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The Thermodynamics of the Formation of Outer-sphere Complexes in Solution

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Data on the thermodynamics of the formation of outer-sphere complexes of coordination compounds of cobalt(III), rhodium(III), iridium(III), platinum(IV), chromium(III), iron(II), ruthenium(II), (III), and osmium(II) have been reviewed. Various regular features of outer-sphere complex formation by inert hydrophilic and hydrophobic cationic complexes with d^6, d^5, and d^3 electron configurations of the central metal ion in aqueous and aqueous-organic solutions have been established. The bibliography contains 144 references.

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I. INTRODUCTION

The formation of outer-sphere complexes[1] is a widespread phenomenon, since most inner-sphere complexes form outer-sphere associates, depending on the composition of the surrounding medium. Detailed studies of outer-sphere complexes (OSC) carried out in recent years have revealed the characteristic features of their formation and new possibilities for their practical application, and this has led to an increased interest in the comprehensive study of OSC.[2]

In the last 15 years, several reviews of the stability and structural characteristics of OSC in solution have been published[2-8]. Reference has been made[1] to a monograph on this topic[9], but this has not yet appeared.

Outer-sphere complexes can be divided into two groups. The first group consists of compounds formed by inert, and the second group of compounds formed by labile (in Taube's terminology) [10] inner-sphere complexes. The OSC of both groups are characterised by high rates of formation and dissociation of the outer coordination sphere[11], that is this sphere is always labile. A large proportion of studies have been carried out for OSC formed by inert coordination compounds. In a number of cases, as a consequence of differences in the rate of formation or in the stability of the inner and outer spheres, it is also possible to carry out qualitative and semi-quantitative studies of the thermodynamics of the formation of OSC by labile inner-sphere complexes[11-18].

Most present-day and earlier studies of OSC have been carried out at a single temperature[19,20]. Only in a few studies have the measurements been made at several temperatures, and the enthalpy and entropy changes for the formation of the OSC calculated from the temperature dependence of the equilibrium constants. The enthalpy changes on OSC formation are small ($<\pm 20-40$ kJ mole^{-1}), and the temperature-coefficient method gives appreciable errors in the determination of small thermal effects[21,22]. Accurate values of the enthalpy and entropy changes can be obtained only by direct thermochemical measurements using highly sensitive calorimeters. Up to the present, all such measurements (except of the heats of two reactions[23]) have been carried out only in the laboratory of the authors of the present review. The aim of the present work is to summarise and discuss critically the data obtained on the thermodynamics of the formation of OSC and to examine other studies of similar content.

Data on the thermodynamics of the formation of OSC by inert cationic complexes of cobalt(III), rhodium(III), iridium(III), platinum(IV), chromium(III), iron(II), ruthenium(II), (III), and osmium(II) are reviewed. Almost all the data relate to aqueous solutions. Some information on outer-sphere interactions in aqueous-organic solvents is also given.

An unsymmetrical standard state[24,25] (that is different for the solvent and the solutes) is used in the study of solutions of electrolytes in general and of OSC in particular. A hypothetical molal (molar) solution with the properties of an infinitely dilute solution is taken as standard for OSC (and for their components). The state of the pure liquid at a definite temperature and pressure is taken as the standard state for the solvent.

The recalculation of the values of the stability constants of the OSC and the enthalpy changes for their formation (from solutions with definite ionic strengths of constant magnitude to the standard state indicated above) is carried out[26] using Vasil'ev's equations[27,28].

The problem of selecting inert salts to keep the ionic strengths constant is solved in various ways. The experience of a large number of studies has shown[26,29] that the perchlorate anion is the most "inert" with respect to hydrophilic cationic complexes, and the fluoride anion the most inert with respect to hydrophobic cationic complexes. This situation (with allowance for the solubility of the background salts) explains why lithium or sodium perchlorates are most frequently used as inert salts in the study of OSC formed by aquoammine, ethylenediamine, and similar hydrophilic complexes. Sodium or potassium fluorides are chosen as inert salts in the study of the OSC of tris(2,2'-bipyridyl), tris(1,10-phenanthroline), and other hydrophobic compounds.

It is of interest to compare the association constants of a number of inert cationic complexes with the perchlorate ion, which is most widely used as inert anion.

The data in Table 1 show that for most cationic complexes with a charge of 1-4, the values of the logarithms of the stability constants of the perchlorate associates are ≥ 1. Increase in the size of the cationic complexes, for example in the series hexammine-, tris(ethylenediamine)-, and tris-(propylenediamine)cobalt(III), leads to a slight decrease in the stability constants (Table 1). A similar change is observed on going from tris(ethylenediamine)cobalt(III) to

tris(ethylenediamine)rhodium(III) or from *trans*-dichlorobis-(ethylenediamine)rhodium(III) to *trans*-dichlorobis(ethylenediamine)iridium(III). On the other hand, for the hydrophobic tris(2,2'-bipyridyl) and tris(1,10-phenanthroline) compounds, the change from iron(II) to ruthenium(II) and osmium(II) leads to an increase in the stability of the perchlorate associates.

Table 1. Logarithms of the association constants of transition metal complexes with the perchlorate ion at 298 K.

Cation	Medium	Method	lg β_1	Refs.
$[Co(en)_2(bipy)]^{3+}$	→0	S	1.66±0.05	[30]
$[Co(NH_3)_6]^{3+}$	→0	El	1.40±0.05	[31—33]
$[Co(NH_3)_6]^{3+}$	0	S	1.47	[34]
$[Co(NH_3)_6]^{3+}$	0	S	1.34	[35]
$[Co(NH_3)_6]^{3+}$	0.1 *M* $NaClO_4$	Sp	0.97	[36]
$[Co(en)_3]^{3+}$	→0	El	1.14±0.05	[32]
$[Co(en)_3]^{3+}$	0	El	1.18	[37]
$[Co(en)_3]^{3+}$	0	El	1.3	[38]
$[Co(en)_3]^{3+}$	1 *M* $NaClO_4$	Sp	—0.35	[39]
$[Co(pn)_3]^{3+}$	→0	El	1.08±0.05	[34]
$[Co(bipy)_3]^{3+}$	→0	S	2.10±0.05	[40]
$[Co(phen)_3]^{3+}$	→0	S	2.50±0.05	[40]
$[Co(NH_3)_5(H_2O)]^{3+}$	0	K	1.47	[41]
$[Co(NH_3)_5Cl]^{3+}$	0	S	1.15	[42]
$[Co(NH_3)_5(SO_4)]^{+}$	0	El	0.80	[43]
$[Co(en)_2(C_2O_4)]^{+}$	0	El	0.02±0.04	[44]
trans-$[Co(en)_2(SCN)Cl]^{+}$	→0	El	1.06±0.04	[45]
$[Rh(en)_3]^{3+}$	→0	El	0.93±0.05	[32]
trans-$[Rh(en)_2Cl_2]^{+}$	→0	El	1.08±0.05	[45]
trans-$[Ir(en)_2Cl_2]^{+}$	→0	El	1.00±0.04	[45]
$[Cr(NH_3)_6]^{3+}$	0	El	1.18±0.03	[46]
$[Cr(NH_3)_6]^{3+}$	0	Sp	1.00	[46]
$[Cr(en)_3]^{3+}$	0	El	1.04	[46]
$[Cr(en)_3]^{3+}$	0	El	1.31	[47]
$[Cr(en)_3]^{3+}$	0	Sp	1.21	[46]
$[Cr(en)_3]^{3+}$	0	Sp	0.90	[48]
$[Pt(NH_3)_6]^{4+}$	0	El	1.51±0.05	[49]
$[Pt(en)_3]^{4+}$	0	El	0.99±0.05	[49]
trans-$[Pt(en)_2Cl_2]^{2+}$	0	El	1.08±0.05	[45]
$[Fe(bipy)_3]^{2+}$	0	El	2.05±0.04	[50]
$[Fe(bipy)_3]^{2+}$	→0	S	2.05±0.05	[38]
$[Fe(bipy)_3]^{2+}$	0	E	2.08±0.06	[50]
$[Fe(phen)_3]^{2+}$	0	E	2.08±0.05	[50]
$[Fe(phen)_3]^{2+}$	→0	S	2.20±0.05	[51]
$[Fe(phen)_3]^{2+}$	0	E	2.13±0.06	[50]
trans-$[Fe(phen)_2(CN)_2]$	→0	S	0.59±0.03	[52]
$[Ru(bipy)_3]^{2+}$	0	El	2.38±0.05	[29]
$[Ru(bipy)_3]^{2+}$	→0	S	2.53±0.06	[29]
$[Ru(phen)_3]^{2+}$	0	El	3.18±0.05	[29]
$[Ru(phen)_3]^{2+}$	→0	S	3.45±0.07	[29]
$[Os(bipy)_3]^{2+}$	0	El	3.38±0.05	[29]
$[Os(bipy)_3]^{2+}$	→0	S	3.40±0.06	[29]
$[Os(phen)_3]^{2+}$	0	El	3.93±0.07	[29]
$[Os(phen)_3]^{2+}$	→0	S	4.32±0.05	[29]

Notation. Cations: en = ethylenediamine, pn = propylenediamine, bipy = 2,2'-bipyridyl, phen = 1,10-phenanthroline. Medium: →0 = extraction into an aqueous solution with zero ionic strength; 0 = recalculated analytically for $I = 0$. Methods: El = electrical conductivity measurement, S = solubility measurement, Sp = spectrophotometrically, K = study of the reaction kinetics, E = extraction.

Doubly-charged hydrophobic complexes[29,53–55] form more stable perchlorate associates than triply- and quadruply-charged hydrophilic cations (Table 1). The non-electrolyte *trans*-dicyanobis(1,10-phenanthroline)iron(II) tends to associate with the perchlorate ion. It should be particularly emphasised that a change in the charge of the coordination compound is not a decisive factor in the formation of perchlorate associates[54]. Many singly-charged cations have the same association constants with perchlorate ion as tris(ethylenediamine)cobalt(III). Judging from the values of the stability constants of the perchlorate associates of tris(ethylenediamine)- and haxamminecobalt(III), increase in the ionic strength of the solution leads to a decrease in the stability of the perchlorate associates (Table 1). The applicability of this regular feature is usually confirmed by published data[29,40,51,53,55], although in some cases there are exceptions [the perchlorate associates of tris(1,10-phenanthroline)-ruthenium(II) and iron(II)].

The ionic strength of the solution has practically no influence on the stability of the associates of coordination compounds with molecules[56,57] and neutral complexes with anions[54]. It should be noted that the values of the stability constants obtained at ionic strengths I which differ in magnitude and in the salts used to establish them can be extrapolated to $I = 0$ using Vasil'ev's equation[27]. This equation uses a distance of maximum approach of the ions equal to 4.9 Å. Change in this quantity over the range 3–6 Å, however, usually has little influence[26,58] on the values of the stability constants at $I = 0$.

Beginning from values of $I \leq 0.2$–0.3, the stability constants can be recalculated to $I = 0$ using Davies' equation[1], but in a number of cases[59–61] it does not lead to the same values as those obtained using Vasil'ev's equation.

Structural changes in the solvent and solvation processes in the second sphere have a significant influence on the formation of OSC in aqueous-organic solutions[62–65]. If the formation of OSC in aqueous solution is represented as the replacement of water molecules in the second sphere by an outer-sphere ligand

$$[MA_N](H_2O)_x(aq) + L(aq) \rightleftarrows [MA_N](H_2O)_yL(aq) + (x-y)H_2O \quad (1)$$

(M is the metal ion, A the inner-sphere ligands, and N their number), then the equilibrium constant of reaction (1) is related to the stability constant of the OSC by the relationship[64]:

$$\beta_e = \beta_1[H_2O]^{x-y} = \beta_1[H_2O]^z \quad (2)$$

Table 2. Logarithms of the stability constants lg β_1 of the outer-sphere complexes $[MA_N]SO_4$ and the equilibrium constants of reaction (1) lg β_e in aqueous methanol solutions at 298 K.[62,63]

MA_N	Methanol, mass %					
	0	10	20	30	40	50
$[Co(NH_3)_6]^{3+}$	3.48 6.97	3.54 6.94	3.68 6.98	3.79 6.97	3.91 6.95	4.08 6.96
$[Co(NH_3)_5Cl]^{2+}$	2.70 6.19	2.79 6.19	2.87 6.17	3.03 6.21	3.16 6.20	3.20 6.18
$[Fe(bipy)_3]^{2+}$	1.45 4.94	1.60 5.00	1.65 4.95	1.75 4.93	1.91 4.95	2.10 4.98

Note. The value of lg β_1 is given in the upper row, and the value of lg β_e in the lower row. The standard deviations for the values of lg β_1 are ±(0.03–0.05).

If equilibrium (1) does not break down in aqueous-organic solutions, and resolvation processes do not take place in the second sphere, it follows from the law of mass action that the role of the organic component often reduces to the role of a diluent of the water, and the correction $[H_2O]^z$ leads to a constant lg β_e in aqueous-organic solutions; z is an integer[64]. For sulphate OSC of hydrophilic and hydrophobic cationic complexes, the introduction of methanol, ethanol,

propanol, acetone, dioxan, and other solvents up to a concentration of 40–50 mass % does not change the values of $\lg \beta_e$ for $z = 2$. For the halide OSC of tris(ethylenediamine)cobalt(III),[65] the introduction of acetone up to 20 mass % does not change the values of $\lg \beta_e$.

Table 2 gives the stability constants in aqueous glycol solutions, where the correction $[H_2O]^z$ does not lead to constant values of $\lg \beta_e$. This case requires verification, since in the system being considered, the introduction of 20 mass % ethylene glycol lowers the value of the stability constant, and at higher ethylene glycol concentrations it increases. To date, this form of dependence of the values of the stability constants on the concentration of the organic component has been noted[66] only for this system. Moreoever, this effect is not observed for sulphate OSC of nitropentamminecobalt(III) in aqueous ethylene glycol solutions (Table 3). Additional verification of this idea for OSC with highly-charged anions, and also extension of the range of solvents and cationic complexes with different charge, containing inner-sphere ligands of different character, are required.

In some systems[67], the replacement of even 80% of water by methanol does not lead to a change in the constant β_e. This indicates the predominant role of the dilution factor.

Table 3. Logarithms of the stability constants[66,67] $\lg \beta_1$ and the equilibrium constants for reaction (1) $\lg \beta_e$ [62,63] for monosulphate OSC of tris(1,10-phenanthroline)iron(II) in aqueous methanol and aqueous ethylene glycol solutions at 298 K.

Solvent	Alcohol, mass %				
	0	20	40	60	80
Methanol	1.54 5.03	1.79 5.08	2.08 5.12	2.45 5.13	2.94 5.12
Ethylene glycol	1.71 5.20	1.59 4.88	1.86 4.90	1.98 4.66	2.36 4.44
Ethylene glycol*	2.55 6.04	2.77 6.04	3.03 6.06	— —	— —

*The data are given for the complex $[Co(NH_3)_5(NO_2)]SO_4$.
Note. See footnote to Table 2.

II. METHODS FOR DETERMINING THE CHANGES IN THERMODYNAMIC FUNCTIONS FOR THE FORMATION OF OUTER SPHERE COMPLEXES IN SOLUTION

The ultimate aim of the study of equilibria in solutions is the determination of the stoichiometry of the forms produced, and the calculation of stability constants and the changes in the thermodynamic functions (enthalpy, entropy, etc.) on complex formation[68]. From these viewpoints it is necessary, in the study of OSC, to establish the stoichiometry of the forms produced by the coordinatively-saturated complex $[MA_N]$ (N is the limiting coordination number) and the outer-sphere ligand L (anion or molecule). This problem is solved by the analysis and mathematical treatment of relationships of the type: solution property–solution composition. For the quantitative solution of this problem it is necessary to establish, in explicit, implicit, or parametric form, the functional relationship between the measured physicochemical property of the solution as a whole and its analytical composition. This functional relationship is established using three fundamental physicochemical concepts, given mathematically[68] by: 1) the material balance equations, 2) the equations of the law of mass action, and 3) equations relating a measured property of the solution as a whole, the partial contributions to this property from the individual chemical forms, and the equilibrium concentrations of these forms.

When an OSC with stoichiometry $[MA_N]L_m$ is formed in solution, the corresponding material balance equations have the form:

$$C_M = \{[MA_N]\} + \sum_m \{[MA_N]L_m\} \quad (3)$$

$$C_L = \{L\} + \sum_m m\{[MA_N]L_m\} \quad (4)$$

where c_M and c_L are the total (analytical) concentrations of the coordination compound $[MA_N]$ and the outer-sphere ligand L.

For the formation of OSC according to Eqn.(1), the corresponding equations of the law of mass action will be

$$\beta_1 = \{[MA_N]L\}/\{[MA_N]\} \cdot \{L\} \quad (5)$$

where β_1 is the concentration stability constant, which depends on temperature, pressure, the chemical character of $[MA_N]$ and L, and the nature of the forming medium. The concentration constant becomes constant if the conditions of a constant ionic medium with respect to the participants of the process being studied are observed [reaction (1)].[68]

The third group of equations is determined by the physicochemical method of study used.

The heats of formation of OSC in solution have been determined using a double differential microcalorimeter with a sensitivity of $(5.52 \pm 0.12) \times 10^{-3}$ J and a cell volume of 10 cm^3. The measurements were made by thermometric titration[59]. The complex compounds were synthesised by the usual methods, and analysed for the metal, hydrogen, carbon, nitrogen, and halogen. The difference between the observed and calculated concentration of the components determined did not exceed 0.5 abs.%. The purity of the synthesised and recrystallised specimens was verified from the published absorption spectra. The salt solutions used in the experiments were prepared from the "analytically pure" or "chemically pure" grade reagents, purified by recrystallising two or three times from water.

The heats of mixing of solutions containing $[MA_N]$ and the background electrolyte $[M'\Phi]$ at I = const with solutions of salts of the outer-sphere ligand M'L were measured. The heats of mixing of $M'\Phi$ with M'L were measured separately in additional experiments.

The heat of complex formation (Q) is related to the enthalpy change (ΔH_m^0) for the formation of the species $[MA_N]L_m$ by the expression

$$Q = V \sum_m \Delta H_m^0 \{[MA_N]L_m\} \quad (6)$$

where V is the volume of the solution, and $\{[MA_N]L_m\}$ represents the equilibrium concentrations of the forms $[MA_N]L_m$.

Eqns.(3)–(5) lead to the equation

$$\frac{Q}{V \cdot c_M} = \sum_m \frac{\Delta H_m^0 \beta_m \{L\}^m}{\left(1 + \sum_m \beta_m \{L\}^m\right)} \quad (7)$$

In most of the systems studied, the stoichiometry of the OSC formed and the values of the stability constants obtained from the results of independent methods of study (for example potentiometry, spectrophotometry, solubility, etc.) have

been used. The values of the stability constants were used to calculate the corresponding enthalpy changes for the formation of OSC from Eqn.(7). In a number of cases, the calculation of ΔH_1^0 and β_1 for single-ligand OSC have been carried out directly from thermochemical data[68].

The values of the free energy changes were calculated from the relationship[68]:

$$\Delta G_i^0 = -RT \ln \beta_i \ . \qquad (8)$$

The corresponding entropy changes for the formation of the OSC were calculated from the equation[68]:

$$\Delta G_i^0 = \Delta H_i^0 - T\Delta S_i^0 . \qquad (9)$$

The values of the changes in the thermodynamic functions are given with their uncertainties in the form of the standard deviations (see Tables 4–12). The results were treated by the least-squares method with allowance for the difference in the accuracy of the experimental data by introducing appropriate statistical weights[68], reflecting the estimates of the dispersions of the results on the measurement of the values of the heat.

III. OUTER-SPHERE COMPLEXES OF COBALT(III)

The outer-sphere complexes of cobalt(III) and the thermodynamics of their formation have been studied in most detail. A review of the study of OSC of cobalt(III) was published in 1970.[5] At that time, however, thermochemical measurements had been carried out for the formation of only the OSC of tris(ethylenediamine)cobalt(III). The studies were carried out in 3.0 M solutions of sodium or lithium perchlorate. The standard state indicated was used[67–77] in thermochemical studies of OSC up to 1975, when the first thermochemical studies[78–80] in dilute solutions with extrapolation of the thermodynamic data to aqueous solutions with zero ionic strength were published. Since 1975, thermochemical studies of the thermodynamics of formation have been carried out in solutions with ionic strengths of 0.1, 0.2, 0.3, 0.4, 0.5, and sometimes 0.75 and 1.0 [26,45,78–94] for the compounds of hexammine-,[79] tris(ethylenediamine)-,[79,81,83] tris(propylenediamine)-,[79] tris(2,2′-bipyridyl)-,[93] tris(1,10-phenanthroline)-,[94] chloro-,[80,87] bromo-,[80,85] nitro-,[80,85] sulphato-,[80,85], acetato-,[82,85] pentamminecarbonato-,[76] oxalato-,[92] malato-,[92] succinato-,[92] phthalato-,[92] tetrammine-, bis(acetylacetonato)-(ethylediamine)-,[88] and acetylacetonato, bis(ethylenediamine)-cobalt(III) [45] with sulphate, thiosulphate, sulphite, selenite, tellurite, and carbonate ions.

The thermochemical method has been used to study halide, thiocyanate, nitrate, carboxylate, and other OSC of cobalt(III). These measurements were made[93–102] in solutions with an ionic strength $I = 3$, maintained by adding sodium or lithium perchlorate.

The enthalpy changes for the formation of the OSC of cobalt(III) have usually been calculated[78–102] using the stability constants of the OSC, determined from potentiometric, solubility, spectrophotometric, and other data.

To illustrate ideas developed below, a small fraction of the data on the thermodynamics of the formation of OSC of cobalt(III) is given in Tables 4–8. Table 4 shows that in aqueous solutions with zero ionic strength, tris(ethylenediamine)-cobalt(III) forms mono- and bis(ligand) OSC with positive values of the entropy change. The enthalpy changes in these processes are small, and lie in the range ±2 kJ mole^{-1}. The differences between the stabilities of the OSC of tris-(ethylenediamine)cobalt(III) with different doubly-charged ligands are slight (Table 4); only the carbonate ion forms comparatively less stable OSC. A regular decrease in the stability constants and the positive values of the entropy changes is observed with increase in the serial number of the added ligand. The entropy changes are ~57–58 J mole^{-1} K^{-1} for the formation of mono-ligand OSC, and ~34 J mole^{-1} K^{-1} for the formation of bis(ligand) OSC.

Table 4. Values of the changes in the consecutive thermodynamic functions for the formation of OSC of tris(ethylenediamine)cobalt(III) at 298 K in aqueous solutions with zero ionic strength[79,103,104].

Ligand	n	$\lg K_n^0$	$\approx\Delta H_n^0$, kJ mole^{-1}	ΔS_n^0, J mole^{-1}K^{-1}
SO_4^{2-}	1	3.40 (3.30)	2.1	56
SO_4^{2-}	2	2.00 (1.80)	1.0	31
$S_2O_3^{2-}$	1	3.40	2.1	57
$S_2O_3^{2-}$	2	1.90	0.8	34
SO_3^{2-}	1	3.40	2.1	59
SO_3^{2-}	2	1.90	—0.8	34
SeO_3^{2-}	1	3.46	2.1	59
SeO_3^{2-}	2	1.85	—0.8	34
TeO_3^{2-}	1	3.32	2.1	59
TeO_3^{2-}	2	1.65	—0.8	34
CO_3^{2-}	1	2.90	1.0	57
CO_3^{2-}	2	1.65	2.9	21
$[Co(NH_3)_4C_2H_2(COO)_2]^+$	1	2.56	5.0	65
$[Co(NH_3)_4C_2H_2(COO)_2]^+$	2	1.40	5.4	38
$[Co(NH_3)_4C_2H_4(COO)_2]^+$	1	2.56	3.4	61
$[Co(NH_3)_4C_2H_4(COO)_2]^+$	2	1.30	2.9	34
$[Co(NH_3)_4C_6H_4(COO)_2]^+$	1	2.42	4.2	61
$[Co(NH_3)_4C_6H_4(COO)_2]^+$	2	1.15	2.1	29

Note. The standard deviations in the determination of the values of $\lg K_n^0$ are ±0.05 for $n = 1$ and $n = 7$, ±(0.07–0.12) for $n = 2$, ±(0.4–0.8) kJ mole^{-1} for ΔH_n^0, and ±(2–3) J mole^{-1} K^{-1} for ΔS_n^0. The improved values[79] used to calculate the enthalpy and entropy changes for the OSC are given in brackets.

Table 5. Values of the changes in the thermodynamic functions for the formation of sulphate OSC of coordination compounds of cobalt(III) at 298 K in aqueous solutions with zero ionic strength[76,79,80,82,92,103].

Cation	n	$\lg K_n^0$	ΔH_n^0, kJ mole^{-1}	ΔS_n^0, J mole^{-1}K^{-1}
$[Co(NH_3)_6]^{3+}$	1	3.40	—2.1	59
$[Co(en)_3]^{3+}$	1	3.30	—2.1	56
$[Co(en)_3]^{3+}$	2	1.80	—1.0	31
$[Co(ph)_3]^{3+}$	1	3.22	—2.5	54
$[Co(ph)_3]^{3+}$	2	1.80	—1.5	30
$[Co(NH_3)_5Cl]^{2+}$	1	2.87	3.6	67
$[Co(NH_3)_5Cl]^{2+}$	2	1.45	0	28
$[Co(NH_3)_5Br]^{2+}$	1	2.80	2.9	64
$[Co(NH_3)_5Br]^{2+}$	2	1.17	1.9	29
$[Co(NH_3)_5(NO_2)]^{2+}$	1	2.88	3.4	67
$[Co(NH_3)_5(NO_2)]^{2+}$	2	1.30	2.1	32
$[Co(NH_3)_5(CH_3COO)]^{2+}$	1	2.80	1.5	59
$[Co(NH_3)_5(CH_3COO)]^{2+}$	2	1.40	1.3	31
$[Co(NH_3)_5(SO_4)]^{+}$	1	2.42	6.3	67
$[Co(NH_3)_5(SO_4)]^{+}$	2	0.60	4.2	25
$[Co(NH_3)_4(CO_3)]^{+}$	1	2.35	5.0	61
$[Co(NH_3)_4(CO_3)]^{+}$	2	0.80	3.4	27
$[Co(NH_3)_4(C_2O_4)]^{+}$	1	2.35	5.0	59
$[Co(NH_3)_4(C_2O_4)]^{+}$	2	1.15	2.9	31

The data in Table 5 show that the stability of the sulphate OSC tends to decrease in the cationic complex order: hexammine- > tris(ethylenediamine)- > tris(propylenediamine)-cobalt(III); there is a slight decrease in the contribution of the entropy component to the free energy change. The

decrease in these quantities is small, however, and lies at the error limit in the determination of the thermodynamic parameters.

Table 6. Values of the changes in the thermodynamic functions for the formation of the monosulphate OSC $[Co(en)_x \cdot (acac)_{3-x}]$ at 298 K and different ionic strengths, maintained using sodium perchlorate and sulphate[88].

I	$\lg \beta_1$	ΔH_1^0, kJ mole^{-1}	ΔS_1^0, J mole^{-1}K^{-1}	I	$\lg \beta_1$	ΔH_1^0, kJ mole^{-1}	ΔS_1^0, J mole^{-1}K^{-1}
	$[Co(en)_2(acac)]^{2+}$				$[Co(en)(acac)_2]^+$		
0	2.49	0.4	46	0	2.05	0.4	38
0.3	1.10	4.2	34	0.3	1.10	2.5	29
0.5	0.80	5.4	34	0.5	0.70	3.8	25
1.0	0.07	8.4	29	1.0	0.22	5.0	21

Note. The standard deviations in the determination of the values of $\lg \beta_1$ are ±(0.03–0.05); ±(0.4–0.8) kJ mole^{-1} for ΔH_1^0; and ±(2–3) J mole^{-1} K^{-1} for ΔS_1^0.

Table 7. Values of the changes in the thermodynamic functions for the formation of the sulphate OSC of tris(2,2′-bipyridyl)- and tris(1,10-phenanthroline)cobalt(III) at 298 K and different ionic strengths[93,94].

I	$-\Delta G_1^0$, kJ mole^{-1}	$-\Delta H_1^0$, kJ mole^{-1}	$-\Delta S_1^0$, J mole^{-1}K^{-1}
	phen		
0	13.0	23	34
0.1	6.3	24	59
0.25	3.7	30.5	59
0.5	2.2	35.5	112
0.75	1.1	42.6	139
	bipy		
0	14.2	25.9 26.4	75
0.1	7.0(5.7)	27.6 43.5	69
0.25	4.55(5.2)	31.4 25.5	90 (67)
0.5	2.7(2.65)	43.1 43.9	134 138
0.75	1.6(1.1)	43.1 53.6	138 176
{0	{13.3}	{29.7}	{54}

Note. The standard deviations of the determinations are ±(0.4–0.6) kJ mole^{-1} for ΔG_1^0; ±(0.8–0.6) kJ mole^{-1} for ΔH_1^0; and ±(3–20) J mole^{-1} K^{-1} for ΔS_1^0.

The values are given for a combination of potentiometric and thermochemical methods; the values in round brackets correspond to purely thermochemical data, and those in braces were obtained by the electrical conductivity method at 293–318 K.

For hydrophilic cationic complexes, the change from the hexammine- [tris(diamine)-] to acidopentammine- and then acidotetramminecobalt(III) leads to a marked decrease in the stability of the OSC with doubly-charged ligands. This decrease in the stability of OSC with decrease in the charge of the central group is accompanied by a regular increase in the positive contribution of the enthalpy component, and is clearly observed for monoligand OSC (Table 5).

The differences in the stability of OSC formed by different acidopentammines of cobalt(III) lie just beyond the error limits in the determination of the changes in the thermodynamic functions (see Table 5). Similar conclusions can be reached about the stability of the OSC of acidotetramminecobalt(III) compounds (Table 5). Sulphatopentamminecobalt(III) forms outer-sphere complexes with stabilities close to those of acidotetrammines of cobalt(III), due to the fact that these complexes have the same charge of +1. The date in Table 5 indicate that the entropy changes are 63 ± 8 J mole^{-1} K^{-1} for the formation of the monoligand OSC of cobalt(III) ammines, and 29 ± 8 J mole^{-1} K^{-1} for the formation of the bis(ligand) OSC.

Table 8. Values of the enthalpy and entropy changes for the formation of associates of amines with coordination compounds of cobalt(III) in aqueous lithium perchlorate or chloride solutions at 298 K.[105]

Cation	L	Medium	$-\Delta H_1^0$, kJ mole^{-1}	$-\Delta S_1^0$, J mole^{-1}K^{-1}
$[Co(NH_3)_6]^{3+}$	NH_3	3 *M* LiCl	4.2	25
$[Co(NH_3)_6]^{3+}$	NH_3	0.2 *M* $LiClO_4$	3.8	21
$[Co(en)_3]^{3+}$	en	3.0 *M* $LiClO_4$	27.6	113
$[Co(en)_3]^{3+}$	en	3 *M* LiCl	29.0	109
$[Co(en)_3]^{3+}$	py	3 *M* $LiClO_4$	18.4	92
$[Co(en)_3]^{3+}$	NH_3	3 *M* LiCl	8.4	42
$[Co(en)_3]^{3+}$	CH_3NH_2	3 *M* $LiClO_4$	12.5	63
$[Co(NH_3)_5(HCOO)]^{2+}$	NH_3	3 *M* $LiClO_4$	9.6	38

Note. The standard deviations of the determinations are ±(0.8–2.0) kJ mole^{-1} for ΔH_1^0, and ±(3–8) J mole^{-1} K^{-1} for ΔS_1^0.

Similar entropy changes are characteristic of the addition of various other doubly-charged anions[78–87,91,92]. The results of Refs.32, 34, and 105–112 were obtained from the temperature dependence of the stability constants of only single-ligand OSC, and most of them confirm the conclusion that the entropy change has the practically constant value given above. Analysis of the data in Ref.111 shows that the enthalpy change for the formation of monohydrogen phosphate OSC of tris(ethyldiamine)cobalt(III) is close to zero, and calculation of the entropy changes gives a value of 63 J mole^{-1} K^{-1}. A study of the association of tris(biguanidine)cobalt(III) with the sulphate ion at 298 K and 308 K[112] showed that the entropy changes for the formation of monoligand OSC are 59 J mole^{-1} K^{-1}. With the assumption that temperature does not influence the stability constant of the mono-oxalato-complex of hexamminecobalt(III),[32,34] we obtain entropy changes of 63 J mole^{-1} K^{-1}. Chloropentamminecobalt(III), even with the quadruply-charged pyrophosphate ion, forms OSC whose entropy changes at 293 K and an ionic strength of 0.1 are 70 J mole^{-1} K^{-1}.[23]

In a number of cases, the formation of OSC in which the number of added ligands is three has been detected[78–102]. The small values of the changes in the thermodynamic functions, however, together with the large errors in their determination and the possibility of a contribution from changes in the activity coefficients, make an unambiguous quantitative discussion of the regular features of the formation of these OSC impossible[113,114].

It is of interest to compare the data of the present authors[80] on the thermodynamics of the formation of OSC of cobalt(III) with published data[114,115] obtained for monoligand complexes from kinetic and sometimes spectrophotometric studies.

The dependence of the acid hydrolysis constant on the sulphate ion concentration for chloropentamminecobalt(III) at an ionic strength of 0.3 and temperatures of 313–328 K [115] made

it possible to determine the association constant, equal to 32.5, and $\Delta G_1^0 = -9.2$ kJ mole^{-1}, $\Delta H_1^0 = -17.2$ kJ mole^{-1}, and $\Delta S_1^0 = -26$ J mole^{-1} K^{-1}. The direct determination of these parameters from potentiometric and thermochemical data[80] gave values of the above functions equal to 14, -8.2 kJ mole^{-1}, 6.3 kJ mole^{-1}, and 48.5 J mole^{-1} K^{-1} respectively. Comparison of the direct and indirect data on the enthalpy and entropy changes for the formation of the sulphate associate of chloropentamminecobalt(III) shows differences even in the signs of these functions.

Doubt must be cast on the values obtained from the kinetic data[115], and also on the published thermodynamic characteristics[116] of the malate and phthalate OSC of chloropentamminecobalt(III). Contrary to the data of Ref.116, these monoligand OSC should be formed with positive enthalpy and entropy changes. The enthalpy and entropy changes at 313 K in 0.3 M sodium perchlorate solutions, however, are respectively -25 kJ mole^{-1} and -53 J mole^{-1} K^{-1} for the malate OSC, and -27 kJ mole^{-1} and -58 J mole^{-1} K^{-1} for the phthalate OSC of chloropentamminecobalt(III).[116] The values of the enthalpy and entropy changes for the formation of phthalate OSC of aquopentamminecobalt(III) in solutions with an ionic strength of 0.3 at 323 K, equal to 24 kJ mole^{-1} and 100 kJ mole^{-1}, obtained[117] from the temperature dependence of the association constants, appear more correct. The latter were determined from the dependence of the rate constants of inner-sphere ligand replacement on the concentration of the outer-sphere ligand.

Since the dependence of the rate constants of hydrolysis, inner-sphere ligand replacement, etc. on the concentration of the outer-sphere ligand is non-linear, the determination of the stability constants of the resulting OSC from kinetic data is difficult, and associated with appreciable errors[118]. In most cases, the influence of temperature on the stability constants of the OSC is weak[119,120], and it is not possible to determine the enthalpy and entropy components of the free energy change.

The successive replacement of ethylenediamine by acetylacetone in the inner sphere of cobalt(III) leads (Tables 5 and 6) to a decreased stability of the monosulphate OSC. The positive contribution of the entropy component tends to get smaller with increase in the number of acetylacetone molecules in the inner sphere of cobalt(III). Published ideas on the reasons for this decrease are contradictory[45]. The decrease in the stability of the hydrate layer[47] and the increase in the donor–acceptor interaction with the π-system of the acetylacetone molecules with an increase in their number in the inner sphere represent[121] equally weighty arguments explaining the decrease in the contribution of ΔS_1^0 to ΔG_1^0.

The formation of monosulphate OSC by the hydrophobic tris(2,2′-bipyridyl)cobalt(III) and tris(1,10-phenanthroline)-cobalt(III), unlike the formation of OSC by hydrophilic cations (Tables 4 and 5), takes place with negative values of the enthalpy and entropy changes (Table 7). The absence of acidic protons, the hydrophobic character of the inner-sphere ligands, and the formation of π-bonds between M and phen (bipy) suggest that the solvation of these cations is determined by the dipole moment of the solvent and van der Waals interaction[93,94].

The reaction of tris(2,2′-bipyridyl)- and tris(1,10-phenanthroline)cobalt(III) with a solvent is determined by the strong hydrophobic character of 1,10-phenanthroline and 2,2′-bipyridyl.[122] The large size of the cationic complexes and the shielding of the central metal ion by the inner-sphere ligands, which form $\pi(M \rightarrow Am)$ bonds, where Am = bipy or phen, weaken the electrostriction interaction of the cationic complex with the solvent molecules. With ion-dipole and van der Waals interactions of the solvent with coordination compounds, hydrophobic hydration may take place[123]. In this case, large ionic complexes such as tris(1,10-phenanthroline)-cobalt(III) do not have a primary hydrate layer, and the influence of their secondary hydration is revealed chiefly in the effect on the structure of water layers adjoining the ions, which increases the degree of ordering. It must be assumed that the formation of associates in this case is accompanied by the combination of the cavities in which the ions are situated, or by the replacement of solvent molecules by the outer-sphere ligand in the secondary hydrate layer. Processes of this kind should not lead to the extensive desolvation processes in the case of highly charged hydrated ions which are observed in the outer-sphere association of sulphate ions with tris(1,10-phenanthroline)cobalt(III), where in contrast to the outer-sphere association of hydrophilic amine compounds of cobalt(III) their formation is accompanied by appreciable negative enthalpy and entropy changes (Tables 4–7).

The data in Tables 4–7 and Refs.14 and 79–94 show unambiguously that the nature of the interaction of coordination compounds with a solvent plays a predominant role in the formation of outer-sphere complexes. Ahrland's criterion[124] for the thermodynamic determination of the type of complex (inner- or outer-sphere) in labile systems is not general; its applicability is restricted to hydrophilic systems, and it cannot be used in hydrophobic systems[93,94].

Thermochemical studies of the reaction of cationic cobalt(III) complexes with amines in the outer sphere are complicated[62] by the high values of the heats of mixing of the solutions of the background electrolytes with amines. For this reason, the thermodynamics of the formation of OSC with amines has been studied[105] only from the temperature dependence of the stability constants of the OSC. The values of the enthalpy and entropy changes obtained in this way are naturally approximate. The quantitative data obtained (Table 8) indicate, however, that the addition of ammonia, ethylenediamine, and pyridine to hexamminecobalt(III) and also to tris(ethylenediamine)- and acetatopentamminecobalt(III) is accompanied by negative enthalpy and entropy changes. The addition of ethylenediamine and pyridine is accompanied by negative enthalpy and entropy changes of greater absolute magnitude than the addition of ammonia (Table 8). The ratio of the thermodynamic functions indicated above is due to the greater complexity of the structures of ethylenediamine and pyridine compared with ammonia.

Published data[26,76,79,81–83,92–94] make it possible to analyse the nature of the influence of the ionic strength of the solution on the formation of OSC. In all the systems examined, except the OSC of tris(2,2′-bipyridyl)- and tris(1,10-phenanthroline)cobalt(III), the ionic strength was maintained using sodium perchlorate. Increase in the concentration of this salt (that is in the ionic strength of the solution) decreases the values of the stability constants of the OSC. This decrease takes place as far as saturated sodium perchlorate solutions, and is due to the association of the cationic complexes with the perchlorate ion. The quantitative characteristics of the first stage of this association were examined in the previous section of the present review.

The contributions of the enthalpy and entropy components of the free energy changes vary in different ways with increase in the ionic strength of the solution for cationic complexes with different charges. In most cases, a decrease in the stability of the OSC of the tris(diamine)-compounds of cobalt(III) accompanies a decrease in the entropy component of the free energy changes at $I = 0$–0.5. The change from $I = 0.5$ to $I = 3.0$ leads to a further decrease in the stability of the OSC with an increase in the endothermicity of OSC formation[26,79,81–83].

For the doubly-charged cationic complexes, for example acidopentamminecobalt(III), and also for the singly-charged sulphatopentammine- and carboxylatotetramminecobalt(III), a decrease in the stability of the OSC is observed with increase in the ionic strength of the solution and the simultaneous increase in the positive enthalpy changes for the formation of the OSC.[26,76,92].

For the mixed coordination compounds $[M(en)_x(acac)_{3-x}]$, increase in the ionic strength of the solution leads to an increase in the positive enthalpy changes and to smaller positive values of the entropy change (Table 6). Increase in the ionic strength of the solution, maintained using sodium fluoride, leads to a decrease in the stability of the OSC of tris(2,2'-bipyridyl)cobalt(III), and also tris(1,10-phenanthroline)cobalt(III), and the absolute values of the negative enthalpy and entropy for the formation of the OSC increase[26,93,94]. The influence of the ionic strength of the solution on the thermodynamic functions for the formation of the OSC is due to the association of the cationic complexes with the ions of the background electrolyte, and also to the dehydrating influence of the added electrolyte.

IV. OUTER-SPHERE COMPLEXES OF RHODIUM(III), IRIDIUM(III), PLATINUM(IV), AND CHROMIUM(III)

The study of the thermodynamics of the formation of OSC by rhodium(III), iridium(III), platinum(IV), and chromium(III) cations using the thermochemical method and extrapolation of the thermodynamic functions to aqueous solutions with zero ionic strength has been much less extensive than that for the corresponding cobalt(III) compounds. The formation of OSC by the tris(ethylenediamine) compounds of all these metals has been studied[45,78,84,92,125–127]; in addition, the formation of OSC with the chloropentammines has been studied for rhodium(III) [90,128] and platinum(IV),[45,86,89] with the tris(propylenediamine) compound for chromium(III),[91] and for the *trans*-dichlorobis(ethylenediamine) compounds for rhodium(III), iridium(III), and platinum(IV).[45] As with the cobalt(III) complexes, the outer-sphere ligands used were the sulphate, thiosulphate, sulphite, selenite, tellurite, and carbonate ions. The reaction of hydroxopentammineplatinum(IV) with chloride and bromide ions has been studied[45,89]. The OSC complexes of hexammine- and tris(1,10-phenanthroline)chromium(III) with sulphate ions have been studied[129,130] at different temperatures by the electrical conductivity method. Some of the data on the thermodynamics of the formation of the OSC of rhodium(III), iridium(III), platinum(IV), and chromium(III) are given in Tables 9–11.

Table 9. Changes in the thermodynamic functions for the formation of monoligand OSC of the tris(ethylenediamine) compounds of chromium(III), rhodium(III), iridium(III), ruthenium(III), and platinum(IV) in solutions with $I = 0$ at 298 K.[29,45,78,84,91,125–128]

L	$-\Delta G_1^0$, kJ mole^{-1}	ΔH_1^0, kJ mole^{-1}	ΔS_1^0, J mole^{-1}K^{-1}
	Cr(III)		
$S_2O_3^{2-}$	19.3 (18.8)	—2.4 (—2.5)	57 (63)
SO_3^{2-}	18.6 (18.4)	—2.3 (—2.3)	56 (55)
SeO_3^{2-}	18.3 (18.0)	1.7 (1.7)	67 (66)
TeO_3^{2-}	18.0 (17.6)	1.4 (1.0)	65 (63)
SO_4^{2-}	17.8 (17.2)	0 (0)	59 (59)
CO_3^{2-}	18.0 (18.0)	1.2 (0.8)	64 (63)
	Rh(III)		
$S_2O_3^{2-}$	20.1 (14.9)	—2.2 (3.4)	60 (61)
SO_3^{2-}	19.3	—2.3	58
SeO_3^{2-}	18.8 (14.9)	—1.7 (7.1)	69 (73)
TeO_3^{2-}	18.8 (14.4)	—1.3 (5.9)	67 (67)
SO_4^{2-}	18.0 (16.5)	0.2 (4.6)	65 (71)
CO_3^{2-}	18.4	0.9	61
	Ir(III)		
$S_2O_3^{2-}$	19.9	—0.8	59
SO_3^{2-}	18.8	1.3	59
SeO_3^{2-}	18.8	—0.4	62
TeO_3^{2-}	18.4	2.1	69
SO_4^{2-}	18.0	—0.8	59
CO_3^{2-}	18.7	2.5	71
	Ru(III)		
$S_2O_3^{2-}$	17.7 (15.9)	—1.3 (4.0)	55 (66)
SO_3^{2-}	17.3 (14.7)	—0.4 (2.1)	56 (58)
SeO_3^{2-}	17.1 (15.9)	—0.4 (6.7)	56 (76)
SO_4^{2-}	17.1 (16.7)	—0.4 (8.4)	56 (84)
	Pt(IV)		
SO_4^{2-}	22.6	—0.4	76
SO_3^{2-}	26.0	—0.8	84

Note. The standard deviations of the determinations are ±(0.3–0.6) kJ mole^{-1} for ΔG_1^0; ±(0.4–0.8) kJ mole^{-1} for ΔH_1^0; and ±(2–4) J mole^{-1} K^{-1} for ΔS_1^0. The data in brackets for Cr(III) are for the OSC of tris(propylenediamine)chromium(III),[91] for Rh(III) they are for the OSC of chloropentamminerhodium(III),[28] and for Ru(III) they are for the OSC of chloropentammineruthenium(III).[31]

Table 10. Changes in the thermodynamic functions for the formation of monohalide OSC of platinum(IV) in solutions with zero ionic strength at 298 K.[45,86,89]

Cation	L	$-\Delta G_1^0$, kJ mole^{-1}	ΔH_1^0, kJ mole^{-1}	ΔS_1^0, J mole^{-1}K^{-1}
$[Pt(en)_3]^{4+}$	Cl^-	9.2	6.3	50
$[Pt(en)_3]^{4+}$	Br^-	8.8	11.7	67
$[Pt(NH_3)_5Cl]^{3+}$	Cl^-	9.2	0.4	34
$[Pt(NH_3)_5Cl]^{3+}$	Br^-	8.4	2.9	38
$[Pt(NH_3)_5(OH)]^{3+}$	Cl^-	8.8	2.9	38
$[Pt(NH_3)_5(OH)]^{3+}$	Br^-	8.0	4.0	40

Note. See footnote to Table 9.

Table 11. Changes in the thermodynamic functions for the formation of monosulphate OSC by *trans*-$[M(en)_2Cl_2]^{2+}$ ions in solutions with zero ionic strength at 298 K.[45]

M	$-\Delta G_1^0$, kJ mole^{-1}	ΔH_1^0, kJ mole^{-1}	ΔS_1^0, J mole^{-1}K^{-1}
Co(III)(Co(en)$_2$(SCN)Cl^{+})	13.0	6.3	63
Rh(III)	12.1	5.4	59
Ir(III)	10.9	3.8	46
Pt(IV)	15.1	5.0	67

Note. See footnote to Table 9.

The data in Tables 9 and 11 show that in aqueous solutions with zero ionic strength at 298 K, all the monoligand OSC with doubly-charged ligands studied are formed with small (less than ±8.4 kJ mole^{-1}) changes in the enthalpy, and positive values of the entropy changes, equal to 63 ± 8 J mole^{-1} K^{-1}. The values of the entropy changes for practically all the OSC of hydrophilic cationic complexes lie in this range. There are only a few systems in which the

entropy changes lie outside this range. They include the sulphate OSC of *trans*-dichlorobis(ethylenediamine)iridium-(III), where $\Delta S_1^0 = 46$ J mole^{-1} K^{-1},[45] and also the sulphate and sulphite OSC of tris(ethylenediamine)platinum(IV), where $\Delta S_1^0 = 76$ J mole^{-1} K^{-1} and 84 J mole^{-1} K^{-1} respectively[76,84]. It is not yet possible to say unambiguously whether these deviations are due to experimental error or to specific features of the formation of the OSC.

In most cases, in contrast to the OSC of amine compounds of cobalt(III), only the formation of monoligand associates by amine compounds of rhodium(III), iridium(III), platinum-(IV), and chromium(III) has been studied. Qualitative and semi-quantitative indications of the formation of multiligand complexes have been reported[29,78,84]. Attempts to determine the thermodynamic characteristics of the formation of even the bis(ligand) OSC of, for example, chromium(III),[78,84] rhodium(III),[78,84] or platinum(IV),[31] however, gave extremely rough or approximate values of the thermodynamic functions. It can only be assumed that the bis(ligand) associates are formed with approximately the same changes in the thermodynamic functions as the OSC of cobalt(III).

The stability of the monoligand OSC of tris(diamine) compounds of rhodium(III), iridium(III), chromium(III), and platinum(IV) decrease in the following order of doubly-charged anions: thiosulphate > sulphite > selenite > tellurite > sulphate ions (Tables 9–11). This is less characteristic of the OSC of amine compounds of cobalt(III). A deviation from the above order is observed for OSC of chloropentamminerhodium(III), where the sulphate associates are more stable than the thiosulphate.

The chloride and bromide associates of tris(ethylenediamine)-, and also chloro- and hydroxopentammineplatinum-(IV), are formed (Table 10) with positive values of the enthalpy and entropy changes. The enthalpy and entropy changes for the formation of the bromide OSC of platinum(IV) are positive and of larger magnitude than those for the formation of the chloride OSC (Table 10). Usually, in the series of "fluoride–iodide" OSC, the absolute magnitude of the entropy changes decrease[71,94], even taking negative values for bromide and iodide OSC,[51,99] and high positive values of the enthalpy and entropy changes are observed only for fluoride OSC.[94] This variation of the enthalpy and entropy changes in the halide ion series is due to hydration factors. The anomalous ratios of the enthalpy and entropy changes for the chloride and bromide OSC of amine compounds of platinum(IV)[45] require verification.

The formation of sulphate OSC of hexamminechromium(III) takes place at values of the enthalpy changes close to zero, and the entropy changes are 63 J mole^{-1} K^{-1}.[127] At the same time, tris(1,10-phenanthroline) chromium(III) adds on sulphate ion with negative values of the enthalpy and entropy changes[126], confirming the thermodynamic data for the corresponding OSC of hydrophilic and hydrophobic cobalt(III) cations (Tables 5 and 7).

On going from the tris(diamine) compounds to the acidopentammines, and then to the *trans*-dichloro- or chloro-(thiocyanato)- (Tables 9–11) -bis(ethylenediamine) compounds of cobalt(III), rhodium(III), and iridium(III), the stability of the OSC decreases in this order for cationic complexes, because of the decrease in the charge on the cationic complexes. The stability of the OSC increases significantly on going from the triply-charged cations of cobalt(III), rhodium(III), and iridium(III) to the quadruply-charged cations of platinum(IV) (Tables 9 and 11).

Interesting relationships are observed in the analysis of data on the stability of the OSC of chloropentammines of cobalt(III) and rhodium(III) (Table 9). The thiosulphate, selenite, and tellurite OSC of chloropentamminecobalt(III) are more stable than the corresponding rhodium(III) compounds. The thiosulphate, selenite, and tellurite ions can transfer charge to the antibonding orbitals of chloropentamminecobalt(III). As a consequence of the greater splitting of the *d* orbitals in the rhodium(III) complexes, the outer-sphere charge transfer in these compounds is less than that in the corresponding cobalt(III) compounds[90,94,130]. For the association of sulphate ions, the charge transfer is slight, because the stabilities of the OSC of the chloropentammines of cobalt(III) and rhodium(III) with the sulphate ion are practically identical.

For most hydrophilic cationic complexes of cobalt(III), rhodium(III), chromium(III), platinum(IV), and iridium(III),[79,81,83,84,123–130] increase in the ionic strength of the solution, maintained by sodium perchlorate, leads to a decrease in the stability of OSC with different ligands L; with increase in I, the positive contribution of the entropy changes decreases. For the sulphate and tellurite OSC of tris(ethylenediamine)-iridium(III), the positive values of the enthalpy changes increase with increase in the ionic strength of the solution.

It should be noted that the dependence of the enthalpy and entropy changes on the ionic strength of the solution is not unique even for the OSC of cationic complexes with similar properties, for example chloropentamminecobalt(III) and chloropentamminerhodium(III).[130] Further studies are necessary to determine the reasons for such marked differences in the changes in the thermodynamic functions.

Table 12. Changes in the thermodynamic functions for the formation of monoligand chloride and sulphate OSC of tris-(2,2′-bipyridyl) compounds of iron(II) and ruthenium(II) at 298 K in aqueous solutions with constant ionic strengths, maintained using sodium fluoride[31,55].

I	$-\Delta G_1^0$, kJ mole^{-1}	ΔH_1^0, kJ mole^{-1}	ΔS_1^0, J mole^{-1}K^{-1}
	Fe(II),Cl$^-$		
0	7.1	4.0	37
0.25	3.6	4.8	28
0.50	2.3	5.4	26
0.75	1.3	6.1	25
	Ru(II), Cl$^-$		
0	11.6(11.5)	0	39
0.25	7.7(8.2)	0.6	28
0.50	6.6(7.6)	1.0	25
0.75	5.5(7.4)	1.0	22
	Ru(II), SO_4^{2-}		
0	12.8	—21.0	—29
0.25	6.4	—16.7	—38
0.5	5.3	—13.8	—29
0.75	4.4	—9.2	—25

Note. The standard deviations of the determinations are ±(0.3–0.5) kJ mole^{-1} for ΔG_1^0; ±(0.4–0.8) kJ mole^{-1} for ΔH_1^0; and ±(2–4) J mole^{-1} K^{-1} for ΔS_1^0. The data for the osmium(II) OSC are given in brackets.

V. OUTER-SPHERE COMPLEXES OF IRON(II), RUTHENIUM-(II), (III); AND OSMIUM(II)

At present, there are only isolated accurate data[34,131,132] on the thermodynamics of the formation of OSC by cationic complexes of iron(II) and ruthenium(II), (III), and information on the composition and stability constants of OSC of

osmium(II). The OSC of amine compounds of ruthenium(III) have been most fully studied by the thermochemical method[29]. Halide, perchlorate, sulphate, thiosulphate, sulphite, and selenite ions were used as outer-sphere ligands. Some of the data on the thermodynamics of the formation of these OSC are given in Tables 9 and 12.

The data in Table 12 and published data[29,53–55,57] indicate that the stability of the OSC of the tris(2,2′-bipyridyl) and tris(1,10-phenanthroline) compounds of iron(II), ruthenium(II), and osmium(II), in the great majority of cases, increases on going from Fe^{II} to Os^{II}; from the tris(2,2′-bipyridyl) to the tris(1,10-phenanthroline) complexes; and with change in the outer-sphere ligands in the order: chloride < bromide < iodide < perchlorate ions.

There is a linear correlation between lg β_1 and the heats of hydration of the outer-sphere ligands[29,31,33]

$$\lg\beta_1 = A + B\,\Delta H^0_{hydr}(L)$$

where A and B are constants for each cationic complex. For the OSC of iron(II), ruthenium(II), and osmium(II) studied, A lies in the range 3.4–8.5, and B in the range 0.018 to 0.062. A linear relationship is also observed between the value of lg β_1 and the reciprocal of the crystal-chemical radius (Goldschmidt) of the outer-sphere anion after allowing an empirical correction of 0.028 nm. The existence of these corrections indicates that in the association of hydrophobic cationic complexes, an important role is played by both electrostatic and hydration factors.

The stability of the above OSC decreases regularly with increase in the serial number of the added ligand. The published data[133,134] indicating deviations from this regular trend require verification. The increase in the stability of the chloride OSC in the order iron(II) < ruthenium(II) < osmium(II) is related to the decrease in the positive contribution of the enthalpy changes.

Studies by the present authors[55,131] have shown that the stability of the OSC depends to a much greater extent on the nature of the central metal ion when the inner sphere contains ligands forming π-bonds than when inner-sphere ligands forming only σ-bonds are present. In some systems (even when the inner sphere contains π-bonds), the differences in the stability of the OSC when, for example, ruthenium(II) is replaced by osmium(II) are small and disappear. This is indicated by the values of the free energy changes for the monochloride complexes of the tris(2,2′-bipyridyl) compounds of ruthenium(II) and osmium(II) in aqueous solutions with zero ionic strength, given in Table 12.

In general, the stability of monoligand OSC of tris(2,2′-bipyridyl) and tris(1,10-phenanthroline) complexes decreases in the following metal ion order: $Os^{II} > Ru^{II} > Co^{III} > Fe^{II}$. The tendency to form π-acceptor bonds increases from Fe^{II} to Os^{II}, that is in the order $3d^6 > 4d^6 > 5d^6$ ions. The hydrophobic properties of the cationic complexes increase in the order indicated, since the influence of the charge on the metal ion on the water molecules becomes weaker as it is shielded by ligands forming π-acceptor bonds. The position of Co^{III} in this series is explained by the decrease in the strength of the hydrophobic properties of the cationic complexes $[CoAm_3]^{3+}$, where Am = phen or bipy, compared with $[MAm_3]^{2+}$, where M = Ru^{II} or Os^{II}, and contradicts simple electrostatic ideas.

The greater stability of the OSC of tris(1,10-phenanthroline) complexes compared with tris(2,2′-bipyridyl) compounds is due to the more hydrophobic properties of 1,10-phenanthroline and the coplanar structure of the inner-sphere molecules of 2,2′-bipyridyl, which increases the size of the complexes $[M(bipy)_3]^{z+}$ compared with $[M(phen)_3]^{z+}$. This effect is not so marked for Co^{II} and Fe^{II}, but is appreciable for Ru^{II} and Os^{II}.

The order of the outer-sphere anions with respect to decreased stability of the OSC of hydrophobic cations is determined by the fact that a decrease in the heat of hydration and an increase in the size of the anions lead to an increase in their tendency to associate with hydrophobic cations. It must be assumed, however, that in these interactions, use is made of the structural cavities of the 2,2′-bipyridyl and 1,10-phenanthroline molecules coordinated to the cations, that is "hydrophobic packets". A number of experimental data[133,134], and also the fact that the maximum number of added ligands in the outer sphere is three[135,136], confirm this. For some tris(2,2′-bipyridyl) and tris(1,10-phenanthroline) complex systems, however, there are indications that a fourth ligand is attached. The question of the existence of these OSC remains open.

Sulphate OSC of tris(2,2′-bipyridyl)ruthenium(II) (Table 12), like the corresponding compounds of other hydrophobic cations, are formed with negative values of the enthalpy and entropy changes. In contrast to the case of the sulphate OSC of tris(2,2′-bipyridyl)cobalt(III), however, a sharp increase in the absolute magnitude of the negative values of the entropy changes is not observed with increase in the ionic strength of the solution.

Sulphate, thiosulphate, sulphite, and selenite OSC have been studied for a number of compounds of ruthenium(III). Tris(ethylenediamine)ruthenium(III) forms more stable OSC than chloropentammineruthenium(III), and this is explained by the charges of the cationic complexes (Table 9). As in the case of other coordination compounds of transition metals, the change from tris(ethylenediamine) OSC to chloropentammine OSC leads to an increase in the positive values of the enthalpy changes (Table 9). At zero ionic strength, OSC of chloropentammineruthenium(III) are formed, with higher values of the entropy changes (up to 84 J $mole^{-1}$ K^{-1}) compared with the OSC of tris(ethylenediamine)- and, probably, nitrosylpentammineruthenium(III) [137] ($\Delta S^0_1 \cong 54-57$ J $mole^{-1}$ K^{-1}), in contrast to the relationship observed for other metals. This is apparently due to the greater dehydration of the cationic complexes on the formation of the OSC of chloropentammineruthenium(III), compared with tris(ethylenediamine)ruthenium(III).

The stability of the OSC of tris(ethylenediamine)ruthenium(III) decreases[29] in the order of outer-sphere ligands: thiosulphate > sulphate > sulphite > selenite > sulphate ions, and that for chloropentammineruthenium(III) in the order: thiosulphate > sulphate > selenite > sulphite ions, but the decrease is small [the free energy changes for tris(ethylenediamine)ruthenium(III) and chloropentammineruthenium(III) in solutions with zero ionic strength are 0.5 kJ $mole^{-1}$ and 1.6 kJ $mole^{-1}$ respectively]. In aqueous solutions with zero ionic strength, the stability of the OSC of ruthenium(III) decreases in the following order of cationic complexes[31]:

$$[Ru(NH_3)_5(NO)]^{3+} > [Ru(en)_3]^{3+} > [Ru(NH_3)_5Cl]^{2+}.$$

The strong π-acceptor properties of the nitrosyl group and the possible resulting change in the actual state of ruthenium from Ru^{III} to Ru^{IV} [138] are responsible for the high stability of the OSC of $[Ru(NH_3)_5(NO)]^{3+}$ compared with those of $[Ru(en)_3]^{3+}$; the replacement of the nitrosyl group in the inner sphere of the cationic complex by chloride ion decreases the stability of the resulting OSC, since the charge on the cationic complex is lowered.

Unlike the OSC of the tris(ethylenediamine) compounds of cobalt(III), rhodium(III),[26,92,125] and chromium(III),[78] for the OSC of tris(ethylenediamine)ruthenium(III),[31] increased ionic strength of the solution leads to an increase in the positive values of the enthalpy changes and to a decrease in the contribution of the entropy component of the free energy.

VI. SOME GENERAL REGULAR FEATURES OF THE THERMODYNAMICS OF THE FORMATION OF OUTER-SPHERE COMPLEXES

Analysis of the data in Tables 4, 5, and 9–12, and the fairly accurate published data[106–109], show that entropy changes of $\Delta S_1^0 = 63 \pm 8$ J mole^{-1} K^{-1} and $\Delta S_2^0 = 29 \pm 8$ J mole^{-1} K^{-1} accompany the addition of the first and second doubly-charged anions to the great majority of hydrophilic coordinately-saturated inert and labile cationic complexes with charges from +1 to +4 in aqueous solutions with zero ionic strength at temperatures close to 298 K. The removal of one solvent molecule from the inner sphere of a cation into an aqueous solution leads to an entropy change of 30.54 J mole^{-1} K^{-1}.[139,140] This value is close to the entropy of fusion of ice[141] and to the entropies of water molecules coordinated, for example, to praseodymium(III) or ytterbium(III).[142] If it is assumed that the difference in the partial molar entropies of the associate and the ligand of the cationic complex is close to zero, it may be concluded that the addition of the first doubly-charged anions in the inner sphere is accompanied by the liberation of two water molecules.

The liberation of two water molecules on the addition, in the inner sphere, of the first doubly-charged anions to both hydrophilic and hydrophobic cationic complexes is indicated by data on the formation constants of OSC in aqueous-organic solutions (Tables 2 and 3). The entropy changes for the formation of OSC by hydrophobic cations (Table 7) do not indicate unambiguously the removal of two water molecules, since they are negative.

It has been suggested that sulphate ions are dehydrated when they add on to cations[106,107]. On the other hand, the difference in the entropy changes in the first and second stages of outer-sphere association provide a basis for assuming that water molecules are liberated as a consequence of dehydration of the cationic complex[26,98,124].

Increase in the ionic strength of the solution should decrease the magnitude of the entropy changes for the formation of OSC, if these changes are related to the dehydration of the anion–ligand, since the water hydrating this anion reaily combines with other ions. This is not observed in all systems, however[26,92,125]. At the same time, for hydrophobic cationic complexes it is necessary to assume that ions can associate by the combination of cavities or the entry of two ions into one cage created by the solvent[123]. In this process, the liberation of water molecules may take place from distant spheres of the hydrated cationic complex or from the anion–ligand.

The great majority of research workers consider that the formation of the first acido-OSC, like that of ordinary ion pairs, can be described[45,106,107] by the electrostatic theories of Bjerrum and Fuoss[143,144]. The processes of OSC formation should take place with a decrease in enthalpy and an increase in entropy[23], since according to these theories it is possible to write

$$\Delta H_1^0, \text{kJ mole}^{-1} = 0.891 \cdot b$$

$$\Delta S_1^0, \text{J mole}^{-1}\text{K}^{-1} = 58.16 \cdot \lg a^0 + 11.3 \cdot b - 49.8$$

where a^0 is the distance of closest approach of the associating ions, $b = z_C z_A e^2/\varepsilon k T a^0$, where z_C and z_A are the charges on the complex and the outer-sphere ligand, e the charge on the electron, ε the dielectric constant of the solvent, and k the Boltzmann constant.

Thus for charges of the associating ions equal to 1, 2, and 3, and $a^0 = 0.357$ nm, the enthalpy changes should be equal to[23] 1.7, 7.1, and 15.9 kJ mole^{-1}, and the entropy changes 5, 73, and 177 J mole^{-1} K^{-1} respectively. Increase in a^0 to 0.714 nm changes these values[23] to 0.8, 3.3, and 8.0 kJ mole^{-1}, and 11.3, 45.2, and 101.7 J mole^{-1} K^{-1}. The data in Tables 5, 10, and 11 show that the model based on the theories of Bjerrum and Fuoss effectively describes the changes in the thermodynamic functions for the formation of OSC by doubly-charged hydrophilic complexes with doubly-charged anions for $a^0 = 0.3–0.5$ nm. The associates of triply-charged hydrophilic cations with doubly-charged anions correspond only approximately to this model. The experimental data indicate, however, that the positive values of the enthalpy changes increase with decrease in the charge on the cationic complex (according to the theory, the positive values of the enthalpy should decrease[23]), and the positive values of the entropy change remain practically unchanged or increase slightly (according to the theory, the positive values of the entropy changes should decrease[23]). The changes in the thermodynamic functions for the formation of OSC by hydrophobic cations with doubly-charged anions (see Table 7) do not agree at all with the theories of Bjerrum and Fuoss[106,107] or with Ahrland's concept[106,107].

On the basis of the fact that the entropy changes for the formation of OSC by hydrophilic cationic complexes with doubly-charged anions are practically constant, and the regular decrease in the stability of the OSC with decrease in the charge of the complex and increase in the positive values of the enthalpy changes, some authors have predicted the values of the thermodynamic functions for the formation of OSC in systems which have not yet been studied[26,45]. For several systems, it has been found that the predicted values are close to those determined experimentally.

The formation of OSC by coordination compounds of cobalt(III), rhodium(III), chromium(III), and platinum(IV) is concentrated electrolyte solutions at 298 K is accompanied by free energy changes in the range ±(2–4) kJ mole^{-1}; the enthalpy and entropy changes lie in the range ±40 kJ mole^{-1} and ±(80–120) J mole^{-1} K^{-1}.[49,57,69–77,92–102] According to Ref. 26, there is a compensation effect between the values of the enthalpy and entropy changes under these conditions.

The lack of data on the thermodynamics of the OSC of inert coordination compounds of the transition metals at present makes a wider generalisation impossible (particularly for multiligand OSC). An increase in the volume of information and an increase in the accuracy and reliability of the experimental data are necessary.

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