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EMPIRICAL APPROACH TO LIGAND EFFECTS ON THE KINETICS OF SUBSTITUTION AND REDOX REACTIONS*

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CONTENTS

A. INTRODUCTION

During the past few years a number of significant results have been reported on the kinetics of substitution reactions at metal ion complexes. The considerable number of data available have encouraged empirical approaches to discover the factors influencing the rates of these reactions. General conclusions have been drawn mainly from studies on the effect of ligands already bound and remaining at the metal ion. We shall term these ligands *non-leaving ligands.* The ligand is frequently described as the electron donor and the metal ion as the electron acceptor. These terms are also used in a different sense for

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* Dedicated to Hermann Hartmann on the occasion of his 60th birthday.

electron transfer reactions, e.g. the reducing agent is considered as the electron donor (ED) and the oxidizing agent as the electron acceptor (EA). For the sake of clarity the terms electron pair donor (EPD) for a Lewis base and electron pair acceptor (EPA) for a Lewis acid respectively[1] will be used throughout the text.

Funahashi and Tanaka[2] correlated rates of substitution with the E_A parameter of Edwards, which as a redox factor has been quoted as being a measure of the extent of electron donation of ligands[3]. Wells[4] questioned, however, whether the oxidative dimerization process is a valid model for acceptor–donor interactions in substitution reactions. Attempts to correlate the rates of dissociation of water molecules from nickel(II) complexes with the Dq values of the non-leaving ligands were unsuccessful[2,5]. Caldin[6] related water-exchange rates to the electron density at the perimeter of the reacting metal ions, which according to Eigen and Wilkins[7] is altered by the local charge density at the ligands present in the coordination sphere. The stronger the electron pair donor (i.e. the ligand) in the coordination sphere of a metal ion, the faster is the water exchange rate[8]. Hunt[9] and Gutmann[1] independently realized that the ligands of a complex have electron pair-donating or withdrawing effects which alter the effective metal ion charge. Good electron pair donors enhance the rate of water replacement[10]. Pearson and Basolo[11] assumed that the π-bonding ability of the remaining ligands enhances the rate of dissociation of a complex.

Langford and Sastri[12] suggested that a good σ-donor ligand would be a good labilizing group. A different view has been put forward by Bennetto and Caldin[13], who have related kinetic data for ligand exchange with structural properties of the solvents. They assumed the solvent fluidity to be an important variable, whereas Shu and Rorabacher[15] suggested steric factors to be responsible for Bennetto and Caldin's results.

Recent studies in non-aqueous solvents[14] confirmed that the strengths of the metal ligand bonds determine the observed variation of rate constants[6-10].

B. THE STRENGTH OF METAL ION–LIGAND BONDS

(i) The concept of donicity

The characterization of metal ion–ligand bond strength by electrochemical quantities has been reported recently[16], and in view of the lack of thermodynamic data the following empirical approach has been presented.

The ability of a ligand to function as an electron pair donor (EPD) towards antimony(V) chloride is represented by the $-\Delta H$ value of the reaction of the EPD with $SbCl_5$ in dilute solution in 1,2-dichloroethane[17,18].

$$\mathrm{EPD} + \mathrm{SbCl_5} = \mathrm{EPD}\cdot\mathrm{SbCl_5};\quad -\Delta H_{\mathrm{EPD}\cdot\mathrm{SbCl_5}} \equiv \mathrm{DN}$$

The negative ΔH value of this reaction was termed "donor number" or *donicity*[17]. Donicities (DN) and dielectric constants (ϵ) for various EPD solvents are listed in Table 1.

TABLE 1

Donicities DN and dielectric constants ϵ of various EPD solvents

Solvent	DN	ϵ
1,2-Dichloroethane (DE)		10.1
Sulphuryl chloride	0.1	10.0
Benzene	0.1	2.3
Thionyl chloride	0.4	9.2
Acetyl chloride	0.7	15.8
Tetrachloroethylene carbonate	0.8	9.2
Benzoyl fluoride	2.0	22.7
Benzoyl chloride	2.3	23.0
Nitromethane (NM)	2.7	35.9
Dichloroethylene carbonate	3.2	31.6
Nitrobenzene (NB)	4.4	34.8
Acetic anhydride	10.5	20.7
Phosphorus oxychloride	11.7	14.0
Benzonitrile (BN)	11.9	25.2
Selenium oxychloride	12.2	46.0
Acetonitrile (AN)	14.1	38.0
Sulpholane	14.8	42.0
Propanediol 1,2-carbonate (PDC)	15.1	69.0
Benzyl cyanide	15.1	18.4
Ethylene sulphite	15.3	41.0
Isobutyronitrile	15.4	20.4
Propionitrile	16.1	27.7
Ethylene carbonate	16.4	89.1
Phenylphosphonic difluoride	16.4	27.9
Methyl acetate	16.5	6.7
n-Butyronitrile	16.6	20.3
Acetone (AC)	17.0	20.7
Ethyl acetate	17.1	6.0
Water	18.0[a]	81.0
Phenylphosphonic dichloride	18.5	26.0
Methanol	19.0	32.6
Diethyl ether	19.2	4.3
Tetrahydrofuran	20.0	7.6
Diphenylphosphonic chloride	22.4	
Trimethyl phosphate (TMP)	23.0	20.6
Tributyl phosphate (TBP)	23.7	6.8
Dimethylformamide (DMF)	26.6	36.1
N-Methyl-ϵ-caprolactam	27.1	
N-Methyl-2-pyrrolidone	27.3	
N,N-Dimethylacetamide (DMA)	27.8	38.9
Dimethyl sulphoxide (DMSO)	29.8	45.0
N,N-Diethylformamide	30.9	
N,N-Diethylacetamide	32.2	
Pyridine (py)	33.1	12.3
Hexamethylphosphoricamide (HMPA)	38.8	30.0

[a] For water as a solvent DN ≈ 33

TABLE 2

DN values extrapolated from NMR data and pK_a values[25]

EPD	pK_a	DN
Pyridine	5.2	33.1
Hydrazine	8.0	44.0
Ethylenediamine	9.9	55.0
Ethylamine	10.6	55.5
Isopropylamine	10.6	57.5
tert-Butylamine	10.8	57.5
Ammonia	9.25	59.0

Systematic studies[1] of interactions between EPD molecules and various electron pair acceptors (EPA) have revealed that the relative order of EPD strengths as observed towards $SbCl_5$ is essentially the same as that observed towards a considerable number of other EPA molecules, such as iodine, phenol, $SbCl_3$, $Sn(CH_3)_3Cl$ or $VO(acac)_2$. However, if the relative donor strengths are determined for "hard" and "soft"[19] EPD molecules towards both a hard EPA and a soft EPA, reversals of donor strengths are possible. For example, an EPD sulphide (soft) will coordinate more strongly towards iodine (soft) than the corresponding oxide, which is hard[20]. The reverse is true for the hard EPA phenol[21]. Furthermore, the application of donicity is not possible when steric factors come into play, as has been observed in the interactions of HMPA and $(CH_3)_3NO$ towards various metal ions[22,23].

For homologous amines a relationship seems to exist between the pK_a values of their corresponding acids and the donicities.

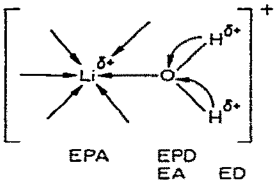
Approximate values for the donicities of halide ions have been derived from thermodynamic data for the reactions

$$[VO(acac)_2AN] + X^- \rightleftharpoons [VO(acac)_2X]^- + AN$$

namely about 14, 20, 26 and 40 for iodide, bromide, chloride and fluoride ions respectively[1,24]. Due to different degrees of solvation in different solvents the actual value in a given solvent may, however, be considerably different from the above values[1,24].

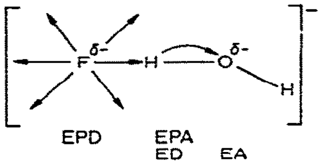
(ii) The functional approach

The functional approach to chemical interactions provides a simplified pattern for the dynamics of electronic changes involved in the course of chemical interactions[1]. It accounts for the fact that coordination leads to changes both in redox properties and in bond properties of already existing bonds. For example, the reducing action of lithium (electron donor = ED) towards water induces the exercise of the Lewis acid function (electron pair acceptor = EPA) at the lithium ion which is hydrated by water molecules functioning as Lewis bases (electron pair donor = EPD). The coordination of water molecules at the metal ion induces the polarization of the O—H bonds of the former. The partial charge transfer of positive charge from the lithium ion to the hydrogen atoms of coordinated water molecules leads to a decrease in net charge at the lithium ion and to an increase in net positive charge at each of the hydrogen atoms.



According to the functional description, a uniform pattern for charge transfer phenomena is provided by considering not only inductive and mesomeric effects within the molecules, but also charge transfer *between* the molecules. In the formalism of the unified treatment all electron density shifts along existing bonds are denoted as ED—EA interactions, although the actual changes in charge density may be very small.

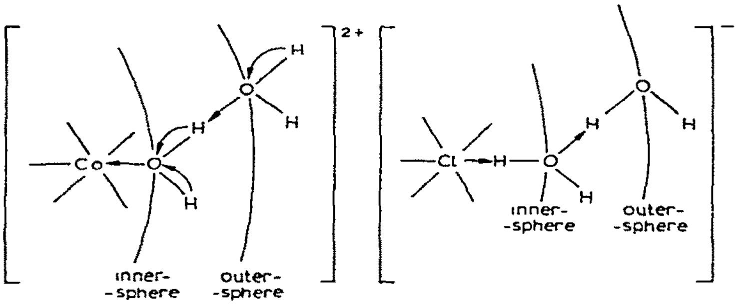
Likewise the oxidizing properties (electron acceptor = EA) of fluorine evoke the exercise of EPD functions at the fluoride ion produced, which is hydrated by the formation of hydrogen bonds accordingly. Since the water molecules act as EPA towards the fluoride ion, the redistribution of the electrons leads to a decrease in net negative charge at the fluoride ion and to an increase in net negative charge at the oxygen atoms of the coordinated water molecules[29a].



(iii) Definition of outer-sphere effects

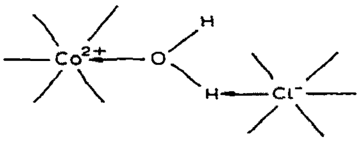
The concept of outer-sphere complex formation introduced by Werner[26] in 1913 refers to the interaction of coordinatively saturated complexes (usually complex ions) with further ligands[27]. The terms "coordination in the second sphere" or "super-complex formation" are sometimes used as well. Unfortunately use is also made of the term "ion-pair", which was introduced by Bjerrum[28] in order to account for conductivity phenomena in more concentrated aqueous electrolyte solutions. The latter term cannot be used for coordination of neutral ligands in the second coordination sphere, but its application to ionic ligands in outer-sphere complexes has led to considerable confusion.

Let us consider an aqueous solution containing both cobalt(II) and chloride ions. Both ions are hydrated with hydration structures not completely known, and indeed outer-sphere effects are involved in coordination of water molecules to water molecules coordinated in the inner hydration sphere[30].



The term *ion-pair* has been designed for the loose contact of such ions in solution and it is understood that the charged coordination centres may be separated by several spheres of water molecules. If both ions have tight solvation shells, interactions between these ions in the sense of outer-sphere coordination is not taking place and consequently the term "outer-sphere coordination" is misleading. Both for the formation and separation of such ion pairs the best approach available remains the elementary electrostatic theory. Cations and anions are coordinated by the solvent molecules in different ways. For example, hydrated cations are coordinated through the oxygen atoms of the water molecules, which function as EPD, while hydrated anions are coordinated through the hydrogen atoms of the water molecules making use of the EPA properties of the solvent molecules. The interactions between the tight solvation spheres of cation and anion are weak and separation is readily accomplished by increasing the dielectric constant of the medium.

On the other hand in this example the chloride ion may penetrate the outer hydration sphere of the cobalt ion to be coordinated directly into the second coordination sphere to form an outer-sphere complex. In this process the ion pair has to undergo considerable changes: even in the first hydration sphere the chloride ion has to lose at least one water molecule while the cobalt ion has to provide one coordination site in the second coordination sphere. Separation of the outer-sphere ligand is not accomplished by increasing the dielectric constant of the medium.



This type of outer-sphere complex may be considered as a non-ionized species consisting of constituents of different charges; the elementary electrostatic approach is no longer satisfactory as dissociation of the charged ligand in the second coordination sphere will involve the coordinating interactions required for the ionization of a covalent substrate in a coordinating solvent[29].

Hence the stabilities of ion pairs and of the corresponding outer-sphere complex are different and equilibria are established in solution between the two types of species, for example

$$\underset{\text{ion pair}}{[\mathrm{Co(OH_2)}_n]^{2+}[\mathrm{Cl(HOH)}_m]^-} \rightleftharpoons \underset{\text{outer-sphere complex}}{[\mathrm{Co(OH_2)}_p\mathrm{Cl(HOH)}_q]^+}$$

with $n > p$ and $m > q$.

Data concerning the existence, composition and stability of such species are often controversial, as research has focussed on the properties of isolated complexes. For interactions in solution the elementary electrostatic theory has frequently been preferred and in this way complex–solvent interactions in solution have hardly been treated from the point of view of coordination chemistry.

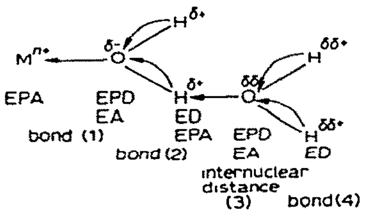
The characteristic features in outer-sphere complexation may be considered as EPD–EPA interactions between coordinated ligands and those to be coordinated. The changes induced in the electronic arrangement of the species are best described by the functional approach to chemical interactions[1] which divides complex compounds according to the functions exercised in complex formation. Hence we shall distinguish between complexes with EPD ligands and with EPA ligands respectively. The course of electronic changes following the coordination of the ligand in the outer-sphere will be different for both types of compounds and we shall term these the *outer-sphere effect for EPD ligands* and the *outer-sphere effect for EPA ligands* respectively. It is obvious that the former effect is more common than the latter.

(iv) The outer-sphere effect for EPD ligands

(a) Hydration of cations

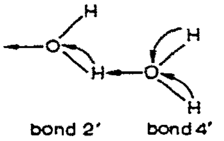
The functional approach[1] emphasizes the electron changes within the molecules induced by coordination. The differences in properties between hydrated and non-hydrated water molecules are due to the increase in EPA properties of the hydrogen atoms of water molecules following coordination to a metal ion. The formation of a coordinate bond between a metal ion and water molecules evokes an electron drift from the hydrogen towards the oxygen atoms of the coordinated water molecules. The O–H bond length is increased and the hydrogen atoms of the coordinated water molecules are more acidic than those of bulk solvent molecules[30]. The water molecules around the first hydration sphere will prefer to interact with the more acidic hydrogen atoms of the coordinated water molecules[16].

This leads to outer-sphere coordination with formation of hydrogen bonds. The bonds between the first and second coordination spheres are stronger than those between uncoordinated water molecules. The electron shift from oxygen atoms of the second-sphere water molecules to hydrogen atoms of the first-sphere water molecules will be continued towards the metal ion–oxygen bonds of the first sphere[16a] and this results in an increase in metal–oxygen coordinate bond strength.



Coordination in additional hydration spheres will still be favoured compared with hydrogen bond formation between uncoordinated water molecules as long as the hydrogen atoms of the outer-sphere water molecules are sufficiently more acidic than those of bulk water molecules.

The bond distances within the hydrated ion as compared to those in bulk water units



are as follows: bond (2) and bond (4) are longer than bonds 2′ and 4′ respectively and bond (4) is not as long as bond (2). All these effects are cooperative in that they all work in the same direction, e.g. bond (1) is shortened by the electron flow from the EPD ligand in the outer coordination sphere towards the inner core, as is indicated from the results of CNDO calculations[16a].

We may formulate the outer-sphere effect for EPD ligands as follows: *outer-sphere coordination by EDP ligands leads to an increase in bond energy in the inner coordination sphere* and hence to an increase in complex stability.

The extent of this effect will be influenced (*a*) by the extent of EPD–EPA interaction between first sphere ligand and coordination centre, e.g. by the strength of the coordinate bond (1); (*b*) by the amphoteric properties of the ligands in the first coordination sphere, and (*c*) by the EPD properties of the outer-sphere ligand.

A very remarkable relationship exists between solvent donicity and chemical shift of the ^{23}Na nucleus in solutions of sodium perchlorate or sodium tetraphenylborate[31,32] in the respective EPD solvents. A nearly straight line (Fig. 1) is observed for different EPD solvents and only water behaves as a much stronger EPD than would be expected on the basis of its donicity. It falls, however, on the line[16] with a donicity of 33. This increased donicity in water as solvent compared with that of water molecules in non-aqueous solvents is due to the outer-sphere effect for water molecules. For water as a solvent the term *bulk-donicity* has been introduced[16] and indeed in solutions of all amphoteric solvents the bulk donicities should be considered rather than the donicities. This concept also proved useful in comparing redox potentials in water and in non-aqueous solvents[16,30,33].

(b) Solvation in solvent mixtures

In mixtures composed of two solvents of different donicities the plot of the ^{59}Co

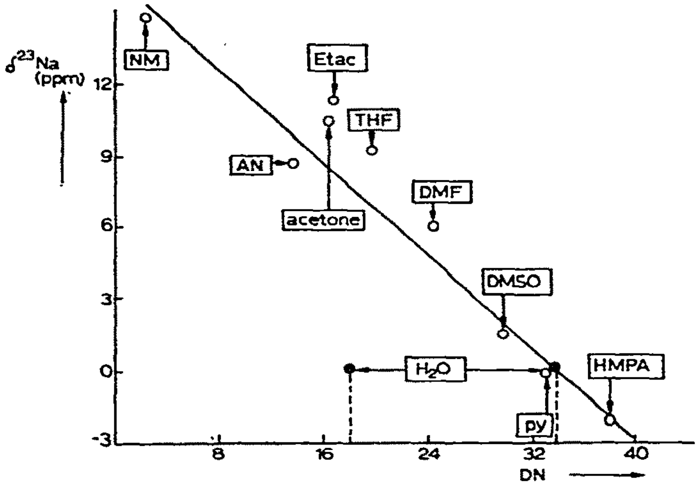


Fig. 1. Relationship between solvent donicity DN and chemical shift of the ^{23}Na nucleus in solutions of $NaClO_4$ in various EPD solvents.

chemical shift in $Co(acac)_2$ vs. bulk solvent composition does not yield a straight line and this is an indication of preferential solvation by one of the two solvents[34,35][*]. The "iso-solvation" point designates the composition at which the chemical shift lies midway between the values for the pure solvents.

In solutions of sodium tetraphenylborate in mixtures of dimethyl sulphoxide (DMSO) and acetonitrile (AN) the iso-solvation point occurs at ≈ 15 mole% DMSO, indicating the not unexpected higher solvating ability of this solvent[36] (Fig. 2). The difference in solvating abilities of acetonitrile and pyridine are less pronounced (iso-solvation point at 40 mole% pyridine), although pyridine has a higher donicity than DMSO. In order to reach a donicity of 26, 20 mole% DMSO or 45 mole% of pyridine are required.

The outer-sphere effect may account for these phenomena, as long as substitution

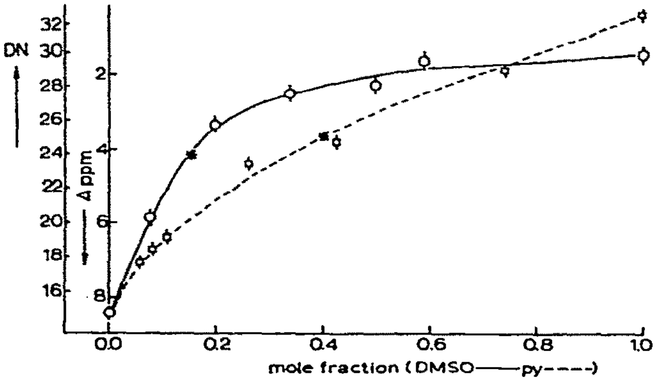


Fig. 2. Chemical shift of ^{23}Na in mixtures of DMSO and py in AN.

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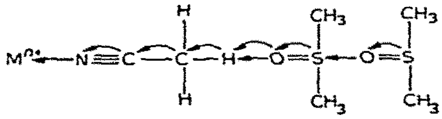
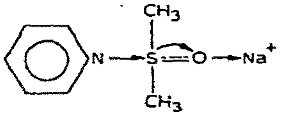
[*] Recently evidence has been found for the preferential solvation of $Cr(DMSO)_6^{3+}$ cations by DMSO in DMSO–NM mixtures. C.H. Langford, R. Scharfe and R. Jackson, *Inorg. Nucl. Chem. Lett.*, 9 (1973) 1033.

in the inner solvation spheres does not take place. Several outer spheres are possible with DMSO, but not with pyridine.



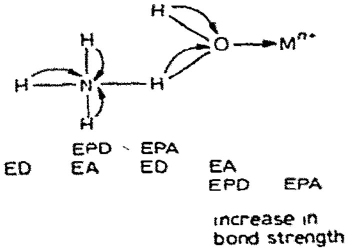
In contrast to pyridine, DMSO is a highly associated liquid with a chainlike structure[37] in which the sulphur atoms act as EPA towards the oxygen atom of another DMSO molecule[38]. A recent study of the Brillouin scattering by pyridine[39] shows extensive disruption of the DMSO structure by pyridine. Addition of small amounts of pyridine to a solution of $NaClO_4$ in DMSO does not displace the latter from the sodium ion, although the donicity is enhanced[40]. The increase in donicity may be due to the outer-sphere effect of pyridine on the metal cation coordinated by DMSO.



The tendency to outer-sphere complexation will be governed not only by the electronic properties, but also by steric effects.

Owing to outer-sphere effects the donicity of a solvent mixture cannot be calculated from the composition and the donicities of the component solvents.

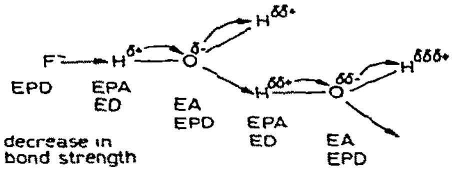
Ammonia has a higher donicity than water, but water shows preferential solvation towards many metal ions. Before ammonia can replace a water molecule in the inner solvation sphere, it forms an outer-sphere complex. In this the metal–oxygen bonds are stronger and the H–O bonds of the inner sphere water molecules weaker than in the hydrated ion.



The interaction may lead to deprotonation of coordinated water molecules with formation of ammonium ion and the hydroxo complex of the metal, which is even more stable than the outer-sphere ammonia complex.

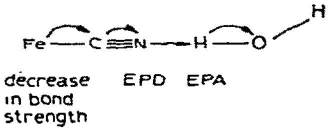
(v) The outer-sphere effect for EPA ligands

Anions are stabilized by coordination with ligands which function as electron pair acceptors towards the electron pair providing anions[1]. In aqueous solution the fluoride ion is coordinated by water molecules through one of their hydrogen atoms[29a]. In this way negative charge is withdrawn from the fluoride ion and transferred through the hydrogen atom to the oxygen atom[16a]. This is reflected in increased EPD properties at the latter. Water molecules coordinated in the first hydration sphere will be able to build up a second hydration sphere by making use of the stronger EPD functions of water molecules coordinated to an anion as compared to those of bulk solvent molecules.



The additional dispersion of the negative charges originally situated at the fluoride ion coordination centre over the oxygen atoms of outer-sphere water molecules leads to a corresponding increase in the bond energies of the inner-sphere coordinate bonds[30].

However in the hexacyanoferrate ion, the nitrogen atoms of the cyanide ligands show basic properties and hence water can be coordinated in the outer sphere with formation of hydrogen bonds. The Fe–C bond is weakened by this outer-sphere coordination and replacement of the water molecules by formic acid in the outer spheres leads to a further weakening of the Fe–C bonds[30].



Hence the outer-sphere effect for EPA ligands may be formulated as follows *outer-sphere coordination by EPA ligands leads to a decrease in bond energy of the inner-sphere metal–ligand bonds.*

C. KINETICS OF SUBSTITUTION REACTIONS

(i) General

Much evidence has accumulated in support of the hypothesis that the rate-determining step of a substitution reaction of octahedral complexes involves the loss of the ligand which is substituted from the inner coordination sphere[7, 41]. This is thought to be preceded by the rapid formation of an outer-sphere complex in which the entering ligand E is coordinated to the inner coordination sphere of the coordination centre.

$$[ML_6]^{n+} + E \rightleftharpoons [L_5ML \leftarrow E]^{n+} \tag{1}$$

If E is a charged ligand, the outer-sphere complex formation is preceded by the formation of an ion-pair.

$$[ML_6]^{n+} + [E_{solv}]^{m-} \rightleftharpoons [ML_6]^{n+}[E_{solv}]^{m-} \tag{2}$$

The overall formation rate constant k_1 is usually formulated as the product of the pre-equilibrium constant K_P (which is a composite constant, namely those of ion pair formation and of outer-sphere complex formation) and the rate constant for the ligand-loss process, i.e. the dissociation rate constant k_{12}.

$$k_1 = K_P k_{12} \tag{3}$$

K_P is usually estimated by means of the Fuoss equation[42], in which the interatomic distances, the electronic charges and the macroscopic dielectric constant are taken into account. The Fuoss equation is applicable to charged ligands only, and a similar equation has been derived for neutral ligands[43].

Equation (3) is generally not applicable to reactions in non-aqueous solvents, as the coordinating properties of the solvents are not taken into account in the estimation of K_P. These are important, however, especially for uncharged ligands involved in the pre-equilibria[1]. Accordingly, different values for K_P were obtained for the reaction of nickel(II) with bipyridyl in different solvents, even in those of similar dielectric constant[13]. Systematic investigations in non-aqueous media will be necessary to discover to what extent the pre-equilibrium constant K_P is related to coordinating effects.

We shall consider the substitution in an octahedral complex.

$$[L'_5M{-}L]^{n+} + E^{m-} \rightleftharpoons [L'_5ME]^{(n-m)+} + L \tag{4}$$

E^{m-} is the entering ligand, L the leaving ligand and L′ the non-leaving ligand. E^{m-}, L and L′ may be solvent molecules or other ligands, solvent exchange being merely a special case of substitution. The rate-determining step of this reaction can be formulated as the dissociation of the ligand to be substituted.

$$[L'_5M{-}L]^{n+} \rightarrow [L'_5M]^{n+} + L \tag{5}$$

It may be anticipated that the rate of rupture of the metal–ligand bond M–L follows the inverse order of the bond strengths. The bond M←L in a complex of the type

$$\underset{\text{EPA}}{[L'_5M}\leftarrow\underset{\text{EPD}}{L]^{n+}}$$

may be considered as the result of the EPA interaction of the ion $[L'_5M]^{n+}$ and the EPD interaction of the ligand L.

While the EPD properties of the ligands may be characterized by their donicity, no corresponding values are available for the EPA properties. The EPA strength of a cation is reduced by increased EPD properties of the ligands L′, and hence the strength of the bond to be dissociated also depends on the nature and on the number of the non-leaving ligands.

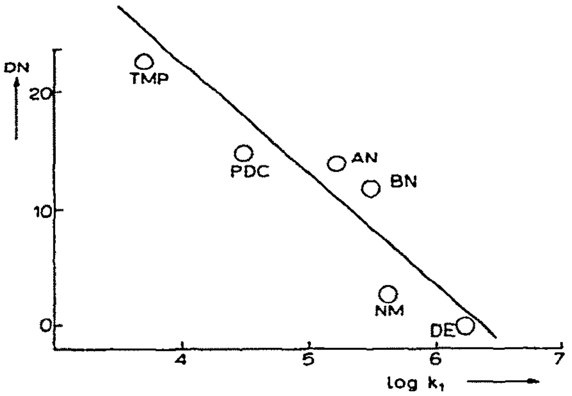


Fig. 3. Plot of donicity DN of L vs. log k_1 for reaction of Cl_5SbL with Ph_3CCl.

(ii) Inner-sphere effects

Three possible cases may be discussed in order to account for the effect of variation of the inner-sphere composition of a complex on the substitution rates.

(a) The leaving ligand is varied

Studies of reactions of the type

$$[Cl_mM{-}L] + Cl^- \rightleftharpoons [MCl_{m+1}]^- + L \qquad (6)$$

have been carried out in different EPD solvents, with L being varied[44].

TABLE 3

Rate constants and equilibrium constants for reaction (7) in different solvents L

L	DN	k_1 (l.mole^{-1} sec^{-1}) at 20°C	k_2 (sec^{-1}) at 20°C	$K_{[SbCl_6]^-}$	
				Kinetically	Spectrophotometrically
DE		1.7×10^6	5	3.5×10^5	$> 10^5$
NM	2.7	4.2×10^5	3	1.4×10^5	$> 10^5$
BN	11.9	3.3×10^5	10	3.3×10^4	
AN	14.1	1.7×10^5	17.5	1.1×10^4	10^5
PDC	15.1	3.4×10^4	16.4	1.3×10^3	3×10^2
$PhPOCl_2$[a]	18.5	1.9×10^2	2	9.6×10^1	4×10^1
TMP	23.0	5.1×10^3	6.5×10^2	7.8×10^0	2×10^0

[a] The considerable deviation with this solvent may be due to the presence of chloride ions.

The rate of solvent substitution at antimony(V) chloride k_1 according to the equation

$$Cl_5Sb{-}L + Ph_3CCl \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [Ph_3C]^+\ [SbCl_6]^- + L \tag{7}$$

was found to be approximately inversely proportional to the donicity of the solvent L, seven solvents having been examined[44] (Fig. 3). The k_1 values are different by 2–3 orders of magnitude for 1,2-dichloroethane and trimethyl phosphate (Table 3).

Reasonable agreement is obtained for the values of the equilibrium constant K as determined spectrophotometrically and kinetically. K is also a function of the ligand donicity, providing a further demonstration of the established relationship between thermodynamic stability and kinetic reactivity[45]. Likewise, the single bond rupture rate constants for the reactions

$$[(H_2O)_5M{-}L]^{2+} + H_2O \overset{k_1}{\rightleftharpoons} [M(H_2O)_6]^{2+} + L \tag{8}$$

L being methanol, water or ammonia, and M being Co or Ni, follow the order of the donicities of the respective ligands[14], Table 4.

Likewise, the rate of substitution in nickel(II) complexes with a series of substituted pyridines

$$[(H_2O)_5Ni{-}py]^{2+} + H_3O^+ \rightleftharpoons [Ni(H_2O)_6]^{2+} + pyH^+ \tag{9}$$

has been found to decrease with increasing EPD properties of the pyridine base[46].

If reactions of type (6) proceed via an S_N2 mechanism, the EPA properties of the metal ion must be considered. The rate-determining step of the reaction

$$[Cl_3Co{-}L]^- + Cl^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [CoCl_4]^{2-} + L \tag{10}$$

can be regarded as the formation of the pentacoordinate transition state.

$$[Cl_3Co{-}L]^- + Cl^- \rightarrow [Cl_4Co{-}L]^{2-} \tag{11}$$

Increasing donicity of the solvent L reduces the EPA strength of $[Cl_3CoL]^-$, and hence lowers the formation rate of the pentacoordinate intermediate. Thus the substitution rate

TABLE 4

Logarithmic values for rate constants for reaction (8) in water

M–L bond	log k_1 (sec^{-1})	M–L bond	log k_1 (sec^{-1})
Ni–CH_3OH	5.9	Co–CH_3OH	6.8
Ni–H_2O	4.5	Co–H_2O	5.9
Ni–NH_3	0.6	Co–NH_3	3.2

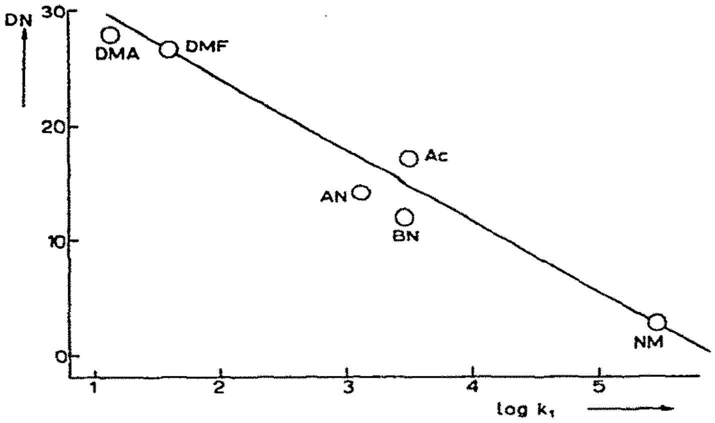


Fig. 4. Plot of donicity DN of L vs. log k_1 for reaction of Cl_3CoL with Cl^-.

is decreased. In fact, the rates vary by four orders of magnitude for nitromethane and dimethylformamide[47]. As expected, the reversed reaction rate k_2 is influenced unnoticeably by the solvent donicity. Again, a relation between kinetic and thermodynamic parameters has been found, as the equilibrium constant K is proportional to the solvent donicity (Table 5).

(b) Non-leaving ligands are varied

The EPA strength of $[L'_mM]^{n+}$ can be changed by varying either the metal ion M or the non-leaving ligands L'. The nature of the metal ion is the main factor determining the overall substitution rate. Unfortunately no characteristic property analogous to donicity has been defined for the EPA strength. (The rate constant for water exchange

TABLE 5

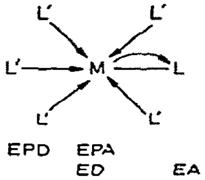
Rate constants and equilibrium constants for reaction (10), in different solvents L in the absence of any electrolyte

EPD solvent L	DN	k_1 (l.mole^{-1}.sec^{-1}) at 20°C	k_2 (l.mol^{-1} sec^{-1}) at 20°C	$K_{[CoCl_4]^{2-}}$ at 20°C	
				Kinetically	Spectrophotometrically
NM	2.4	3×10^5	≈ 3	1×10^5	8×10^4
BN	11.9	2.9×10^3	0.4	8×10^3	5×10^3
AN	14.1	1.3×10^3	1	1×10^3	9.7×10^2
AC	17.0	3.1×10^3	0.6	5×10^3	4.1×10^3
DMF	26.6	4×10^1	1.2	3×10^1	2.9×10^1
DMA	27.8	1.4×10^1	0.2	9×10^1	5×10^1

is not always inversely proportional to the ionic radius for metals of a given charge-type. Deviations have been regarded as being due to partly filled *d*-orbitals on the metal ion which can cause considerable complications interpreted in terms of crystal-field stabilization and the Jahn–Teller effect[48].)

Within a homologous series of hydrated metal ions the increase in substitution rate is paralleled by a decrease in the hydration bond energy[1]. It might therefore be expected that in non-aqueous solutions the substitution rate in a solvate will be an inverse function of the solvation enthalpy. We shall discuss in more detail only the variation of L′ with M being kept constant.

Coordination of the ligands L′ to the central ion M leads to an increase in electron population at M, which induces an electron shift from M to L.



The M–L bond is increasingly weakened by increasing donicity of L′. This will be manifested in an increase in M–L bond rupture rate, and substitution reactions proceeding through an S_N1 mechanism will be faster. Hoffmann and co-workers[49, 50] studied substitution reactions of the type

$$[L'_5Ni{-}L]^+ + L' \underset{k_1}{\overset{k_1}{\rightleftharpoons}} [L'_6Ni]^{2+} + L \qquad (12)$$

where L, a univalent anion, was kept constant and the EPD solvent L′ varied. In terms of an S_N1 mechanism the bond rupture of Ni–L is rate-determining. It was found that the rate constants k_1 increase dramatically with increasing donicity of L′. For both Cl^- and SCN^- as ligand L, the rates varied by eight orders of magnitude[49] on going from methanol to ammonia as L′ (Table 6). Desai et al.[51] have found that water exchange rates in

TABLE 6

Rate constants k_1 for reaction (12) in different solvents L′

L′ in $[L'_5NiSCN]^+$	DN	k_1 (sec^{-1})
CH_3OH	19[a]	3×10^{-1}
DMSO	30	7×10^{1}
H_2O	33	10^{3}
NH_3	59	10^{7}

[a] The bulk donicity of methanol is higher.

TABLE 7

Water-exchange rate constants k_1 in some Ni^{II} complexes in water

Complex	$\log k_1$	Complex	$\log k_1$
$[Ni(OH_2)_6]^{2+}$	4.5	$[Ni(terpy)(OH_2)_3]^{2+}$	4.5
$[Ni(NH_3)(OH_2)_5]^{2+}$	5.4	$[Ni(bipy)(OH_2)_4]^{2+}$	4.7
$[Ni(NH_3)_2(OH_2)_4]^{2+}$	5.8	$[Ni(bipy)_2(OH_2)_2]^{2+}$	4.8
$[Ni(NH_3)_3(OH_2)_3]^{2+}$	6.4		

aquoamminenickel(II)-complexes are increased by increasing the number of ammonia molecules in the inner coordination sphere of nickel(II). Ammonia is a stronger EPD than water and hence the EPA strength of the Ni^{II} complex is reduced accordingly upon substitution of water by ammonia ligands. On the other hand, bipyridyl[51] and terpyridyl[52] do not produce these effects and cause only a small change in the water's lability, because the donicities of these ligands are similar to those of pyridine and to the bulk donicity of water[16] (Table 7). Likewise the rates for nickel–malonate complex formation according to

$$[NiL(OH_2)_n]^{2+} + mal \rightleftharpoons [NiL(OH_2)_{n-2}\,mal]^{2+} + 2\,H_2O \tag{13}$$

are only slightly different depending on whether L is water, pyridine or bipyridyl, whereas increase in donicity of L brings about an increase in the rate constants[53].

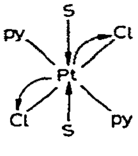
The incorporation of water molecules into the inner coordination sphere of nickel(II)–methanol solvates enhances the rate of methanol exchange[54, 55]. $[Ni(OH_2)_5(CH_3OH)]^{2+}$ is the most labile of solvated Ni^{II} ion species in methanol–water mixtures. Alcohols have lower bulk donicities than water and hence the EPA strength of all possible $[NiL_5]^{2+}$ ions in these solutions is least for $[Ni(OH_2)_5]^{2+}$. The rate of dissociation of CH_3OH from $[Ni(OH_2)_5(CH_3OH)]^{2+}$ is therefore greater than for any other composition in water–methanol solvate[14]. The rate constant for nickel–methanol bond rupture in this species is approximately 800 times larger than the rate constant established for breaking the nickel–methanol bond in $[Ni(CH_3OH)_6]^{2+}$ and it is 20 times larger than the rate constant for nickel–water bond ruptures in $[Ni(OH_2)_6]^{2+}$, as in the latter the $Ni–OH_2$ bond is stronger than the Ni–methanol bond in $[Ni(OH_2)_5(CH_3OH)]^{2+}$.

The same interpretation — the variation of the EPA strength by variation of the inner coordination sphere ligands — is applicable to ligand exchange in tetrahedral complexes. Pignolet and Horrocks[56] found that the lability of ligands L in complexes of the type $[L'_2ML_2]$ (M = Co, Ni) increases in the order

$$L' = I^- < Br^- < Cl^-$$

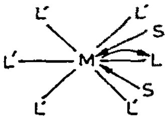
The EPA strength of $[L'_mM]^{n+}$ is varied not only by variation of L′ but also by variation of the coordination number. Rare-earth metal ions react much more rapidly than expected on the basis of the charge–radius rule[6]. The comparatively high water-exchange rates for these trivalent ions have been attributed to their coordination numbers greater than six[57].

The effect of the solvent on the rate of chloride ion exchange at [*trans*-$Pt(py)_2Cl_2$] is not related to the dielectric constant, but to the coordinating properties of the solvent[58]. The solvent S is considered to occupy sites in the inner coordination sphere and to weaken the Pt–Cl bonds.



A relation between rate constant and solvent donicity cannot be expected, because Pt^{2+} is a soft Lewis acid.

For octahedral complexes the term *solvent-assisted dissociation* mechanism ("SAD" mechanism) has been suggested[59]. It is applied to solvent effects that happen when solvent molecules slip in when the bond between the metal ion and the leaving group is stretched beyond a critical length and hence enhance the dissociation of L.



The SAD mechanism has been well established for non-aqueous substitution reactions in which X in the $[Co(en)_2AX]^{n+}$ cation[59] is replaced, and has been discussed in terms of competition between solvent and solute for a position in the inner solvation shell of the complex. It has been widely applied in interpreting the dissociation rate constants for various solvation reactions[15,60].

(c) Substitutions at unmixed solvates $[MS_6]^{n+}$

We have seen that the rupture rate of the bond $L'_5M{-}L$ is drastically increased with increasing donicity of the non-leaving ligands L' and decreasing donicity of the leaving ligand L. A difference of eight orders of magnitude is found[49] in the rupture rates of the Ni–NCS bond in $[(MeOH)_5Ni{-}NCS]^+$ and $[(NH_3)_5Ni{-}NCS]^+$. The difference in donicities between MeOH and NH_3 is about 40. The rate constants for the substitution of the solvent S in $SbCl_5S$ differ by three orders of magnitude, S being dichloroethane and trimethyl phosphate. The difference in donicities[44] is $\Delta DN \approx 20$. Thus we expect no large effect of donicity on substitution reactions of $[MS_6]^{n+}$, where all ligands have the same donicity.

For substitution reactions at octahedral unmixed solvates in different solvents, the rate-determining step may be represented

$$[MS_6]^{n+} \rightarrow [MS_5]^{n+} + S \qquad (14)$$

Increase in EPD properties of the solvent molecules S again leads to an increase in solvate bond strength, but the EPA strength of $[MS_5]^{n+}$ is simultaneously decreased. Thus the effect of the leaving ligand is opposite to that of the non-leaving ligand and hence the substitution rates should hardly be influenced by the ligand donicities, e.g. they should be nearly levelled in different solvents.

In fact, small differences are observed for the exchange rates between solvent molecules S coordinated to a metal ion and bulk solvent molecules S* in various EPD solvents as found from NMR measurements.

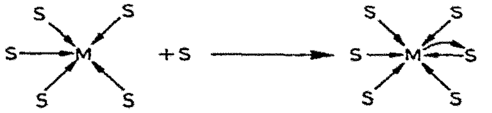
$$[MS_6]^{n+} + S^* \rightleftharpoons [MS_5S^*]^{n+} + S \tag{15}$$

Appropriate solvent exchange data have previously been tabulated[12, 13].

Effects become more obvious, however, if solvents of vastly different donicities are compared. MacKellar and Rorabacher[14] have found that solvent exchange proceeds, relatively to aqueous solutions, more rapidly in ammonia and less rapidly in methanol (Table 8).

The difference in bond rupture rates in methanol and ammonia is only two orders of magnitude; hence the differences are even smaller, if solvents of similar donicities are compared.

Since five EPD molecules contribute to the overall EPA strength of the intermediate $[MS_5]^{n+}$, it is reasonable that increase in EPD donicity should cause the relative decrease in EPA strength of $[MS_5]^{n+}$ to be larger than the relative increase in EPD donicity[60a]. As a consequence the solvent exchange rates increase with increasing solvent donicity. Ligands of high donicity result in a more stable five-coordinate metal ion intermediate relative to its six-coordinate ground state than do ligands of weaker donicity[14]. Increase in bond strength of the existing bonds in the species $[MS_5]^{n+}$ will weaken the sixth bond being formed.



(16)

It might be an unusual thought to consider the equivalence of all six metal ion–ligand bonds in solution as only statistically valid. In other words, the solvated ion should perhaps not be considered a perfectly rigid unit, but rather dynamic as involving continuous

TABLE 8

Solvent exchange rates for Ni^{II} solvates in different solvents

Complex	Solvent	log *k*
$[Ni(CH_3OH)_6]^{2+}$	CH_3OH	3
$[Ni(OH_2)_6]^{2+}$	H_2O	4.5
$[Ni(NH_3)_6]^{2+}$	NH_3	5

rapid interchanges in bond energies within certain limits. A distinction between a stable symmetric complex with equal bonds and the suggestion above might be possible by analyzing the vibrational spectra including isotope substitution.

(iii) Other effects

Since rate constants depend on the EPD property of the leaving ligand and the EPA property of the remaining intermediate, it is reasonable to assume that the bond strength is the dominating factor in the overall rate of a substitution reaction. However, dielectric effects and outer-sphere effects must also be considered, especially when either complexes with identical inner-sphere composition or unmixed solvates $[MS_6]^{n+}$ are reacted in different solvents S or solvent mixtures. For unmixed solvates it has been pointed out that increasing donicity of S is compensated to a great extent by decreasing EPA strength of $[MS_5]^{n+}$.

(a) Ion pair effects

For charged entering ligands E the first step of the substitution reaction is the association of the cationic and anionic species to form an ion pair. The extent of ion pair formation is dependent on the electronic charges and the ionic radii of the reactants as well as the dielectric constant of the medium. Increasing charges and decreasing dielectric constant favour ion pair formation, the equilibrium constant of which influences the pre-equilibrium constant K_P and thus the overall formation rate constant k_1 according to eq. (3). For given k_{12}, k_1 will be decreased by an increase in the dielectric constant of the medium. If substitution reactions of complexes in which the ligands have comparable coordinating properties are considered, the dielectric constant may considerably contribute to the observed rate. This ion pair effect or dielectric effect on K_P can be sufficient to prevent the trend of the bond strengths being manifested by the change in the dissociation rate constant k_{12}.

For example, Pearson and Ellgen[41] have found that with nickel(II) solvates $[NiS_6]^{2+}$, only neutral ligands react at a slower rate in methanol than in water, as predicted from the trend of bond strengths. Monovalent anions react at about the same rate in methanol as in water, whereas divalent anions react even faster in methanol. Likewise the bimolecular formation rate constants for the reaction of $[NiS_6]^{2+}$ with thiocyanate have been found to be similar for dimethyl sulphoxide and methanol[49,50]. The smaller dielectric constant of methanol overcomes the higher donicity of DMSO.

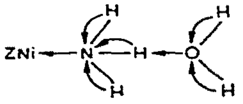
(b) Outer-sphere effects

The outer-sphere effect for EPD ligands causes an increase in coordinate bond strength of the inner sphere and hence a decrease in dissociation rate of the inner sphere ligand. On the other hand, the dissociation rate will be increased by the outer-sphere effect for EPA ligands, as the inner-sphere coordinate bond is weakened.

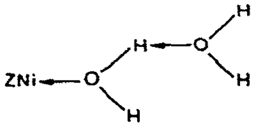
Shu and Rorabacher[15] studied the kinetics of solvent–ammonia exchange on Ni^{II} as a function of methanol–water solvent composition. In order to minimize inner-sphere effects a quinquedentate ligand Z has been complexed to the Ni^{II} ion leaving a single coordination site available for solvent–ammonia exchange.

$$ZNi{-}NH_3 + S \underset{k_2}{\overset{k_1}{\rightleftharpoons}} ZNi{-}S + NH_3 \tag{17}$$

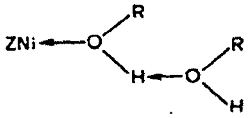
Both the dissociation rate k_1 and the formation rate k_2 are increased with increasing methanol content of the solvent mixture and this is attributable to the different extent of outer-sphere effect for water and methanol respectively. The nickel–ammonia bond is strengthened by outer-sphere complexation.



The effect is less pronounced for methanol than for water. If water is substituted in the outer sphere by methanol the $Ni{-}NH_3$ bond is weakened and hence the dissociation rate is increased accordingly. Likewise the formation rate k_2 is increased with increasing methanol content. In pure water the hydrate complex



is present. In water–methanol mixtures H_2O is partly replaced by methanol in the outer sphere and the nickel–water bond is weakened. At high methanol content, even water molecules in the inner sphere are replaced and in anhydrous methanol the complex

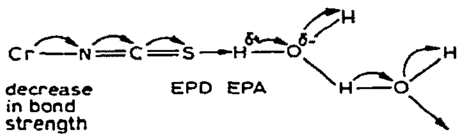


is present, in which the metal–inner-sphere ligand bonds are weaker than in any other complex under consideration. Hence k_2 reaches its maximum value.

Casazza and Cefola[61] found that the rate of the reaction of Ni^{II} ion and acetylacetone giving monoacetylacetonate–nickel(II) is increased by addition of 2-propanol to the aqueous solution. They considered the change in the dielectric constant of the solvent mixture within a range of dielectric constant between 24 and 26 to be responsible for the change in rate. However, within this small range of dielectric constant a difference in rate constant of nearly 100% is observed. Desai et al.[51] observed a linear relationship between rate of water substitution and inner-sphere composition in aquoamminenickel(II) complexes in water without noticeable change in dielectric constant of the medium. Since the dielectric constant in water–methanol mixtures is also a linear function of solvent composition[62], there is a linear relationship not only between rate and dielectric constant, as pointed out by Casazza and Cefola[61], but also between rate and solvent composition. Since the inner sphere remains intact, there should be a continuous change in outer-sphere composition with change of medium composition. 2-Propanol in the second coordination sphere strengthens the Ni–OH_2 bonds to a smaller degree than water. The very rapidly increasing rates in propanol–water mixtures of low water content indicate a continuous change from outer-sphere to inner-sphere coordination of propanol at the metal ion, the highest lability for the metal–propanol bond being expected in $[(H_2O)_5Ni(ROH)]^{2+}$.

Likewise, the ligand exchange kinetics of $[M(DMSO)_6]^{2+}$ in mixed solvents DMSO–nitromethane and DMSO–methylene chloride is independent of the composition of the solvent, although the dielectric constants of nitromethane and methylene chloride are very different[63]. Both solvents are, however, poorly coordinating and hence no outer-sphere effect is found.

On the other hand, the rate constant for the solvolysis of $[Cr(NH_3)_2(NCS)_4]^-$, the ion of Reinecke's salt, with replacement of thiocyanate, is greater in solvents of the ROH type than in non-hydrogen bonding solvents such as nitromethane or dioxane[60]. Likewise Thomas and Holba[64] reported a decrease in rate for the aquation of $[Cr(en)(NCS)_4]^-$ in water–methanol mixtures with increasing methanol content. These phenomena may be regarded as due to the outer-sphere effects of the EPA ligands, by which the metal–inner-sphere ligand bond is weakened.



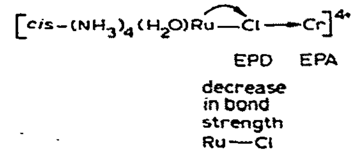
Outer-sphere effects due to EPA ligands are responsible for the acid catalysis of certain aquation reactions. The role of H^+ may be simply the labilization of the leaving group, hydronium ions having considerably stronger EPA properties than water molecules. Thus an increase in rate with decreasing pH value has been reported for reactions of the type[65, 66]

$$[L'_5CrX]^{2+} + H_2O \xrightarrow{H^+} [L'_5CrOH_2]^{3+} + X^- \qquad (18)$$

Metal ions, acting as EPA, may be capable of outer-sphere coordination. The rate of loss of a chloride ion from the first coordination sphere of the complex

$[cis\text{-}(NH_3)_4(H_2O)Ru\text{–}Cl]^+$

is 30 times as fast in the presence of chromium(III) ions[67]. These are coordinated to the chloride to give an outer-sphere complex. Owing to the outer-sphere EPA effect for Cr^{3+}, the Ru–Cl bond is weakened.



D. KINETICS OF REDOX REACTIONS

(i) General

Rates of redox reactions of metal ion complexes demonstrate a tremendous sensitivity to a change in the ligands. The intimate relationships between coordination and redox properties have recently been formulated by means of the functional approach[30] and this should also be useful for a better understanding of the kinetics of redox reactions.

For redox reactions two different limiting types of mechanisms can be distinguished.

(1) Outer-sphere mechanism. The inner coordination spheres of the reactants remain intact and no ligand is common to the coordinating spheres of both the reducing and the oxidizing agents. The actual electron transfer takes place through an outer-sphere complex, for example[68]

$$[Cr(bipy)_3]^{2+} + [Co(NH_3)_6]^{3+} \rightleftharpoons [(bipy)_2\overset{e^-\ \curvearrowright}{Cr(bipy)(NH_3)Co}(NH_3)_5]^{5+} \tag{19}$$

(2) Inner-sphere mechanism. The electron transfer is preceded by substitution of a ligand from one reactant into the coordination sphere of the other to form a bridged complex. In this complex the two metal ions are connected through one or more bridging ligands common to both coordination spheres, through which the actual electron transfer takes place. An example of this type is the reaction[69]

$$[(H_2O)_6Cr]^{2+} + [ClCo(NH_3)_5]^{2+} \rightleftharpoons [(H_2O)_5\overset{e^-\ \curvearrowright}{Cr \leftarrow ClCo}(NH_3)_5]^{4+} + H_2O \tag{20}$$

This type of mechanism is expected to be influenced by the extent of EPA—EPD interaction between coordination centres and ligands. As has been pointed out in this presentation, strong EPD—EPA interactions between the coordination centre and the ligands are characteristic of substitution-inert complexes, and redox reactions between two substitution-inert complexes will probably proceed through an outer-sphere mechanism. Thus for the reaction of $[Cr(bipy)_3]^{2+}$ with $[Co(NH_3)_6]^{3+}$, an outer-sphere mechanism is reasonably clear[68]. Even if only one reactant is inert and has no possible bridging ligands such as complexes with ammonia, an outer-sphere mechanism is again probable, for instance for the reaction[68]

$$[Cr(OH_2)_6]^{2+} + [Co(NH_3)_6]^{3+} \rightleftharpoons [Cr(OH_2)_6]^{3+} + [Co(NH_3)_6]^{2+} \tag{21}$$

In other cases, however, inner-sphere intermediates are likely to be formed and involved in the course of the actual electron transfer.

(ii) Outer-sphere mechanism

Let us consider the general outer-sphere reaction

$$\underset{\text{reductant}}{[L_m\overset{e\ \curvearrowright}{M_1]^{z+} + [M_2}} \underset{\text{oxidant}}{L'_n]^{z'+}} \xrightarrow{k_1} [L_mM_1]^{(z+1)+} + [M_2L'_n]^{(z'-1)+} \tag{22}$$

where L are the ligands at the reducing metal ion M_1 and L′ the ligands at the oxidizing metal ion M_2.

While the extent of EPD–EPA interaction determines the rate of a substitution reaction, the rate of an outer sphere redox reaction should be determined by the ED strength of the reducing agent and the EA strength of the oxidizing agent[1,30]. Increase in donicity of the ligands leads to a decrease in oxidizing properties and to an increase in reducing properties[30]. Thus the rate k_1 is increased with increasing donicity of the ligands L, when the oxidant is kept constant. Conversely the rate k_1 will decrease with increasing EPD strength of the ligands L′ of the oxidizing agent, when the reductant is kept constant.

$[V(OH_2)_6]^{2+}$ is oxidized more rapidly[70] by I_2 than I_3^-; the EA property of iodine in I_3^- is less than that of pure iodine. The donicity of ammonia is higher than that of pyridine and hence ammonia complexes are reduced at lower rates than the pyridine analogues[71–74] (Table 9).

Anbar and Hart[75] found that the ligands have profound effects on the rates of reduction of complex ions with hydrated electrons. The rate of reduction increases within the series of ligands

$$CN^- < F^- < Cl^- < I^-;\ NH_3 < H_2O$$

This order parallels the decreasing EPD properties of the ligands[24]. Likewise, the outer-sphere reduction rate of $[Co(NH_3)_5X]^{2+}$ by $[Cr(bipy)_3]^{2+}$ or by $[Ru(NH_3)_6]^{2+}$ is increased by changes in the ligands X^- in the order[68, 73]

$$F^- < Cl^- < Br^- < I^-$$

In a similar way $[Co(NH_3)_6]^{3+}$ is not reduced as rapidly as $[Co(NH_3)_5(OH_2)]^{3+}$, as the donicity of ammonia is greater than that of water[68, 73].

Since the counter-ions present in the solutions could conceivably act as pseudo-bridges between two reacting cations or between two reacting anions respectively[79], it is not surprising to find that the rates depend on the nature and concentrations of the counter-ions[79].

TABLE 9

Outer-sphere oxidation rates of $[Cr(OH_2)_6]^{2+}$

Oxidant	k_1 (mole.l^{-1}.sec^{-1})
$[Co(NH_3)_6]^{3+}$	8.9×10^{-5}
$[Co(NH_3)_5py]^{3+}$	4.3×10^{-3}
$[Ru(NH_3)_6]^{3+}$	$2.0 \times 10^{+2}$
$[Ru(NH_3)_5py]^{3+}$	$3.4 \times 10^{+3}$

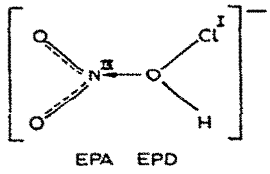
(iii) Inner-sphere mechanism

The consideration of the effect of the ligands on the rates of inner-sphere reactions brings us back to the field of coordination chemical reactions. In terms of the functional approach inner-sphere redox reactions may be defined as redox reactions initiated by EPA–EPD interactions between the reactants. The mechanism for such reactions can be considered as occurring in at least four steps, namely (1) loss of one or more ligands from the labile partner, (2) formation of a bridged complex, (3) electron transfer and (4) subsequent dissociation into the products. The bridged complex is formally called a *precursor complex* before the EA–ED interaction takes place and a *postcursor complex* after the EA–ED interaction has taken place[76]. The postcursor complex dissociates according to the relative stabilities of the possible products. The stabilities depend mainly on the relative EPA properties of the metal ions connected by the bridging ligand(s). The EPA strength increases with increasing oxidation number[1]. The atoms or groups forming the bridge will generally prefer the metal ion of higher oxidizing properties and hence a ligand transfer from the reduced to the oxidized form is frequently observed. For instance, the oxidation of $[Cr^{II}(OH_2)_6]^{2+}$ by $[Co^{III}(NH_3)_5Cl]^{2+}$ has been shown to involve chloride transfer from the oxidizing to the reducing agent[77]. The postcursor for this reaction may be formulated as

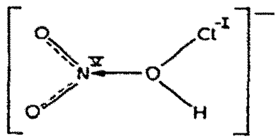
$$[(H_2O)_5Cr^{III}\leftarrow Cl-Co^{II}(NH_3)_5]^{4+}$$

Both $[(H_2O)_5Cr]^{3+}$ and $[Co(NH_3)_5]^{2+}$ are competing for the chloride ion. Since the former is the stronger EPA, $[(H_2O)_5Cr^{III}Cl]^{2+}$ and $[Co^{II}(NH_3)_5]^{2+}$ are formed initially.

Oxygen-18 labelling indicates that the oxidation of $[NO_2]^-$ by HOCl proceeds via oxygen atom transfer[78, 79]. EPA–EPD interactions between the reactants lead to the precursor complex, $[NO_2]^-$ acting as EPA.



After electron transfer the postcursor complex

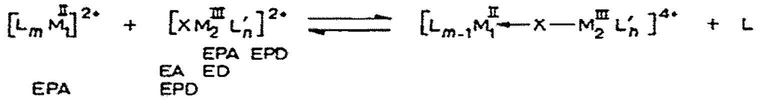


dissociates into $[O_2N]^+$ and Cl^-, both competing for coordination to OH^-. Since $[O_2N]^+$ is the stronger EPA, the products are HNO_3 and Cl^-.

The effect of the ligands on inner-sphere redox reactions may vary. We have to distinguish between bridging and non-bridging ligands, the latter not being in a position to bind to both metal centres at the same time. The question whether the EPD–EPA interactions or the EA–ED interactions are rate-determining must also be considered.

The reducing agent may be $[L_mM_1]^{2+}$ and the oxidizing agent $[XM_2L'_n]^{2+}$, L and L′ being neutral ligands and X^-an univalent bridging ligand. The possible reaction schemes are[80]:

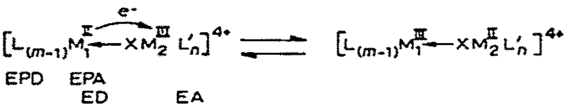
Scheme 1: The formation of the precursor complex is rate-determining, e.g. electron transfer occurs rapidly as soon as the precursor complex is formed.



$$[L_m\overset{II}{M_1}]^{2+} + [X\overset{III}{M_2}L'_n]^{2+} \rightleftharpoons [L_{m-1}\overset{II}{M_1}\leftarrow X - \overset{III}{M_2}L'_n]^{4+} + L \qquad (23)$$

Assuming a pure S_N1 mechanism for the substitution at the M_1 centre, the reaction rate will increase with increasing DN of L according to a decreased EPA strength of M_1 and will be independent of the oxidizing agent. Assuming a borderline mechanism between S_N1 and S_N2 for precursor formation, the rate will also be increased with increasing DN of X^-. According to the functional approach the EPD strength of X^-also increases with increasing DN of L′.

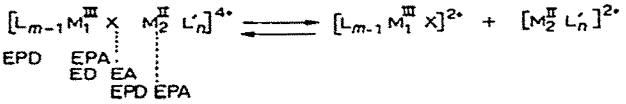
Scheme 2: The precursor complex is readily formed and the rate of transformation to the postcursor complex is relatively slow, i.e. the electron transfer is rate-determining.



$$[L_{(m-1)}\overset{II}{M_1}\leftarrow X\overset{III}{M_2}L'_n]^{4+} \rightleftharpoons [L_{(m-1)}\overset{III}{M_1}\leftarrow X\overset{II}{M_2}L'_n]^{4+} \qquad (24)$$

In this case the ligands L and L′ will have the same effect on the rate as in outer-sphere reactions. The rate increases with increasing donicity of L and decreasing donicity of L′. The bridging ligand X^-will act as conductor of the electrons. The ability to channel electrons should increase with increasing ED properties of X^-.

Scheme 3: The overall reaction rate depends on the rate of the bond rupture in the postcursor complex. We assume the usual pathway, i.e. the bridging ligand remains at the oxidized complex ion.



$$[L_{m-1}\overset{III}{M_1}X \quad \overset{II}{M_2}L'_n]^{4+} \rightleftharpoons [L_{m-1}\overset{III}{M_1}X]^{2+} + [\overset{II}{M_2}L'_n]^{2+} \qquad (25)$$

The rate of rupture of the bond $X{-}M_2$ is increased with increasing donicity of L′, because of the decreased EPA strength of $[M_2L'_n]^{2+}$, and is increased with decreasing EPD strength of X^-. The EPD strength of $X^-$is decreased with decreasing donicity of $X^-$and increasing EPA strength of $[L_{m-1}M_1]^{3+}$. The latter is increased with decreasing donicity of L according to the functional principle. A summary is given in Table 10.

Because of the different effects of the ligands on the different reaction steps it is not possible to predict the change in rate of inner-sphere reactions caused by changing the ligands. On the other hand it should be possible to obtain further information about the

TABLE 10

Effect of increasing donicity of the ligands L and L′ on the rate of a redox reaction, $[M_1L_m]^{2+}$ being the reductant and $[XM_2L'_n]^{2+}$ being the oxidant

Mechanism	L	L′	X⁻
Outer-sphere	Increase	Decrease	Decrease
Inner-sphere			
Scheme 1	Increase	No effect[a]	No effect[a]
	Increase	Increase[b]	Increase[b]
Scheme 2	Increase	Decrease	No effect; increase with increasing ED strength
Scheme 3	Decrease[c]	Increase[c]	Decrease[c]
	Increase[d]	Decrease[d]	Decrease[d]

[a] Assuming an S_N1 mechanism for precursor formation.
[b] Borderline mechanism between S_N1 and S_N2 for precursor formation.
[c] X^- remains at the oxidized complex.
[d] X^- remains at the reduced complex.

reaction mechanism if the dependence of the overall reaction rate on the EPD functions of the ligands is known. Thus decrease of the rate coefficients k_1 and k_2 in the reaction

$$[\mathrm{Fe(EPD)_6}]^{3+} + \mathrm{Fe(cp)_2} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [\mathrm{Fe(EPD)_6}]^{2+} + [\mathrm{Fe(cp)_2}]^{+} \qquad (26)$$

with increasing DN of EPD suggests that the rupture of the bridged complex may be rate-determining[81].

Examples of Scheme 1 are many vanadium(II) redox reactions, for instance reactions between various Co^{III} complexes[82] of the type $[Co(CN)_5X]^{3-}$ and $[V(OH_2)_6]^{2+}$. The agreement of kinetic data such as k, ΔH^* and ΔS^* for these reactions with those for V^{II} substitutions suggests that the rate is controlled primarily[80] by the loss of a water molecule coordinated to vanadium(II). This interpretation is also established by the fact that for different complexes similar values of k have been found, X^- being Cl^-, Br^-, SCN^-, N_3^- and H_2O.

Reactions following Scheme 2 are usually believed to be the most common reaction pattern[80]. In this case the ligand substitution rates are considerably higher than the measured overall redox reaction rate.

The rate of H_2O substitution[79] on the centre of $[Cr(OH_2)_6]^{2+}$ is as high as $10^8 - 10^9$ sec^{-1}, whereas the rate of reduction[83] of $[Cr(OH_2)_5Cl]^{2+}$ by $[Cr(OH_2)_6]^{2+}$ amounts to 3.3×10^1 $mole^{-1}.sec^{-1}$. Transfer of the bridging ligand has been shown to take place. According to Scheme 2, a fall in the value of k is expected with increasing donicity of the ligands on the oxidizing agent L′. The reduction rate of $[cis\text{-}Cr(NH_3)_4H_2OCl]^{2+}$ has been estimated[84] as 1.3×10^{-1} $mole.l^{-1}.sec^{-1}$ and of $[Cr(NH_3)_5Cl]^{2+}$ as 8.8×10^{-2} $mole.l^{-1}.sec^{-1}$.

Less pronounced differences between substitution rates and overall redox reaction rates have been found for Cr^{II} reductions of some cobalt(III) complexes, which have rate con-

TABLE 11

Inner-sphere oxidation rates of $[Cr(OH_2)_6]^{2+}$ reacting via Scheme 2

Oxidant	k_1 (mole.l^{-1}.sec^{-1})
[*cis*-$Co(en)_2NH_3Cl]^{2+}$	2.3×10^5
[*cis*-$Co(en)_2H_2OCl]^{2+}$	4.2×10^5
[*cis*-$Co(en)_2pyCl]^{2+}$	9.4×10^5
$[Co(NH_3)_5F]^{2+}$	2.5×10^5
$[Co(NH_3)_5Cl]^{2+}$	6.0×10^5
$[Co(NH_3)_5Br]^{2+}$	1.4×10^6
$[Co(NH_3)_5I]^{2+}$	3.4×10^6

stants[81] of about 10^5–10^7 mole.l^{-1} sec^{-1}. It has been claimed[85,86] that the reason for the similarity in rate constants is that the substitution on the Cr^{2+} centre limits the rate and that the mechanism of these reactions belongs to Scheme 1 rather than to Scheme 2. However, the effect of the ligands on the reaction rates suggests Scheme 2. It has been pointed out[87] that non-bridging ligand effects are of the same significance in outer-sphere reductions as in inner-sphere reductions of cobalt(III). The rate increases with decreasing DN of the ligands L′ of the complex [*cis*-Co(en)$_2$L′Cl]$^{2+}$, NH^3 being less effective[88] than H_2O and py (Table 11). The same values of *k* should be expected for H_2O and py, the bulk donicity of water being similar to the donicity of pyridine. However, in these octahedral complexes py seems to be more weakly coordinated, possibly due to steric hindrance.

The bridging ligands accelerate the reduction of $[Co(NH_3)_5]^{2+}$ by Cr^{2+} in the order[89] $F^- < Cl^- < Br^- < I^-$ (Table 11). This order may parallel the increasing ED properties of the halides. Thus we propose that the overall rate of reductions of Cr^{II} by Co^{III} complexes is determined by the electron transfer, the fastest inner-sphere Cr^{II} reductions being limited by the substitution on $[Cr(OH_2)_6]^{2+}$.

Movius and Linck[67] reported that the reduction by Cr^{2+} of $[Ru(NH_3)_5Cl]^{2+}$ may proceed by the mechanism of Scheme 3. If Scheme 3 is actually followed, we should expect *k* to increase with increasing donicity of L′, as is in fact found[90], whereas the opposite would be true for Scheme 2. Some data are given in Table 12.

TABLE 12

Inner-sphere oxidation rates of $[Cr(OH_2)_6]^{2+}$ reacting via Scheme 3

Oxidant	k
$[Ru(H_2O)_5Cl]^{2+}$	$1.2 + 0.36/a_{H^+}$(mole.l^{-1}.sec^{-1})
[*cis*-$Ru(NH_3)_4H_2OCl]^{2+}$	1.2×10^2(sec^{-1})
$[Ru(NH_3)_5Cl]^{2+}$	4.6×10^2(sec^{-1})

E. CONCLUSION

The application of the functional approach in connection with the concept of donicity enables a unified and general description of the effect of a change in the coordination sphere of metal ion complexes on the rates of their substitution and redox reactions. It is now possible for the first time to rationalize diversified kinetic information and to reconcile hitherto unrelated facts. This concept is qualitative by nature and does not allow quantitative predictions. On the other hand it does disclose a number of semiquantitative relationships and it may serve as a useful guide for predicting changes in rates due to changes of ligands, solvents or solvent composition.

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