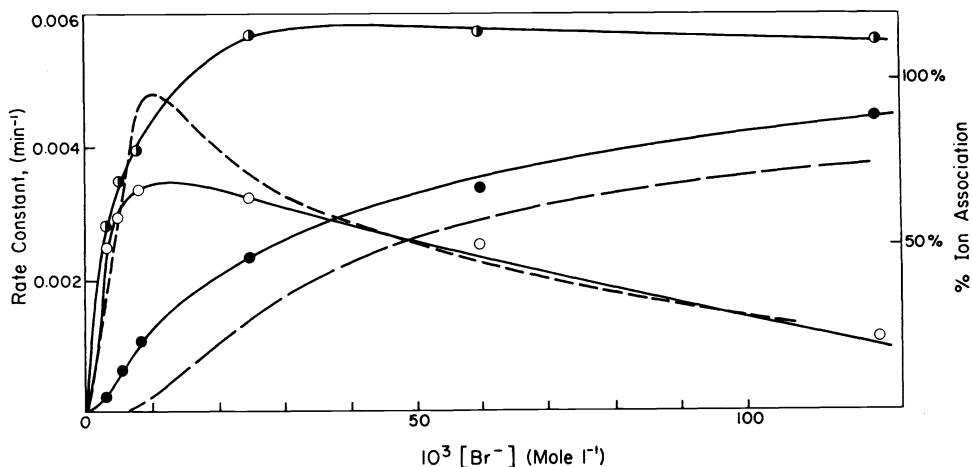
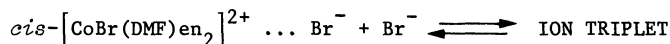


Fig.1. Dependence k_c , k_t and (k_c+k_t) on bromide ion concentration for the reaction: $cis-[CoBr(DMF)en_2]^{2+} + Br^- \rightarrow cis-$ and $trans-[CoBr_2en_2]^+ + DMF$ at $45^\circ C$, and the percentage of the reactant complex (total concentration $\sim 8 \times 10^{-3} \text{ mol dm}^{-3}$) initially as $cis-[CoBr(DMF)en_2]^{2+} \cdot Br^-$ and $cis-[CoBr(DMF)en_2]^{2+} \cdot 2Br^-$. \circ , k_c+k_t (the rate constant for loss of $cis-[CoBr(DMF)en_2]^{2+}$); \bullet , k_t (the rate constant for formation of the product); \bullet , k_c (for the cis -product); -----, % ion pair; — — —, % ion triplet (data from Ref.16).

Figure 1 shows the dependence of the rate and steric course of the substitution on bromide ion concentration. Also in this figure is the best estimate of the concentration of the ion-pair and the ion-triplet formed in the reaction



The results clearly confirm that once the one bromide ion is present in the first solvation sphere of the complex a maximum rate of substitution is established. This rate approximates to the rate at which the complex exchanges solvent in the absence of bromide ion, and confirms that the presence of only one bromide ion in the first sphere of solvation is sufficient to guarantee that bromide ion entry follows a dissociative act in breaking a Co - DMF bond.

In contrast however, the presence of the second bromide in the solvation sphere, that is the existence of the ion-triplet species, is registered by the increase in the ratio of $cis-[CoBr_2en_2]^+$ to $trans-[CoBr_2en_2]^+$ in the product. It is an inescapable conclusion that interchange in the ion-pair favours the cis -product while the ion-triplet favours the complex. It must be emphasized that this is a kinetic phenomenon and is additional to the well established increased thermodynamic stability of $cis-[CoX_2en_2]^+$ and $cis-[CrX_2en_2]^+$ ions compared to their $trans$ -isomers at high X^- concentration which owes its origin to the substantially higher ion association constants of dipolar cis -isomers compared with the analogous $trans$ -ions (Ref.19&20) (e.g. for Cr when $X = Cl^-$, $K_{ip}(cis) = 291$ and $K_{ip}(trans) = 25$ in DMSO).

These results suggest that in the first solvation sphere of octahedral complexes there are specific sites which for an anion are of significantly lower free energy and that these sites

are filled in stepwise equilibria. Figure 2 is a diagrammatic representation of the ion-triplet in the present system. The ${}^1\text{Br}^-$ ion is in the more stable site, as in the ion-pair, which in interchange favours the *trans*-product, whereas the ${}^2\text{Br}^-$ is in the site occupied in the ion-triplet only. This species favours *cis*-formation.

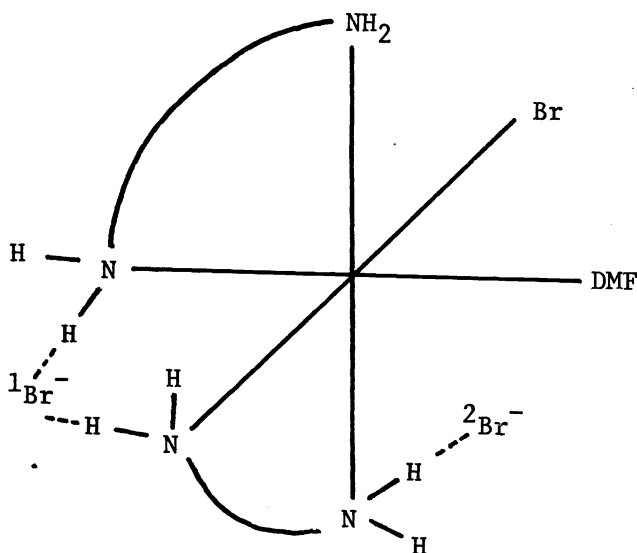


Fig. 2. Diagrammatic representation of the ion triplet $\text{cis-}[\text{CoBr}(\text{DMF})\text{en}_2]^{2+} \cdot 2\text{Br}^-$ showing ${}^1\text{Br}^-$ the site occupied in the ion pair and ${}^2\text{Br}^-$ the second site, occupied only in the ion triplet.

The nature of these specific sites, which are a simple extension of the structure of the coordination sphere into the first solvation sphere are a reflection of the charge, the dipole moment and hydrogen-bonding interactions. The role of these hydrogen-bonding forces are most easily seen in the ion aggregation in dipolar aprotic solvents, where the anions are relatively poorly solvated (Ref.1), and the anions compete for hydrogen-bonding sites on the complex with the solvent molecule. Such specific interactions lead to ion association constants which are highly solvent dependent even with groups of solvent which are of similar dielectric constant, ϵ (Table 1).

TABLE 1: Ion association constants (K_{ip} , 25°C)

Solvent	ϵ	K_{ip}	
		$\text{cis-}[\text{CoCl}_2\text{en}_2]^+ \text{Cl}^-$	$\text{trans-}[\text{CoCl}_2\text{en}_2]^+ \text{Cl}^-$
CH_3OH	32.7	280	< 10
DMF	36.7	8560	180
$(\text{CH}_3)_2\text{SO}$	46.7	397	100
DMA	37.8	20000	

Data from references 19 and 21.

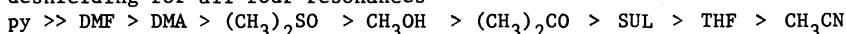
These results re-emphasize the effect of the dipole moment of the *cis*-species already discussed but also show that of these dipolar aprotic solvents, $(\text{CH}_3)_2\text{SO}$ with strong H-bond acceptor properties (Ref.1&22) competes more favourably with the chloride ion for the favoured site than do the other solvents DMF and DMA. The low result in CH_3OH is complicated further by the H-bonding interaction between the chloride ion and the solvent.

The nature of the site in the above system has been defined by pmr studies (Ref.19) which clearly show that two nitrogen protons, those *trans* to the *cis* chloro-ligands and along the octahedral edge *trans* to the edge occupied by these chloro-ligands, are more deshielded in the ion pair and as a result their absorption is shifted to lower fields. It is thus clear that at least for these *cis*-complexes hydrogen bonding between the ligands in the co-ordination sphere and ions in the solvation sphere is an extension of the metal centred structure and produces marked kinetic and thermodynamic consequences.

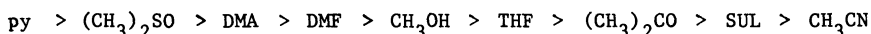
The results described above are not new but serve to emphasize structural relationships in solution which are often forgotten. Too little attention has been paid to structure outside the co-ordination sphere, not only in non-aqueous solvents but also in water. Much of the early work on inorganic reaction mechanisms concentrated on the steric course of aquation and base hydrolysis reactions. Almost all attempts to rationalize these results were dependent on discussions of the relative stabilities of transition states in which the reactant, in a structural sense, was seen to be only the metal and its co-ordination sphere. It must be remembered that in all these systems the nucleophile is the solvent water and that the solvation sphere water is as much a part of the reacting structure as the co-ordination sphere. Certainly the extended structure either through the nitrogen protons on ethylenediamine ligands, or through hydrogen-bonding of solvent to ligands such as carbonate, chloride or nitrite must influence steric course. The weakness of ion association in these systems in water, is not only a function of the anion solvation but is also due to occupation of structural sites in the solvation sphere by water molecules in an acceptor role.

The subtleties of the structural relationship between the co-ordination sphere and the first solvation sphere and the importance of hydrogen bonding are most clearly demonstrated by a most elegant recent investigation by Hawkins et al. (Ref.23) in which they studied the proton nmr and solvent induced circular dichroism of *trans*- $[\text{CoX}_2(\text{R-pn})_2]^+$ ions, where X = Cl and Br and R-pn = R-propane-1,2-diamine, in a wide range of solvents. In these *trans*-complexes extended structure is not enhanced by the existence of a dipole moment as in the above *cis*-complexes, but is a function only of charge and hydrogen bonding which manifest in complex-solvent interactions as well as ion association.

An analysis of the 270 MHz pmr spectra in the NH-region (Figure 3) leads to a relative order of deshielding for all four resonances



which differs only slightly from the order of donor power established by both Mayer and Gutmann (Ref.24) and Popov (Ref.25-27).



Hawkins believes that the lower position held by $(\text{CH}_3)_2\text{SO}$ in his series is due to the small size of the anisotropic shielding effect of S = 0.

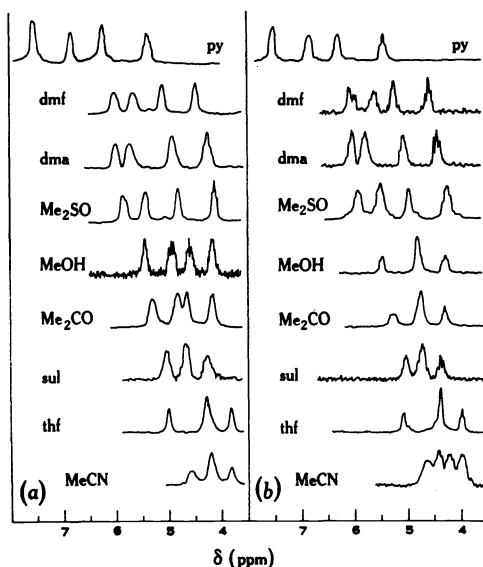
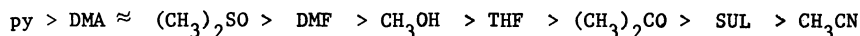


Fig. 3. 270-MHz pmr spectra for NH region of *trans*- $[\text{CoX}_2(\text{R-pn})_2]\text{BPh}_4$; a, X=Cl; b, X=Br. Taken from Ref.23.

In addition to this general effect of solvent deshielding it was found that the most strongly deshielding solvents discriminated more significantly between equatorial (eq) and axial (ax) nitrogen protons, expressed as $\Delta\delta_{\text{NH}} = \delta_{\text{NH}_{\text{eq}}} - \delta_{\text{NH}_{\text{ax}}}$. In respect to this discrimination the order is



The differences which occur between the order for general deshielding and the discrimination order are accounted for in terms of specific steric effects.

The above was studied using tetraphenylborate salts which show no evidence for ion association. However both chloride and bromide salts showed strong interactions between these ions and the nitrogen protons indicating strong ion association. It was found that there was insignificant discrimination between equatorial and axial protons in this respect. This contrasts with the behaviour of the *cis*-complexes discussed earlier where the dipole moment of the complex leads to significant discrimination between protons in the ion pair.

For aprotic solvents the chloride ion had a significantly larger deshielding effect than the bromide while the reverse was true in protic solvents. This is consistent with previous studies of ion association (Refs.19,20,28) for complex ions of this type and reflects a greater hydrogen-bonding component in the solvation of chloride ion in protic solvents, and better solvation of the more polarizable bromide ion in dipolar aprotic solvents.

The magnitude of the solvent induced circular dichroism is shown in Figure 4 in which the high energy ${}^1A_{1g} \rightarrow {}^1A_{2g}$ Cotton effect shows a progressive change from a positive rotational strength in pyridine to a negative rotational strength in sulpholane, in the order:

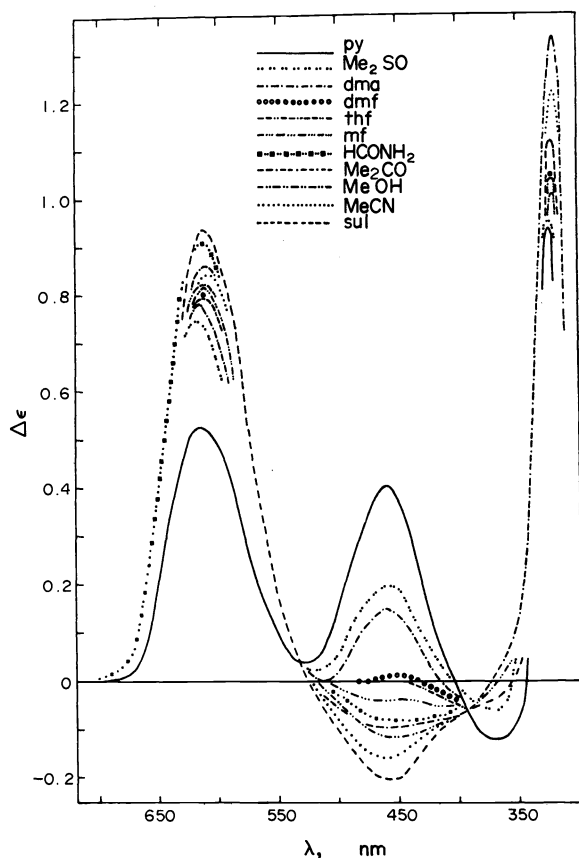
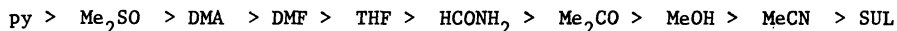


Fig. 4. C.D. spectra of *trans*-[CoCl₂(R-pn)₂]BPh₄ in various solvents. Taken from Ref.23.

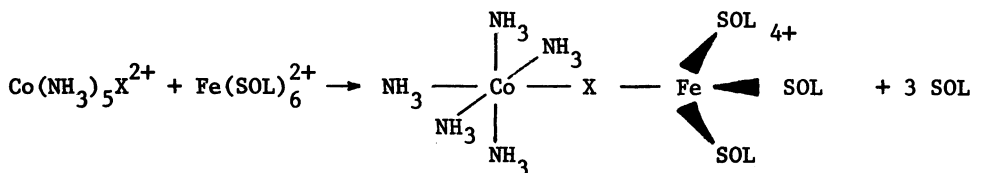
This effect is due to the development of asymmetric nitrogen donor groups through the preferential solvation of the $N-H_{eq}$ compared to the $N-H_{ax}$. The preferential solvation of the equatorial nitrogen proton with S configuration can be related to asymmetry in the related complexes with the ligand (S)-N-methyl-(R)-propane-1,2-diamine where the methyl group adopts the preferred equatorial orientation.

All this work although secondary to the substitution studies that introduced it gives a new perspective to our understanding of the structural relationship between the co-ordination sphere and the solvation sphere of metal complexes and the important role of the hydrogen bond. I believe strongly that information which will be gained from further studies on these systems will lead to a greater understanding of the extended ion centred order in the solvation of simple metal cations where the only difference in principle is the lability of substitution in the first sphere.

ELECTRON TRANSFER REACTIONS OF METAL COMPLEXES

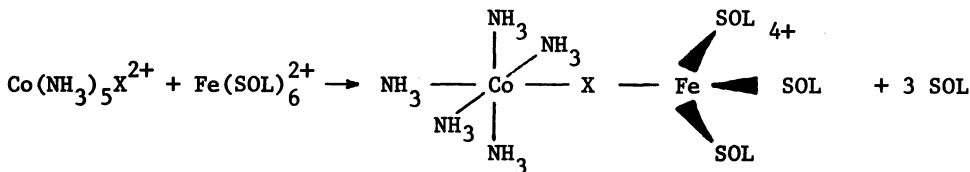
The two basic mechanisms for electron transfer in metal complex systems have been well established for some years (Refs.29-31). The first, the outer sphere mechanism, requires a close approach of the two complex ions followed by electron transfer between orbitals of the complex, the co-ordination spheres remaining intact until electron transfer occurs. The dependence of the rate of electron transfer on the nature of the solvent was treated initially by Marcus (Ref.32). The solvent effects on these reactions can be accounted for in terms of coulombic energy and entropy changes derived from outer sphere re-organization.

The more interesting systems from the point of view of solvent effects are those which react by the formation of a bridged intermediate in which one ligand is shared by each of the metal ions. Electron transfer occurs through this bridging ligand. Two possible intermediates of this type are shown in Figures 5 and 6 for the reduction of $Co(NH_3)_5X^{2+}$ by iron(II). Mechanisms involving the formation of bridged intermediates as precursors to electron transfer are known as "inner sphere".



(SOL \equiv DMF or $(CH_3)_2SO$; X \equiv Br, Cl, N_3 and NCS.)

Fig. 5. Transition state for inner-sphere electron transfer (both metals octahedral)



(SOL \equiv DMF or $(CH_3)_2SO$; X \equiv Br, Cl, N_3 and NCS.)

Fig. 6. Transition state for inner sphere electron transfer (Co, octahedral; Fe, tetrahedral).

The majority of the work on these reactions has been confined to aqueous solution and the small amount of the work in non-aqueous solvents produced little interest because neither the rates of reaction nor the kinetic forms were sensitive to solvent change. However, many important features were missed because of concentration on alcohols as alternative solvents (Refs.29-31, 33-35) and the preoccupation with rates rather than activation enthalpies and entropies. More recent work in dipolar aprotic solvents shows that many of the features which had been postulated from studies in water are confirmed beyond question for non-aqueous systems. In particular, the greater stability of the bridged intermediates allow confirmation of their existence by observation of their spectra (Ref.36). These studies have led to stereochemical information about these precursor complexes by careful studies of ΔH^* , ΔS^* and ΔV^* (Refs.13,36-39).

Table 2 summarizes the available data for the reduction of a series of $\text{CoX}(\text{NH}_3)_5^{2+}$ species by iron(II) in three solvents. This work has since been extended to $\text{X} = \text{N}_3$ and NCS (Ref.40) which behave similarly to $\text{X} = \text{Br}$ and Cl , contrasting markedly with the fluoro-system.

TABLE 2. Comparison of rate parameters in $(\text{CH}_3)_2\text{SO}$, DMF and H_2O with $\text{Fe}(\text{II})$ as reductant

Solvent		$\text{CoBr}(\text{NH}_3)_5^{2+}$	$\text{CoCl}(\text{NH}_3)_5^{2+}$	$\text{CoF}(\text{NH}_3)_5^{2+}$
$\text{H}_2\text{O}^{\text{a,b}}$	k_2 (25°C) $\text{mol}^{-1} \ell \text{s}^{-1}$	0.92×10^{-3}	1.60×10^{-3}	7.6×10^{-3}
	ΔH^* kJ mol^{-1}	65.2	60.6	56.0
	ΔS^* $\text{JK}^{-1} \text{mol}^{-1}$	-84	-96	-96
	ΔV^* (35°C) $\text{cm}^3 \text{mol}^{-1}$	6.4	8.7	10.7
$(\text{CH}_3)_2\text{SO}^{\text{c,d}}$	k_2 (25°C) $\text{mol}^{-1} \ell \text{s}^{-1}$	2.51×10^{-3}	9.7×10^{-3}	4.73
	ΔH^* kJ mol^{-1}	91	90	37.0
	ΔS^* $\text{JK}^{-1} \text{mol}^{-1}$	8	16	-108
	ΔV^* (35°C) $\text{cm}^3 \text{mol}^{-1}$	0	3.8	10.3
DMF ^e	k_2 (25°C) $\text{mol}^{-1} \ell \text{s}^{-1}$	4.2×10^{-3}	18.7×10^{-3}	33.9
	ΔH^* kJ mol^{-1}	97	90	39
	ΔS^* $\text{JK}^{-1} \text{mol}^{-1}$	8	-3	-118

a. Ref.41, b. Re-calculated by R.van Eldik, D.A.Palmer and H.Kelm (Ref.13) from data in Ref.42

c. Ref.13 d. Ref.38 e. Ref.36.

f. Calculate as kK from separately determined values of k and K .

The X = F system transfers from water to $(\text{CH}_3)_2\text{SO}$ and DMF with an increase in rate, largely from a decrease in activation enthalpy but with little change in the negative ($\sim -100 \text{ JK}^{-1}$) entropy of activation. In contrast the X = Br and Cl systems show very little solvent induced change of rate at 25°C but extraordinarily large changes in ΔH^* and ΔS^* . Compared with water ΔH^* is increased by $\sim 30 \text{ kJ}$ and the ΔS^* becomes more positive by $\sim 100 \text{ JK}^{-1}$. Our interpretation of these results is to account for these massive changes in activation parameters in terms of a change in the stereochemistry of iron atom in the precursor complex. Figures 5 and 6 illustrate the two models showing that in those cases with more positive ΔS^* the iron(II) atom is tetrahedral in the precursor complex. In the tetrahedral case two extra solvent molecules are released in the bridge formation. Work on the solvation of simple ions in $(\text{CH}_3)_2\text{SO}$ (Refs. 43 & 44) suggests that the entropy change associated with the release of a molecule of $(\text{CH}_3)_2\text{SO}$ from the coordination sphere to the bulk solvent is of the order $48 \text{ JK}^{-1}\text{mol}^{-1}$. On this basis the anticipated entropy of activation for the tetrahedral case would be more positive by $\sim 100 \text{ JK}^{-1}\text{mol}^{-1}$. The activation enthalpy must be greater in such cases because of the need to break two extra metal solvent bonds although this requirement would be compensated by the reduction of steric crowding around the iron atom and by solvation of the lost solvent molecules.

More recently we have studied the reduction of $\text{cis}[\text{CoCl}_2\text{en}_2]^+$ in $(\text{CH}_3)_2\text{SO}$ (Ref. 45) and these results are compared with the data for the reduction of $\text{CoF}(\text{NH}_3)_5^{2+}$ and $\text{CoCl}(\text{NH}_3)_5^{2+}$ in $(\text{CH}_3)_2\text{SO}$ in Table 3.

TABLE 3. Comparison of the rate parameters in $(\text{CH}_3)_2\text{SO}$ with Fe(II) as reductant

	ΔH^* kJ mol^{-1}	ΔS^* $\text{JK}^{-1} \text{ mol}^{-1}$	N^a
$\text{CoF}(\text{NH}_3)_5^{2+}$	37	-108	1
$\text{CoCl}(\text{NH}_3)_5^{2+}$	90	16	3
$\text{cis}[\text{CoCl}_2\text{en}_2]^+$	70	-40	2^b

- a. N = the number of $(\text{CH}_3)_2\text{SO}$ molecules released in the formation of the precursor complex.
- b. N based on a precursor complex involving double Cl bridge and octahedral iron(II) coordination (Figure 7).

The case of the reduction of $\text{cis}[\text{CoCl}_2\text{en}_2]^+$ has some importance because of interest in whether a double chloro-bridge exists, a point that remained uncertain following studies of this and analogous reactions in water (Ref. 46). Further, a question must be answered concerning the stereochemistry of the iron(II) in the precursor complex. If the precursor complex was bridged by only one chloro-ligand then in $(\text{CH}_3)_2\text{SO}$ tetrahedral co-ordination about the iron atom would be expected, and thus three $(\text{CH}_3)_2\text{SO}$ molecules ($N = 3$ in Table 3) would be released as in the case of the $\text{CoCl}(\text{NH}_3)_5^{2+}$ reduction. However, if the *cis*-disposition of the two chloro-ligands on the cobalt led to a double bridge, the frozen octahedral geometry on the cobalt(III) atom is likely to encourage the retention of octahedral geometry at the iron(II) atom. Such a reaction leads to the release of two solvent molecules ($N = 2$ in Table 3) in the formation of the precursor complex (Figure 7). If the double chloro-bridge was to exist coupled with tetrahedral co-ordination of the iron(II) atom a value of $N = 4$ is expected.

The entropies of activation in Table 3 provide extraordinarily powerful evidence for double bridged-octahedral structure in Figure 7 in that a change in N from 1 to 2 yields a more positive ΔS^* by $60 \text{ JK}^{-1}\text{mol}^{-1}$ and a change from 2 to 3 produces a change of $56 \text{ JK}^{-1}\text{mol}^{-1}$.

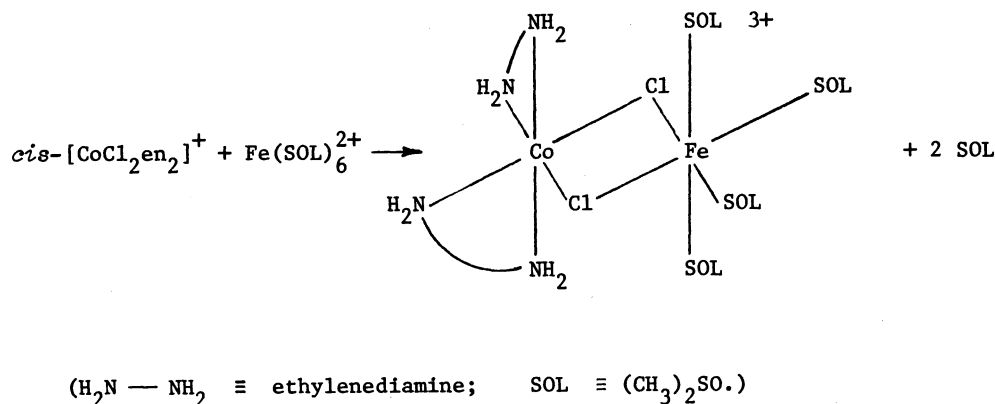


Fig. 7. Transition state for inner sphere electron transfer with two bridging ligands (both metals octahedral).

In all this discussion the recent work of van Eldik, Palmer and Kelm (Ref.13), and Sullivan and Stranks (Ref.39) on the volume of activation (Table 2) has been ignored. It is clear that there is no extraordinary change in ΔV^* in the reactions of either $\text{CoCl}(\text{NH}_3)_5^{2+}$ or $\text{CoBr}(\text{NH}_3)_5^{2+}$ consistent with the changes in entropy. Initial work on activation volume studies has supported quite justifiable claims that the interpretation of activation volumes is inherently simpler than the interpretation of the corresponding entropy data (Refs.5-13). There seems little doubt that for many systems this will be true. However in the present cases (Table 2 and 3) and related studies (Refs.40&45) the magnitude of the activation entropy changes and the internal consistency found over an increasing range of systems makes it difficult to deny our interpretation based on stereochemical changes. Indeed it seems impossible to support the claim of van Eldik, Palmer and Kelm (Ref.13) that:

"To sum up, we conclude that the observed changes in k , ΔH^* , ΔS^* and ΔV^* for the reduction of $\text{CoX}(\text{NH}_3)_5^{2+}$ ($X = \text{F}, \text{Cl}, \text{Br}$) by $\text{Fe}(\text{II})$ in $(\text{CH}_3)_2\text{SO}$ may be explained in terms of the same mechanism as found in water, namely an inner sphere, electron transfer rate determined process. Variations in these parameters are then due to changes in solvation and the introduction of steric crowding rather than changes in the co-ordination number of iron(II)."

We believe that this interpretation places far too much importance on the constancy of ΔV^* and pays little attention to elegant interpretation of very large changes in ΔS^* . Since there seems to be no plausible model which could account for these entropy results we question whether there are not limitations in their simple approach to the interpretation of ΔV^* in these systems.

There is no doubt that a significantly more positive ΔV^* would be expected if there was a change in the stereochemistry of the iron atom resulting in the release of the extra solvent molecules. The question that must be answered is, "If there is a change in stereochemistry for the $X = \text{Cl}$ and Br systems, what other significant change in volume occurs which compensates for the release of solvent molecules?" The answer must lie in the difference in volume of the separate octahedral iron(II) complex and the contribution made to the precursor complex by a tetrahedral iron(II) centre.

It is well established that labile first row transition metal ions such as iron(II) and cobalt(II) and ions such as zinc(II), which are octahedral with solvent co-ordination, take on tetrahedral geometry with more polarizable ligands such as I^- , Br^- and Cl^- (Ref.38). It is also established that $(\text{CH}_3)_2\text{SO}$ can co-ordinate to metals through both the oxygen and sulfur donor groups. We suggest that the change from octahedral iron(II) to tetrahedral iron(II) could easily be accompanied by a change in the mode of co-ordination from oxygen to the more polarizable sulfur donor with an accompanying compaction of the size of the co-ordination sphere of the iron(II) centre. Under these circumstances no increase in ΔV^* is expected for the $X = \text{Cl}$ and Br cases to correspond with the large increases in ΔS^* .

Finally, in summary, I hope to have achieved the following in the presentation of this lecture:

(1) To have emphasized the need to recognise a metal complex and its reactions as not only a problem of the metal ion and its co-ordination sphere, but as a problem involving a structural unit which contains the second sphere. A recognition of this is not only vital to an understanding of substitution reactions but will also lead to a more enlightened approach to model making in areas such as the solvation of simple metal ions.

(2) To have presented a case for the use of data for ΔH^* , ΔS^* and ΔV^* in a way which will

lead to more detailed structural knowledge of reaction intermediates. I must emphasize, even if in the above case I prove to be incorrect, that it is naive to suggest values of ΔV^* will always be easier to interpret and more productive of information than values of ΔS^* .

Finally, I wish to thank Dr. Peter Schuster and Dr. Viktor Gutmann for the compliment they paid me in asking me to present this lecture and in addition to acknowledge the financial assistance given to me by the Conference Organizers and the University of Western Australia, and the Australian Research Grants Committee which continues to support this research.

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