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Outer-sphere Interactions in Solutions of Labile Complexes

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The principal methods for the investigation of outer-sphere interactions in solutions of labile inner-sphere complexes are arranged systematically and analysed. The modern views on the thermodynamics and structure of outer-sphere complexes are discussed and the reliability of certain hypotheses and models is examined from the standpoint of the comparison of the results of different experimental methods and theoretical ideas. A number of features of the outer-sphere interaction in solutions are formulated in relation to outer-sphere associated species formed by 3*d* metals, using certain data about the associated species of *s*, *p*, and *f* metals as well as outer-sphere associated species of inert complex cations.
The bibliography includes 203 references.

CONTENTS

I. Introduction 631
II. Methods for the investigation of the outer-sphere interaction of labile complex cations 631
III. Outer-sphere complexes of transition metals (*d* metals) 634
IV. Outer-sphere complexes of non-transition (*s*, *p*), lanthanide, and actinide elements (*f* metals) 637
V. Certain features of the outer-sphere interaction of labile outer-sphere complexes 639

I. INTRODUCTION

Outer-sphere interaction is a phenomenon as common as the formation of inner-sphere complexes[1]. Certain problems of the theory and practice of outer-sphere association in solutions have been examined in a number of reviews[2-10]. However, in these studies attention was concentrated on the outer-sphere complexes (OSC) formed by inert Werner complexes, i.e. complexes which are formed and dissociated at a low rate and which are saturated with respect to the coordination number of the central atom[1-8]. As regards labile complexes or complexes which rapidly exchange ligands, over a period shorter than 1 min for a 50% degree of reaction, outer-sphere reactions involving them have been investigated mainly in relation to complex anions[2,3] such as $[ZnBr_4]^{2-}$, $[BiCl_6]^{3-}$, $[Fe(SCN)_6]^{3-}$, and $[AgCl_2]^-$.

Complex cations, for example, $[Co(NH_3)_6]^{3+}$, $[Cr(H_2O)_6]^{3+}$, and $[Rh(NH_3)_5Cl]^{2+}$ usually function as the coordination centres of the OSC. Anions, both simple and complex, play the role of ligands in the vast majority of cases. This can be explained by the high tendency of anions to exhibit electron-donating properties. Inert complex anions are probably capable of forming an outer (second) coordination sphere of a definite configuration, which has been confirmed by numerous investigations[1-14]. The ability of labile complex cations, for example $[Ni(NH_3)_6]^{2+}$ and $[Co(H_2O)_6]^{2+}$ to undergo outer-sphere interaction and procedures for its investigation have not so far been the subject of independent reviews. At the same time the number of systems with labile inner-sphere complexes is many times greater than the number of systems with inert compounds and the interactions in such systems are much more complicated.

Together with the increased theoretical interest in labile outer-sphere complexes[1-10], the latter also attract attention from the practical point of view, particularly in the field of homogeneous catalysis[1,12,15] and in the regulation of biological molecular processes—oxygen and energy transfer in cells, ionic equilibria in the reactions of enzymes, and other most important biological phenomena[12].

The equilibria in labile systems containing outer-sphere complexes and the thermodynamic interpretation of the experimental results associated with them have been transformed into an important and serious problem[5-10], in view of the almost simultaneous occurrence of both inner-sphere and outer-sphere interactions.

The aim of the present review is to examine critically methods for the experimental investigation of the outer-sphere interaction of labile complex cations with different ligands, to survey and analyse literature data on the thermodynamics of this type of OSC, to carry out a comparison with the results of the study of the OSC of inert cations, and to outline certain ways in which this field in the chemistry of coordination compounds can be developed.

II. METHODS FOR THE INVESTIGATION OF THE OUTER-SPHERE INTERACTION OF LABILE COMPLEX CATIONS

There exist various approaches to methods for the investigation of the outer-sphere interactions of labile complex cations as a function of an inner-sphere process, which complicates the study of the OSC.

1. Outer-Sphere Interaction Uncomplicated by Inner-Sphere Complex Formation

The most convenient method for the investigation of outer-sphere interactions for labile complex cations of different composition involves carrying out experiments in solutions containing an excess of inner-sphere ligands. This excess should almost completely suppress the dissociation of the inner sphere and should not influence appreciably the formation of the OSC investigated. This situation can only be created in systems with comparatively stable inner-sphere compounds. The absence of measurable dissociation of the inner-coordination sphere makes it possible to study the formation of OSC by any methods used in the investigation of labile inner-sphere interaction.

The formation of 1 : 1 OSC can be represented in the general form as follows:

$$[ML_N] + A \rightleftarrows [ML_N] \ldots A$$

where L and A are inner- and outer-sphere ligands (the charges have been omitted) and N is the limiting coordination number of the first sphere.

Potentiometry, which is one of the most exact and widely used methods for the investigation of inner-sphere complex formation, has been employed in the study of the association of tris(ethylenediamine)cadmium with sulphate ions in 3.0 N

aqueous solutions of mixtures of sodium perchlorate and sulphate[11,13]. Measurements were made of the changes in the e.m.f.'s of cells with ion transport comprising a cadmium amalgam electrode, where diffusion potentials were determined experimentally[13]. The dissociation of tris(ethylenediamine)-cadmium(II) was suppressed by an excess of ethylenediamine. The measured changes in the e.m.f. were related to the formation of OSC of the type $[CdEn_3](SO_4)_n^{2-2n}$ only; the values of n and the stability constants were determined by Leden's method[1].

The changes in the solubilities of a number of sparingly soluble salts containing the tris(ethylenediamine)nickel(II) ion in solutions with increasing concentrations of outer-sphere ligands and in the presence of a constant excess of ethylenediamine served as a basis for the determination of the stability constants of the OSC $[NiEn_3].L_n^{z-zn}$, where z is the charge of the ligand and L are chloride, sulphate, thiosulphate, and carbonate ions. The conductimetric method has been used[15] to study the monoligand OSC of tris(ethylenediamine)- and tris(propylenediamine)-cobalt(II) in aqueous solutions at low ionic strengths. The thermochemical method[14] led to the determination of the stability constants and enthalpies and entropies of formation of a number of tris-(ethylenediamine)nickel(II) OSC.

Electronic spectroscopy using charge transfer bands in the ultraviolet has been employed in the investigation of the OSC of tris(ethylenediamine)cobalt(II)[15,16] and a number of other cations[17]. The NMR method yielded information about the thermodynamics and structure of numerous OSC of tris(pyrazolyl)borate[18–22] as well as bis(acetylacetone)dipyridinecobalt(II)[23] in several non-aqueous solvents such as cyclohexanone or chloroform. The absorption of ultrasound has been used to investigate the OSC of tris(1,10-phenanthroline)zinc(II).[24] Extraction has been used for the same complexes and mixed complexes with acetylacetone[25]. It served as a basis also for the determination of the formation constants of the OSC of tetra(γ-picoline)dicyanatocobalt(II).[26] The influence of the composition of the external medium on the width of the EPR spectral line has been demonstrated[27].

The high stability of the hydration shell of alkali and alkaline earth metal cations as well as lanthanide ions in many instances makes it possible to investigate numerous OSC of the aquo-complexes of these metals with simple and complex anions using various research techniques[28,29]. However, in such systems there is a possibility of the superposition of the inner-sphere effect on the outer-sphere association. The degree of such superposition depends greatly on the stability of the hydration shell and the nature of the outer-sphere ligands.

2. Simultaneous Formation of Inner- and Outer-Sphere Complexes

The simultaneous formation of inner-sphere complexes (ISC) and OSC is frequently encountered in systems containing aquated cations. The effect of the outer-sphere interaction is then manifested to the maximum extent before the formation of the first inner-sphere complex[1] and is sharply reduced in subsequent coordination stages.

Processes involving the joint formation of monoligand inner- and outer-sphere complexes from an aquated metal ion $M(H_2O)_N$ and the ligand (here and in the general cases discussed below the ionic charges are omitted to simplify the formulation) can be represented by the equations:

$$\begin{array}{ccc} M(H_2O)_N + L & \underset{}{\overset{k_{1,2};\,\omega_{01}}{\rightleftharpoons}} & [M(H_2O)_N]\cdot L \\ \uparrow\downarrow\beta_{n,0} & & \downarrow\uparrow k_{2,3};\ k_{3,2},\ K_\Pi \\ [M(H_2O)_{N-n}L] + nH_2O & & \end{array} \qquad (1)$$

where n is the number of binding sites in the ligand in the given process. Thus the inner-sphere complexes examined are labile and the OSC are formed at very high rates[3,4], the equilibrium constants for the formation of 1 : 1 complexes can be characterised by the following expressions:

$$\omega_{01} = \frac{\{[M(H_2O)_N]\cdot L\}}{\{[M(H_2O)_N]\}\cdot\{L\}}, \qquad (2)$$

$$\beta_{10} = \frac{\{[M(H_2O)_{N-1}\cdot L]\}\cdot\{H_2O\}}{\{[M(H_2O)_N]\}\cdot\{L\}}. \qquad (3)$$

The square brackets define the Werner coordination sphere and the braces denote activity or concentration if the activity coefficients are constant. The subscripts to the constants indicate the number of attached inner- and outer-sphere ligands.

The ratio of the constants represented by Eqns.(2) and (3) characterises the conversion of the OSC into the inner-sphere complex:

$$K_\Pi = \frac{\{[M(H_2O)_{N-1}\cdot L]\}\cdot\{H_2O\}}{\{[M(H_2O)_N]\cdot L\}} = \frac{\beta_{10}}{\omega_{01}}. \qquad (4)$$

In systems with labile complexes it is difficult to separate the effects of the formation of inner- and outer-sphere species for their quantitative assessment. The majority of physicochemical properties or quantities (electrical conductivity, electrode potential, optical density, heat of formation, and others), characteristic of OSC and ISC, are manifested as the general property of the solution. The reactions involving the formation of OSC and ISC under equilibrium conditions are virtually identical with the parallel reactions and any property of the solution is related to the amounts of complexes by the general expression

$$\bar{P} = \sum_{i=0}^{i=n} \alpha_i\, p_i, \qquad (5)$$

where α_i are the fractions of different types of complexes and p_i are the partial values of a certain physicochemical parameter $\bar{P}$ for each type of complex. Since it is impossible to obtain the exact value of p_i either experimentally or theoretically, only an approximate solution of Eqn.(5) and an approximate determination of β_{10} and ω_{01} are possible[1,37,39,40,45,46].

The majority of the formation constants of the complexes determined previously and compiled in the literature[28,29] contain information about the overall stability of two components:

$$K = \frac{\{[M(H_2O)_N]\cdot L\}\cdot(1/\{H_2O\}) + \{[M(H_2O)_{N-1}\cdot L]\}}{\{[M(H_2O)_N]\}\cdot\{L\}} = \beta_{10} + \omega_{01}. \qquad (6)$$

At the present time extensive data have accumulated, which permit a separate estimation of the β_{10} and ω_{01} with a certain degree of approximation.

The spectrophotometric method has been greatly developed for the solution of problems of outer-sphere interactions. Changes in absorption in the visible region in the electronic spectra of d and f metals have been observed in a large number of examples[37,38] for solutions containing inner-sphere forms[31–34]. We may note that the presence of OSC does not affect the intensity and positions of the absorption bands in the visible part of the spectrum, but affects the absorption in the ultraviolet, where intense charge-transfer bands are present[34,35]. In many cases[36–38] it is possible to assign the absorption bands to different types of complexes. The difficulty of the quantitative determination of β_{10} and ω_{01} is associated, as for a number of other methods, with the fact that the partial molar extinction coefficients of the OSC and ISC (ε_{01} and ε_{10}) are unknown. These quantities can be estimated approximately[39,40]. The neglect of one of the forms present in smaller amounts[41–44] yields doubtful results,

because the degree of approximation to the exact stability constants[45,46] is difficult to determine.

The most successful approach probably involves the use of the change in the activity of water in the course of the formation of the ISC [see Eqn.(1)]. Spectrophotometric measurements for aqueous organic solutions make it possible to obtain separately the values of β_{10} and ω_{01}.[45,47] A disadvantage of this method is the necessity to extrapolate the formation "constants", more precisely coefficients, characterising the equilibria in non-aqueous solutions to the conditions in an aqueous solution.

Using a familiar method[48] for the calculation of the stability constants of 1 : 1 complexes in the visible region of the spectrum, where $\varepsilon_{01} = \varepsilon_{00}$, it is possible to obtain the following relation[45]:

$$\frac{d\bar{\varepsilon}}{d[L]} = \frac{1}{\beta_{10}^{org}(\varepsilon_{10} - \varepsilon_{00})}\left(\frac{\varepsilon_{00} - \bar{\varepsilon}}{[L]}\right)^2, \qquad (7)$$

where ε_{10} and ε_{00} are the molar extinction coefficients of the ISC and the free metal respectively.

The values of $\varepsilon_{10} - \varepsilon_{00}$ and ε_{10} can be found from $\beta_{10}^{org}(\varepsilon_{10} - \varepsilon_{00})$ and β_{10}^{org} (obtained for an aqueous–non-aqueous solution) by extrapolating the experimental values to the concentration ranges where absolute non-aqueous and aqueous solutions exist. In this case the errors due to the slight changes in absorption in the region of transitions in the electronic absorption spectrum forbidden by the selection rule are usually added to the inaccuracies associated with the extrapolation.

The method of chemical relaxation developed by Eigen and his coworkers[49-51] theoretically makes it possible to find separately the formation constants of OSC and ISC, provided that there is a significant difference between the kinetics of their formation. For $k_{12} = 10^{10} - 10^{12}$ mol s^{-1} [see Eqn.(1)], the constant k_{23} is frequently in the range 10^3–10^9 s^{-1}. If it is possible to obtain separately the relaxation times corresponding to the formation of the OSC and the ISC, then the problem of the calculation of their formation constants can be solved unambiguously. In practice one usually obtains a single relaxation time corresponding to the slow state of the process, i.e. the formation of the ISC. This relaxation time (τ) depends on both the fast and slow processes:

$$\tau^{-1} = \frac{k_{12}([M] + [L])k_{23} + k_{21}k_{32}}{k_{21} + k_{23}}, \qquad (8)$$

where [M] and [L] are equilibrium concentrations.

Bearing in mind that $k_{21} \gg k_{23}$, we obtain

$$\tau^{-1} = k_{23}\omega_{01}([M] + [L]) + k_{32},$$

where $\omega_{01} = k_{12}/k_{21}$.

Thus the values of $k_{form} = k_{23}\omega_{01}$ and $k_{diss} = k_{32}$, obtained from kinetic experiments, make it possible to determine β_{10}:

$$K = k_{23}\omega_{01}/k_{32} = K_{II}\omega_{01} = (\beta_{10}/\omega_{01})\,\omega_{01} = \beta_{10}.$$

The difficulty consists in the determination of the exact relaxation data under standard conditions. Using this method, Eigen and Tamm[50] calculated the equilibrium constants K_{II} for a series of 3*d* aquo-anions in sulphate solutions.

In some kinetic studies it has been suggested that the amplitude and form of the relaxation curve be used[52,53] to calculate the parameters of the equilibria involving OSC and ISC when these are present jointly. The two methods yield a difference between the stability constants approximately by a factor of two. The experimental accuracy of the kinetic data is still unsatisfactory for the determination of reliable data for the stability of the OSC. More than others, this method can yield an unambiguous solution, provided that the experimental technique is improved and is applied more widely to problems of the OSC.

During recent years, the NMR and EPR methods have contributed greatly to the study of outer-sphere interaction[54-58]. The separation of the effects with their aid as well as other methods is difficult owing to the rapid exchange of the ligands in the inner sphere of labile complexes[59,72]. The difference between the two forms of complexes in solution is limited by the condition $1/\tau = (\sqrt{2})\pi\Delta\nu_0$, where $1/\tau$ is the rate of the exchange reaction and $\Delta\nu_0$ is the difference between the frequencies of maximum absorption for the two forms in the absence of exchange. Thus, when the lifetime of any one form is too short ($< 10^{-3}$ s), i.e. there is rapid exchange, then ν_{10} and ν_{01} cannot be determined separately. This obtains virtually for all labile complexes.

However, the NMR and EPR methods yield very valuable structural data, obtained under the conditions of a slow exchange of atoms containing resonating nuclei or electrons[55,56]. For example, the formation of ISC together with OSC in solutions of certain copper salts has been demonstrated from the change in the *g*-factor[57,58]. OSC in the presence of different anions have been found on the basis of the line width in the hyperfine structure of the EPR spectrum of manganese(II).[60-62]

Comparison of the variations of the signal intensity and the hyperfine splitting line width in the EPR spectra made it possible to find the ratio of the OSC and ISC in solutions of the dithionate[63-65] and perchlorate[66] of manganese(II).

The NMR chemical shifts[67-69], the relaxation times[70], and the paramagnetic shift[71-76] in the resonance of the ^{1}H, ^{19}F, ^{17}O, and (to a lesser extent) heavier nuclei have been used to investigate outer-sphere interactions. In most cases the formation of a mixture of ISC and OSC was noted in solutions of inorganic salts of transition metals (Cu, Mn, Co, Ni), including solutions where complex anions were present: SiF_6^{2-}, GeF_6^{2-}, SnF_6^{2-}, and BF_4^-.[71,74-76] An attempt has been made[71] to calculate β_{10} and ω_{01} for compounds of a series of metals with the above ligands from the changes in the paramagnetic shifts of the ^{19}F signal. However, the assumptions made led to extremely approximate equilibrium constants.

Relatively inert complexes, for example aluminium sulphates[77,78], give rise to resonance absorption bands of the ISC $[Al(H_2O)_5(SO_4)]^+$ and the hexa-aquo-form $[Al(H_2O)_6]^{3+}$, which can be determined separately, but no calculations have been made by the NMR method on the two forms of complexes present jointly in these systems.

The possibility of using the rate of exchange of water in the aquo-ions of metals in the presence of non-aqueous additives has been demonstrated[74-76,79]. In this case differences are observed between the chemical shifts of inner- and outer-sphere water. The development of this method apparently makes it possible to differentiate quantitatively the OSC and ISC in mixed solvents.

The "probe" method has been used[80] to investigate the outer-sphere interaction of labile aquo-ions of the elements in the first transition series. Methylene chloride and carbon tetrachloride have been used as the outer-sphere probes. On the basis of measurements of the longitudinal (T_1) and transverse (T_2) proton relaxations, the formation of a series of OSC $[H_4Mn(H_2O)_6]_nCl_m$, where $n = 2$–4 and $m = 4$–6, in manganese(II) chloride solutions has been demonstrated[81].

In certain favourable cases vibrational spectroscopy has been used successfully as a quantitative and qualitative method for the study of outer-sphere interactions. The characteristic absorption of SCN^-, CN^-, SO_4^{2-}, and PO_3^- ions serves as a source of information about the OSC and ISC in solutions of many metal salts[82-87]. For example, the absorption bands due to the stretching vibrations of the S–O bond in the sulphate ion in the range 850–1400 cm^{-1} make it possible to identify ISC and OSC. It has been possible to demonstrate approximately[82] the presence of 8, 50, and 12% of ISC in

sulphate solutions of nickel(II), indium(III), and cerium(III) salts. Analogous data have been obtained for sulphate solutions of aluminium(III)[83,84] as well as Mn^{2+}, Co^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, and Cd^{2+} in the presence of SCN^-.[85-87]

The difficulties in the quantitative estimation of the ratio of the concentrations of OSC and ISC are due to the lability of the complexes and the necessity for an accurate determination of the absorption intensity in aqueous solutions. Qualitative data have been obtained for solutions of metal perchlorates, nitrates, and sulphates from Raman spectra[88-92].

The potentiometric method has been used recently[93-95] for the simultaneous detection and subsequent calculation of the formation constants of the OSC and ISC in solutions of copper(II) chloride and bromide and manganese(II), cobalt(II), and zinc(II) chlorides. These studies were performed for a variable salt composition, which entailed the variation of the activity of water. The equilibrium constants were determined by extrapolating the concentration "constants" obtained to zero and unit activities of water. The dependence of the composition of the complexes on the activity of water, discussed above [see Eqn.(1)], and not the method of measurement plays the main role in this instance. The disadvantages of the method include the necessity to measure the equilibrium constants under non-equivalent conditions in the ionic medium and inaccurate extrapolation.

The calorimetric method sometimes makes it possible to solve the problem of whether OSC or ISC predominate. Owing to the liberation of water molecules [see Eqn.(1)] from the inner sphere on formation of the OSC, the values of $\Delta H°$ and $\Delta S°$ should be more positive when the inner sphere complex does not form strong covalent bonds. On this basis, the complexes formed in solution can be assigned either to the inner-sphere type (the ΔH and ΔS for the complex formation reactions are more positive than for the reactions involving other ligands) or to the outer-sphere type. This method of identification can be referred to as the thermodynamic criterion. Hypotheses concerning the application of a thermodynamic criterion of the type of complex formation on this basis have been put forward by both Vasil'ev and Yatsimirskii[96-100] and subsequently in Ahrland's papers[9,10].

Comparison of the values of $\Delta H°$ and $\Delta S°$ for labile and inert complexes makes it possible to make a qualitative choice in a number of instances between inner- and outer-sphere compounds[9,10,101-107]. A more reliable application of this principle is hindered by the lack of thermodynamic complex formation data obtained by calorimetric measurements and referred to zero ionic strength.

The inner- and outer-sphere complexes can be identified by measuring the specific volumes or compressibilities of solutions[108]. The sensitivity of solutions to pressure should be greater when ISC predominate[108-111]. This can be explained by the theoretically greater compressibility of ISC solutions compared with OSC solutions, because the degrees of hydration and electrostriction change more on formation of ISC. For example, the changes in the partial molar volumes of solutions for manganese(II) and magnesium(II) sulphates[109] are from −7,4 to −10 ml mol^{-1} and from −9.5 to 6.9 ml mol^{-1} when the concentration is changed from 5×10^{-4} M to 2×10^{-2} M respectively. The different directions of the changes $\overline{\Delta V}$ permit a conclusion concerning the different types of complexes formed.

The proof of the influence of the outer sphere of aquocations on the structure and properties of the solutions has also been obtained from compressibility data[110,111]. On the other hand, dilatometric measurements of the compressibilities of cobalt(III) complexes[111] in solutions containing OSC and ISC do not allow the formulation of a criterion for differentiating between these two types of complexes although the changes $\overline{\Delta V}$ for complexes with similar structures were regular.

An effective although rarely used method for the investigation of OSC in solutions is X-ray diffraction. The results of the determination of the interatomic distances in the OSC $[M(H_2O)_6]^{2+}...Cl^-$, where M = Cd(II), Co(II), or Cu(II), have been published[112]. The M–Cl distance is 4.42 Å. The distances for the ISC are much smaller: 2.27–2.60 Å.[113] The existence of OSC has been established by X-ray diffraction for associated gadolinium chloride species[114] in which the Gd–Cl distances are 4.5–5.0 Å, while in the ISC the Gd–Cl bond length is 2.8 Å.

The above brief survey of experimental methods leads to the conclusion that the study of inner- and outer-sphere complex formation is on the whole developing rapidly and involves the employment of the latest methods. Important structural results have been obtained with the aid of microwave spectroscopy, chemical relaxation, and X-ray diffraction. On the other hand, the study of the equilibria and the thermodynamics of the ISC and OSC in labile systems is advancing slowly. The problem can be probably to a large extent solved by devising apparatus whereby one can measure chemical relaxation with a high accuracy and by developing experimental and computational NMR techniques in combination with the development of the theory of solutions[115-117].

III. OUTER-SPHERE COMPLEXES OF TRANSITION METALS (*d* METALS)

Unambiguous information about the thermodynamics of the structure of OSC has been obtained for systems where outer-sphere association is not complicated by the inner-sphere interaction. Unfortunately such studies have been made only for a small number of OSC and should be extended further.

Data have now been obtained[14] on the association of tris(ethylenediamine)nickel(II) in 3.0 *N* aqueous sodium perchlorate solutions containing also the sodium salt of the ligand (Table 1). It follows from these results that the stability of the OSC decreases in the following sequence of outer-sphere anions: $S_2O_3^{2-} > SO_4^{2-} > CO_3^{2-} > Cl$, which is analogous to the sequence for tris(ethylenediamine)cobalt(III) [4] and many other inert complexes[15,30]. The existence of this sequence has been explained[4] by the changes in the charges and polarisabilities of the anions.

Table 1. The overall association constants of tris(ethylenediamine)nickel(II) with certain anions in 3.0 *N* solutions of sodium perchlorate and the sodium salt of the ligand at 25.0 °C according to solubility data[14] for $[NiEn_3]SO_4$.

Ligand ion	ω_{01}	ω_{02}
Chloride	0.08	—
Sulphate	0.70 (0.66) *	0.20 (0.57) *
Carbonate	0.58	0.06
Thiosulphate	0.92 (0.83) **	0.16 (0.22) **

* The solubilities of $[NiEn_3][PtCl_6]$ are indicated in brackets.

** According to the solubility of $[NiEn_3]S_2O_3$.

The enthalpies (−1.7 kcal g-ion^{-1}) and entropies (−5.7 e.u.) of formation show[14] that the addition of a sulphate ion to tris(ethylenediamine)nickel takes place as a result of the enthalpy component of the free energy. On the other hand,

inert tris(ethylenediamine) complexes combine with sulphate ions as a result of the increase of entropy[4]. The causes of this phenomenon require explanation.

It is of interest to note that tris(ethylenediamine)cadmium(II) forms associated species with sulphate ions having the same equilibrium constant[11] as the species formed by tris(ethylenediamine)nickel(II). This demonstrates the influence of the charge of the complex cation on the association and a very small contribution of other factors. However, tris(ethylenediamine)cobalt(II)[16] has a much smaller capacity for interaction with sulphate ions, which conflicts with the conclusion that the charge exerts the dominant influence. We believe that the properties of the OSC noted here have still been very little investigated and require extensive tests in relation to other examples.

A number of studies[18-22] of the OSC of labile but extremely strong complexes of cobalt(II), the inner sphere of which is saturated by the tridentate tripyrazolylmethane ligands, have been published. The OSC were studied by NMR. Measurements were made of the chemical shifts of the proton or ^{19}F signals for the outer-sphere ligands consisting of different molecules and ions. The outer-sphere ligands were pyridine, aniline (or its substituted derivatives), methanol, acetonitrile, acetone, benzene, hexane, hexafluorophosphorus(V), etc. It was shown that neutral molecules add to the outer sphere along the z axis[18,19], while anions add along the x axis[21]. This difference was explained by the contribution of electrostatic and van der Waals forces to the formation of outer-sphere bonds. The contribution of the latter was confirmed[22] by the increase of the association constants with increase of the dipole moment of the solvent. The results of these studies demonstrated the presence in the outer-sphere of a different configuration which determines the catalytic effect[20].

An analogous study by NMR was carried out[23] for bis(acetylacetone)dipyridinecobalt(II) in cyclohexanone. The stepwise interaction with chloroform and methyl chloride was investigated and it was observed that the outer-sphere association takes place as a result of the decrease of enthalpy accompanied by a sharp diminution of entropy (−20 e.u. in each coordination stage). It was shown that the outer-sphere ligands are coordinated via hydrogen atoms directed towards the inner-sphere ligands in the equatorial plane.

Table 2. The extinction coefficients ($\bar{\varepsilon}$) of copper(II), cobalt(II), and nickel(II) ions in 1 M Li_nL solutions at an ionic strength of 3.0 ($LiClO_4$).

Ligand ion	Cu^{2+} (λ = 800 nm)	Type of complex	Co^{2+} (λ = 510 nm)	Type of complex	Ni^{2+} (λ = 720 nm)	Type of complex
Perchlorate	11.9	OSC	5.5	OSC	2.2	OSC
Sulphate	12.1	OSC	5.6	OSC	2.3	OSC
Fluoride	>12.5	OSC,ISC	5.5	OSC	2.2	OSC
Chloride	22.1	ISC	6.0	OSC	2.2	OSC
Bromide	21.8	ISC	5.9	OSC	2.2	OSC

An extraction study[26] demonstrated the occurrence of successive double addition of chloroform to the outer-sphere of dithiocyanatotetrakis(γ-picoline)cobalt(II) via hydrogen bonds formed between chloroform and the picoline π electrons.

However, in the case of labile ISC systems the greatest amount of data has been obtained for acido-OSC formed by the complexes of transition elements of the first series with F^-, Cl^-, Br^-, SO_4^{2-}, NO_3^-, etc. In these systems both types of complex formation occur simultaneously, inner- and outer-sphere associated species being produced. In such cases the absorption spectrum in the visible region, due to the breakdown of symmetry in the inner sphere, undergoes a change in intensity. Table 2 presents data concerning the variation of the absorption of certain cations under comparable conditions[39,101-103].

Table 3. Thermodynamic data for inner- and outer-sphere complex formation (at 25 °C) involving inert and labile complexes according to the equilibria:

$$[ML_6]^{n+} + A^z \rightleftarrows [ML_6]^{n+}\cdot A^z \rightleftarrows [ML_5\cdot A]^{n-z} + H_2O$$

Compn. of complex in soln.	ΔH°, kcal mol^{-1}	ΔS°, cal mol^{-1} K^{-1}	Ionic strength	Type of complex	Refs.
$[Cr(H_2O)_5SO_4]^+$	7.2	29	1.0*	ISC	10
$[Cr(H_2O)_6]^{3+}\cdot SO_4^{2-}$	0	5	1.0*	OSC	10
$[Cr(H_2O)_5Cl]^{2+}$	5.0	23.3	0	ISC	118
$[Cr(H_2O)_5Cl]^{2+}$	6.6	—	5.1	ISC	119
$[Cr(H_2O)_6]^{3+}\cdot Cl^-$	−0.43	−1.7	1.0	OSC	120
$[Co(NH_3)_5SO_4]^+$	3.7	17	1.0	ISC	32,10
$[Co(NH_3)_5SO_4]^+\cdot SO_4^{2-}$	1.6	16.5	0	OSC	126
$[Co(NH_3)_5Cl]^{2+}\cdot SO_4^{2-}$	−4.1**	−6.2	0.3	OSC	121
$[Co(NH_3)_5Br]^{2+}\cdot SO_4^{2-}$	0.85	16	0	OSC	126
$[Co(NH_3)_5Br]^{2+}\cdot SO_4^{2-}$	0.7	15	0	OSC	126
$[Co(NH_3)_5(H_2O)]^{3+}\cdot SO_4^{2-}$	−0.3	4	1.0	OSC	32,10
$[Co(NH_3)_6]^{3+}\cdot Cl^-$	0.6	—	1.0	OSC	122
$[Co(NH_3)_6]^{3+}\cdot SO_4^{2-}$	−0.5	14.2	0	OSC	126
$[Rh(NH_3)_5Cl]^{2+}\cdot SO_4^{2-}$	1.1	17	0	OSC	125
$[Rh(NH_3)_5Cl]^{2+}\cdot CO_3^{2-}$	4.9	22	0.5	OSC	125
$[Rh(NH_3)_5Cl]^{2+}\cdot CO_3^{2-}$	1.0	16	0	OSC	125
$[IrEn_3]^{3+}\cdot CO_3^{2-}$	−0.2	13.7	0	OSC	125
$[CoEn_3]^{3+}\cdot SO_4^{2-}$	2.0	10	0.5	OSC	125
$[CoEn_3]^{3+}\cdot SO_4^{2-}$	1.4	14	0	OSC	125
$[CoEn_3]^{3+}\cdot SO_4^{2-}$	−0.5	13.5	0	OSC	126
$[CoEn_3]^{3+}\cdot SO_4^{2-}$	0.3	6.5	0.5	OSC	126
$[Co\,Dipy_3]^{3+}\cdot SO_4^{2-}$	−8	−13	0	OSC	15
$[Co\,Phen_3]^{3+}\cdot SO_4^{2-}$	−6	−10	0	OSC	15
$[CuCl]^+$	2.9	7.0	3.0	ISC	101
$[CuCl]^+$	3.2	10.6	4.0	ISC	127
$[NiCl]^+$	1.10	2.9	4.0	OSC,ISC	127
$[CoCl]^+$	0.62	1.3	4.0	OSC	127
$[MnCl]^+$	1.40	4.5	4.0	ISC,OSC	127
$[ZnCl]^+$	1.2	4.8	4.0	ISC,OSC	127
$[FeCl]^{2+}$	4.2	16	1.0	ISC	10
$[FeCl]^{2+}$	3.4	16	3.7	ISC	10
$[CuBr]^+$	3.0	7.5	3.0	ISC	101
$[CuBr]^+$	0.9	2.8	2.0	ISC,OSC	123
$[CuBr]^+$	1.0	3.0	2.0	ISC,OSC	123
$[NiBr]^+$	0.08	−0.27	2.0	OSC	123
$[NiBr]^+$	2.8	5.5	3.0	ISC,OSC	101
$[CoBr]^+$	2.20	3.5	3.0	ISC,OSC	101
$[CoBr]^+$	0.15	0	2.0***	OSC	123
$[ZnBr]^+$	0.0	−2.75	4.5	OSC	124
$[CuSO_4]$	1.22	14.6	0	ISC,OSC	10,123
$[CuSO_4]$	0.38	2.0	4.0	OSC	127
$[NiSO_4]$	0.41	14.1	0.0	OSC	10
$[NiSO_4]$	0.58	3.0	3.0	OSC	101
$[NiSO_4]$	−0.11	2.2	4.0	OSC	127
$[CoSO_4]$	0.50	13.9	0	OSC	10
$[CoSO_4]$	0.62	3	3.0	OSC	101
$[CoSO_4]$	−0.64	0.1	4.0	OSC	127
$[FeSO_4]$	0.56	12.0	0	OSC	123
$[MnSO_4]$	0.61	15.2	0	OSC	10
$[MnSO_4]$	2.3	7	3.0	ISC,OSC	101
$[MnSO_4]$	1.4	4.5	4.0	ISC,OSC	127
$[ZnSO_4]$	0.63	13.5	0	OSC	123
$[ZnSO_4]$	0.72	3.5	3.0	OSC	101
$[ZnSO_4]$	0.57	4.7	4.0	OSC	127
$[NiS_2O_3]$	0.11	1.2	1.0	OSC	105
$[CoS_2O_3]$	0.12	1.2	1.0	OSC	105
$[CuF]^+$	3.2	15.5	3.0	ISC	103
$[MnF]^+$	3.6	10.5	3.0	ISC	103
$[CoF]^+$	3.3	14.0	3.0	ISC	103
$[NiF]^+$	1.4	8.0	3.0	OSC,ISC	103
$[ZnF]^+$	2.2	11.5	3.0	OSC,ISC	103
$[CuClO_4]^+$	−1.55	−6.8	1.0	OSC	106
$[NiClO_4]^+$	−1.26	−5.8	1.0	OSC	106
$[CoClO_4]^+$	−0.65	−1.2	1.0	OSC	106
$[MnClO_4]^+$	−1.24	−5.4	1.0	OSC	106
$[ZnClO_4]^+$	−1.04	−4.0	1.0	OSC	106

* At 60 °C.

** Determined from the temperature variation of the formation constant.

*** At 40 °C.

The results in Table 2 indicate at least the coexistence of OSC and ISC for the majority of associated copper(II) species and predominantly ISC for cobalt(II) and nickel(II).

The results of the measurements of the heats of formation of these complexes lead to the same conclusion. Table 3 presents the experimental $\Delta H°$ and $\Delta S°$ obtained by different workers together with qualitative estimates of the dominant types of complexes in the reaction mixture. The data for inert complexes, which form only OSC, are included as selection criteria.

The numerical data in Table 3 permit the utilisation of the thermodynamic criterion described above and lead to a conclusion concerning the dominant type of complex formation in systems comprising the labile compounds. The analogy with inert OSC in terms of thermodynamic properties is apparently fully justified, since kinetic properties should not influence the thermodynamics of the compounds. The OSC of inert "hydrophilic" complex cations are characterised by low values of ΔH and as a rule by positive values of ΔS, while the corresponding quantities for the ISC are more positive. Ionic strength has little influence on the ΔH for the complexes but, it apparently should have a significant influence on the entropies of formation of the OSC, since in this case the outer sphere is desolvated[105,106]. On the other hand, careful calorimetric measurements for the OSC formed by inert complexes[15,30,125,126] demonstrated that the entropy is approximately constant at $\Delta S° \cong 15$ e.u. for "hydrophilic" complex cations of any charge and doubly charged anions at zero ionic strength. By analogy, it is sometimes possible to decide which type of OSC predominates in the case of labile aquo-complexes and other "hydrophilic" complexes (Table 3).

In conformity with the thermodynamic criterion, the majority of the results obtained agree with spectroscopic measurements on solutions of salts of 3*d* metals. Unfortunately the amount of calorimetric data on complex formation at zero ionic strength is still inadequate. The development of studies on these lines is essential. On the other hand, one should point out the limitations of the thermodynamic criterion. It is inapplicable to "soft" acceptors and donors and to "hydrophobic" ions {see the OSC of $[CoDipy_3]^{3+}$ and $[CoPhen_3]^{3+}$, Table 3} whose hydration and solvation processes contribute less to the free energy[9,10,15,30].

Aruga[105,106] assigned the monoligand associated cobalt(II) and nickel(II) thiosulphate species in solutions as well as the manganese(II), cobalt(II), nickel(II), copper(II), and zinc(II) nitrate and chlorate species predominantly to the class of outer-sphere complexes in view of the negative values of ΔS at an ionic strength of 1.0. For $\Delta S = -1.2 - -6.8$ e.u., ΔH was $-0.65 - -1.55$ kcal mol^{-1}, which apparently characterises the interaction of ions of class *a*.

Larsson[107] calculated $\Delta S°$ for the dissociation of the OSC of the type MSO_4, where $M^{2+} = Mg^{2+}$, Zn^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, or Ca^{2+}. These functions were found to be in the range between -14.7 and -17.8 e.u. Theoretically the partial molar entropies $\Delta S°$ for the OSC differ from those for the ISC by the entropy of liberation of water (7.3 e.u.). Then judging from the $\Delta S°$, zinc(II) and magnesium(II) sulphates should exist in the form of the OSC, while calcium(II) and cadmium(II) should be predominantly in the form of ISC.[107]

As mentioned above, the stability constants of the ISC and OSC can be determined separately with certain approximations, but in the majority of methods no estimate of the degree of approximation is made. The most reliable results have been so far obtained by relaxation and spectrometric methods, the dependence of the equilibria on the composition of the solvent being used in the latter case. Table 4 gives a systematic list of the results of the determination of the stability constants of the OSC and ISC by different methods in systems comprising labile complexes. Table 4 also includes the results of the determinations of the overall stability constants for systems in which the appearance of both types of compounds has been demonstrated, the type of complex being determined on the basis of the experimental criteria of each method.

Many of the results in Tables 3 and 4 demonstrate unambiguously the dominance of the outer-sphere interaction in aqueous solutions of the salts of many ions of 3*d* elements. Nickel(II), cobalt(II), and copper(II) ions form mainly outer-sphere species of the type $\{[M(H_2O)_6].L\}$, while manganese(II) and iron(III) complexes have a mixed composition. The stability of purely outer-sphere species varies in the majority of systems in accordance with the following series of metals: $Cu^{2+} > Ni^{2+} \geqq Co^{2+} > Mn^{2+} \ll Fe^{3+}$, which constitutes a complete analogy with inner-sphere complex formation and corresponds to the same extent with the energy of stabilisation by the crystal field.

The size of the ligands apparently also plays a definite role in the formation of the ISC. Large polyatomic ions SO_4^{2-}, NO_3^-, ClO_3^-, and SiF_6^- form ISC more rarely than the monatomic ions F^- and Cl^-. The stability series for the OSC with different ligands is as follows:

$$F^- > SO_4^{2-} > ClO_3^- \simeq NO_3^-, \quad Cl^- > Br^-.$$

The ISC and OSC of bivalent manganese, cobalt, nickel, and copper have been studied systematically[71] by NMR on the basis of chemical, paramagnetic, and isotopic shifts, line widths, and spin–spin and hyperfine interaction constants. The ligands were the fluoride and oxide fluoride complexes of a number of metals. These large ions formed mainly OSC. If it is assumed that the assumptions made[67,71] in the calculation of the association constants do not introduce large errors, then the tendency of these ions towards the formation of both ISC and OSC diminishes in the following sequences:

$$MoO_2F_4^{2-} > WO_2F_4^{2-} > TiF_6^{2-} > SnF_6^{2-} > GeF_6^{2-} > SiF_6^{2-} > BF_4^-;$$
$$Fe^{2+} > Mn^{2+} > Co^{2+} > Ni^{2+} > Cu^{2+}.$$

These sequences are determined not only by the charges and dimensions of the ions but also by the nature of the M–F bond and the lability of the hydration shell of the cation.

However, the extremely significant difference between the data for the stabilities of the associated species under consideration is striking. The stability constants of such species are much higher, according to the results of new investigations[71] than those based on the results of earlier studies, although the methods of investigation and conditions were analogous.

It is of interest to note that molybdenyl and tungstyl tetrafluorides interact[71] via the fluoride ions in the *trans*- and *cis*-positions with respect to oxygen, forming equatorial and axial OSC with the cations, the former predominating.

The association of the cation with the perchlorate ions of the supporting salt plays a significant role in outer-sphere complex formation. The dependence of the stability constants on the ionic strength of the solution should be greater than is in reality the case. Nevertheless, despite the competition by the perchlorate ions, the ligand series quoted here confirm the occurrence of a predominantly ionic interaction, as has in fact been suggested for outer-sphere complex formation[7].

A common feature of the OSC is their low thermodynamic stability. When the overall complex formation reactions lead to stable complexes, for example, those of iron(III) with acetate or formate ions, the OSC are not manifested thermodynamically and play only a kinetic role.

Table 4. The stability constants of inner- and outer-sphere 1 : 1 complexes of the aquo-ions of *d* elements with different ligands (at 25.0°).

Ligand	β_{10}, ω_{01} or $\beta_{10}+\omega_{01}$	Ionic strength	Type of complex	Method of determination*	References
			Cu^{2+}(aq.)		
SO_4^{2-}	178	0	OSC	SP	42
SO_4^{2-}	6.0	1.0	OSC	SP	127
SO_4^{2-}	5.0	3.0	OSC	SP	38,39,101
SO_4^{2-}	2.3	3.0	OSC	SP	127
SO_4^{2-}	3.3	4.0	OSC	SP	127
NO_3^-	2.0	0	OSC	SP	45
NO_3^-	1.4	1.0	OSC	KIN	106,128
NO_3^-	0.40	3.0	OSC	SP	45
ClO_3^-	2.2	1.0	OSC	KIN	106,128
F^-	11.4	3.0	ISC,OSC	SP,C	103
Cl^-	0.87	3.0	ISC	SP	39,45
Cl^-	0.80	2.39	ISC	SP	93
Cl^-	0.58	3.0	ISC	SP	127
Cl^-	1.72	0	ISC	SP	42,45
Cl^-	1.63	0	ISC	SP	93
Cl^-	0.95	4.0	ISC	SP	127,1
Br^-	0.28	3.0	ISC,OSC	SP	38,38,101
Br^-	0.25	1.857	ISC,OSC	SP	95
Br^-	0.60	4.0	OSC	SP	127,1
SCN^-	82	3.0	ISC,OSC	SP	38
SiF_6^{2-}	0.8	1.0	ISC	NMR	71
SiF_6^{2-}	5	1.0	OSC	NMR	71
GeF_6^{2-}	0.8	1.0	ISC	NMR	71
GeF_6^{2-}	5	1.0	OSC	NMR	71
SnF_6^{2-}	0.7	1.0	ISC	NMR	71
SnF_6^{2-}	5	1.0	OSC	NMR	71
TiF_6^{2-}	1.0	1.0	ISC	NMR	71
TiF_6^{2-}	7	1.0	OSC	NMR	71
			Ni^{2+}(aq.)		
SO_4^{2-}	120	0	OSC	SP	127
SO_4^{2-}	1.8	3.0	OSC	S,P	38
SO_4^{2-}	3.2	4.0	OSC	SP	127
F^-	5.8	3.0	OSC	C,P	103
Cl^-	1.63	0	OSC	SP	127
Cl^-	0.20	1.0	OSC	SP	129
Cl^-	0.27	3.0	OSC	SP	38
Cl^-	0.50	3.0	OSC	SP	127
Cl^-	0.39	—	OSC	P	94
Br^-	1.04	0	OSC	SP	127
Br^-	0.13	1.0	OSC	SP	129
Br^-	0.15	3.0	OSC	SP	38
SCN^-	21.7	3.0	OSC	SP	38
SCN^-	12	—	ISC	IR	85
SCN^-	3	—	OSC	IR	85
GeF_6^{2-}	15	1.0	OSC	NMR	71
GeF_6^{2-}	1.7	1.0	ISC	NMR	71
SnF_6^{2-}	15	1.0	OSC	NMR	71
SnF_6^{2-}	1.7	1.0	ISC	NMR	71
SiF_6^{2-}	15	1.0	ISC	NMR	71
SiF_6^{2-}	1.7	1.0	ISC	NMR	71
TiF_6^{2-}	17	1.0	OSC	NMR	71
TiF_6^{2-}	1.9	1.0	OSC	NMR	71
NO_3^-	1.02	1.0	OSC	KIN	106, 128
ClO_3^-	2.2	1.0	OSC	KIN	106, 128
			Co^{2+}, (aq)		
SO_4^{2-}	102	0	OSC	SP	127
SO_4^{2-}	1.65	1.0	OSC	SP	129
SO_4^{2-}	1.70	3.0	OSC	S,P	38
SO_4^{2-}	3.2	3.0	OSC	SP	127
F^-	4.4	3.0	OSC	C,P	103
Cl^-	2.2	0	OSC	SP	127
Cl^-	0.43	1.0	OSC	SP	129
Cl^-	0.57	3.0	OSC,ISC	SP	38
Cl^-	0.32	—	OSC	P	94
Cl^-	0.43	—	ISC	P	94
Br^-	1.7	0	OSC	SP	127
Br^-	1.17	1.0	OSC	SP	129
Br^-	0.19	3.0	OSC	SP	38
Br^-	0.41	3.0	OSC	SP	127
SCN^-	18.7	3.0	OSC,ISC	SP	38
SiF_6^{2-}	25	1.0	OSC	NMR	71
SiF_6^{2-}	2.0	1.0	ISC	NMR	71
CrF_6^{3-}	25	1.0	OSC	NMR	71
CrF_6^{3-}	2.2	1.0	ISC	NMR	71

Table 4 (Cont'd.)

Ligand	β_{10}, ω_{01} or $\beta_{10}+\omega_{01}$	Ionic strength	Type of complex	Method of determination*	References
			Co^{2+}(aq.)		
TiF_6^{2-}	33	1.0	OSC	NMR	71
TiF_6^{2-}	2.8	1.0	ISC	NMR	71
			Fe^{3+}(aq.)		
SO_4^{2-}	580	4.0	ISC,OSC	SP	130
SO_4^{2-}	5.0	3.0	ISC,OSC	P	132
Cl^-	14.4	4.0	ISC,OSC	S,C	130
Cl^-	3.0	1.0	ISC	KIN	131
Cl^-	2.2	1.0	OSC	KIN	131
Br^-	2.3	4.0	OSC,ISC	SP,S,C	130
SCN^-	155	4.0	ISC	SP,S	130
$HCOO^-$	$3.4\cdot10^3$	4.0	ISC	SP	130
CH_3COO^-	$2.9\cdot10^5$	4.0	ISC	SP	130
			Mn^{2+}(aq.)		
SO_4^{2-}	22.4	0	ISC,OSC	P	127
SO_4^{2-}	3.3	1.0	ISC,OSC	P	127
SO_4^{2-}	1.7	3.0	ISC,OSC	P	107
SO_4^{2-}	1.62	3.0	ISC,OSC	SP	101
Cl^-	2.68	0	ISC,OSC	P	127
Cl^-	1.7	3.0	ISC,OSC	P	62
Cl^-	0.78	3.0	ISC,OSC	P	127
Cl^-	0.22	3.0	OSC	EPR	62
Br^-	1.53	0.0	ISC,OSC	P	127
Br^-	1.34	3.0	ISC,OSC	SP	62
Br^-	0.4	3.0	ISC,OSC	P	127
Br^-	0.17	3.0	OSC	EPR	62
$S_2O_4^{2-}$	18	—	OSC	EPR	63
$S_2O_4^{2-}$	4	—	ISC	EPR	63
SCN^-	9.4	3.0	ISC,OSC	SP	130

* Notation: SP = spectrophotometry; KIN = kinetic method; C = calorimetry; S = solubility; P = potentiometry.

It is noteworthy that the thermodynamics of the formation of OSC change fundamentally[15] on passing from "hydrophilic" to "hydrophobic" complex cations. The thermodynamic parameters examined above, which indicate the structure of the associated species, are valid only when the outer-sphere ligands interact with "hydrophilic" complex cations.

Analysis of data on the stability of the OSC of 3*d* metals shows that the order in which the stabilities vary for a series of metals depends little on the nature of the anion in the outer sphere. This indicates a major role of the central atom in the outer-sphere bond, the latter being subjected to its influence owing to the alteration of the properties of the coordinated inner-sphere ligand.

IV. OUTER-SPHERE COMPLEXES OF NON-TRANSITION (*s*,*p*), LANTHANIDE, AND ACTINIDE ELEMENTS (*f* METALS)

Metals whose valence is determined solely by *s* and *p* electrons exist in aqueous solution as singly- and doubly-charged ions. These are, in particular, alkali and alkaline earth metals. The stability of the hydration shells of these ions is high and increases with decrease of their atomic weight.

Aqueous solutions of the majority of salts of these metals with singly charged anions contain only outer-sphere associated species at concentrations below the total hydration limit. The stability of these species usually increases with decrease of the stability of the solvation shell from lithium to caesium and from beryllium to barium[28,29]. The tendency towards association with hydroxide, fluoride, acetate, and lactate, and similar ions varies in the opposite direction, indicating the dominant influence of the inner sphere interaction.

The 1–2- and 2–2-valent electrolytes based on these metals frequently exist in dilute aqueous solutions in the form of outer-sphere associated species. The contribution of the inner-sphere interactions in such solutions increases sharply, becoming dominant on passing from 1–2- to 2–2-valent electrolytes, on replacement of weakly polarisable anions by highly polarisable anions with a high electron-donating capacity, and with increase of the concentration of the solutions. The validity of the above postulates is confirmed by the satisfactory agreement between the results obtained using different experimental techniques[28,29].

Fairly extensive information about the thermodynamics of associated species formed by complex anions with alkali and alkaline earth metal cations has been examined by Mironov[2,3]. It shows unambiguously that complex anions are in many respects analogous to simple anions as regards their capacity for addition to the outer-spheres of alkali and alkaline earth metal aquo-cations. However, the outer-sphere association of unstable complex anions with cations usually leads to the additional incorporation of simple anionic ligands in the inner sphere of the complex anion as a result of the decrease of the negative charge of the entire associated species owing to the interaction of the complex anions with the alkali or alkaline earth metal cation[2]:

$$K^+ + [PbCl_3(H_2O)]^- \rightarrow K^+ \ldots [PbCl_3(H_2O)]^- \xrightarrow{+Cl^-} K^+ \ldots [PbCl_4]^{2-} + H_2O\,.$$

The interaction of triply and quadruply charged anions with alkali and alkaline earth metal cations is determined by the nature of the anions. In these systems the anions are usually incorporated in the inner coordination sphere, displacing water, and forming mixtures of ISC and OSC only occasionally in a small number of systems[2,3]. Judging from the infrared spectra of solutions, a good example of such OSC[86] is provided by magnesium and calcium compounds with certain doubly, triply, and quadruply charged ligands of the type of $CH_3PO_4^{2-}$, $CH_3P_2O_7^{3-}$, and $AP_3O_{10}^{4-}$, where A is adenosine. It is of interest to note that these ligands also form mainly OSC with doubly charged manganese, cobalt, and nickel ions, but are incorporated in the inner spheres of copper(II) and zinc(II).[86] In our view the validity of these postulates requires confirmation.

On the other hand, the interactions of alkali and alkaline earth cations (as well as cations of *p* and *f* metals even with singly charged anions at fairly high concentrations of aqueous solutions lower the symmetry of complex ligands. Thus Raman spectra demonstrate unambiguously[90] the decrease of the symmetry of the nitrate ion to C_{2v}. This effect weakens in the following sequence of cations:

$$Th^{4+} > In^{3+} > Cu^{2+} > Hg^{2+} > Ce^{3+} > Ca^{2+} > Zn^{2+} > Al^{3+} > Ag^+ > Na^+ \simeq K^+ \simeq NH_4^+\,.$$

It is believed[90] that the decrease of the symmetry is the result of the formation of ion pairs. Raman bands corresponding to the M–O bond have not been observed, but, bearing in mind the low sensitivity of Raman spectra, the presence of covalent bonds cannot be fully ruled out in all the systems investigated. One may assert[135] that only OSC are formed in solutions of alkali metal nitrates, but, judging from a comparison of the Raman and infrared spectra, the nitrate ion is partly incorporated in the inner spheres of zinc(II), copper(II), mercury(II), calcium, indium(III), and cerium(III) cations[136,137].

The decrease of the symmetry of the ligand cannot be always regarded as a criterion of the occurrence of the ISC or OSC interaction, since the tetrahedral structure of the sulphate and perchlorate ions is not distorted[135] by certain cations. In dilute solutions the sulphate ion, for example, does not in fact enter into the inner spheres of many cations, but, with increase of concentration, the main bulk of the OSC are converted into ISC. This has been observed[83] for the sulphate complexes of aluminium and certain other metals[138,139].

It has been shown[140,141] that *s* and *p* metals in perchlorate solutions bind and polarise outer sphere water and induce structure formation in the latter more vigorously than *d* elements, which are more likely to have a structure breaking effect on the outer-sphere water. Consequently the formation of OSC by *s* and *p* metals should be more accurately regarded as substitution or displacement of outer-sphere water molecules. Studies[53,142–144] of the association of beryllium(II) with sulphate ions, which have been discussed in detail[143], are of interest from this point of view. As an illustration, Table 5 presents the thermodynamic functions for the outer-sphere complex $[Be(H_2O)_4].SO_4$ and for its conversion into the inner-sphere complex $[Be(SO_4)(H_2O)_3]$ obtained from measurements of the relaxation time of the pressure jump[144] and by an iterative procedure[52–54,142].

Table 5. Thermodynamic constants for the formation of $[Be(H_2O)_4].SO_4$ and for its conversion into $[Be(SO_4)(H_2O)_3]$ at 25 °C and zero ionic strength of the solution[143].

Complex and equilibrium	ω_{01} (K_Π)	ΔH°, kcal mol^{-1}	ΔS°, e.u.	ΔV°, cm^3 mol^{-1}
$[Be(H_2O)_4]\cdot SO_4 \rightleftarrows [Be(SO_4)(H_2O)_3]$	100±20 (0.65±0.1)	1.4±0.8 (0.9±0.3)	14.0±0.3(2.2±1.5)	10±3 (3±2)

The data in Table 5 show that OSC predominate in the system of beryllium sulphate complexes, being formed with increase of entropy and molar volume. These OSC consist of $Be(H_2O)_4^{2+}$ tetrahedra and sulphate ions in contact with three water molecules of tetraaquoberyllium[143]. The entropy of formation of OSC by tetrahedral aquo-complexes is the same as that of the formation of "hydrophilic" OSC having an octahedral structure[15,30].

Aluminium and gallium sulphate complexes have been investigated by the analogous method involving the measurement of the pressure jump[145]. The predominance of OSC has been observed to an even greater extent for these compounds in solutions at ionic strengths of 0.1 than for beryllium. Here the equilibrium constant for the transformation of the OSC into the ISC is in the range 10^{-2}–10^{-1}.

Comparison of aluminium(III), gallium(III), and indium(III) monosulphate complexes shows that in this series the contribution of the inner-sphere interaction to the overall complex formation increases from aluminium(III) to indium(III). The considerable contribution or complete dominance of the OSC of metals with singly charged anions in aqueous salt solutions has been pointed out in many studies[134,146–166]. An increase of the degree of formation of OSC is observed with increase of the concentration of the supporting salt. The decrease of the activity of water under these conditions, of the kind which occurs after the introduction of non-aqueous solvents, has a particularly marked influence on the nature of the complexes of the light lanthanides[162]. This is associated with the greater stability of the aquo-complexes of the yttrium group compared with the cerium group[156].

The influence of non-aqueous solvents on the formation of the OSC of the lanthanides is determined mainly by the dielectric constant of the medium, while the formation of ISC is greatly influenced by the electron-donating properties of solvent molecules[163]. However, doubtful claims have been

made[156] that erbium(III) does not form ISC in methanol; certain objections have been made to this claim[165]. There has also been disagreement in the estimates for the formation of OSC by lanthanides, for example as regards the linkage of the perchlorate ion in the inner sphere[162,165] and the purely inner-sphere nature of fluoride and iodate associated species[155]. The cause of the presence of a covalent bond between lanthanide and nitrate ions in aqueous solutions[167] and of the absence of such a bond in tributyl phosphate solutions[147] has not been elucidated.

The attempts to solve the problem concerning the inner- and outer-sphere nature of the complexes of lanthanides with singly charged anions on the basis of the enthalpies and entropies of formation yielded doubtful results. This is because the above functions are small and are usually determined from the temperature variation of the equilibrium constants[28,29]. This can be seen in relation to the complexes with SO_4^{2-} and $Fe(CN)_6^{3-}$; on passing to doubly and triply charged anions, the contribution of lanthanide ISC increases[168-172].

The OSC of the actinide ions have been investigated in less detail than those of lanthanide ions. The chloride, thiocyanate, and polyaminocarboxylate complexes of tervalent actinides have been thoroughly investigated. Inner-sphere polyaminocarboxylate complexes of the actinides are more stable than those of the lanthanides[173-176]. The stability constants of the chloride complexes in 1–4 M solutions in LiCl are almost identical for tervalent actinides and lanthanides with the same ionic radii[150,177]. Only OSC are formed under the conditions indicated[150]. In solutions 10 M in LiCl the actinides (III) form mainly ISC,[178] like the lanthanides, the actinide complexes being more stable than the lanthanide complexes. An analogous situation has been observed[151,174,179-183] also on comparing the stability constants of lanthanide and actinide nitrate and thiocyanate complexes. In view of the similarity of the stability constants, it is possible to determine the type of coordination (in the inner or outer sphere) by analysing the enthalpies and entropies of formation[151,174,180].

Appreciable differences have been observed in the behaviour of the OSC of the actinides relative to the corresponding lanthanide complexes. In aqueous solutions of lanthanide chlorides and perchlorates without added ligands only OSC are formed[184], as in dilute solutions of the nitrates. Judging from the heats of dilution of solutions of these salts, their behaviour is determined by a two-group effect[184], i.e. by the influence of the properties of the cerium and yttrium group. The apparent molal enthalpies of aqueous solutions of these salts increase with increasing radius of the cations (as is shown particularly clearly for the chlorides), which is associated with the presence of hydration shells in the cations. A similar effect has not been observed for the actinide complexes.

Actinide(III) sulphate complexes probably involve the same contribution of the outer-sphere interaction as their lanthanide analogues, i.e. approximately 10%.[169,185] The formation of OSC on interaction of thorium(IV) and neptunium(IV) with sulphate ions[10,186] does not produce a notable effect.

The principal causes responsible for the contributions of different types of forces to the formation of OSC and ISC have been discussed[187]. Analogous but more general attempts had been made also in earlier studies[1-10,188].

V. CERTAIN FEATURES OF THE OUTER-SPHERE INTERACTION OF LABILE OUTER-SPHERE COMPLEXES

The above postulates and certain literature data quoted below make it possible to formulate a number of features of the outer-sphere interaction.

In the majority of systems of labile complexes the coordination "centres" forming the outer (second) coordination sphere are, as for the inert complexes, coordination-saturated cations and to a lesser extent anions. Complex cations with a labile first coordination sphere as well as those with an inert first coordination sphere interact consecutively with the ligands in the second sphere, which are located at definite points in space determined by the inner-sphere ligands. This has been satisfactorily confirmed[18-23,189,190] by the study of inert and, especially, labile OSC in which the strength of the bonds in the second sphere is as a rule much smaller than in the first. The forces of such interaction are predominantly electrostatic: $[ML_6]^{n\pm}...A^{m\pm}$.

At the same time numerous experimental data on the equilibria involving inert and labile[3-5,14,15] compounds, particularly neutral species[16], based on structural data obtained by NMR[18-23,67-80], EPR[27,62-65], and X-ray diffraction[112] as well as the influence of non-aqueous additives[45,47,95,198,199] confirm the important role of the inner-sphere ligand[5,143,199] in outer-sphere interactions. The donor–acceptor interaction of the outer-sphere ligand with the active centres of the inner sphere is outstanding in this respect. This type of interaction includes also hydrogen bonding[138]. The interaction can be represented schematically by $[M(L_6\text{-}l)]...A$, where $(L_6\text{-}l)$ are ligands containing free electron-donating or electron-accepting atoms l.

The coordination number, structure, nature of the bond, and the influence of OSC on the inner sphere are determined by the type of the $l \leftrightharpoons A$ interaction. The concept of the outer-sphere complex becomes much broader in this approach.

The thermodynamic properties of the OSC are determined by the contributions of the electrostatic and donor–acceptor interactions. In many systems the thermodynamic strengths of the binding of the ligands in the first and second coordination spheres are comparable[2]. In such cases it is usually impossible to observe a stepwise outer-sphere interaction. The first ligand, having become attached to the outer-sphere, then passes to the inner sphere. For example, anionic ligands[43-45,127] behave in this way in relation to solvated cations. In the systems indicated the effect of the outer-sphere interaction is manifested most clearly after the addition of the first ligand and then diminishes sharply[82] when the first ligand has been incorporated in the inner sphere.

The features examined above refer to the addition of the first ligand to the outer sphere. As in the stepwise interaction in the second sphere, this ligand adds to energetically favourable positions, determined by geometrical factors, within the complex cation with a saturated inner sphere[18-23]. The systems considered can be divided into three groups: (a) systems in which the formation of OSC greatly predominates; (b) systems with comparable amounts of OSC and ISC; (c) systems in which the formation of ISC greatly predominates. Systems of the first and third types can be studied by the usual methods, neglecting the formation of ISC or OSC. The majority of systems are of this kind.

The principal complications arise in the presence of comparable amounts of OSC and ISC. The formation of OSC and ISC is greatly influenced by the ionic strength of the solution and non-aqueous additives[45,127,189,191]. An increase of ionic strength and of the fraction of the non-aqueous additive reduces the contribution of the OSC and increases that of the ISC. A fairly considerable decrease of ionic strength can lead to the formation of OSC alone, while an increase of the amount of the non-aqueous additive, which lowers the dielectric constant of the medium, can lead to the formation of ISC only. These factors can be used in estimating the contributions of the OSC and ISC in systems where their amounts are comparable.

If the complex formation proceeds via the mechanism initial ions ⇋ OSC ⇋ ISC [see equilibrium (1)], then the overall equilibrium constant K_1 can be formulated thus: $K_1 = \omega_{0,1} + \beta_{10} = \omega_{0,1}(1 + K_{\Pi})$.

We shall consider the influence of certain factors on $K_1, \omega_{0,1}$, and K_{Π} when ionic bonds predominate. For a series of identically charged cations, a number of changes occur when their radii increase[188].

1. The M–L attraction diminishes with increase of the distance between M and L. This effect entails a decrease of $\omega_{0,1}$ and K_{Π}.

2. The extent of local hydrolysis diminishes owing to the depolarisation of the inner-sphere water, which leads to a decrease of $\omega_{0,1}$.

3. (a) The degree of hydration of the cation diminishes, i.e. there is a partial displacement of water, which facilitates the entry of the anion into the coordination sphere;

(b) the degree of hydration of the cation decreases without the displacement of water from its first coordination sphere, which facilitates the incorporation of L into the first coordination sphere of M. Both these effects increase K_{Π}.

4. The energy of the stabilisation of the aquo-cation, arising as a result of the polarity of the water in the second sphere, progressively diminishes as L approaches M, which leads to a decrease of $\omega_{0,1}$ and K_{Π}.

Sometimes when M and L have electrostatic properties similar to those of the dipolar water molecules, the increase of K_{Π} by the third and fourth factors can be selective in relation to the enhancement of the M–L interaction or the increase of the dipole moment of water.

Using the above factors, it is possible to explain the characteristic features of the changes in many formation constants of OSC and ISC.

In the vast majority of the OSC examined the bond between solvated M and L is predominantly ionic, being complicated by the operation of dispersion and van der Waals forces as well as the contributions of the hydrogen bonds and charge transfer in accordance with the scheme M ← L.[194–197] As a rule the charges (or the charge and the dipole moment of L) as well as the radii of M and L determine the stability of the OSC formed. The contribution of the energy of stabilisation by the crystal field or the covalence of the M–L bond can increase K_{Π} and the sum $\beta_{10} + \omega_{0,1}$. From these standpoints, it is possible to account for the increase of the stability of the OSC with increasing charges on M and L, but the fraction of the OSC relative to the sum of the complexes then diminishes.

Analysis of the thermodynamics of the formation of the ISC and OSC leads to a thermodynamic criterion, which determines the type of complex predominant in the system. New thermodynamic results require correction for the conditions under which the criterion is applied: it is applicable only to "hydrophilic" cations and partly to "soft" anions, in terms of Pearson's terminology, which form OSC with a predominantly ionic bond.

The available literature data[28,29] for the OSC in systems of labile OSC refer mainly to acceptors M of class *a*, i.e. "hard" ions. For these acceptors, the overall stability of the halide complexes diminishes in the sequence of the anions $F^- \gg Cl^- > Br^- > I^-$. The contribution of the OSC to the overall effect of the interaction usually increases in the opposite sequence (from I^- to F^-), although frequently large, for example, complex anions with identical charges, form compounds with M, in which there is an increased contribution of the OSC.[2,3]

For copper(II) complexes, an increased tendency for ligands to enter the inner sphere compared with nickel(II) and cobalt(II) has been observed[38,45,127,133]. This property can probably be accounted for by the anisotropy[197] of the copper(II) ISC formed due to the Jahn–Teller effect.

Regardless of their composition, structure, and charge, all the "hydrophilic" complex cations form monoligand OSC on interaction with doubly charged anions, for which $\Delta S^\circ \cong 15$ e.u. in solutions at zero ionic strength[15]. This constancy of ΔS°, which so far is not altogether explicable, has been observed mainly for inert complexes and, if it is confirmed for labile systems, the problem of the identification of OSC will be solved.

Data for the variation of the stability of OSC and of their contribution to the overall complex formation effect as a function of the nature of the central ion are contradictory, although a correlation with the number of *d* electrons has been sometimes noted[127,192]. However, it is clear that the series of central ions corresponding to the variation of the stability of OSC and ISC are different[127]. These differences increase with increasing degree of covalence of the M–L bond in the first coordination sphere and with increase of the complexity of the interaction of the inner- and outer-sphere ligands.

Outer-sphere coordination entails a change in the length of the inner-sphere bond[198,199] in consequence of the enhancement of the polarisation of ligands. This induces a far-reaching rearrangement of the inner sphere, which is manifested by the enhancement of the acid properties of the metal aquo-ion[199], a change of the structure of the inner-sphere complex in the melt[200] and in the crystal[201], a change in the stretching vibration frequencies of the bonds[202,203], and ultimately a change in the reactivity of the compound[203]. All these phenomena, which fit within the framework of the fundamental concept of the mutual influence of ligands, have the specific features of an individual property of outer-sphere complexes, and can be referred to as the outer-sphere effect.

However, the insufficiency of data on the thermodynamics, structure, and kinetic properties of the OSC greatly hinders the extension of the generalisations. In order to be able to reach deeper conclusions, a considerable increase of the amount of information in this field is necessary.

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