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CHEMISTRY OF THE OUTER-SPHERE COMPLEXES

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CONTENTS

A. INTRODUCTION

The term outer-sphere complex formation refers to the interaction of coordinatively saturated complex ions with further ligands. Some other terms are also used for this phenomenon: coordination in the second sphere, super-complex formation, ion-pairing; for reasons mentioned later we prefer outer-sphere complex formation. The concept was originally introduced by Werner[1] in 1913, and since then much work has been done in this field. Nevertheless the data concerning the existence, composition and stability of such species are often controversial, although their importance in determining the behaviour of different complex systems cannot be disputed. The aim of the present paper is to survey critically the information so far available on the stability of outer-sphere complexes, to discuss the factors which determine their stability, to examine their role in ligand substitution and redox reactions and to indicate possible lines of research to clarify the situation.

In most cases the coordination sphere of the central ion is saturated. In the absence of other complex forming ligands the coordination sites are occupied by the molecules of the solvent (S). With increasing concentration of the ligand (L) the coordinated solvent molecules are gradually displaced by L, until the MeL_N complex (N is the coordination number) is formed. The residual affinity of these complexes for the other species present in the solution is greatly determined by the charge of the complex. If the ligand is a neutral molecule the charge of each complex is equal to the charge of the central ion (m), while if the ligand is an anion of charge l, the charge of the species $MeS_{N-n}L_n$ is $m-nl$. If the complex species are negatively charged the interaction of the complex anion with metal ions may be expected. Species such as $KFe(CN)_6^{3-}$ formed by this interaction may be regarded as transitions to the binuclear complexes and will not be treated in this review*.

By similar reasoning if the resultant charge of the inner-sphere complex is positive interaction may occur with ligand anions or dipoles. It follows that besides the series of inner-sphere complexes (MeS_N, MeS_{N-1},L... MeL_N) a series of outer-sphere complexes ($MeS_{N-n}L_nX_x$, where X may be L or another ligand) may occur; the value of x is usually 1 or 2 and there is no example where its value exceeds 4. This makes treatment of the successive complex equilibria much more complicated, and a clear cut distinction between inner-sphere and outer-sphere coordination is only seldom possible. Treatment is very favourable if the inner-sphere complex is inert. In such cases there are no changes in the inner-sphere and uptake of the ligand(s) in the outer-sphere can be studied quite separately. The results of such studies can also be considered in the treatment of the analogous labile systems.

B. DETECTION OF OUTER-SPHERE COMPLEX FORMATION AND DETERMINATION OF STABILITY CONSTANTS

(i) General remarks

When only outer-sphere coordination need be considered, *i.e.* systems where the inner-sphere complexes are inert, the same experimental approach and calculation methods can be applied as in the case of the study of successive complex formation. Optical rotatory dispersion measurements can be used even more extensively. Whilst a change in optical rotatory power can be used in the equilibrium study of labile complexes only if the ligand is optically active, in the case of inert

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* It should be mentioned, however, that even cationic complexes may react with another metal ion, if the ligand bound has a further unshared pair of electrons. For example there are interactions between the following pairs of ions: silver(I) and monothiocyanatopentaamminecobalt(III), silver(I) (or mercury(II)) and *cis*- and *trans*-dithiocyanatotetraamminecobalt(III)[3] and silver(I) and chloropentaaquochromium(III)[4] ions.

complexes outer-sphere complex formation can be followed polarimetrically if the inert complex itself is asymmetric.

However, even in these relatively simple systems some special problems arise. It may be expected that in outer-sphere complex formation, if specific forces are involved at all these must be much less pronounced than in the case of direct interactions of metal ions with ligands. Therefore, the principle of constant ionic medium[5] can be enforced very cautiously. The favourite non-complex forming ligands, nitrate and perchlorate, are not as innocent as in the case of inner-sphere complex formation. On the other hand the stability of the outer-sphere complexes is fairly small in most cases, consequently fairly concentrated solutions must be used.

The situation is much more complicated if the simultaneous formation of inner- and outer-sphere complexes occurs. The normal equilibrium analysis cannot distinguish the corresponding outer- and inner-sphere complexes $Me(H_2O)_5L$ and $Me(H_2O)_6L$. This means that the stability constant of the first complex obtained by the usual methods (β_1) is a composite constant:

$$\beta_1 = \frac{[Me(H_2O)_5L]+[Me(H_2O)_6L]}{[Me(H_2O)_6]\cdot[L]} = \beta_{1,0}+\beta_{0,1}. \tag{1}$$

Similar considerations are valid for the analogous corresponding inner- and outer-sphere complexes. It may occur that the same kind of ligands are simultaneously bound in the inner- and the outer-sphere. The normal equilibrium analysis cannot distinguish between the "isomeric" species. In general it may be written that

$$\beta_n = \sum_{i=0}^{n} \beta_{i,(n-i)} \tag{2}$$

where the second subscript refers to the number of ligands bound in the outer-sphere.

(ii) Study of inert complexes

a) Rate of dialysis.—From the rate of dialysis the molecular or ionic weight of the species can be calculated[6]. Brintzinger and coworkers studied a number of complex systems by this method. Brintzinger and Osswald[7] proposed the formation of outer-sphere complexes of general formula CoX_6Y_4, where X stands for ligands bound directly, while Y may be SO_4^{2-}, $C_2O_4^{2-}$ or HPO_4^{2-}. These and similar results were considered to be very strange and critical studies by Jander and Spandau[8] and by Kiss and Acs[9] proved that the membranes used by Brintzinger were unsuitable; the size of the pores is critical and slightly narrow pores may result in too high ionic weights. These criticisms completely invalidated the reliability of Brintzinger's work, nevertheless it was important because it called attention to a very important problem.

b) Polarographic studies.—Laitinen *et al.*[10] observed a shift in the half-wave potential and a decrease in the diffusion current in the polarographic reduction of $Co(NH_3)_6^{3+}$ as a function of the anion. They explained these phenomena by the formation of outer-sphere complexes. After some similar observations[11,12] some quantitative studies were performed. Laitinen and Grieb[13] have determined some association constants from the shift of the half-wave potential, while Tanaka, Ogino and Sato[14] calculated such constants from the decrease of the diffusion current. Methods were elaborated for the determination of the stability constants of outer-sphere complexes from the kinetics of the polarographic reduction by Vlcek[15] and from the chronopotentiometric transition time by Tanaka and Yamada[16]. These latter methods have the advantage that they can be applied to both the reversible and irreversible electrode processes.

c) Conductivity measurements.—Under proper experimental conditions, quantitative information can be obtained for the stability of outer-sphere complexes[17] from the conductivity of mixtures of an inert complex with different salts. Recently Hughes and Tobe[18] studied outer-sphere complex formation in acetone using a continuous variation approach. The results indicated a very strong interaction and the stability constant could not be calculated. Considering, however that in the systems studied the successive formation of several outer-sphere complexes occurs, the results must be regarded with some reservation.

d) Solubility measurements.—In testing the validity of the Debye–Hückel theory many solubility measurements with salts of different inert complexes were made by Brönsted *et al.*[19] Davies[20] pointed out that the enhanced solubility can be explained by formation of outer-sphere complexes. The experimental error in these measurements is fairly small. Takashima[21] has determined the solubility of $Co(NH_3)_6Cl_3$ in HCl. He observed that the solubility reaches a minimum value in 5–8 *M* HCl solution and on further increasing the concentration of the hydrochloric acid the solubility increases. He suggests that the solubility of $Co(NH_3)_6Cl_3$ in HCl is greater than in water. I feel that it is more likely that at high chloride activity a $Co(NH_3)_6Cl_4^-$ species is formed leading to an increased solubility. Further experiments are needed to clarify this interesting phenomenon. Solubility experiments by Larsson[22] indicated the formation of outer-sphere complexes involving neutral ligands in the outer-sphere.

e) Liquid–liquid extraction measurements.—This technique is widely used in the study of successive complex formation but has received much less attention than it deserves in the determination of stability constants of outer-sphere type complexes. Larsson[23,24] has studied the extraction of some cobalt(III) complexes into octanol-2 and cyclohexanone in the presence of different ligands. The fact that in the case of the $Co(NH_3)_6^{3+}$-salicylate system the distribution coefficient as a function of salicylate concentration exhibits a definite maximum, indicates the formation of a negatively charged species $Co(NH_3)_6L_4^-$ (L = salicylate anion). Another important observation[23] is that different ligands (salicylate and cyclohexanone) are simultaneously bound in the outer-sphere. The outer-sphere complexes of the tris-(phenanthroline)-iron(II) complex can also be determined by extraction[25]. An interesting phenomenon was found by Vydra and Přibil[26]. They observed that excess phenanthroline enhances the extraction of the $Fe(phen)_3I_2$ complex. This seems to indicate that phenanthroline is coordinated in the outer-sphere at least in the organic solvent.

f) Ion-exchange studies.—Larsson[24,27] undertook some studies with anion exchange resins. The results are semiquantitative but they strongly support the formation of the following species: $Co(NH_3)_6Cl_4^-$, $Co(NH_3)_6Br_4^-$, $Co(NH_3)_6(SO_4)_3^{3-}$ and $Co(NH_3)_6(S_2O_3)_3^{3-}$. These data are in line with the explanation given on the solubility behaviour of $Co(NH_3)_6Cl_3$.

g) pH Measurements.—This method can be used in case of the uptake of basic ligands in the outer-sphere. Measurements with the glass electrode were applied by Archer, East and Monk[28] to follow the association of chloropentamminecobalt(III) with malonate, phthalate, tartarate, maleate, succinate and malate. Caton and Prue[29] determined the stability constant of $Co(NH_3)_6OH^{2-}$ by measuring the OH^- concentration of solutions of $Co(NH_3)_5(OH)_3$. The OH^- concentration was determined from the rate of decomposition of diacetone alcohol which is catalyzed by hydroxide ions.

h) Nuclear magnetic resonance studies.—Alei[30] studied the association between hexaquochromium(III) ion and perchlorate ion (water) using an NMR method. The effect of the paramagnetic ion on the chemical shift of ^{17}O nuclei in enriched water was measured as a function of Cr^{III} and ClO_4^- concentration. The results show outer-sphere association both with water and perchlorate. Stengle and Langford[31] developed another NMR technique. They studied the effect of a paramagnetic ion on the relaxation time of nearby nuclei. The association of some chromium(III) complexes with PF_6^- and F^- ions was observed.

i) Spectrophotometric methods.—The effect of the different anionic ligands on the spectra of some cobalt(III) complexes was observed by Kiss and Czeglédy[32]. Later Linhard[33] estimated the association constant of the $Co(NH_3)_6I^{2+}$ complex from spectrophotometric data. Since then many studies have been made; in fact this technique is one of the most popular in the study of outer-sphere complex formation. In most cases the concentration of the inert complex is kept at a constant value and the absorbancy is measured as a function of the ligand concentration, and *vice versa*[37]. Millen and Watts[34] elaborated another method where the ratio of the inert complex to the ligand is constant but their absolute concentration is changed by dilution. Recently some studies were also made in non-aqueous solvents[34-36]. Posey and Taube[50] observed a remarkable change in the molar absorbances of $Co(NH_3)_6{}^{3+}$ and $Co(NH_3)_6SO_4{}^+$ with temperature. This possibility must be considered in the evaluation of spectrophotometric data.

It is worthwhile to mention the serious discrepancy of some data obtained spectrophotometrically. Evans and Nancollas[38] determined the stability constants of the $Co(NH_3)_6X^{2-}$ (X = Cl, Br, I, N_3) complexes at constant ionic strength $I = 0.054$. King, Espenson and Visco[39] found much lower stability constants at $I = 0.9$. The main reason for this discrepancy is probably the different ionic strength, not only because of the considerable difference between the activity coefficients in the two media, but also because of the likelihood of the uptake of perchlorate in the more concentrated solution. A systematic study of these and similar systems seems to be very important.

j) Polarimetry and circular dichroism.—These techniques are perhaps the most powerful ones in the study of outer-sphere complex formation. They provide not only another possibility for the determination of stability constants, but also give important information on the structure of the outer-sphere complex and on the mode of the bonding therein. Werner[40] observed that the optical rotation of the various asymmetric complex ions depends strongly on the nature of the counter ion. Jaeger[41] made similar observations measuring the rotation dispersion curves of different complexes. Kirschner *et al.*[42] attributed the effect of the counter ion to the formation of outer-sphere complexes. They found an interesting correlation between the equivalent molecular rotation ($[\alpha])_E$ and the ionic potential of the counter ion. $[\alpha]_E$ is defined as

$$[\alpha]_E = [\alpha]M/n$$

where M = molecular weight, n = number of optically active complex ions per molecule, and $[\alpha]$ = specific rotation. Ionic potential is equal to the ratio of ionic charge to the ionic radius. However, it is not advisable to attribute any deeper chemical meaning to this relationship. The $[\alpha]_E$ values obtained by the authors depend both on the stability and the molar rotation of the different outer-sphere complexes formed. It is possible that either of these properties is related to the ionic potential, but the relationship is not likely to be simple. Kirschner and Bhatnagar[43] studied polarimetrically outer-sphere complex formation with complex ions whose activity is due not to the asymmetry of the complex as a whole but to an optically active ligand. Larsson[44,45] studied the rotation as a function of the ligand concentration and evaluated stability constants. Smith and Douglas[46] pointed out that the analysis of the circular dichroism spectra gives a more solid basis for conclusions than the study of the absorption spectra or the optical rotatory dispersion curves. Larsson *et al.*[47,48] elaborated a method for the determination of stability constants of outer-sphere complexes from the dependence of circular dichroism on the ligand concentration. The data obtained by this method are in agreement with the stability constants evaluated from polarimetric measurements. Experiments were also made in non-aqueous media[49].

k) Kinetic studies.—Taube and Posey[50] found that the rate of the reaction

$$\mathrm{Co(NH_3)_5H_2O^{3+} + SO_4{}^{2-} \rightarrow Co(NH_3)_5SO_4{}^{+} + H_2O}$$

is almost independent of the concentration of the sulphate ion over a wide range. They explained this fact by a pre-equilibrium leading to the formation of an outer-sphere type complex the rearrangement of which gives the final products of the reaction. Later studies revealed that this behaviour is quite general[51] and the mechanism of such reactions can be represented by the following scheme:

$$\begin{aligned}
&\mathrm{R_5MeX^{m-x} + L^{l-}} \overset{k_{01}}{\rightleftharpoons} \mathrm{R_5MeXL^{m-x-l}}\\
&\mathrm{R_5MeX^{m-x} + L^{l-}} \xrightarrow{k_1} \mathrm{R_5MeL^{m-l} + X^{x-}}\\
&\mathrm{R_5MeXL^{m-x-l}} \xrightarrow{k_1} \mathrm{R_5MeL^{m-l} + X^{x-}}
\end{aligned}$$

where R_5 represents the ligands which are not displaced. The rate is given by

$$w = \frac{k_1 + k_2 K_{01}[L^{l-}]}{1 + K_{01}[L^{l-}]}\,[\mathrm{complex}]. \qquad (3)$$

The rate constants and the stability constant of the outer-sphere complex can be obtained by measuring the rate as a function of $[L^{l-}]$. If almost the total amount of the complex is converted to the outer-sphere complex, the rate is independent of the concentration of L^{l-}. The primary importance of the study of these displacement reactions is not the determination of the stability of outer-sphere complexes, but the comparison of the rate data with stability constants derived from independent experiments. This comparison gives a deeper insight into the mechanism of the reactions and indicates the reliability of the stability data.

l) Stability constants survey.—The stability constants of outer-sphere type complexes involving inert complex ions are collected in Table 1. The symbols and abbreviations are the same as were used in the standard collection of stability constants[52], but the data are arranged according to the inert complexes and not to the ligands. In addition to the data tabulated, there are observations of outer-sphere complexes with many other inert ions and ligands[42,43,46,47,49,53], but these data do not indicate even the composition of the complexes and their inclusion is not merited.

It appears from the Table that there are dramatic differences among the published data for many complexes. Sometimes the different experimental conditions may be responsible for the discrepancies. In several cases, however, the

TABLE 1

STABILITY CONSTANTS OF OUTER-SPHERE COMPLEXES INVOLVING INERT COMPLEX IONS

Ligand	*Method**	*Temp.*	*Medium*	*log equilibrium constant*	*Ref.*
			$Co(NH_3)_6^{3+}$		
OH^-	pH, kin	25	O corr	$\beta_{01} = 1.85$	56C
Cl^-	cond	25	O corr	$\beta_{01} \sim 1.48$	51J
Cl^-	sp	25	$I = 0.054$	$\beta_{01} = 1.87 \pm 0.02$	53E
Cl^-	sp	35	$I = 0.054$	β_{01} 1.96 ± 0.02	53E
Cl^-	sp	35.1	$I = 0.9$	β_{01} -0.70	59K
Cl^-	ix	20	var	RL_n[a]; $n = 1,2,3,4$	62La
Br^-	sp	25	$I = 0.054$	β_{01} 1.66 ± 0.02	53E
Br^-	sp	35	$I = 0.054$	β_{01} 1.71 ± 0.02	53E
Br^-	sp	35.1	$I = 0.9$	β_{01} -0.70	59K
Br^-	ix	20	var	RL_n; $n = 1,2,3,4$	62La
I^-	sp	20	var	β_{01} 1.58	44L
N_3^-	sp	25	$I = 0.054$	β_{01} 1.30 ± 0.04	53E
N_3^-	sp	35	$I = 0.054$	β_{01} 1.20 ± 0.05	53E
NH_3	sol	20	1 M NH_4ClO_4	β_{01} -0.62 ± 0.09 β_{02} -1.31	58L
NH_3	sp	20	1 M NH_4ClO_4	β_{01} -0.40 ± 0.3	58L
$P_3O_9^{3-}$	cond	25	O corr	β_{01} 4.43	52M
$P_4O_{12}^{4-}$	cond	25	O corr	β_{01} 5.74	52M
SO_4^{2-}	sol	25	O corr	β_{01} 3.53 ± 0.015	30D
SO_4^{2-}	cond	25	O corr	β_{01} 3.56	51J
SO_4^{2-}	sp	25	O corr	β_{01} 3.94 ± 0.02	56B
SO_4^{2-}	sp	24.5	O corr	β_{01} 3.32[b]	56P
SO_4^{2-}	sp	25	O corr	β_{01} 1.89	58D
SO_4^{2-}	pol	25	$I = 0.1$	β_{01} 2.09 ± 0.1	61V
SO_4^{2-}	ix	20	var	RL_n; $n = 1.2.3$	62La
SO_4^{2-}	pol	25	$I = 0.1$	β_{01} 1.83 ± 0.05	66T
SO_4^{2-}	pol	25	$I = 0.1$	β_{01} 1.96 ± 0.04	67T
SO_4^{2-}	pol	25	O corr	β_{01} 3.30	67T
$S_2O_3^{2-}$	sol	25	O corr	β_{01} 3.62	51D
$S_2O_3^{2-}$	sp	15	$I = 0.05$	β_{01} 3.20 ± 0.14	55G
$S_2O_3^{2-}$	sp	25	$I = 0.05$	β_{01} 3.26 ± 0.13	55G
$S_2O_3^{2-}$	sp	35	$I = 0.05$	β_{01} 3.26 ± 0.13	55G
$S_2O_3^{2-}$	ix	20	var	RL_n; $n = 1.2.3$	62La
oxalate	cond	25	O corr	β_{01} 3.40	51P
malonate	gl	25	O corr	β_{01} 3.54	51P
succinate	gl	25	O corr	β_{01} 2.94	51P
glutarate	gl	25	O corr	β_{01} 3.18	51P
adipate	gl	25	O corr	β_{01} 3.34	51P
phthalate	gl	25	O corr	β_{01} 3.74	51P
maleate	gl	25	O corr	β_{01} 4.20	51P
fumarate	gl	25	O corr	β_{01} 2.36	51P
salicylate	dis	20	var	RL_n; $n = 1,2,3,4$	62Lb
salicylate + cyclohexanone	dis	20	2-octanol	β_{01} -0.12 ± 0.025[c]	62Lb
				β_{02} -0.62 ± 0.09	62Lb
acetone	sol	20	1 M NH_4ClO_4	cpx formation	58L
			$Co(en)_3^{3+}$		
OH^-	sp	15	$I = 0.0103$	β_{01} 1.40	67C
OH^-	sp	25	$I = 0.0103$	β_{01} 1.42	67C

* Footnotes on p. 103.

TABLE 1 *(continued)*

Ligand	*Method*	*Temp.*	*Medium*	*log equilibrium constant*	*Ref.*
OH^-	sp	35	I = 0.0103	β_{01} 1.44	67C
OH^-	sp	25	I = 0.0103 (10% w/w dioxan)	β_{01} 1.66	67C
OH^-	sp	25	I = 0.0103 (20% w/w dioxan)	β_{01} 2.01	67C
OH^-	sp	25	I = 0.0103 (30% w/w dioxan)	β_{01} 2.46	67C
OH^-	sp	25	I = 0.0103 (40% w/w dioxan)	β_{01} 3.10	67C
OH^-	sp	24	I = 0.0103, D_2O	β_{01} 1.46[d]	67C
OH^-	sp	25	I = 0.0103, D_2O (10 w/w dioxan)	β_{01} 1.68[d]	67C
OH^-	sp	25	I = 0.0103, D_2O (20% w/w dioxan)	β_{01} 2.03[d]	67C
OH^-	sp	25	I = 0.0103, D_2O (30% w/w dioxan)	β_{01} 2.48[d]	67C
OH^-	sp	25	I = 0.0103, D_2O (40% w/w dioxan)	β_{01} 3.12[d]	67C
Cl^-	cond	25	O corr	β_{01} 1.72	51J
Cl^-	pol	25	O corr	β_{01} 1.26	55L
Br^-	sp	25	I = 0.054	β_{01} 1.32 ± 0.1	53E
Br^-	sp	35	I = 0.054	β_{01} 1.37 ± 0.02	53E
N_3^-	sp	25	I = 0.054	β_{01} 1.06 ± 0.03	53E
N_3^-	sp	35	I = 0.054	β_{01} 0.93 ± 0.035	53E
NO_3^-	pol	25	O corr	cpx formation	55L
$P_3O_9^{3-}$	cond	25	O corr	β_{01} 4.40	52M
$P_4O_{12}^{4-}$	cond	25	O corr	β_{01} 5.77	52M
SO_4^{2-}	cond	25	O corr	β_{01} 3.45	51J
SO_4^{2-}	pol	25	O corr	β_{01} 2.72	55L
SO_4^{2-}	rot	20	var	RL^+ and RL_2^-	62Lc
SO_4^{2-}	pol	25	I = 0.1	β_{01} 1.99 ± 0.065	67T
SO_4^{2-}	pol	25	O corr	β_{01} 3.23	67T
$S_2O_3^{2-}$	rot	20	var	β_{01} 1.81 β_{02} 2,60 RL_3^{3-}	62Lc
$S_2O_3^{2-}$	rot	20	2 M $NaClO_4$	β_{01} 2.00 β_{02} 3.95 β_{03} 4.23	65L
$S_2O_3^{2-}$	CD[f]	20	2 M $NaClO_4$	RL_n; n = 1,2,3,4	66La
$S_2O_3^{2-}$	sp	20	2.88 M $NaClO_4$	β_{01} 0.11 ± 0.035	67O
SeO_3^{2-}	CD	20	2 M $NaClO_4$	β_{01} 2.11 ± 0.02 β_{02} 3.92 ± 0.015 β_{03} 4.46 ± 0.09 β_{04} 5.15 ± 0.2	66Lb
SeO_3^{2-}	sp	20	2.88 M $NaClO_4$	β_{01} 0.07 ± 0.2	67O
$Fe(CN)_6^{4-}$	rot, CD	20	$C_{Na}{}^+ = 2$ M I = 2–5	β_{01} 0.39 ± 0.085 β_{02} 1.62	67La
$Fe(CN)_6^{4-}$	rot, CD	20	I = 0.2	β_{01} 1.98 ± 0.01 β_{02} 3.85 ± 0.4	67La
			$Co(pn)_3^{3+}$		
Cl^-	cond	25	O corr	β_{01} 1.60	51J
$P_3O_9^{3-}$	cond	25	O corr	β_{01} 3.64	52M
$P_4O_{12}^{4-}$	cond	25	O corr	β_{01} 4.59	52M
SO_4^{2-}	cond	25	O corr	β_{01} 3.76	51J
			$Co(NH_3)_5H_2O^{3+}$		
SO_4^{2-}	sp	24.5	O corr	β_{01} 3.276[e]	56P
CrO_4^{2-}	sp	25	O corr	β_{01} 5.49	64S

TABLE 1 *(continued)*

Ligand	*Method*	*Temp.*	*Medium*	*log equilibrium constant*	*Ref.*
			$Co(NH_3)_5F^{2+}$		
SO_4^{2-}	pol	25	I = 0.1	β_{01} 1.85	61V
			$Co(NH_3)_5Cl^-$		
Cl^-	sol	25	O corr	β_{01} 1.00	65A
Cl^-	sol	35	O corr	β_{01} 1.00	65A
N_3^-	sol	25	O corr	β_{01} 1.07	65A
N_3^-	sol	35	O corr	β_{01} 0.96	65A
NO_3^-	sol	25	O corr	β_{01} 1.04	65A
SO_4^{2-}	pol	25	I = 0.1	β_{01} 1.88	61V
SO_4^{2-}	sol	25	O corr	β_{01} 2.45	65A
SO_4^{2-}	sol	35	O corr	β_{01} 2.52	65A
ClO_4^-	sol	25	O corr	β_{01} 1.15	65A
ClO_4^-	sol	35	O corr	β_{01} 1.04	65A
acetate	sol	25	O corr	β_{01} 0.7	65A
acetate	sol	35	O corr	β_{01} 0.45	65A
glycollate	sol	25	O corr	β_{01} 1.45	65A
malonate	gl	25	O corr	β_{01} 2.27	65A
malonate	gl	35	O corr	β_{01} 2.31	65A
malonate	sol	25	O corr	β_{01} 2.32	65A
malonate	sol	35	O corr	β_{01} 2.30	65A
phthalate	gl	25	O corr	β_{01} 2.54	65A
phthalate	gl	35	O corr	β_{01} 2.63	65A
phthalate	sol	25	O corr	β_{01} 2.51	65A
phthalate	sol	35	O corr	β_{01} 2.52	65A
tartarate	gl	35	O corr	β_{01} 2.00	65A
tartarate	gl	35	O corr	β_{01} 1.98	65A
tartarate	sol	25	O corr	β_{01} 2.12	65A
tartarate	sol	35	O corr	β_{01} 2.08	65A
maleate	gl	25	O corr	β_{01} 2.52	65A
maleate	gl	35	O corr	β_{01} 2.52	65A
maleate	sol	25	O corr	β_{01} 2.47	65A
maleate	sol	35	O corr	β_{01} 2.51	65A
succinate	gl	25	O corr	β_{01} 1.99	65A
succinate	gl	35	O corr	β_{01} 2.04	65A
succinate	sol	25	O corr	β_{01} 1.94	65A
succinate	sol	35	O corr	β_{01} 1.92	65A
malate	gl	25	O corr	β_{01} 2.01	65A
malate	sol	25	O corr	β_{01} 1.99	65A
malate	sol	35	O corr	β_{01} 1.98	65A
			$Co(NH_3)_5N_3^{2+}$		
SO_4^{2-}	pol	25	I = 0.1	$\beta_{01} \sim 1.18$	61V
			$Co(NH_3)_5NO_2^{2+}$		
SO_4^{2-}	pol	25	I = 0.1	β_{01} 1.69 ± 0.01	61V
			$Co(NH_3)_5NO_3^{2+}$		
SO_4^{2-}	pol	25	I = 0.1	β_{01} 1.59 ± 0.1	61V
			$Co(NH_3)_5(CH_3CO_2)^{2+}$		
SO_4^{2-}	pol	25	I = 0.1	β_{01} 1.65 ± 0.1	61V

TABLE 1 *(continued)*

Ligand	*Method.*	*Temp.*	*Medium*	*log equilibrium constant*	*Ref.*
			$Co(NH_3)_5SO_4^+$		
SO_4^{2-}	pol	25	I = 0.1	β_{01} ~1.00	61V
			cis-$Co(en)_2Cl_2^+$		
Cl^-	sp	25	I ~0.02, methanol	β_{01} 2.13	57P
Cl^-	kin	35	methanol	β_{01} 2.40 ± 0.04	65B
Cl^-	sp	30	O corr DMSO	β_{01} 2.42 ± 0.01	66Ma
Cl^-	sp	30	O corr DMF	β_{01} 3.71 ± 0.01	66Ma
Cl^-	sp	30	O corr DMA	β_{01} 4.31 ± 0.01	66Ma
Cl^-	sp	20	O corr DMSO	β_{01} 2.50 ± 0.01	66Ma
Cl^-	sp	25	O corr DMSO	β_{01} 2.44 ± 0.01	66Ma
Cl^-	sp	30	O corr DMF	β_{01} 3.71 ± 0.01	66Mb
Br^-	sp	25	I ~ 0.02	β_{01} 1.54	57P
Br^-	sp	30	O corr DMF	β_{01} 2.99 ± 0.005	66Ma
I^-	sp	30	O corr DMF	β_{01} 2.93 ± 0.01	66Mb
N_3^-	kin	25	I ~ 0.02	β_{01} 1.63	57P
acetate	kin	25	I ~ 0.02	β_{01} 0.38	57P
			trans-$Co(en)_2Cl_2^+$		
Cl^-	sp	30	O corr DMF	β_{01} 2.25 ± 0.01	66Mb
			trans-$Co(en)_2(SCN)_2^+$		
SCN^-	ix	20	var	RL_n, n = 1,2	60L
SCN^-	dis	20	var	RL_n, n = 1.2	60L
SCN^-	sol	20	3 M $NaClO_4$	β_{01} −0.52 ± 0.04	60L
ClO_4^-	sol	20	3 M $NaClO_4$	cpx formation	60L
salicylate	dis	20	var	cpx formation	62Lb
			trans-$Co(en)_2NO_2H_2O^{2+}$		
Br^-	cond	25	acetone	stable RL_3	65H
Br^-	cond	25	DMF	stable RL_2	65H
SCN^-	cond	25	acetone	stable RL_2	65H
			cis-$Co(en)_2ClDMF^{2+}$		
Cl^-	sp	4.8	O corr DMF	β_{01} 4.09 ± 0.01	66Lc
Cl^-	sp	12.2	O corr DMF	β_{01} 4.10 ± 0.01 β_{02} 6.28	66Lc
Cl^-	sp	21.3	O corr DMF	β_{01} 4.13 ± 0.01 β_{02} 6.23	66Lc
Cl^-	sp	30	O corr DMF	β_{01} 4.17 ± 0.01 β_{02} 6.08 ± 0.02	66Lc
Br^-	sp	1.6	DMF	β_{01} 3.44	66Lc
Br^-	sp	11.6	DMF	β_{01} 3.63	66Lc
Br^-	sp	20.6	DMF	β_{01} 3.81	66Lc
Br^-	sp	30	DMF	β_{01} 3.96 ± 0.01	66Lc
			cis-$Co(en)_2BrCl^+$		
Br^-	sp	1.4	DMF	β_{01} 2.92 ± 0.01	66Lc
Br^-	sp	21.1	DMF	β_{01} 2.85 ± 0.01	66Lc
Br^-	sp	30	DMF	β_{01} 2.83 ± 0.01	66Lc
			$Cr(H_2O)_6^{3+}$		
SCN^-	sp	25	I = 1.2	β_{01} 0.00	55P
SCN^-	sp	25	O corr	β_{01} 0.85	55P

TABLE 1 *(continued)*

Ligand	*Method*	*Temp.*	*Medium*	*log equilibrium constant*	*Ref.*
PF_6	nmr	25	var	weak RL	65S
CrO_4^{2-}	sp	25	I = 1	RL	55K
SO_4^{2-}	sp	46.2–84	I = 1	β_{01} 1.08 ± 0.11[f]	62F
SO_4^{2-}	pol	25	I = 0.1	β_{01} 1.60	66T
			$Cr(NH_3)_6^{3+}$		
SO_4^{2-}	pol	25	I = 0.1	β_{01} 1.76 ± 0.06	66T
SO_4^{2-}	pol	25	I = 0.1	β_{01} 1.78 ± 0.05	67T
SO_4^{2-}	pol	25	O corr	β_{01} 3.14	67T
			$Cr(en)_3^{3+}$		
OH^-	sp	25	I = 0.0103	β_{01} 0.78 (extrapolated)	67C
OH^-	sp	25	I = 0.0103 (10% w/w dioxan)	β_{01} 1.11 (extrapolated)	67C
OH^-	sp	25	I = 0.0103 (20% w/w dioxan)	β_{01} 1.41	67C
OH^-	sp	25	I = 0.0103 (30% w/w dioxan)	β_{01} 1.85	67C
OH^-	sp	25	I = 0.0103 (40% w/w dioxan)	β_{01} 2.48	67C
OH^-	sp	25	I = 0.0103 D_2O	β_{01} 1.26[d] (extrapolated)	67C
OH^-	sp	25	I = 0.0103 D_2O (10% w/w dioxan)	β_{01} 1.43[d]	67C
OH^-	sp	25	I = 0.0103 D_2O (20% w/w dioxan)	β_{01} 1.72[d]	67C
OH^-	sp	25	I = 0.0103 D_2O (30% w/w dioxan)	β_{01} 2.11[d]	67C
OH^-	sp	25	I = 0.0103 D_2O (40% w/w dioxan)	β_{01} 2.69[d]	67C
F^-	nmr	25	var	>1	65S
PF_6^-	nmr	25	var	0	65S
SO_4^{2-}	pol	25	I = 0.1	β_{01} 1.76 ± 0.05	67T
SO_4^{2-}	pol	25	O corr	β_{01} 2.77	67T
			$Cr(pn)_3^{3+}$		
F^-	nmr	25	var	RL	65S
PF_6^-	nmr	25	var	RL	65S
			$Cr(NH_3)_5H_2O^{3+}$		
Cl^-	sp	23.27	0.158 $NaClO_4$	β_{01} < 0.34 (λ 220)	67D
				β_{01} 0.11 ± 0.30 (λ 218)	67D
				β_{01} 0.77 ± 0.14 (λ 216)	67D
SCN^-	sp	23.27	0.158 $NaClO_4$	β_{01} 0.98 ± 0.30 (λ 265)	67D
				β_{01} 1.06 ± 0.1 (λ 260)	57D
				β_{01} 0.98 ± 0.15 (λ 255)	67D
oxalate^{2-}	kin	50	I = 0.5–2.7	β_{01} 0.28 ± 0.04	67K
$HC_2O_4^-$	kin	50	I = 0.5–2.7	β_{01} −0.07 ± 0.05	67K
			$Cr(en)_2Cl_2^+$		
F^-	nmr	25	var	β_{01} 0.48	65S
PF_6^-	nmr	25	var	RL	65S

TABLE 1 *(continued)*

Ligand	*Method*	*Temp.*	*Medium*	*log equilibrium constant*	*Ref.*
			$Pt(en)_3^{4+}$		
Cl^-	sp	25	O corr	β_{01} 1.04	60N
Cl^-	sp	10	O corr	β_{01} 1.17 ± 0.03	63G
Cl^-	sp	25	O corr	β_{01} 1.24 ± 0.02	63G
Cl^-	sp	40	O corr	β_{01} 1.29 ± 0.02	63G
Cl^-	CD	20	var	RL_n, n = 1,2	67Lc
Br^-	sp	25	O corr	β_{01} 0.90	60N
Br^-	sp	10	O corr	β_{01} 1.14 ± 0.03	63G
Br^-	sp	25	O corr	β_{01} 1.18 ± 0.01	63G
Br^-	sp	40	O corr	β_{01} 1.25 ± 0.01	63G
I^-	sp	10	O corr	β_{01} 1.11 ± 0.015	63G
I^-	sp	25	O corr	β_{01} 1.14 ± 0.015	63G
I^-	sp	40	O corr	β_{01} 1.20 ± 0.01	63G
SCN^-	sp	10–25	O corr	cpx formation	63G
NO_3^-	sp	25	O corr	β_{01} −0.10	60N
SO_4^{2-}	sp	25	O corr	β_{01} 3.52	60N
SO_4^{2-}	CD	10	var	RL_n, n = 1,2,3	67Lc
ClO_4^-	sp	25	O corr	cpx formation	60N
			$Pt(en)_2Cl_2^{2+}$		
Cl^-	sp	20	$I \approx 0.5$	$\beta_{01} < -1.00$	63G
I^-	sp	20	$I \approx 0.5$	β_{01} 0.11	63G
			$Pt(en)_2Br_2^{2+}$		
Br^-	sp	20	$I \approx 0.5$	$\beta_{01} < -1.00$	63G
			$Fe(phen)_3^{2+}$		
I^-	dis	25	O corr	β_{01} 1.92 ± 0.08	67N
				β_{02} 3.22 ± 0.02	67N

en = ethylenediamine; pn = propylenediamine; DMF = dimethylformamide; phen = *o*-phenanthroline; sol = solubility data; pol = polarography; nmr = nuclear magnetic resonance; kin = kinetic studies; cond = conductivity studies; ix = ion exchange; sp = spectrometric studies; dis = distortion methods; gl = glass electrode; rot = measurement of optical rotation power; CD = measurement of circular dichroism.

[a] R represents the inert complex ion written at the head of each section of the table;

[b] $\log \beta_{01} = 3.322 - \dfrac{6.102\sqrt{I}}{1+2\sqrt{I}}$;

[c] $\beta_{01} = \dfrac{[Co(NH_3)_6Sal_3ch]}{[Co(NH_3)_6Sal_3]\,[ch]}$; $\beta_{02} = \dfrac{[Co(NH_3)_6Sal_3ch_2]}{[Co(NH_3)_6Sal_3]\,[ch]^2}$.
Sal = salicylate; ch = cyclohexanone.

[d] The inner-sphere ligand is ethylenedi[$^2H_4$]amine.

[e] $\log \beta_{01} = 3.276 - \dfrac{6.10\sqrt{I}}{1+1.5\sqrt{I}}$;

[f] β_{01} is independent of the temperature.

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reasons for the contradictory results are not clear. This is especially true of Larsson's data[44,45,47,48] obtained by polarimetry and circular dichroism which indicate the formation of as many as four successive outer-sphere complexes, while the data obtained by spectrophotometry and by conductivity measurements can be fully explained by the formation of one complex. According to Bjerrum[54] the peculiar shape of the curves obtained by Larsson can be explained by considering that both the *dextro* and the *levo* form of $Co(en)_3{}^{3+}$ exist as an equilibrium mixture of four conformations[55], each with its own optical rotation; this equilibrium is disturbed by the formation of outer-sphere complexes. The fact that the concentration-dependence of both the rotation and the circular dichroism curves can be quantitatively described by a series of successive stability constants does not support this explanation. Nevertheless it would be necessary to follow Berrum's suggestion to make similar measurements with the optically active tris-(1,2-cyclohexanediamine)cobalt(III) complex which exists in one conformation only.

Some conclusions from the tabulated constants will be drawn in section C but the scarcity of available data evidently prevents any broader generalisation. It appears that the most important requirement for further work in this field would be to obtain reliable information on the existence and stability of outer-sphere complexes of the perchlorate ion and to look for other anions whose tendency for outer-sphere complex formation is very small. For this purpose the application of the different relaxation techniques seems helpful.

(iii) Study of labile complexes

In systems where the inner-sphere complexes are labile the main problem is the distinction between inner- and outer-sphere type complexes. Reliable methods for this purpose were only developed in the last few years; consequently the amount of data available is even less than in the case of inert complexes.

a) Spectrophotometry.—Smithson and Williams[56] pointed out that the charge transfer spectra, but not the crystal field spectra of transition metal ions, are influenced by the formation of outer-sphere complexes. The weak crystal field bands in the visible region due to forbidden *d-d* transitions, depend upon the splitting of the *d* states. This splitting is a function of the polarisation of the central ion by the ligand and therefore depends on a high negative power of the distance of separation (possibly r^{-5}). Changes in the outer-sphere are expected to have very little effect upon these bands. However the u.v. bands are charge transfer bands and their wavelength depends more nearly on r^{-1} than r^{-5} since in the interaction-expression one (or both) of the states contains terms in r^{-1}. Therefore these bands will be influenced by both the inner and the outer-sphere complex formation but to a much greater extent by the latter. It follows from the nature of this phenomenon that the two types of complexes cannot be definitely distinguished, the effect of outer-sphere complex formation may be disguised by simultaneous inner-sphere association.

b) Comparison of stability constant determined by different methods.—The equilibrium analysis provides stability constants (K_n) which as has already been stressed, are, in fact, composite constants. The different methods should give the same values for these composite constants, within experimental error. Nevertheless it is frequently claimed (see the discussion in Jørgensen's paper[57]) that comparison of the constants obtained by different methods gives information on the stability of the corresponding outer- and inner-sphere complexes. However, this is possible only if values of the "intensive factors" of the corresponding complexes are known. In general, these "intensive factors" are just as unknown as the stability constants. Fronaeus and Larsson[58], studying the $Ni^{2+}-SCN^-$ system by infra-red spectrometry assumed that the C–N stretching frequency of the outer-sphere complex $Ni(H_2O)_6SCN^+$ "the intensive factor" is the same as that of the free ligand. Thus they could calculate the stability constant of the inner- and outer-sphere complexes separately:

$$\beta_{1,0}\ 12 \pm 2; \qquad \beta_{0,1} = 3 \pm 2.$$

c) Thermodynamic considerations.—The dependence of the equilibrium constant on the ionic strength can be described by the original Debye-Hückel equation or by its extended form:

$$\log K_1{}^0 = \log K_1 - \frac{\Delta z^2 A \sqrt{I}}{1 + B å \sqrt{I}} \tag{4}$$

where $K_1{}^0$ and K_1 are the first stability constants for $I = 0$ and $I > 0$, respectively, A and B are constants, å is the "closest approach" of the ions and Δz^2 is determined by the charges of the ions. Evidently the value of å depends on whether the ions are in direct contact (inner-sphere complex) or are separated by a water molecule (outer-sphere complex). However, the physical meaning of the å parameter is not clear enough to allow such a distinction. Furthermore å does not refer to a single complex but to the pair of the corresponding inner- and outer-sphere complexes. This remark is also valid for the following speculations which try to distinguish between the two types considering enthalpy and entropy of formation.

Rossotti[59] has stated that a less favourable entropy change is expected for the formation of an outer-sphere complex than for the corresponding inner-sphere one. Therefore when the entropy change is substantially less than expected from the charges and sizes of the ions it is reasonable to assume that outer-sphere complexes are predominantly formed. This principle was used by Choppin *et al.*[60–62] in studying different lanthanide and actinide complexes. They believe that sulphate and propionate form inner-sphere, while monovalent inorganic ligands form outer-sphere complexes with these metal ions.

Duncan and Kepert[63] have thoroughly examined the thermodynamics of the reaction

$$\mathrm{Me_{aq}}^{m+} + \mathrm{L_{aq}}^{l-} = \mathrm{MeL_{aq}}^{m-l}.$$

The free energy change of this reaction is given as

$$-RT\ln K = \Delta G^0 = G^0(\mathrm{MeL}^{m-l})_{aq} - G^0(\mathrm{Me}^{m+})_{aq} - G^0(\mathrm{L}^{l-})_{aq}, \tag{5}$$

where K is the equilibrium constant of the reaction, while the G^0's are the standard free energies. They found that for a series of complexes with common ligand and different metal ions, two different relationships may hold: i) ΔG^0 values decrease with increasing $G^0(\mathrm{Me}^{m+})_{aq}$; ii) ΔG^0's are nearly independent of $G(\mathrm{Me}^{m+})_{aq}$. They think that the first type of behaviour is characteristic for inner-sphere complexes, while the second indicates the formation of outer-sphere complexes. The explanation, according to Duncan and Kepert, is that when two ions interact without serious distortion of the hydration shells, the energy of the interaction is primarily determined by the ionic charges and the distance between them. The radius of the hydrated ions being fairly similar for ions of the same charge, we may expect that the energy of interaction will not change to a great extent in the formation of outer-sphere complexes. It must be borne in mind, however, that for the outer-sphere complex only one molecule of solvent is assumed to separate the metal ion and the ligand, therefore the aforementioned reasoning is not completely logical.

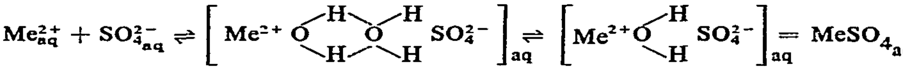
d) Comparison of successive stability constants.—As Bjerrum[64] has pointed out, the ratio of the logarithm of the successive stability constants can be described as the sum of three terms

$$\log K_n/K_{n+1} = T_n = S_n + E_n + R_n. \tag{6}$$

S_n represents the statistical term which is determined by the number of available and occupied coordination sites, E_n is the electrostatic term which represents the electrostatic contribution of the work necessary to form MeL_{n+1} from MeL_n, while R_n ("rest effect") contains all the other effects. Manning[65-67] calculated these different terms in the formation of inner- and outer-sphere complexes. From comparison of the theoretical values with the experimentally found ratio he claims to be able to determine the type of complex. I believe that this method cannot be regarded as reliable. First of all the uncertainty of the ratios is much greater than that of the absolute values of the constants the experimental error of which is considerable. The calculation of the statistical term in the case of outer-sphere complex formation is fairly arbitrary. The consideration of the electrostatic term is also arbitrary because the distance and the dielectric constant must be chosen. This may result in several hundred per cent differences. The rest effect is completely neglected. He declares that the sulphates of the lanthanides are outer-sphere complexes whereas Choppin on the basis of thermodynamic considerations finds just the opposite. It seems quite evident that both type of complexes are formed simultaneously but neither of the suggested methods can tell us the distribution of these complexes, or can indicate which type predominates.

e) Relaxation methods.—The formation of the complex MeL from the solvated metal ion and the ligand takes place in several distinct steps. Although these elementary reactions are extremely rapid, the different relaxation techniques developed by Eigen *et al.*[68] provide a possibility for their study. Among the different techniques ultrasonic absorption measurement[69] and the temperature-jump method[70,71] are especially well-suited for the study of outer-sphere complex formation.

That the formation of MeL occurs in successive steps is reflected in the fact that a single relaxation time cannot be assigned to each step. Eigen and Tamm describe the formation of the sulphato complexes of the bivalent metal ions with the following scheme:



$$\mathrm{Me^{2+}_{aq}} + \mathrm{SO^{2-}_{4_{aq}}} \rightleftharpoons \left[\mathrm{Me^{2+}\,O{\begin{smallmatrix}\diagup H \diagdown \\ \diagdown H \diagup\end{smallmatrix}}O{\begin{smallmatrix}\diagup H \\ \diagdown H\end{smallmatrix}}\,SO_4^{2-}}\right]_{aq} \rightleftharpoons \left[\mathrm{Me^{2+}O{\begin{smallmatrix}\diagup H \\ \diagdown H\end{smallmatrix}}\,SO_4^{2-}}\right]_{aq} = \mathrm{MeSO_{4_{aq}}} \quad (7)$$

The first step represents, in fact, a series of diffusion-controlled processes which, however, can be regarded as a single step. The second step is the formation of the outer-sphere complex which is followed by the transformation to the inner-sphere complex. Similar schemes are valid for other pairs of metal ions and ligands. The analysis of the relaxation spectra gives information on the distribution of the corresponding inner- and outer-sphere complexes. Unfortunately only a few system have been studied, but it is expected that these techniques will rapidly come into general use. The results show that in the case of all systems where different oxyanions were applied as ligands, a considerable fraction of the monocomplexes exist as outer-sphere complexes; in many systems the outer-sphere complexes even predominate. For the sulphates of Be^{2+}, Mg^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+} [69] and Al^{3+} [71] it was found that only about 10% of the monosulphatocomplexes occurs in the inner-sphere form.

C. STABILITY AND STRUCTURE OF OUTER-SPHERE COMPLEXES

The fundamental reason for the interaction of coordinatively saturated complexes with further ligands resulting in outer-sphere complexes is the electrostatic attraction between the inner-sphere complex and the ligand. Bjerrum[73] treated the problem from purely electrostatic considerations and defined a distance between oppositely charged ions within which they are regarded as being associated. This distance, q, is arbitrarily chosen so that the work of separation of the ions should be four times the mean kinetic energy per degree of freedom:

$$q = \frac{z_+ z_- e^2}{2DkT} \tag{8}$$

where z_+ and z_- are the charges of the ions, e is the charge of the electron, D is the dielectric constant of the medium, k is the Boltzmann constant and T is the absolute temperature. Then the association constant is given by

$$K = \frac{4\pi N}{1000}\int_a^q \exp\left[\frac{-z_+z_-e^2}{DkT}\right] r^2\, dr \tag{9}$$

where a is the radius of the central ion and r is the distance between the centres of the two ions. It follows that the higher the charge of the ions and the smaller the dielectric constant of the medium, the greater will be the tendency for the formation of the complexes. It appears from the data of Table 1 that the experimental data support this view. The fact that *cis*-$Co(en)_2Cl_2{}^+$ forms a much more stable outer-sphere complex with Cl^- then the *trans* isomer[35] is also in accordance with the electrostatic considerations, since the *cis* isomer has a dipole moment while the symmetrical *trans* isomer has not. However, simple electrostatic considerations can hardly explain the interaction of electrically neutral or even negatively charged species with further anions. (One must remember, however, that the Kossel–Magnus theory could explain, by elementary electrostatic reasoning, the formation of highly charged complex anions from the central metal ion and the ligands.) The following experimental observations seem to be in conflict with the simple electrostatic view:

i) Formation of anionic species by overcompensation of the original positive charge by the uptake of several anions in the outer-sphere. Evidence was obtained by anion exchange experiments (62La), liquid–liquid distribution (62Lb), optical rotation studies (65L, 66La, 66Lb, 67La) and by conductivity measurements (65H). Most of these highly important data came from the same laboratory.

ii) Sometimes there is no evidence for complex formation when it would be expected from consideration of the charges of ions. *e.g.* Larsson[74] found no interaction between $Co(en)_3{}^{3+}$ and $Fe(CN)_6{}^{3-}$.

iii) The fact that the stability constants of many outer-sphere complexes are larger than that of the corresponding inner-sphere complexes.

Considering that ligands of the outer-sphere may be bound by hydrogen bonds to the ligands of the inner-sphere, this last mentioned fact is easily understandable. It seems very likely that hydrogen bonds play a very important role in the formation of outer-sphere complexes. Comparative studies using protic and aprotic solvents would throw more light on the phenomenon.

The other facts mentioned under i) and ii) suggest that besides the simple electrostatic interactions charge transfer also occurs and this contributes to the stabilisation of the outer-sphere complexes. That a certain degree of charge transfer takes place during the outer-sphere complex formation follows from the spectroscopic observations of Kiss and Czeglédy[32] and particularly of Linhard[33]. The charge-transfer bands of $Co(NH_3)_5X^{2+}$ ($X = F, Cl, Br, I$) are gradually shifted towards shorter wavelength in the order $I^- > Br^- > Cl^- > F^-$[75], the donation of electronic charge from halogen to metal decreasing in the same sequence. The same phenomenon was observed with $Co(NH_3)_6^{3+}$ with changing halide ion[33], suggesting that the electronic interaction is transmitted by the NH_3 molecules of the inner-sphere. An especially pronounced effect was observed by Baker and Phillips[76] in a series of $Cr(bipy)_2Cl_2X$ and $Cr(phen)_2Cl_2X$ complexes (X = I, N_3, SCN, Br, Cl; bipy = 2,2'-bipyridyl, phen = 1,10-phenanthroline) which can be attributed to the easier electronic interaction through the conjugated ligands. It must be mentioned that this last-mentioned study was made with solid complexes only; it would be very important to investigate the outer-sphere complex formation in solution.

A charge transfer from the ferrocyanide ion to the cobalt(III) center in $[Co(en)_3{}^{3+}]_4[Fe(CN)_6{}^{4-}]_3$ could explain the formation of the second complex the great increase of the absorption in the visible and the decrease in the inertness of the inner-sphere[77]. A comparative study of the $Cr(en)_3{}^{3+}$–$Fe(CN)_6{}^{4-}$ system would be crucial in judging the validity of this explanation because in the chromium(III) complex the tendency for the charge transfer is evidently much less.

Although interaction between $Pt(en)_2Cl_2{}^{2+}$ and Cl^- is expected to occur on purely electrostatic considerations, Poë[78] assumes that the halogen in the inner-sphere is partially oxidized and reacts with a further halide ion just as free halogen molecules from charge transfer complexes with halide ions.

Two important questions arise in connection with the structure of outer-sphere complexes:

i) What is the configuration of the outer-coordination sphere?

ii) Is chelation possible in the outer-sphere?

At present it is very difficult to give a definite answer to these questions. There is no doubt that the ligands in the outer-sphere have a preferred spatial arrangement. Brady[79] on the basis of an X-ray study of solutions of $ErCl_3$ suggests that the central ion is octahedrally coordinated by water molecules while two chlorides are held in the outer-sphere occupying *trans* positions on the edges of the octahedron. Mason and Norman's studies[49] on circular dichroism indicate that the $PO_4{}^{3-}$ is situated over the centre of the face of the octahedron in the $Co(en)_3PO_4$ outer-sphere complex. Hydrogen bonds between the amine groups and the oxyanion contribute to the stability of the complex. It is very likely that the configuration of the outer-sphere in the case of a given inner-sphere complex depends on properties of the ligands both in the outer- and in the inner-sphere. These studies indicate the formation of cyclic structures in the outer-sphere and the stability constants of Table 1 also give some basis for the assumption that chelation operates in the outer-sphere complexes. Peacock and James (51P) found that the association constant of $Co(NH_3)_6^{3+}$ with maleate is one hundred times greater than with fumarate. It is interesting that the stability constant of the oxalate complex is a little less than that of the malonate complex; this is easy to understand considering the greater distance of the coordination sites in the outer-sphere.

Further evidence for chelation is given by the data of Archer, East and Monk (65A) according to which the stability of the dibasic outer-sphere complexes of $Co(NH_3)_5Cl^{2+}$ with anions of dibasic organic acids is much greater than the stability of the acetate complex.

D. THE KINETIC IMPORTANCE OF OUTER-SPHERE COMPLEXES

(i) Substitution reactions

The role of outer-sphere complex formation in substitution reactions has already been dealt with in sections B, *(ii)*, *k* and B, *(iii)*, *e*, therefore only one additional remark is made. It is reasonable to expect that the S_N2 mechanism involving a pre-equilibrium between the reactants will occur in the case of substitution reactions of four coordinated square-planar complexes. The kinetic studies indicate such pre-equilibria[80]; however, these association products are not outer-sphere complexes. In such cases the entering ligand is directly bound to the central ion, *i.e.* the inner coordination sphere is expanded. These species signify a transition from the normal inner-sphere complexes to the outer-sphere complexes and were termed "anisotropic complexes" by Jørgensen[57]. Evidently, a clearcut distinction between outer-sphere complex formation and the expansion of the coordination sphere is not possible.

(ii) Redox reactions

Although it is clearly true that outer-sphere complexes must play an important role in redox reactions between a cationic complex and an uncharged or anionic ligand, there are no quantitative data in this respect. Therefore, in the following, the treatment will be restricted to the possible role of the inert complexes in catalytic reactions[81].

The catalytic effects of complexes are generally associated with transient changes in the inner coordination sphere. However, if the catalyzed reaction is faster than the substitution reaction of the catalyst complex, this explanation cannot be correct. There are some cases where the catalytic activity of inert complexes is beyond doubt. Here outer-sphere complex formation may be responsible for the catalytic effects. The enormous repulsive forces which hinder the reaction between two anionic reactants dramatically decrease if one of the reactants is incorporated into an outer-sphere complex, the resultant charge of which is opposite. The catalytic effect of $Co(NH_3)_6{}^{3+}$ in the reaction between persulphate and iodide ions[83] can be explained by such an effect.

Another possibility is electron mediation by the inert complex. Infra-red spectroscopic studies[82] indicate an electronic interaction between the ligands in *trans* positions. As was mentioned in sections B, *(ii) i* and B, *(iii)* an electronic interaction exists between the central metal ion and the ligands in the outer-sphere, the inner-sphere complex can act as an electronic mediator. It may be anticipated that the more polarizable the inner-sphere ligands and the central ion, the more efficient is the inert complex in transferring the electrons of the outer-sphere ligands. A condition for such a mechanism is the simultaneous coordination of the reactants in the outer-sphere. There is evidence for the preferred formation of a mixed ligand outer-sphere[25] complex $Fe(phen)_3S_2O_8I^-$. It follows, however, from the nature of the phenomenon that it is very difficult to find definitive experimental evidence for such a mechanism.

E. CONCLUSIONS

In spite of the many discrepancies in the composition and stability of outer-sphere complexes it is proven that an inner-sphere complex may take up more than one ligand in the "second sphere". The data suggest that the spatial arrangement of the ligands in this sphere is determined by the properties of the inner-sphere complex and of the ligands. Therefore the term "ion-pair formation" is not adequate. On the other hand the term "second sphere" may imply the possibility of a third coordination sphere too. It is very likely, however, that the distribution of the ligands beyond the second sphere cannot be dealt with by the mass action law. Hence outer-sphere complex formation coordination seems to be the most appropriate term.

Simple considerations and the experimental evidence obtained so far indicate that outer-sphere complex formation is an ubiquitous phenomenon. The mechanism of different reactions involving metal ions is greatly influenced by the stability and the structure of these complexes. After surveying the present state of the chemistry of the outer-sphere complexes I am forced to use the hackneyed expression "much more research is necessary to get a deeper understanding of the phenomena and for the solution of the inconsistencies". There is no doubt that work in this exciting field will be rewarding for careful and imaginative coordination chemists.

ADDENDUM

Recently Ogino and Saito[84] have pointed out that it is possible to learn from spectrophotometric study whether the antipodes of an asymmetric inert complex form outer-sphere complexes of different stability with an optically active ligand. The method was tested by studying the racemic mixture of $Co(en)_3^{3+}$-*d*-tartaric acid system. At 25° and $I = 0.1$ the following stability constants were determined:

d-Co(en)$_3^{3+}$ -d-tartrate, log $\beta_{01} = 1.41$

l-Co(en)$_3^{3+}$ -d-tartrate, log $\beta_{01} = 1.32$

Notations d- and l- refer to the sign of the optical rotation at 589.3 mμ (sodium D-line).

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