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Reactivity of transition metal solvates

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ABSTRACT. Reactivity data are generalised for one of the most important classes of complexes, solvates, which are quantitatively nearly unstudied. Various approaches to studying and describing the reactivity are compared with respect to solvation of the reagents and the transition state. The specifics and mechanism of ligand substitution in pure and mixed organic solvents are found. The reactivity of simple (homoleptic) and mixed solvates toward macrocycles is examined in detail using porphyrins as an example. The kinetic method of indicator reactions is applied to porphyrins in order to study the state of transition metal salts in organic solvents and the stability of the coordination spheres of acidosalts (MX_n^{n-2}), acidosolvates (MX_2S_{n-2}) and their transition states. The concentration dependence of the rate constant of an indicator reaction is demonstrated to be due to a change in the inner coordination sphere and a shift of equilibria between the various coordination complexes.

A bibliography with 38 citations is included.

Contents

I. General concepts of the reactivity of complexes 996
II. Kinetics of complexation in organic solvents 1000
III. Indicator reactions and the stability of *d*-metal coordination spheres 1001

I. General concepts of the reactivity of complexes

The reactivity of a compound refers to the rate at which the given compound reacts with others. The rate constant at 298 K, k_v^{298}, is used as a measure of the reactivity of a compound in a series of similar reactions.[1] The number of chemical reactions in which one compound or another participate can be practically infinite. However, the rates differ dramatically from reaction to reaction. Therefore, the reactivity of any compound refers to a specific reaction or at least a specific type of reaction (acid–base, complexation, redox, etc.). The rate constant is related to the free energy of activation

$$\Delta G^{\neq} = -RT \ln k_v - RT \ln \frac{kT}{h}, \quad (1)$$

which is determined by the energy and structural changes occurring during activation in the transition state (Fig. 1). Hence, the numerical values of k_v^{298} and ΔG^{298} are controlled by the mechanistic subtleties of the fundamental reaction step.

The free energy of activation contains two components. These involve energy (energy E or enthalpy of activation $\Delta H^{\neq}$) and structure (entropy of activation $\Delta S^{\neq}$)

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}. \quad (2)$$

According to the basic equation of the theory of absolute reaction rates[2]

$$k_v^{298} = \varkappa \frac{\kappa T}{h} \exp(S_0/R) \exp(-\Delta H_0^{\neq}/RT). \quad (3)$$

For complicated reactions, which include ligand substitution in solvates, the coefficient representing surmounting of the potential barrier by the reagents, $\varkappa$ (transmisison coefficient), cannot be found. It is usually taken equal to unity. The enthalpy of activation is less frequently used in kinetic calculations than the activation energy, which is usually found graphically using the Arrhenius equation. The quantities $\Delta H^{\neq}$ and E are interrlated

$$\Delta H^{\neq} = E - RT. \quad (4)$$

At 298 K, the difference between $\Delta H^{\neq}$ and E is 2.5 kJ mol^{-1}. The enthalpy of activation for a complicated chemical reaction in solution is determined by the energy change resulting from the cleavage of some and the formation of other chemical bonds, the energy difference of electrostatic repulsion and attraction, and the energy changes due to loss or addition of solvent molecules in the transition state. The entropy of activation is related to the probability of forming the transition state, i.e. to the steric relationship of the reaction centres in the reacting reagents. If the solvent actively participates in the reaction (as a reagent and as a strongly solvating species), this is reflected in $\Delta S^{\neq}$. As a rule, desolvation favours conversion from the transition state to the final one and increases $\Delta S^{\neq}$. Conversely, additional solvation reduces the probability of generating the transition state and reduces $\Delta S^{\neq}$. Especially complicated situations are encountered in complexation involving macrocycles where the macrocyclic effect appears.[3] The quantities $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are interrelated for formation of complexes with porphyrins. Desolvation of the reagents in the transition state increases the energy requirements for their activation, i.e. the increase of $\Delta S^{\neq}$ causes $\Delta H^{\neq}$ to increase. Solvation in the transition state is energetically favourable but structurally unfavourable. Therefore, a decrease of $\Delta S^{\neq}$ decreases $\Delta H^{\neq}$. This is known as the kinetic compensation effect,[1] which is mathematically described by

$$\Delta H^{\neq} = a + b\Delta S^{\neq}, \quad (5)$$

where a and b are coefficients. The transition state serves as a manifestation of the chemical form of the mass action.[4] The complexity of this action is reflected in the activation mechanism of the fundamental chemical reaction.

The reactivity of complexes has been well studied and is well documented in a monograph.[5] This refers not to ligand substitution processes in complexes but to a change of the chemical nature of coordinated ligands under the influence of outer-sphere species. There are no broad systematic data for the reactivity of coordination (complex) compounds in substitution reactions of some ligands by

others, except for the case water ⇋ ligand. Existing books[6–8] contain only anecdotal kinetic data for these reactions. Ligand substitution in solvates apparently obeys the same rules as substitution of water molecules in aqua complexes. Their stoichiometric mechanisms[8] are apparently also similar.

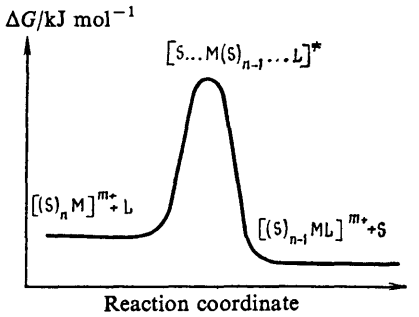


Figure 1. Coordinate and transition state of an $S_N2(I)$ solvate coordination reaction.

Let us examine in general the mechanisms of complexation in solution. The limiting steps of ligand substitution reactions are usually classified by their molecularity. Unimolecular, bimolecular and termolecular reactions differ in the number of species used in forming the transition state (and in activating the reagents). The duration of the fundamental step is $\sim 10^{-13}$ sec. The theory of termolecular reactions in solutions is complicated and not fully solved.[2] Bimolecular reactions are more numerous. Representing as a reagent the ligand (L or X^-) entering the coordination sphere of the complex, these reactions are denoted by the symbol S_N2 (according to Ingold–Hughes). This stands for substitution of a ligand by another nucleophilic ligand in the complex

$$[M\ (S)_n]^{m+} + L \rightleftharpoons [M(S)_{n-1}L] + S \ldots \quad . \tag{6}$$

In this instance, L should be an electron donor, i.e. have an O, N, S, Hal, etc. atom with a negative charge or an electron pair or both. Therefore, H_2O, NH_3, solvents derived from them, H_2S, all solvents with $-S-R$ bonds, $R-S-R$, $R_2S=O$, R_2SO_2, and certain others are nucleophiles. According to the Langford and Gray classification,[8] three types of bimolcular reaction mechanisms can be distinguished: *D*, dissociative; *A*, associative; and *I*, interchange. The *D*-mechanism of substitution includes two steps and presumes two possible routes for its occurrence. If the solvent loss step is fast and the second step of ligand L or X^- addition is slow

$$[M(S)_n]^{m+} \overset{-S}{\rightleftharpoons} [M(S)_{n-1}] \overset{+L}{\rightleftharpoons} [M(S)_{n-1}L], \tag{7}$$

then the $S_N2(D)$ mechanism is observed. If the first step is slow and the second fast, then the reaction wil be monomolecular (its rate does not depend on [L]). Such a mechanism is denoted $S_N1(D)$. Both *D* mechanisms are equally probable. Realisation of one or the other depends on the nature of the metal and solvent. In both instances, the intermediate formed is $M(S)_{n-1}$, a solvate with coordination number smaller than maximal by one unit.

The associative mechanism (*A*) is less probable for solvates since it is caused by deformation of the initial coordination sphere of $[M(S)_n]^{m+}$ by the substituting ligand L

$$M(S)_n]^{m+} + L \rightleftharpoons [M(S)_nL]^{m+} \rightleftharpoons S + [M(S)_{n-1}L]^{m+}. \tag{8}$$

If the coordination number *n* does not reach the maximal value in a given solution, then one stable form of the coordination sphere simply rearranges into another. The species $[M(S)_{n-1}L]$ becomes an intermediate and a stable solvate. On the other hand, the intermediate $[M(S)_nL]^{m+}$ with a strained coordination sphere converts to the stable solvate $[M(S)_{n-1}L]$. This is an example of the $S_N2(A)$ mechanism. Hence, intermediates of different stability with a coordination number greater than *n* of the initial solvate can form in the $S_N2(A)$ mechanism.

The interchange mechanism (*I*) is very common. In this mechanism, movement along the reaction coordinate causes the M–S bond to stretch and then cleave whereas the M–L bond forms and strengthens. Both processes occur simultaneously (Fig. 1). this is the $S_N2(I)$ mechanism

$$[M(S)_n]^{m+}L \rightleftharpoons [L \ldots M(S)_{n-1} \ldots S]^{*} \rightleftharpoons S + [M(S)_{n-1}L]^{m+}. \tag{9}$$

Reactions of this type are often encountered, even in organic chemistry. Their occurrence is due to the large deformation of the coordination sphere or organic radical at which substitution is occurring. Langford and Gray[8] assume incorrectly that an outer-sphere intermediate (for example, $[M(S)_n \ldots L]^{m+}$) is formed in $S_N2(I)$ reactions. An outer-sphere complex forces the reaction to take path *D* or *A* and not the interchange route.

The activation mechanisms of the reacting species or their separate fragments are very important. Langford and Gray[8] prefer to differentiate two activation mechanisms: associative activation (denoted '*a*') and dissociative activation ('*d*'). The symbols '*a*' and '*d*' coincide with (*A*) and (*D*). Obviously the entering group L contributes greatly to activation in stoichiometric *A* processes; the leaving group S, in *D*. Also, interchange mechanisms with associative I_a and dissociative activation I_d, where the principal contribution to the activation comes from the leaving group S, should be differentiated in $S_N2(I)$ processes.

We discovered and studied[9] a large group of $I_{a,d}$ reactions with associative–dissociative activation where the entering and leaving groups contribute equally to the activation. In order to find the stoichiometric mechanism of the reaction (S_N1, S_N2, S_E1, S_E2, *A*, *D*, *I*) It is necessary to study the substitution kinetics, find the kinetic equations and investigate the influence of the nature and concentration of entering and leaving groups on the type of kinetic equation. Fulfilment of a first-order kinetic equation

$$-\frac{dC_{solvate}}{dt} = k_v C_{solvate}, \tag{10}$$

suggests that the substitution reaction is unimolecular, dissociative, and $S_N1(D)$. If a second-order kinetic equation is obeyed

$$-\frac{dC_{solvate}}{dt} = k_v C_{solvate} C_L, \tag{11}$$

a bimolecular associative $S_N2(A)$ or interchange $S_N2(I)$ mechanism is expected.

The mechanistic subtleties, also called the intimate[8] or activational mechanism (this last term is more definitive) must be found by studying the temperature dependence in a series of substitution reactions involving various entering and leaving ligands. The presence or absence of a dependence of the enthalpy of activation

$(\Delta H)^{\neq}$ on the nature of L and S enables the activational mechanism (I_a, I_d or $I_{a,d}$) of the reactions to be defined as interchange substitution of ligands. Due to a lack of experimental data, the mechanism was not examined where activation involves accompanying ligands (X^-) in mixed and similar complexes $[MX_m(S)_{n-m}]$ in addition to inner-complex and macrocyclic compounds.[8] Complicated mechanisms with multi-centered interactions in the transition state are possible here.

Determination of the stoichiometric and activational contributions to the reaction mechanism still does not provide a comprehensive understanding. A model of the transition state must be constructed. The type of reaction centres and orbitals used in the chemical interaction in addition to the role of the solvent in forming the transition state (solvation of the transition state) can be determined by changing the structure of its component parts and the nature of the medium. Quantum-chemical calculations of the potential energy surface must be performed.

Therefore, the term 'reaction mechanism' represents a complicated and gradual transition of the starting reagents into the final products that is examined on a molecular and electronic level.

A large volume of experimental data exists on formation in aqueous solutions of complexes involving metal salts and ligands. Almost all monographs on coordination chemistry in aqueous solutions treat this topic.[6-8,10-15]

The stability of complexes is controlled by the dynamic equilibrium of two opposing processes: substitution of H_2O by ligands (direct process) and substitution of ligands by H_2O (reverse process). The stability constant of a complex K_s reveals which process predominates. If $K_s > 1$, the formtiton reaction predominates; if $K_s < 1$, dissociation prevails. If $K_s = 1$, $k_v^f = k_v^d$.[16] It is very important to obtain data on the mechanism and transition state of both complexation steps. Since complexation (if it is true complexation) is reversible, the reaction passes through the same transition state on moving forward or backward along the reaction coordinate.

Complexation in mixed solvents is more complicated. This can give rise to mixed solvate and ligand coordination spheres $[MX_mS_1S_2]$, $[MX_{m-p}L_pS_1S_2]^{m-p}$, $[ML_mS_1S_2]^{m+}$, $[MS_{1m}S_{2n-m}]$, $[M(S_1)_n]^{m+}$, $[M(S_2)_m]^{m+}$ and all intermediate forms. The quantity K_s in binary solvents (even more complicated in ternary systems) is determined by the simultaneous occurrence of very many reactions in equilibrium with each other. More often than not the dependence of K_s on solvent composition in these complicated systems provides no definitive information on the reaction. For this, the kinetics of all competing reactions must be studied. Such a fruitful approach has previously been used.[17]

Let us examine substitution of water in aqua complexes by other ligands. Analysis of the data in Table 1,[8] which contains experimental values of the rate constants (k_H^{298}, sec^{-1}) for substitution of H_2O in $[Pt(dien)OH]^{2+}$, indicates that the substitution accelerates where the chemical affinity of the ligand for Pt^{2+} increases.

The high rate of 'substitution' by OH^- is not due to the chemical affinity of hydroxide for Pt (it is not large compared with other ligands[11]) but to the extensive inner-sphere ionisation of H_2O. This is supported by the fact that the rate of exchange of Cl^-, Br^- and I^- by X^- is completely independent of the presence of OH^- in solution.[8]

Data for the influence of the nature of the solvent on the rate of substitution of $^{35}Cl^-$ by $^{36}Cl^-$ in *trans*-$[Pt(py)_2Cl_2]$ are presented in Table 2. The substitution includes a formation step of two solvates *trans*-$[Pt(py)_2S(Cl)_2] \rightleftharpoons [Pt(py)_2SCl]^+$ and conversion of the latter into $[Pt(py)_2Cl^{36}Cl]$. It is clear from Table 2 that formation of $[Pt(py)_2Cl_2S]$ or $[Pt(py)_2Cl_2S_2]$ and their conversion into $[Pt(py)_2SCl]^+$ strongly affects the reaction rate and changes its mechanism. The ligand exchange rate is especially high if such solvates are not formed (in C_6H_6 and CCl_4) or if the solvent can solvate the leaving ligand (DMSO, H_2O, CH_3NO_2, ROH). If the solvent can solvate Pt^{II} but not the leaving ligand [DMF, $(CH_3)_2CO$, $CH_3CO_2C_2H_5$], the ligand substitution rates are minimal.

Table 1. Rate of H_2O substitution by a ligand in $[Pt(dien)OH_2]^{2+}$ in aqueous solution at 298 K*.[8]
$[Pt(dien)OH_2]^{2+} + X^- \rightleftharpoons [Pt(dien)X]^+ + H_2O$.

Ligand	$10^2 k_H^{298}$, s^{-1}	Ligand	$10^2 k_H^{298}$, s^{-1}	Ligand	$10^2 k_H^{298}$, s^{-1}
Cl^-	0.52	NO_2^-	0.090	OH^-	very fast
I^-	3.9	SCN^-	1.45	Py	0.19

*The uncertainty in the rate constants given here and below is from 5 to 20%.

Table 2. Solvent influence on exchange rate of Cl^- in *trans*-$[Pt(py)_2Cl_2]$ at 298 K.[8]

Solvent	$10^5 k_H$, s^{-1}	Solvent	$10^5 k_H$, s^{-1}
H_2O	3.5	DMF	10^{-3}
DMSO	380	$(CH_3)_2CO$	10^{-2}
CH_3NO_2	3.2	$CH_3COOC_2H_5$	10^{-2}
C_2H_5OH	1.3	*m*-$C_6H_4(CH_3)OH$	10^{-1}
n-C_3H_7OH	0.42	C_6H_6	10^2
trans-C_4H_9OH	0.10	CCl_4	10^4

The ligand substitution rate depends mainly on solvation of the leaving ligand X^- in complexes where the central atom is coordinatively saturated and is incapable of further solvation, for example, $[Co(en)_2X_2]^+$ (Table 3).

Before commenting on Table 3, attention should again be drawn to the very unfortunate terminology that for some unknown reason complicates the coordination chemistry of ligand substitution reactions.[6-8] This concerns solvolytic dissociation of acidocomplexes, for example:

$$[CoL_mX_{n-m}]^{z+} + S \rightleftharpoons [CoL_mX_{n-m-1}(S)]^{z+1} + X^-, \qquad (12)$$

in which the Co–X bond is completely broken by the solvent. If H_2O acts as S, then reaction (12) represents hydrolytic dissociation. Reactions of type (12) have incorrectly been called 'solvolysis' or 'hydrolysis'[6-8] since in general chemistry hydrolysis (solvolysis) means splitting of water (solvent) into ions with subsequent bonding

by a cation, anion or neutral molecule. Therefore, the term 'acid hydrolysis' in the sense used before[6,8] does not correspond to the actual process. The term 'base hydrolysis' is just as incorrect.[6,8]

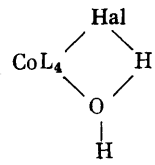
Table 3. Rate of hydrolytic dissociation of the Co–X bond at 298 K in Co^{III} complexes.[8]
$[CoL_mX_{n-m}]^{z+} + H_2O \rightleftharpoons CoL_mX_{n-m-1}(H_2O)]^{z+1} + X^-$.

Complex type	Ancillary ligand (L)	Leaving ligand (X^-)	Rate constant, $10^4 k_v$, sec^{-1}
$[Co(L)_2Cl_2]^+$	en	Cl^-	0.32
$[Co(L)_2Cl_2]^+$	1.2-pn	Cl^-	0.62
$[Co(L)_2Cl_2]^+$	2.3-bn (*d, l*)	Cl^-	1.5
$[Co(L)_2Cl_2]^+$	2.3-bn (*meso*)	Cl^-	4.2
$[Co(L)_2Cl_2]^+$	$H_2N-[C(CH_3)_2]_2-NH_2$	Cl^-	330
$[CoL_4L'X]^{2+}$	NH_3, H_2O	Cl^-	$2.2 \cdot 10^{-2}$ *
trans-$[CoL_4X_2]^+$	NH_3	Cl^-	18
cis-$[CoL_4X_2]^+$	NH_3	Cl^-	very fast
$[CoL_5X]^{2+}$	NH_3	Br^-	$6.3 \cdot 10^{-2}$
trans-$[CoL_2L'X_2]^+$	en, NH_3	Br^-	$1.2 \cdot 10^{-2}$
trans-$[CoL_2X_2]^+$	en	Br^-	1.4
trans-$[CoL_2XX']^+$	en	Br^-, NO_2^-	40
cis-$[CoL_2X_2]^+$	en	Cl^-	2.5
cis-$[CoL_2L'X]^{2+}$	en, NH_3	Cl^-	$1.4 \cdot 10^{-2}$ **
trans-$[CoL_2L'X]^{2+}$	en, NH_3	Cl^-	$4.0 \cdot 10^{-3}$
cis-$[CoL_2XX']^+$	en	Cl^-, NO_2^-	1.1
trans-$[CoL_2XX']^+$	en	Cl^-, N_3^-	2.5
$[CoL_5X]^{2+}$	NH_3	NO_3^-	0.27
$[CoL_5X]^{2+}$	NH_3	I^-	0.083
$[CoL_5X]^{2+}$	NH_3	Br^-	0.063
$[CoL_5X]^{2+}$	NH_3	Cl^-	0.017
$[CoL_5H_2O]^{3+}$	NH_3, H_2O	NH_3	0.058
$[CoL_5X]^{2+}$	NH_3	SO_4^{2-}	0.012
$[CoL_5X]^{2+}$	NH_3	$H_2PO_4^-$	$2.6 \cdot 10^{-3}$
$[CoL_5X]^{2+}$	NH_3	CH_3COO^-	$1.2 \cdot 10^{-3}$
$[CoL_6]^{3+}$	NH_3	NH_3	10^{-6}
$[CoL_5X]^{2+}$	NH_3	F^-	$8.6 \cdot 10^{-4}$
$[CoL_5X]^{2+}$	NH_3	SCN^-	$5.0 \cdot 10^{-6}$
$[CoL_5X]^{2+}$	NH_3	N_3^-	$2.1 \cdot 10^{-5}$
$[CoL_5X]^{2+}$	NH_3	NO_2^-	very slow
$[CoL_5X]^{2+}$	NH_3, OH^-	NH_3	very slow
$[CoL_5X]^{2+}$	NH_3	PO_4^{3-}	very slow
$[CoL_4L'X]^{2+}$	NH_3, H_2O	Cl^-	0.035
$[CoX_5X']^{3-}$	X=CN⁻	$X=N_3^-$	$5.8 \cdot 10^{-4}$
$[CoX_5X']^{3-}$	X=CN⁻	X^-=SCN⁻	$2.7 \cdot 10^{-4}$

* T=293 K; ** T=308 K.

Investigation of ligand (Cl^-, Br^-) substitution in Co^{III} complexes with a mixed coordination sphere containing covalently bound and difficultly exchangeable molecular ligands [NH_3, en = $NH_2(CH_2)_2NH_2$; 1,2-pn = $CH_3CH(NH_2)CH_2NH_2$; 2,3-bn = $CH_3CH(NH_2)CH(NH_2)CH_3$] and relatively readily substituted acidoligands enables some useful conclusions to be drawn (Table 3). Chelating ligands (diamines) hinder dissociation of the $Co^{III-Hal}$ bond (where Hal is a halogen) more than NH_3. However, adding methyls to the diamine increases the rate of dissociation by weakening the Co–Hal bond and creating steric hindrances that stabilise the $[CoL_2Hal]^{z+}$ species with coordination number 5. Therefore, the rate constant for removal of Cl^- from the tetramethylethylenediamine complex is three orders of magnitude greater than that for the ethylenediamine complex. Obviously the dissociation takes the same path, *D*, with preliminary loss of Cl (Br^-) due to solvation and substitution by H_2O. The *trans*- and *cis*-effects are evident in $[CoL_2X_2]^+$ and $[CoL_4X_2]^+$ in which L is a diamine or NH_3, respectively. The presence of NO_2^- or N_3^- *trans* to Cl^- accelerates dissociation of the Co–Cl bond by 4–8 times. An analogous effect of Br^- on a bond *trans* to Co–Br is seen. Susbtitution of NH_3 by Br^- in the position *trans* to Br^- in *trans*-$[Co(en)_2LX]^{2+}$ accelerate the reaction by almost two orders of magnitude.

In an analogous situation, Cl^- weakens the Co–Cl bond by almost 200 times. The *cis*-effect was unexpectedly large in Co^{III} complexes. The *cis*-effect in these Co^{III} complexes is apparently even stronger than the *trans*-effect. All of the changes in the dissociation rate are probably not assignable to only the electronic influence of the atom *trans* or *cis* to the Co–Hal bond. An analysis of Table 3 leaves no doubt that other factors, especially solvation, play a large role. For example, the *cis*-effect in Co^{III} complexes on dissociation in H_2O can be visualised as stabilisation of species



due to an intramolecular H-bond.

Data on the structural and energy activation parameters and systematic investigations of the kinetics in nonaqueous and mixed solvents are not available. Therefore, the role of solvation in solvolytic dissociation of Co^{III} complexes cannot be found.

The mechanism of substitution of an anion X^- by water or a molecule of another solvent is apparently very complicated.[6] The role of the H-bond $X^-...H_2O$, which should be large, is not overlooked. The rate of cleavage of Co–X in $[CoL_5X]^{2+}$ increases in the halide series from F^- to I^- (for F, Cl, Br and I, k_v is 8.6×10^{-4}, 1.7×10^{-2}, 6.3×10^{-2} and 8.3×10^{-2} sec^{-1}, respectively). The reduction of the Co–X bond strength in this order affects the dissociation kinetics. Other anions in aqueous solution fall into the following order of dissociation rate: NO_3^- (0.27) > SO_4^{2-} (0.012) > $H_2PO_4^-$ (2.6×10^{-3}) > $CH_3CO_2^-$ (1.2×10^{-3}) > N_3^- (2.1×10^{-5}) > SCN^- (5×10^{-6}). This also clearly demonstrates the role of strengthening the Co–X bond in the dissociative mechanism *D*. Apparently a drop in the rate generally corresponds to an increase in K_s of $[Co(NH_3)_5X]^{2+}$.[6]

The K_s of these complexes borrowed from previous work[6] are presented in Table 4. Comparison of k_v and K_s indicates that a known correlation exists between the ease of breaking the Co–X bond and the stability of $[Co(NH_3)_5X]^{2+}$.

However, the relative dissociation rates and K_s do not agree. It should be remembered that K_s is not a measure of the M–X bond strength since formation of the complex in solution is related to desolvation of the reagents. The results presented in Table 3 leave open the possibility that Co^{III} complexes and those of other M^{III} dissociate by an interchange mechanism $S_N2(I_{a,d})$. The dissociation rate constants of $[CoL_4Cl_2]^{2+}$ can be several hundreds of times greater than k_v^{298} of $[CoL_5Cl]^{2+}$ whereas the corresponding ones for Rh^{III} complexes are the same. This suggests a possible bimolecular *cis* attack of the reagent (including solvent molecules) on the central atom near the Co–X bond.[6] For strongly covalent Rh^{III} chloride complexes, the attacking molecules contribute insufficiently to activation of a system reacting by the S_N2 mechanism to cause it to occur.

Kinetic data for substitution reactions of water in octahedral Co^{III} complexes and in other M^{III} and M^{II} complexes are very interesting to the chemistry of solvates.

Table 4. Rate constants of $[Co(NH_3)_5X]^{2+}$ at 298 K in aqueous solution.[6]
$[Co(NH_3)_5H_2O]^{3+} + X^- \leftrightharpoons [Co(NH_3)_5X]^{2+} + H_2O$.

Anion	K_s^{298}	Anion	K_s^{298}	Anion	K_s^{298}
NO_3^-	0.018	SO_4^{2-}	12.4	NO_2^-	10^{10}
Br^-	0.37	F^-	25	H_2O	0.018
Cl^-	1.25	CNS^-	470	NH_3	$2.5 \cdot 10^4$
$H_2PO_4^-$	7.4	OH^-	$2 \cdot 10^8$	–	–

Table 5. Kinetic parameters of H_2O substitution in the coordination sphere of $[CoL_5H_2O]^{3+}$, where L = NH_3, at 298 K in aqueous solutions.[6]
$[Co(NH_3)_5(H_2O)]^{3+} + X^- \leftrightharpoons [Co(NH_3)_5X]^{2+} + H_2O$.

X⁻	k_v, $dm^3\ mol^{-1}\ sec^{-1}$	Outer-sphere association constant*, sec^{-1}	Outer-sphere–inner-sphere conversion constant**, sec^{-1}
Cl^-	$2.1 \cdot 10^{-6}$	–	–
Br^-	$2.5 \cdot 10^{-6}$	–	–
NO_3^-	$2.3 \cdot 10^{-6}$	–	–
CNS^-	$1.3 \cdot 10^{-6}$	4.5	$2.9 \cdot 10^{-7}$
$H_2PO_4^-$	$2.0 \cdot 10^{-6}$	2.75	$7.3 \cdot 10^{-7}$
SO_4^-	$1.5 \cdot 10^{-5}$	11.2	$1.3 \cdot 10^{-6}$
NH_3	$2 \cdot 10^{-6}$	–	–
H_2O	$6.6 \cdot 10^{-6}$	–	$6.6 \cdot 10^{-6}$

*Formation constant of the associate of the complex with X^-.
**Conversion with loss of H_2O.

Rate constants for H_2O substitution in $[Co(NH_3)_5H_2O]^{3+}$ are given in Table 5. The substitution rate of H_2O by the acidoligand in octahedral monosolvates within experimental and calculational uncertainty is independent of the nature of X^- and averages $k_v \approx 2 \times 10^{-6}$ $dm^3\ mol^{-1}\ sec^{-1}$. Such a small rate constant is indicative of a rather covalent $Co^{III}-H_2O$ bond. Even for NH_3 the rate constant of H_2O substitution has such a value. The rate of exchange of H_2O by SO_4^{2-} is slightly greater. There is no doubt that the substitution reaction of H_2O in octahedral Co^{III} complexes follows the dissociative mechanism S_n1 (or D)

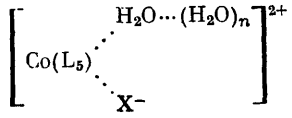
$$[CoL_5H_2O]^{3+} \underset{\text{fast}}{\overset{\text{slow}}{\rightleftharpoons}} [CoL_5]^{3+} + H_2O, \quad (13)$$

$$[CoL_5]^{3+} + X^- \underset{\text{slow}}{\overset{\text{fast}}{\rightleftharpoons}} [CoL_5X]^{2+}. \quad (14)$$

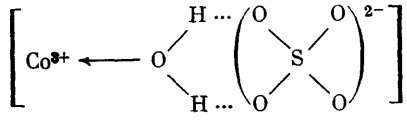
Therefore, the mechanism here is different from that of $[ML_3H_2O]^{2+}$, where M = Pt^{II} and others.

It has been proposed[6] that reaction (13) passes through formation of an outer-sphere encounter complex and that anion X^- enters the inner sphere from the outer. However, this does not provide a very detailed mechanism since outer-sphere associates (complexes) occur in practically all solutions of complexes and participate in practically all reactions. The intermediate $[CoL_5]^{3+}$ apparently does not accumulate (the probability of its formation is very small) during reaction of $[CoL_5H_2O]^{3+} + X^-$. It is a highly reactive species and reacts immediately. The high charge of the central atom facilitates this. The water exchange rate, i.e. dissociation of the $M-OH_2$ bond, in $[M(H_2O)_6]^{2+}$ is very fast[17] (k, sec^{-1}: Cr^{2+}, 7×10^9; Mn^{2+}, 3×10^7; Fe^{2+}, 3×10^6; Co^{2+}, 10^6; Ni^{2+}, 3×10^4; Cu^{2+}, 8×10^9).

Owing to the low covalency of the $M^{II}-H_2O$ bond in octahedral complexes, the probability of removing a water molecule from the coordination sphere of $[M(H_2O)_6]^{2+}$ is very large. Therefore, intermediates $[M(H_2O)_5]^{2+}$ are formed in one concentration or another on coordination of aquasolvates with various ligands. A different situation ensues for M^{3+} solvates. The transition state arising through exchange of a solvent molecule for X^- in octahedral complexes sterically shielded by ligands can be represented as the system



with a Co...OH_2 bond. From this H_2O migrates into the bulk solvent (into a vacancy in the second corodination sphere). As a result, a very weak bond to X^- forms. The reaction occurring by this path is second-order. The constant k_v in this instance does not depend on the nature of X^- since the energy demands for activation with any X^- are determined by the same process, cleavage of the $Co^{III}-OH_2$ bond and removal of H_2O. Entry of SO_4^{2-} (Table 5) into the Co^{III} aquasolvate introduces substantial corrections into the process since removal of H_2O is enhanced by SO_4^{2-}. There is a probability of forming the associate



II. Kinetics of complexation in organic solvents

We will now examine the reactivity of complexes in nonaqueous solvents, without touching upon the broad range of aqueous–organic solutions where the composition of the solvates is, as a rule, unknown. It has been correctly noted[6] that ability to investigate the kinetics and mechanisms of a reaction involving complexes in nonaqueous media is limited by the very low solubility of many complexes.

A very important feature of complexation in organic solvents[16] is the weaker solvation of simple acidoligands and the strong solvation of complicated organic acidoligands, especially inner-sphere types. Water readily forms solvates of simple inorganic acidoligands (F^-, Cl^-, Br^-, I^-, NO_3^-, ClO_4^-, SO_4^{2-}, etc.) and enhances solvolytic dissociation of complexes with these ligands and formation of simple solvates. If the acidoligand contains a hydrocarbon residue, water does not solvate it. Such an anion is unstable in aqueous solution

and remains within the complex or in the solid as a salt. The opposite picture is seen in many organic solvents.

Transition metal cations can be solvated more strongly in nonaqueous solvents than in water [for example, DMSO, DMF, NH_3, amines, simple chain polyethers (glymes), crown ethers, their N and S derivatives, etc.[18]] and more weakly (alcohols, simple monoethers, ketones, carboxylic esters, alkylsuphides, alkylphosphines, etc.). Solvation can be practically absent (alkanes, cycloalkanes) or very weak (alkenes, arenes).

Hence, the contribution of partial or complete loss of the solvation sphere on complexation in organic media to the energy and entropy of activation can be greater or less than in aqueous medium.

It is usually weaker than in H_2O. The structuring of the organic solvents can have a substantial effect on the reactivity of solvates. The possibilities of outer-sphere complexation and substitution of X^- in octahedral complexes (Table 6) with release of them into the outer sphere drop sharply.

Table 6. Rate constants of Co—X bond dissociation in organic solvents (k_v, sec^{-1}) at 303 K.[6]

Solvent	Complex		
	trans-$[Co(En)_2Cl_2]^+$	*trans*-$[Co(En)_2NO_2(Cl)]^+$	*trans*-$[Co(En)_2NO_2(Br)]^+$
H_2O	$1.2\cdot10^{-4}$	$2.8\cdot10^{-3}$	$4.2\cdot10^{-3}$
DMSO	$3.7\cdot10^{-5}$	$1.4\cdot10^{-4}$	$8.0\cdot10^{-4}$
DMF	$5.8\cdot10^{-6}$	$5.4\cdot10^{-5}$	$6.9\cdot10^{-4}$
Methanol	$2.0\cdot10^{-5}$	$2.0\cdot10^{-4}$	–

The rate of solvolytic dissociation of the Co^{III}—Hal bond decreases in the order H_2O > DMSO, CH_3OH > DMF. This is probably a result of the decreased total chemical affinity of the solvent for Hal and Co^{III}.

The ability of Co^{III} cationic complexes to form outer-sphere associates with X^- depends on the *cis*- or *trans*-configuration of $[CoL_4XY]^+$ and is determined by the size of the dipole moment of the complexes, the relative permittivity of the solvent and the degree of solvation of X^-.[6] Outer-sphere complexes (ion pairs) are formed more readily for *cis*-complexes than for *trans*-complexes.

A large amount of experimental data has been accumulated on reactions of *d*-metal solvates with porphyrins.[9,19] Porphyrins are far from the only ligands that can be used effectively to study the complex-forming reactivity of *d*-metal solvates.

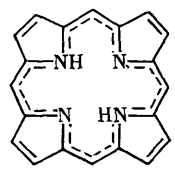
The method developed has been called the kinetic method of porphyrin indicator reactions.

III. Indicator reactions and the stability of *d*-metal coordination spheres

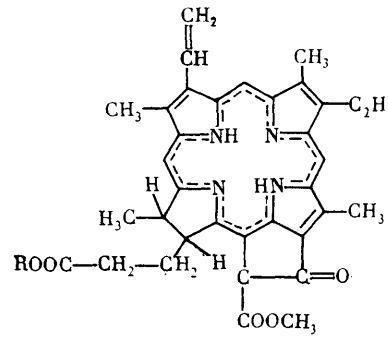
An indicator reaction between a solvate and a porphyrin (H_2P) (I) to form a porphyrin complex (MP)

$$[MX_mS_{n-m}] + H_2P \rightarrow MP + 2HX + (m-2)X^- + (n-m)S, \quad (15)$$

is a unique instrument for studying various solvate coordination spheres. Their composition in various salts, the relative stability of the M—S bond, and the variability as a function of solvent can all be found.[9,19,20]



(I)
Porphyrin nucleus



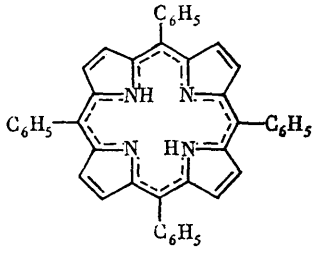
(II)
Chlorophyll ligand ($R = C_{20}H_{39}$)

A series of studies[21–28] has been carried out on the influence of the organic solvent and the structure of the transition-metal coordination sphere on the kinetics of complex formation with the most important natural porphyrin, the chlorophyll ligand (II). It was discovered that the inner coordination sphere of the metal determines the rate in addition to the energy and entropy of activation of the coordination. Therfore, coordination of H_2P by metal salts was called[20] the kinetic indicator reaction of porphyrins. The kinetic parameters of these reactions are very sensitive to the composition of the metal solvate coordination sphere, i.e. to the number and nature of ligands S and X^-.

Indicator reactions of porphyrins lie at the base of the kinetic method for studying the structure and properties of solvates. There apparently are few ligands that can be used successfully to study the change of composition, structure and properties of metal solvates as a function of concentration, solvent, temperature, the presence of force fields, etc., owing to the stringent requirements placed on kinetic indicator reactions.[20] The kinetic indicator reaction (15) should have a simple stoichiometry, i.e. its product should be the 1:1 complex (one metal per one ligand). Complexes with the indicator ligand should be kinetically and thermodynamically stable.[9] They should retain their composition and geometric configuration over the whole range of concentration changes of the coordinating solvent S and the acidoligands X^-. The reaction should proceed slowly enough to be easily controlled by ordinary chemical kinetics. One of the reagents should have a specific, accurately determined property, for example, a distinctive electronic absorption spectrum (EAS) with strong absorption bands. Porphyrins satisfy all these requirements. They form highly stable complexes MP of 1:1 composition. Their rate of formation is easily measured. Metalloporphyrins have distinctive EAS with very large molar absorption coefficients (ε) that reach 200 000. Therefore, formation of metal complexes with porphyrins is an ideal indicator reaction enabling a retention or change of the $[MX_m(S)_{n-m}]$ coordination sphere to be easily and quickly detected.

Ethanol homosolvates of MCl_2 (M = Fe, Co, Cd, Hg and Pd), $M(NO_3)_2$ (M = Co, Ni, Cu, Zn, Cd and Ag), $M(CH_3CO_2)_2$ (M = Co, Ni, Cu and Zn), MI_2 (M = Cd and Hg),[21–26] homosolvates of $Cu(CH_3CO_2)_2$ with monohydric alcohols, acetone, ethylacetate, dioxane, CH_3CO_2H, DMF, py and XL,[27–29] binary heterosolvates of $Cu(CH_2CO_2)_2$ and $Zn(CH_3CO_2)_2$ in CH_3CO_2H—ROH (R = CH_3,

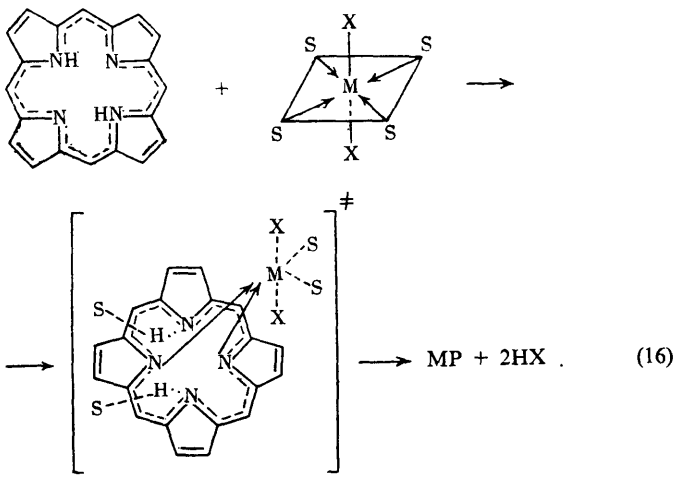
C_2H_5, C_5H_{11}), CH_3CO_2H-py, CH_3CO_2H-dioxane, CH_3CO_2H-acetone,[20,30] binary heterosolvates of Co^{II} and Zn^{II} acetates in CH_3CO_2H-ethylacetate, CH_3CO_2H-ethyleneglycol, CH_3CO_2H-monoethanolamine, $CH_3CO_2H-CH_3OH$, CH_3CO_2H-DMF, $CH_3CO_2H-DMSO$, CH_3CO_2H-py, $CH_3CO_2H-H_2O$, $CH_3CO_2H-n-C_4H_9OH$ [31] and other solvates have been studied using indicator reaction (15) and II and tetraphenylporphine (III) as ligands. Systematic investigations carried out in our laboratory and those of others[9,20,31,32] demonstrated that the reaction of solvates of divalent 3*d*-metals with porphyrins in organic solvents follows very complicated kinetic laws.



(III)

The formation rate of MX_2 complexes with II, III and other porphyrins in addition to the energy and entropy of activation of reaction (15) are determined primarily by the steric relationship of both reagents, i.e. the macrocyclic effect;[3] the electronic structure of the porphyrin reaction centre (H_2N_4); the nature of the chemical bond $M^{2+}\leftarrow S$, i.e. the nature of M and S; the presence of acidoligands X^- in the inner sphere and their number and nature; the compatibility of the various solvents S_1, S_2, etc., in the inner sphere of heterosolvates; the polarity and donor–acceptor nature of solvents S_1, S_2, etc. as media in which the reagents are activated, the solvation or desolvation of the transition state $[MX_2.H_2P]^{\neq}$; the removal of H^+ and X^- after overcoming the potential barrier; and the formation of metalloporphyrins MP or their solvates $(S)_iMP$.[33]

Compared with all other known complexation reactions, indicator reaction (15) proceeds extraordinarily slowly. Its rate typically is 10^6 times less than that of the other reactions. The bimolecular multicentered mechanism, denoted $S_{EN}2$ by the Ingold–Hughes classification or $I_{a,d}$ by Langford–Gray, is responsible for this. The transition state is formed by loss of two solvent molecules (S) from the inner sphere of the solvate, the weak coordinative interaction M←P, and lengthening of the two N–H...S bonds in the porphyrin:



$\longrightarrow MP + 2HX$. (16)

The reaction with porphyrins of coordinatively saturated complexes, for example $HgCl_4^{2-}$ or HgI_4^{2-}, that do not contain solvent molecules also follows a bimolecular mechanism.[9] In this instance atoms are not lost from the coordination sphere as the transition state is approached. The coordination sphere of MX_4^{2-} in the transition state is probably only deformed. This produces instead of the tetrahedral configuration a distorted octahedron with two vacant coordination sites that are necessary for bonding to two tertiary N atoms of the porphyrin. The reaction mechanism is also denoted $S_{EN}2$. The octahedral acidocomplexes $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_5H_2O]^{2-}$ or the covalent molecular-ligand complexes $[Co(NH_3)_6]^{3+}$ and $[Co(NH_3)_5H_2O]^{3+}$ do not have the required number (two or more) of solvent molecules to experience compression of the coordination sphere. Therefore, the above salts cannot react with porphyrin even under forcing conditions.

Porphyrins are molecular ligands that lose two H^+ during complex formation. Therefore, complexation reaction (15) follows a $S_{EN}2$ mechanism. Hence, H_2P is simultaneously electrophilic and nucleophilic.

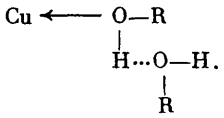
Table 7. Kinetics of formation of Cu(Chl) from $[CuAc_2(S)_4]$ and the chlorophyll ligand in organic solvents (S).[9]

S	k_7^{298}, $dm^3\ mol^{-1}\ sec^{-1}$	E, $kJ\ mol^{-1}$	$\Delta S^{\neq}$, $J\ mol^{-1}K^{-1}$	*DN* *
CH_3OH	4.45	58	−17	(30)
C_2H_5OH	1.65	44	−96	(32)
n-$C_5H_{11}OH$	0.555	113	126	(25)
CH_3COCH_3	0.905	46	−67	17
$O(CH_2CH_2)_2O$	0.046	72	−25	14.8
CH_3COOH	5.30	44	−79	20
$(CH_3)_2NCHO$	0.036	79	−8	26.6
C_5H_5N	0.0092	96	37	33.1
C_9H_7N	0.028	100	+63	32
$CH_3COOC_2H_5$	0.515	61	−63	17.1

*Estimated *DN* are given in parentheses.

An examination of the indicator reaction mechanism would seem to indicate that its rate and activation parameters should depend on the structure and stability of the inner coordination sphere in general and on the structure and stability of the solvation sphere in particular. The rates of formation of complexes from homosolvates of $[CuAc_2(S)_4]$ in various solvents are listed in Table 7. The stability constants of the homosolvate salts have not been determined. The relative stability of the copper acetate solvation sphere can be judged from the donor numbers (*DN*). It is clear from Table 7 that the reaction rate tends to decrease at the same time as the activation energy increases and *DN* increases, i.e. as the strength of the Cu–S bond increases and the solvation sphere becomes stronger. However, there are several exceptions to this rule. Methanol forms a stronger solvate and reacts faster than ethanol and especially propanol. Attention should be drawn to the donor numbers in parentheses in Table 7. In alcoholic solutions $SbCl_5$ is extensively solvolysed. Therefore, it is difficult to determine the electron-donating ability of alcohols relative to $SbCl_5$.

In estimating the change of electron-donor properties of various alcohols relative to metal salts, their structure and known properties should be considered. Methanol should form stronger solvates than ethanol firstly because conditions are favourable for formation of a second solvation sphere in its solvates. This second sphere stabilises the first by forming H-bonds to coordinated CH_3OH. As the alkyl chain lengthens, steric hindrances to the interaction are created



This interaction facilitates formation of the second and successive alcohol solvate spheres. Secondly, the electron-donor ability of the electron pair of the alcohols depends little on the size of the alkyl group, i.e. on its inductive effect. Therefore, the electron- and proton-donor properties of uncoordinated CH_3OH and C_2H_5OH are almost identical. The higher $\Delta S^{\neq}$ and E for methanol are due to the presence of a second solvation sphere.

The rate of coordination of solvates by porphyrins is affected by the exchange conditions of coordinated solvent molecules with the medium. The rate of exchange substantially decreases and the conditions for it worsen for alcohols as the length of the alkyl chain and other large molecules increases. This feature of solvates formed by large molecules has been called steric hindrances of the solvation sphere.[9] They are created during attack of the solvation sphere of such a hugh reagent as a porphyrin. We are inclined to assign the increase in energy and entropy of activation and the decrease of reaction rate of $CuAs_2$ solvates with pentanol, dioxane, DMF, py and quinoline to steric hindrances of the solvation sphere. As we suppose, such hindrances lead not only to loss of two solvent molecules but also to deformation of the remaining sphere of ancillary ligands.[34] There is no doubt that steric hindrances created by a huge coordination sphere will affect the kinetics of reactions between many large ligands with a shielded reaction centre.

An important property of the indicator reaction (15) is the dependence of its rate on the concentration of a 3*d*-metal salt (the so-called 'concentration' dependence of the rate constant) and of a coordinating or uncoordinating salt background,[25,26,35] where the porphyrin does not change but the structure of the coordination sphere of the 3*d*-metal salt does. Results characterising the influence of concentration of 3*d*-metal salt on the formation rate of chlorophyll (Chl) analogues with Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+} and Cd^{2+} are presented in Table 8.

Evidently the coordination spheres of $[CuAc_2(C_2H_5OH)_4]$ are rather stable as the salt concentration changes from 2.5×10^{-4} to 25×10^{-4} mol dm^{-3} since the concentration dependence of k_v is very weak. The dependence of k_v on salt concentration increases in the order $CdAc_2 < Co(NO_3)_2 < Ni(NO_3)_2$. This order apparently corresponds to the ease with which the composition and structure of the coordination sphere changes and the number of solvate forms increases, i.e. the stability of the coordination sphere of $[MX_2(S)_4$ decreases.

Therefore, the kinetic method of porphyrin indicator reactions enables the uniqueness or variety of solvate coordination spheres to be judged. It follows from Table 8 that ethanol solvates of Ni^{2+} and especially Co^{2+}, compared with those of Cu^{2+} and Cd^{2+}, have a much lower ability to complex porphyrins. However, the reactivity of solvates can depend strongly on the nature of the porphyrin and solvent. It is important that not only k_v but also more frequently E and $\Delta S^{\neq}$ change on changing the composition of the solvate.[9,19,26,35]

The methanol solvate of $CoCl_2$ (Table 9) has many forms in solution. Therefore, the concentration dependence of k_v is very strong. Increasing the concentration of $CoCl_2$ in methanol shifts the equilibrium toward the stable forms of low reactivity. The situation is the same for $CoAc_2$ in methanol.

Table 8. Coordination-sphere stability of solvates and concentration dependence of formation rate constants (k_v) of metalloporphyrins, chlorophyll (MChl) analogues, in ethanol at 298 K.[9]
$MX_2 + H_2Chl \rightarrow MChl + 2\,HX$.

MX_2	$10^4\,C_{MX_2}$, M	True k_v, dm^3 mol^{-1} sec^{-1}	E, kJ mol^{-1}	$\Delta S^{\neq}$, J mol^{-1} K^{-1}
$CdAc_2$	1.25	1.55	13	−62
	3.75	1.55	–	–
	25	0.75	–	–
$Zn(NO_3)_2$	2.5	0.415	59	−67
	25	0.0720	59	−52
$Co(NO_3)_2$	25	0.00295	100	44
	250	0.00189	75	−44
$Ni(NO_3)_2$	2.5	0.0394	99	60
	25	0.0095	65	−64
$CuAc_2$	2.5	1.64	44	−109
	25	1.60	44	−109

Table 9. Influence of a salt background on coordination-sphere stability of methanol solvates in Co(Chl) formation reactions.[20]
$H_2Chl + [CoX_m(S)_{n-m}] \rightarrow Co(Chl) + 2\,HX + (m-2)\,X^-$.

Reagent salt MX_2	Background salt MX	Concentration of reagent salt, $c\,10^3$ M	k_v^{298}, dm^3 mol^{-1} sec^{-1}	E, kJ mol^{-1}	$\Delta S^{\neq}$, J mol^{-1} K^{-1}
$Co(NO_3)_2$	–	2.5	$2.56 \cdot 10^{-3}$	43	−161
$Co(NO_3)_2$	3M $LiNO_3$	2.5	$2.40 \cdot 10^{-2}$	56	−87
$CoCl_2$	–	2.5	$1.78 \cdot 10^{-3}$	65	−93
$CoCl_2$	–	25	$3.10 \cdot 10^{-4}$	67	−87
$CoCl_2$	2M LiCl	2.5	$4.90 \cdot 10^{-3}$	52	−114
$CoCl_2$	2M LiCl	25	$1.89 \cdot 10^{-3}$	50	−128
$CoAc_2$	–	2.5	$1.32 \cdot 10^{-2}$	99	+52
$CoAc_2$	–	25	$3.40 \cdot 10^{-3}$	83	−15
$CoAc_2$	2M LiAc	2.5	$1.11 \cdot 10^{-3}$	–	–
$CoAc_2$	2M LiAc	25	$1.13 \cdot 10^{-3}$	86	−12

Addition of LiAc stabilises the form $[CoAc_4]^{2-}$. This causes the dependence of k_v on $CoAc_2$ concentration to vanish.

A detailed analysis of the kinetic data demonstrated that the dependence of k_v (and also E and $\Delta S^{\neq}$) on 3*d*-metal salt concentration is mainly determined by the change of properties of $MX_2(S)_{n-2}$. Similar changes of k_v in aqueous solutions have usually

been ascribed to a change of the salts activity coefficient. For the example involving 3*d*-metal salts in organic solvents that are incapable of solvolytic dissociation

$$MX_2(S)_{n-2} \overset{+S}{\rightleftharpoons} [MX(S)_{n-1}]^+ + X^- \quad (17)$$

$$[MX(S)_{n-1}]^+ \overset{+S}{\rightleftharpoons} [M(S)_n]^{2+} + X^- \quad (18)$$

the reaction proceeds without involving the ions, i.e. with a small change of salt activity coefficient as classically interpreted.

As the salt concentration increases, the geometry of the solvate can change owing to a shift of autocomplexation equilibria, the isomerisation *cis*-octahedron $\rightleftharpoons$ *trans*-octahedron, changes in the degree of solvation

$$MX_2(S)_4 \rightleftharpoons MX_2(S)_2 + 2S,$$

loss of the second solvation sphere, a reduction of the solvating ability of the solvent, salt dimerisation, etc.

In this instance, the lack of a concentration dependence of k_v (and also $\Delta S^{\neq}$ and E) is consistent with a stable salt coordination sphere within the given concentration range. On the other hand, the presence of such a dependence means that the initial coordination sphere is unstable and changes.

Kinetic data for the indicator reaction (15) occurring in the presence of a salt background (Table 9) suggest whether the complex coordination sphere is stable and if stabilising conditions can be found.

It follows from Table 9 that the inert (noncoordinating) background salt $LiNO_3$ has a different effect from that of a coordinating salt (LiCl, LiAc) which can provide inorganic ligands (Cl^-, Ac^-) for the Co^{II} solvate.

Lithium nitrate does not change the EAS of $Co(NO_3)_2$. It can be concluded on the basis of the EAS[35] that $Co(NO_3)_2$ in methanol exists as the octahedral complex $[Co(CH_3OH)_6]^{2+}$. In the presence of $LiNO_3$, ion pairs of the type shown below can form

$$Co^{2+} \longleftarrow \overset{CH_3}{\underset{|}{O}}—H\cdots NO_3^-$$

and partially $Co^{2+} \leftarrow NO_3^-$.

Therefore, NO_3^- ions reduce the stability of the solvate. The formation rate of Co(Chl) increases almost 10 times on adding $LiNO_3$. The energy and entropy also considerably increase. Free methanol molecules are practically nonexistent in 3 M $LiNO_3$. Therefore, the acceleration of the indicator reaction can be attributed to weakening of the bonds in the fragments

$$Co^{2+} \longleftarrow \overset{CH_3}{\underset{|}{O}}—H,$$

associated with NO_3^- in addition to a decrease of solvation in the transition state ($\Delta S^{\neq}$ increases by 74 J mol^{-1} K^{-1}; the activation energy, by 13 kJ mol^{-1}). The increased solvation in the transition state apparently destabilises the latter.

In the presence of a coordinating salt background, the Co(II) solvate is transformed into complex acidoligands $[CoCl_4]^{2-}$, $[CoCl_5]^{3-}$, etc. The promoting action of the salt background becomes weaker (LiCl) or changes into inhibiting action (LiAc) as a result of stabilisation of the solvate coordination spheres in $[CoX_n]^{2-n}$.

The existence of a concentration dependence in the system $H_2Chl + CoCl_2 + LiCl$ leaves no doubt that the series of acidocomplexes $[CoCl_3]^-$, $[CoCl_4]^{2-}$ and $[CoCl_5]^{3-}$ exists in the presence of LiCl in methanol. These differ little from each other in entropy and enthalpy of activation. Lithium acetate converts the $CoAc_2$ solvate into a single stable coordinated form $[CoAc_4]^{2-}$. This is kinetically 10 times less active in the indicator reaction where Co(Chl) is formed. The lack of a concentration dependence of k_v^{298} in methanolic LiAc is consistent with the lack of other coordinated forms of $CoAc_2$.

However, the effect of background salts on the stability of 3*d*-metal solvates depends strongly on the organic solvent. It has been found[25] that LiCl slows the coordination of the CoX_2 solvate with H_2Chl in *n*-pentanol, in contrast with methanol. However, LiAc accelerates it. This opens wide possibilities for using indicator reactions to study the influence of solvent containing salt on the solvates of a reagent. Even more promising is the use of this method to investigate mixed solvates of 3*d* -metals in binary organic solvents.

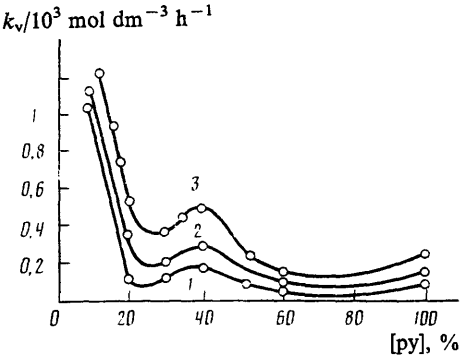


Figure 2. Dependence of formation rate constant of Cu(Chl) in CH_3CO_2H—py on medium composition at: 298 (*1*), 318 (*2*), 328 K (*3*).[30]

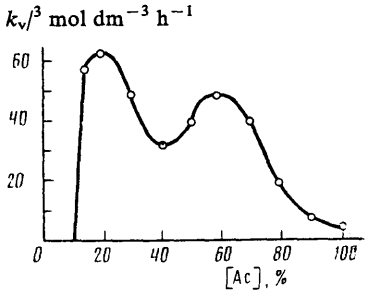


Figure 3. Dependence of formation rate constant of Cu(Chl) in CH_3CO_2H—CH_3COCH_3 on medium composition at 298 K.[30]

Formation of the analogues Cu(Chl) and Zn(Chl) in the systems CH_3CO_2H—coordinating solvent and py—coordinating solvent has been studied.[30] For concentrations of coordinating solvent in CH_3CO_2H from 0 to 100%, kinetic curves of composition *vs.* property were obtained. Lots of composition—rate of indicator reaction (Figs. 2 and 3), composition—activation energy (energy curves), and composition—entropy of activation (structure curves) (Fig. 4) all have peaks.

Concentration dependences of the formation rate of Cu(Chl) from $CuAc_2$ and H_2Chl in the systems CH_3CO_2H–py and CH_3CO_2H–acetone are plotted in Figs. 2 and 3, respectively. These data reflect the change of properties of the binary solvent (its solvating ability) and the change of stability of Cu^{II} solvates as a function of medium composition. Addition of a strongly coordinating component (py, ROH, acetone, dioxane, etc.) to CH_3CO_2H causes a gradual destruction of its dimeric structure $(HAc)_2$, accumulation of solvates $CH_3CO_2H...S$ and a subsequent transition to the structure of the solvent. As the medium composition changes, the mixed solvation sphere of $[MX_2(CH_3CO_2H)_4]$ converts successively to a mixed solvent sphere $[MX_2(CH_3CO_2H)_{4-m}S_m]$†, and then to $[MX_2(S)_{n-2}]$. Formation of $[MX(S)_{n-1}]^+$ and $[M(S)_n]^{2+}$ is also possible.

It is noteworthy that solvates of only divalent cations are examined here. Solvates of MX_3 and MX_4 do not react with porphyrins under ordinary conditions and cannot presently be investigated by porphyrin indicator reactions.

It has been demonstrated[36] that small additions of a second component to a pure solvent greatly changes the structure of the latter, causing either a loss of structure (destabilisation) or higher degree of structure (stabilisation). Destabilisation of the intrinsic solvent structure increases its solvating power whereas stabilisation reduces it.

In our opinion, the increased rate of reaction (15) observed in the majority of cases in CH_3CO_2H with small additions of a strongly coordinating solvent is due to destruction of $(CH_3CO_2H)_2$ dimers and an increased solvation of the transition state [cf. equation (16)] in addition to the destabilisation of the CH_3CO_2H–cation bond that favours reaction (16).

It can be stated that where two or more molecules of a weakly coordinating solvent enter the coordination sphere of *d*-metals they make a poor match. If a strongly coordinating solvent (S_c) enters the inner sphere of MX_2, the effective charge on the metal decreases, the initial M–S bonds are destabilised, and the ability to substitute S increases. In all probability, a similar type of competition for a coordination site arises between any pair of solvents differing in donor–acceptor numbers.

The change of kinetic parameters with large additions of a coordinating component,[20] as demonstrated previously,[31] is caused by substitution of HAc by S_c in the first solvation sphere. Thus, all mixed (HAc–py) $CuAc_2$ solvates are less active than the pure HAc ones. The maximal complexation rate is reached with 40% py. This can be attributed to the special properties of the CH_3CO_2H–py associate that dominates the solvent structure in this range. The second maximum on the curve corresponds to accumulation of the associate and produces a maximum in E and $\Delta S^{\neq}$ (Fig. 4). The first maximum at 20% py represents complete substitution of the very weak ligand CH_3CO_2H by the strongly coordinating py. In HAc and alcoholic solutions, $CuAc_2$ is known[31] to exist as a dimer. However, Cu_2Ac_4 has been found to be unreactive toward porphyrins.

Addition of a strongly coordinating solvent to an HAc solution shifts the equilibrium of the dimer

$$2[CuX_2(S)_{n-2}] \rightleftharpoons [Cu_2X_4(S)_4] + (n-6)S, \qquad (19)$$

where X^- is any carboxylate, toward the monosolvate. As the dimer breaks up, the monosolvate $[CuX_2(S_c)_{n-2-m}(HAc)_m]$ accumulates, i.e. HAC is lost from the inner sphere. This process occurs in parallel with the change in composition of the solvation sphere of the monosolvate, which is present in small quantities in HAc (about 0.1%) and alcoholic solution, and corresponds exactly to this change.

The dimers and their break-up by large amounts of S_c undoubtedly affect k_v. However, they do not change the nature of the dependence of k_v on solvent composition (Fig. 2) and even more the nature of the structure–kinetic curves (Fig. 3) since they do not affect the energy and entropy of activation.

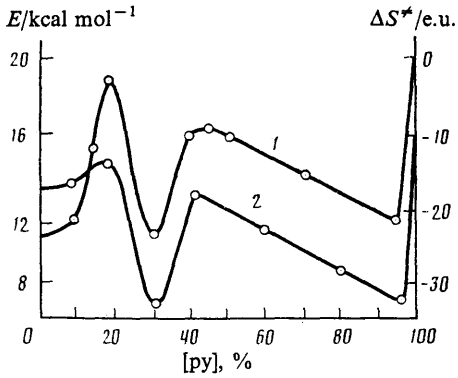


Figure 4. Dependence of energy (*1*) and entropy of activation (*2*) for Cu(Chl) formation in CH_3CO_2H–py on medium composition at 298 K.[20]

This conclusion is also supported by the fact that the curves shown in Figs. 2 and 3 are completely identical if the total concentration of $CuAc_2$ is changed by 10–100 times.

The kinetics of complexation in the mixed solvent HAc–acetone are especially interesting. The reaction sharply accelerates and the rate constant increases three times with even 1% acetone added. In view of the weak basicity and small size of $CO(CH_3)_2$, such an effect cannot be related to a change of properties of HAc as a solvent. The activity of the first mixed acetone–HAc solvate in reaction (15) is so high that even trace amounts cause a large effect. It can be assumed that acetone (ketones) is highly effectively coordinated to copper salts since π-backbonding is possible.

The path of the composition–rate curves suggests that all mixed acetone solvates of $CuAc_2$ are more highly reactive than HAc solvates, which are some of the most reactive solvates (Table 7). It is assumed that the first maximum on curve *1* (Fig. 2) corresponds to the first mixed solvate $[CuAc_2(C_2H_6CO)(HAc)_3]$; the minimum, to the second; and the third, to the third solvate $[CuAc_2.(C_2H_6CO)_3(HAc)]$. The solvate $[CuAc_2(C_2H_6CO)_4]$ is six times less active than $[CuAc_2(HAc)_4]$.

We are inclined to ascribe the elevated reactivity of mixed acetone solvates to the *trans*-effect of acetone in octahedral copper complexes and to its labilising action on bound HAc.[20] The catalytic action of acetone was also observed for Co^{II} salts. The *trans*-effect is proposed to occur in mixed HAc solvates of $CoAc_2$ with py, DMSO and DMF. It can stabilise the transition state of an indicator reaction.

The rate of complexation of tetraphenylporphine (H_2TPP) is slower for all mixed acetone–HAc solvates of $ZnAc_2$ than for the

†The inner coordination sphere is shown in square brackets; the outer sphere is not indicated.

pure HAc solvate. In these instances, there are no maxima on the composition–rate curves. The minima in the energy and entropy on the composition–energy (entropy) of activation curves correspond to the maximal accumulation of mixed acetone–HAc solvates of $CoAc_2$.

Individual rate constants for reactions involving mixed solvates of $ZnAc_2$ and $CoAc_2$ were first obtained by Golubchikov.[31] In these reactions one (k_1) or two (k_2) molecules of HAc in the inner sphere are replaced by a coordinating solvent. The data presented in Table 10 show that entry of one solvent molecule of any kind into the solvation sphere of $ZnAc_2$ instead of weakly bound HAc decreases the coordinating ability by about 2 times; two molecules, by 4–15 times. Under analogous conditions the reactivity of $CoAc_2$ in saturated solvents (excluding monoethanolamine) changes little. The strong catalytic effect in py, DMSO and DMF may be due to a *trans*-effect. Monoethanolamine forms a monosolvate $\{CoAc_2(HAc)_2[NH_2(CH_2)_2OH]\}$ in which the chelate is tightly bound to Co^{II} by the NH_2-group and weakly by the OH-group. In our opinion, the 10-fold increase of rate of coordination to monoethanolamine is explained by the interaction of the OH-group in the transition state with the leaving HAc ligand or an ancillary Ac^- ligand. This enhances the reaction.

Table 10. Individual rate constants of tetraphenylporphine coordination by $ZnAc_2$ and $CoAc_2$ solvates $MAc_2(HAc)_4$, $MAc_2(HAc)_3(S)$ and $MAc_2(HAc)_2(S)_2$ at 298 K.[31]

Reagent salt	Coordinating solvent (S_c)	Rate constants, $dm^3\ mol^{-1}\ sec^{-1}$		
		k_0	k_2	k_1
$ZnAc_2$	HAc	38.5	–	–
	Py	39.0	26.8	6.4
	DMSO	37.8	18.8	2.3
	DMF	39.5	14.1	–
	Butanol	39.0	19.1	8.2
	H_2O	18.7	10.9	5.0
$CoAc_2$	HAc	0.100	–	–
	Py	0.095	0.478	0.670
	DMSO	0.109	0.199	1.21
	DMF	0.079	0.71	–
	Butanol	0.105	0.111	–
	H_2O	0.083	0.064	0.043
	Methanol	0.096	0.096	0.096
	Ethanol	0.106	0.110	–
	Ethyleneglycol	0.105	0.090	0.037
	Monoethanolamine	0.100	0.97	–

A combination of porphyrin indicator reactions and thermodynamic methods is especially effective for investigating the reactivity of individual solvates by the kinetic method. This approach has been successfully used to investigate the state of Cu^{II} carboxylates, including dimers, in binary solvents (consisting of coordinating and weakly coordinating solvents[37,38]).

In conclusion, the special role of solvates in the coordination chemistry of solutions must be emphasised. The chemistry of complexes begins with just these complexes, which are formed during dissolution of metal salts in aqueous and nonaqueous solvents. Methods for preparing the complexes are based on substitution of solvent–ligands by ligands of any other type (molecular, acidoligands, inner-sphere, macrocyclic, etc.). The lack of sufficient data on the structure, stability and reactivity of solvates impedes development of many concepts of the theory of ligand substitution, the theory of their stability in solutions, and the optimal methods of synthesis. Taking into account the importance of solvates to electrochemistry, hydrometallurgy, analytical chemistry of nonaqueous solutions, homogeneous and heterogeneous catalysis, biochemistry and other practically important areas it becomes obvious that efforts need to be focussed on a systematic study of them.

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