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Outer-sphere Complexes of Tervalent Cobalt

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Certain theoretical postulates concerning the formation of outer-sphere complexes have been described. Various approaches to the investigation of these compounds have been considered. Data are presented showing the necessity to take into account the packing term in unitary cratic thermodynamic functions of outer-sphere complexes. Methods for and the results of investigations of various classes of cobalt(III) outer-sphere complexes have been discussed. It is suggested that the formation of transition metal outer-sphere complexes takes place in steps as a result of directional forces. Like inner-sphere interactions, this process takes place in accordance with limiting and characteristic co-ordination numbers. The types of bonds involved in the formation of outer-sphere complexes have been examined.
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1. INTRODUCTION

Interest in the study of outer-sphere complexes (OSC) increased sharply in the last ten years because outer-sphere coordination processes determine the mechanisms and the rates of many reactions, provide a more profound understanding of catalysis [1], yield a partial model of the transition state, and lead to the discovery of new methods for the isolation, purification, and detection of many metals [2,3], and also have a marked effect on inner-sphere interaction. Many types of complex compounds exist in aqueous solutions solely because of outer-sphere association [4,5]. Recently a number of theoretical postulates have been formulated [6] concerning the formation of such complexes. The data on the thermodynamics and structure of cobalt(III) outer-sphere complexes have played an important role in the formulation of these postulates but the complexes have not so far been reviewed.

This paper constitutes an attempt to review and examine critically the published data and also the results obtained by the author of the review and his coworkers for cobalt(III) outer-sphere complexes.

Complexes of di- and ter-valent cobalt are most frequently encountered [3]. A characteristic feature of most of the cobalt(III) complexes is a low rate of inner-sphere electrolytic dissociation and a constant coordination number of six [7,8]. The compounds have an octahedral configuration. Almost all cobalt(II) complexes are labile and their coordination number is four or six [9].

At present cobalt(III) outer-sphere complexes have been investigated in greatest detail compared with analogous compounds of other metals. This situation arose partly because of the inertness of the inner sphere of cobalt(III) and the lability of the outer-sphere complexes. The low rate of dissociation of the inner-sphere complex made it possible to investigate the cobalt(III) outer-sphere complexes by many methods used for the study of labile inner-sphere coordination [10] and it also permitted the application of the most effective modern methods, such as, for example, circular dichroism spectroscopy [11]. The outer sphere complexes of other metals such as chromium, platinum, rhodium, iridium, etc. frequently have advantages, which are indicated in the description of the properties of the cobalt(III) complexes, but for various reasons [5] these complexes have not been investigated systematically.

The study of cobalt(II) outer sphere complexes is difficult because of the high lability of the inner sphere of this ion, but infrared [12,13], Raman [14], and electronic spectroscopy [15-18] permits the study of outer-sphere complexes in these and other systems with similar properties. The most promising approach for the investigation of cobalt(II) outer-sphere complexes is a combination of thermodynamic and electronic spectroscopic methods [15-17]. The methods proposed for the study of outer-sphere complexes in the present author's earlier investigations [4,5,19-27] are also suitable for the study of the analogous cobalt(II) complexes.

2. SOME GENERAL DATA ON OUTER SPHERE COORDINATION

According to Werner's theory, all saturated complex compounds are capable of outer-sphere interaction. However, the theoretical postulates formulated at present

concerning the formation of outer sphere complexes [6] are valid only for transition metal, lanthanide, and probably actinide compounds. Ions of other metals are capable of outer-sphere association but the occurrence of outer-sphere coordination has not been demonstrated for them. In fact the study of the outer-sphere interaction of ions with filled *d* orbitals indicates the absence of stepwise outer-sphere coordination [28].

Numerous literature data show [5,6,29-47] that the capacity of transition metals for interaction is determined by the main and subsidiary valences and also by additional specific forces, the effect of which is directed to fixed positions in space. The nature of these forces is determined by the nature of the Werner complexes functioning as the central groups of the outer sphere complexes. The directional effect of the additional forces determines the stereochemistry of the second coordination sphere.

Like inner-sphere interaction, outer-sphere complex formation processes take place in stages and involve a decrease in the strength of the bond between the outer-sphere ligands and the inner sphere on going from the nth to the $(n + 1)$th outer-sphere ligand. Sometimes deviations from this rule are observed [4,5]. This happens when inner-sphere coordination is superimposed on the outer-sphere interaction or when the activity coefficients of the interacting and product ions are altered. Similar deviations may be attributed also to the geometrical characteristics of the outer coordination sphere.

Outer-sphere interaction, like inner-sphere complex formation, is characterised by limiting and characteristic coordination numbers [6]. Inner-sphere complexes with octahedral configuration have limiting outer-sphere coordination numbers of 8 and 12 and characteristic numbers of 2 and 4. An especially large number of octahedral inner-sphere cobalt(III) complexes coordinate four outer sphere ligands [30,38-42,45,46]. There are few data on outer-sphere complexes the central ions of which are Werner complexes with tetrahedral and square configurations. According to theoretical considerations [6], one may assume that tetrahedral complexes have limiting outer-sphere coordination numbers of 4 and 6 and a characteristic number of 4. The outer-sphere coordination numbers of complexes with a square configuration are probably 2 and 4.

The charge, dimensions, geometrical configuration, and type of inner-sphere ligand, the electronic state of the Werner complex, and also the nature of the medium, temperature, and pressure determine the stability, structure, and number of ligands combined in the outer-sphere complex. However, the charge and dimensions of inner-sphere complexes do not influence the coordination numbers of the outer-sphere complexes. These characteristics have a major effect on the thermodynamic functions of outer-sphere coordination [4]. A decrease of the dielectric constant of the medium and an increase of the electron-accepting properties of the inner-sphere complex usually increase the stability of the outer-sphere complex.

The sites of contact between the outer-sphere ligands and the inner-sphere complex are points with the most effective charges of the interacting species. The centres of the edges or faces of the octahedral and tetrahedral complexes and the reactive atoms of the inner-sphere ligands [31,43,44,47] not involved in inner-sphere interaction frequently form the closest bond in the outer sphere complex.

Comparison of data on the stability of typical ion pairs and triplets with the stability typical of outer-sphere coordination complexes shows [5] appreciable differences between these two groups of association complexes. The difference consists in the characteristic coordination number. The latter is unity for typical ion pairs and triplets. Saturated complex cations (in the sense of Werner's theory) show a much higher capacity for outer-sphere coordination than complex anions [5]. The latter rarely form stable-outer sphere complexes in which they behave as the central group. Both complex and simple anions have a pronounced capacity for addition to central groups as ligands. The explanation is that all anions tend to exhibit electron-donating properties and do not have appreciable electron-accepting properties.

The interaction between ions and molecules of water or another highly polar solvent leads to the formation around the ions of three concentric shells [48-50] and therefore the overall concentration (C_M) of a conventionally free ion M can be expressed [51] by the equation

$$C_M = \sum_{n=0}^{N} \sum_{n_1=0}^{N_1} \sum_{n_2=0}^{N_2} ([MS_n]S_{n_1}S_{n_2}), \qquad (1)$$

where N, N_1, and N_2 are the maximum numbers of solvent molecules S in the first, second, and third solvation shells of the ion M. The square brackets in this equation define the first solvation shell and the symbols of the substances in round brackets denote their equilibrium concentrations. The ionic charges have been omitted for simplicity.

The first solvation shell of the association complexes is identical in many ions with the Werner coordination sphere [52-58]. The second solvation shell of the association complex is characterised by a lower degree of order in the solvent structure than in the pure solvent. The bond between the solvent molecules in the second shell and the ion M is usually formed via the molecules of the first shell but $N_1 > N$. [59] The state of the solvent molecules in the third solvation shell does not differ fundamentally from that in the pure solvent and $N_2 \gg N_1$.

Inner-sphere complex formation in solutions is a process in which the solvent molecules in the Werner coordination sphere of the central ion are displaced by any ligand other than the solvent molecule [60]. Such a process is always accompanied by the formation of a direct bond between the central atom and the ligand.

It is suggested that outer-sphere complex formation be regarded [61,62] as a process in which solvent molecules in the second shell of the association complex, with the composition defined by formula (1), are substituted. Such a process is accompanied by the formation of bonds between the central ion M and the outer sphere ligand A via an inner sphere ligand L and by secondary interaction between M and A as a result of charge transfer from A to the antibonding orbitals of ML_n. [35]

The formation of a successive series of outer-sphere complexes of the central group $[ML_nS_{N-n}]$ may be represented by the equilibrium

$$[ML_nS_{N-n}]S_{N_1} + q[AS_P] \rightleftarrows [ML_nS_{N-n}]A_qS_x + (qP + N_1 - x)S, \qquad (2)$$

where $q = 1, 2, 3, \ldots$ The above formulation of reaction (2) is valid if the addition of each outer-sphere ligand is accompanied by the elimination from $[ML_nS_{N-n}]S_{N_1}$ of an arbitrary number of solvent molecules.

When outer-sphere complex formation occurs in solution with a high concentration of inert salts, then one or several ions of the inert salt are detached from the central group together with solvent molecules in the course of reaction (2). This postulate has been found to hold in practice [30].

The equilibrium constant for reaction (2) ($^{p}\omega_{nq}$) is related to the stability constant ω_{nq} of the outer-sphere complex $[ML_nS_{N-n}]A_qS_x$ formed by the equation

$$\omega_{nq} = {}^{p}\omega_{nq} \cdot (S)^{x-N_1-qP} \qquad (3)$$

when the activity coefficients of all three components of equilibrium (2) are constant and arbitrarily set equal to unity.

The equilibrium constants for reaction (2) and similar processes, expressed on the molal and molar scales consist of a unitary component, characterising the nature of the interacting species, and a packing or cratic component, defined by the number of interacting species [63]. The packing term in equilibrium (2) is $(S)^{x-N_1-qP}$.

Some time ago Bjerrum pointed out [64] the necessity to correct the equilibrium constants for the packing term. This has also been noted in other investigations [65,66].

Gurney [63] examined the problem of the standard state in the study of solutions starting with the concept of the separation of the overall entropy of the process into unitary and cratic components. The difference between the standard states of the solvent (pure solvent) and the solute (hypothetical or real solutions) makes it necessary to take into account two components of the equilibrium constant—the free energy and entropy terms. Only the use of the mole fraction scale eliminates the asymmetry in the choice of the standard state for the solvent and solution, but this method of expressing concentrations is inconvenient in practice [67].

It is interesting to note that the correction of the formation constants of outer-sphere complexes for the cratic terms eliminates many contradictions in data on the stability of these compounds [30]. Unfortunately there are very few literature data necessary for such correction of the thermodynamic functions of both inner-sphere and even more so outer-sphere complexes.

The enthalpy of complex formation in solutions is a unitary constant when it is determined from thermochemical measurements. The cratic term varies with temperature and therefore the process enthalpies calculated from the temperature variation of the equilibrium constants can differ fundamentally from the values obtained from thermochemical measurements.

3. FIRST STUDIES ON OUTER-SPHERE COMPLEXES OF TERVALENT COBALT

The first studies on cobalt(III) outer sphere complexes in solution were made by Brintzinger as early as 1935. [38, 39, 68] The author notes [38] the necessity to distinguish two types of complex: comparatively simple complexes such as hexamminecobalt(III) chloride, aquopentammine-cobalt(III) bromide, etc. and more complicated compounds where saturated complexes (in the sense of Werner's theory) play the role of the central ion or ligand. According to Brintzinger [33], the central ion in the latter type of complex may be any complex cation and anion and therefore there are many more of the complicated complexes than of the simple complexes. The above postulates put forward by Brintzinger are valid also in the light of modern investigations. It is necessary to make only one modification namely that complex anions show little tendency to behave as coordination centres in outer-sphere complexes compared with complex cations.

Brintzinger demonstrated [38,39,68] the formation of a large number of outer-sphere complexes by dialysis and also by transport measurements.

The molecular weight data for outer-sphere complexes found by dialysis have been criticised [7,29] on account of the error involved. Indeed this method is unsuitable for the accurate determination of the number of molecules of water or another solvent in various solvation shells of an association complex the composition of which is represented by formula (1), [29] but it frequently makes it possible to determine the molecular weight of complex ions [69] and outer-sphere association complexes [39] with adequate reliability [70]. Moreover, the validity of Brintzinger's data showing that hexamminecobalt(III) ions move towards the anode in the presence of an excess of outer-sphere anionic ligand species is unequivocal [70] and the critics of Brintzingers investigations unfortunately did not take this into account.

The first studies of cobalt(III) outer-sphere complexes showed that in 2 M solutions of sodium nitrate hexaammine, trisethylenediamine-, and various acidopentammine-, and acidotetrammine-complexes of cobalt(III) do not interact appreciably with nitrate ions [69]. However, in 2 M ammonium sulphate solutions, in 1.5 M potassium oxalate solutions [38], in 0.5 M potassium hexacyanoferrate(II) solutions [68], and in 1.5 M potassium pyrophosphate solutions [39] all the above and a number of other simple and mixed cobalt(III) complexes form outer-sphere complexes with a coordination number of 4 when the outer sphere ligands behave as monodentate species. Immediately after their preparation, cobalt in these solutions migrates to the anode under the influence of an electric field. Thus the first studies on cobalt(III) outer-sphere complexes already demonstrated unambiguously the addition of several anionic ligands in the outer sphere.

The addition to CoL_N^{3+} complexes of even one hexacyanoferrate(II) ion leads to the formation of a negatively charged association complex. Consequently further addition of outer-sphere ligands cannot occur because of electrostatic forces. Similar situations are encountered also in other systems. However, many investigators still believe that the interaction between complex and outer-sphere ions in aqueous solutions is virtually non-existent [29] or can be accounted for [7,8,67,71] within the framework of the theory of electrostatic interaction. The results of Brintzinger's work and other early investigations of cobalt(III) complexes have been discussed in detail in a number of monographs [7, 72,73].

4. TWO APPROACHES TO THE STUDY OF COBALT(III) OUTER SPHERE COMPLEXES

The present author's work showed [4,5,74-77] that the association of any ions in any solvent can be characterised quantitatively on the basis of the law of mass action (LMA). A knowledge of the true composition of the interacting and product species is necessary for such description of the process. Hence it follows that the association of saturated complexes (in Werner's sense) with outer sphere ions is also a process obeying the law of mass action. The validity of this postulate is confirmed by numerous investigations [5].

Many workers believe [78-82] that the dissociation of complexes in aqueous solutions into complex and outer-sphere ions should be characterised by formal activity coefficients. There exists a view that large complex ions show less tendency towards association than simple ions. A number of objections have also been made [83-86] to the use of the law of mass action to characterise quantitatively association interactions with participation of complex ions. However,

recent measurements of osmotic coefficients and activity coefficients of hexammine- and acidopentamminecobalt(III) complexes disprove [87-91] the view that outer-sphere interaction can be usefully characterised with the aid of the activity coefficients of complex salts. These data confirm the view expressed by the author of this review more than ten years ago [92] and constitutes the second approach to the study of outer-sphere complexes with calculation of the law of mass action constants on the basis of measured activity coefficients. The first approach to the study of such complexes consists in a direct determination of the changes in thermodynamic functions in the course of outer-sphere interaction.

A pronounced dependence of the outer-sphere complex formation constants on the concentration of complex salts was observed [81] in early measurements of activity coefficients. New studies have shown [87-90] that, with a correct approach to the calculation of the outer-sphere association constants from the activity coefficients, the association constants remain invariant over a wide range of the concentrations of various salts. Moreover, it has been observed that the activity coefficients of numerous acidopentamminecobalt(III) salts are much lower than those of simple electrolytes of a similar type and do not pass through a minimum even in solutions at concentrations of about 2.5 M.

Very convenient methods have now been developed [87-91] for the calculation of the thermodynamic functions of outer-sphere complexes with one ligand from osmotic and activity coefficients. These methods have been used to investigate cobalt(III) outer-sphere complexes.

5. ALLOWANCE FOR THE PACKING TERM OF THE UNITARY CRATIC FUNCTIONS OF COBALT(III) OUTER-SPHERE COMPLEXES

The principal standard state used in the study of stepwise outer-sphere coordination is a solution with a high and constant ionic strength maintained by means of inert salts. Studies on solutions with variable ionic strengths cannot yield accurate thermodynamic characteristics of outer-sphere complexes, since there is no way of finding the activity coefficients of individual ions (particularly complex ions) in solutions with high concentrations of ligand ions, where the majority of outer-sphere complexes are formed.

The thermodynamic functions of outer-sphere complexes referred to solutions with various constant ionic strengths as standards can be adjusted to zero ionic strength [93-97] but various complications frequently arise in such recalculations [98,99]. For example [30], in aqueous solutions with perchlorate ion concentrations of about 0.1 M, hexamminecobalt(III) ions form association complexes with perchlorate ions in which the latter are probably separated from the complex ion by water molecules. The location of perchlorate ions in the third coordination shell of the association complex, the composition of which is represented by formula (1), is confirmed by the absence of an appreciable effect of perchlorate ions on the electronic spectra of hexamminecobalt(III) and the circular dichroism spectra of (+)-trisethylenediaminecobalt(III). [32] The formation of cobalt(III) outer-sphere complexes in aqueous lithium or sodium perchlorate solutions is accompanied by the partial dissociation from the conventionally free central group of one or several perchlorate ions [30,100], which requires the introduction into the unitary-cratic values of the thermodynamic functions of outer sphere complexes of a correction for the packing effect. Recently the present author developed [30] an approximate method for applying such a correction. It is interesting to note that an increase of temperature from 25° to 45°C reduced sharply the cratic terms of the thermodynamic functions for formation of hexamminecobalt(III) halide complexes.

The need to apply a correction for the packing effect follows from numerous data [41,101-104]. For example, it has been shown [102] that the chloropentamminecobalt(III) ion forms with perchlorate ions, usually regarded as inert, more stable association complexes than with nitrate, chloride, azide, and acetate ions. Electrophoretic studies have shown [103,104] that cobalt complexes with three molecules of ethylenediamine, 2,2′-dipyridyl, and 1,10-phenanthroline also interact with perchlorate ions more strongly than with many other singly-charged ions.

A particularly striking example of the necessity to take into account the packing term follows from the work of Larsson [41], who investigated the association of *trans*-dithiocyanatobisethylenediaminecobalt(III) with thiocyanate ions in 3 M aqueous solutions of a mixture of sodium perchlorate and thiocyanate at 20°C by an ion-exchange method. The calculations without a correction for the packing term led to the detection of only the complex with a single ligand having a stability constant of 0.30. This constant could not account for various properties of the system investigated. The use of an extraction method enabled Larsson to investigate the perchlorate association complexes of *trans*-dithiocyanatobisethylenediaminecobalt(III) and to introduce a correction for the packing term. After applying the correction, it was found that three thiocyanate complexes are formed in the system, with overall stability constants of 1.42, 0.88, and 0.30.

6. METHODS FOR THE INVESTIGATION AND CERTAIN GENERAL FEATURES OF COBALT(III) OUTER-SPHERE COMPLEXES

It can now be regarded as proved that all coordination-saturated complex cobalt(III) cations are capable of stepwise coordination in the outer sphere of various anions [30,32] and also molecules [93,105-108] with electron-donating properties. The outer-sphere coordination of ligands by inner-sphere cobalt(III) complexes involves an increase of the intensity of the charge-transfer bands in electronic spectra [109,110] and is equally reflected in the results of thermodynamic studies of outer-sphere complexes [30].

The study of the addition of a seventh ammonia molecule [107,108], of outer-sphere ethylenediamine molecules [93,105], and a number of other ligands [30,44,47] made a considerable contribution to the proof of the occurrence of outer-sphere coordination by cobalt(III) complexes. These investigations showed that the stepwise outer-sphere interaction constants are independent of the methods of determination and the ratios of their logarithms yield reasonable values for the statistical and ligand effects [29] when the correct limiting coordination numbers for the second shell are employed [6].

Interesting data on the stepwise formation of cobalt(III) outer-sphere complexes were obtained in studies on circular dichroism spectra [30-32,35,36,45,46,111-113], since this method is free from the many disadvantages characteristic of customary electronic spectroscopy and measurements of optical rotatory dispersion [11]. The high sensitivity of circular dichroism spectra and different signs of the dichroic molar absorption coefficients in successive stages of outer-sphere coordination made it possible to investigate accurately the stepwise outer-sphere interaction.

The circular dichroism spectra of the selenite complexes of (+)-trisethylenediaminecobalt(III) were investigated with particular care. The results obtained by Larsson[31] agreed well with the present author's data[45] but the stability constants calculated in these investigations[31,45] were inexplicably high[30,114]. This finding can be accounted for by the presence of several conformations of (+)-trisethylenediaminecobalt(III).[114] Moreover, it is now clear[30] that data on dichroic absorption cannot always be used for the simultaneous determination of the stability constants and molar dichroic absorption coefficients, because the latter may be zero, which greatly distorts the stability constants. Despite these limitations, the study of circular dichroism spectra in combination with data from thermodynamic methods gives a clear idea about the stereochemistry and bonds in the outer-sphere complexes of cobalt(III) and a number of other metals[111,115].

The stability of a large series of cobalt(III) outer-sphere acido-complexes in dilute aqueous and non-aqueous solutions with variable ionic strengths was investigated conductimetrically[10,116-119]. The stability constants calculated from the data obtained by this method are usually referred to solutions at zero ionic strengths as standards. Conductimetric measurements were used to determine the thermodynamic functions of outer-sphere complexes with one ligand only.

Electronic spectroscopy has been most frequently used to investigate cobalt(III) outer-sphere complexes[120-131], the data thus obtained permitting the calculation of the stability constants (the first and more rarely the second stability constants) and to solve approximately the problem of the nature of the outer-sphere coordination bonds.

A number of studies on the thermodynamics of cobalt(III) outer-sphere complexes were made by the solubility method[30,97-100,132-136]. Measurements were made of the solubility of sparingly soluble iodates[133-135], perchlorates[97-100], hexacyanoferrates(III),[136] and other hexa- or pent-amminecobalt(III) salts in solutions with different concentrations of outer-sphere ligands. In a number of other studies[133] the solubility of sparingly soluble salts containing outer-sphere ligands was investigated as a function of the concentration of inner-sphere cobalt(III) complexes.

Studies on the kinetics of complex formation[61,62,102,137-142] and various versions of the potentiometric method[30,135,143,144] made a considerable contribution to the thermodynamics of cobalt(III). Outer-sphere complexes with the anions of weak acids were investigated[120,135,144] by pH titration. The study of the redox potentials of the cobalt(III)–cobalt(II) system proved very useful and promising in the investigation of cobalt(III) outer-sphere complexes[30,143]. The use of electrodes reversible with respect to the outer-sphere anionic ligands is less suitable because the stability of the majority of outer-sphere complexes is comparatively low and therefore the equilibrium and overall concentrations of the ligands are almost equal.

In studies on the outer-sphere complexes of various metals the e.m.f.'s of cells with ion transport were usually measured. The conventional diffusion potentials of such cells were determined experimentally in accurate investigations[28,30,145] but normally they were calculated from the Henderson equation. The latter method of finding the diffusion potentials is unreliable[28,30] in studies on unstable complexes. Cells without transport have not so far been used to investigate outer-sphere complexes although this approach may prove to be very useful[146].

Isolated studies have been made on cobalt(III) outer-sphere complexes by extraction[34,41], ion-exchange[40,41], and electrophoretic[103,104] methods.

Interesting data on chromium(III)[147,148] and iron(III)[149] outer-sphere complexes were obtained by nuclear magnetic resonance. Recently this method was applied also in the study of cobalt(II) outer-sphere complexes[44,150].

Several systems with stepwise cobalt(III) outer-sphere complex formation were investigated polarimetrically[33,35,42,136]. Trisdiaminecobalt(III) compounds were studied. The investigations led to the determination of the composition and the calculation of the stepwise outer-sphere coordination constants and also the demonstration that there is no difference in the tendency towards the formation of outer-sphere complexes by the racemate and the dextro- and leavo-rotatory isomers[30]. However, the stability constants found from the polarimetric measurements are frequently inaccurate[114] and optically active outer-sphere ligands interact in different ways with dextro- and leavo-rotatory isomers[151].

Infrared spectroscopic studies led to a number of conclusions concerning the nature of the chemical bond in cobalt(III) outer-sphere complexes and to the solution of the problem of the stability of these complexes[152-154]. However, it should be noted that the applicability of the infrared spectroscopic method in the study of outer-sphere complexes is limited and the method is altogether inapplicable to dilute solutions. This is also true of Raman spectra.

The polarographic[155-163] and amperometric[164] methods proved to be useful in the study of cobalt(III) outer-sphere complexes. The shift of the half-wave potential or the changes in diffusion current[159] following the addition of the outer-sphere ligands to cobalt(III) complexes were measured by these methods.

The possibility of using the chronopotentiometric transition to study cobalt(III) outer-sphere complexes has been justified theoretically[165] and confirmed experimentally.

This isopiestic[87-91] and thermochemical[30,93,105,166,167] methods have been shown to be promising.

So far there are no literature data on the thermodynamic functions of cobalt(III) outer-sphere complexes with an outer-sphere coordination number greater than unity referred to solutions at zero ionic strength as standards. Possibly modern methods for the conversion of the thermodynamic functions from one standard state to another will help fill this gap[168-170].

7. HEXAMMINE COBALT(III) COMPLEXES

Numerous data have been published[10,41,71,95-100,103,104,106,116,123,171-177] on the stability of single-ligand outer-sphere complexes where the central group is the hexamminecobalt(III) ion, but the enthalpies and entropies of formation of these compounds have not been determined with adequate reliability; on the other hand the formation of polyligand complexes has been studied only in isolated cases[34,41,100,104].

An advance in the study of hexamminecobalt(III) complexes has been the demonstration of the formation of an outer-sphere chelate ring. This has been shown[175] by investigating the ultraviolet and circular dichroism spectra of a solution of hexamminecobalt(III) perchlorate in the presence of an excess of diethyl-(+)-tartrate ions. The appearance of a new absorption band in the spectrum of this system at about 3000 Å was attributed to charge transfer from the outer-sphere ligand to the complex ion and to a d–d electronic transition.

The contradictory nature of the literature data on the stability of single ligand (particularly chloride and bromide) complexes of hexamminecobalt(III) has been the subject of several controversies [4,5,40,100,126]. The reason for these controversies were examined in earlier publications [4,40,98].

Certain thermodynamic functions for a number of hexamminecobalt(III) complexes with various anions have been determined with sufficient reliability to allow their comparison. These data show that the stability of single-ligand association complexes of this cation increases in the following series of anions: lactate [134] < thiocyanate [134] < hydroxide [137] < iodide [97] < azide [97] < bromide [97] < chloride [97] < < tartrate [134] < malonate [134] < sulphate [95] < sulphite [124] < < thiosulphate [174] < fluoride [30] < oxalate [10] < triphosphate [119] < tetraphosphate [119]. The logarithm of the stability constant increases in this series from 0.68 to 4.44 at 25°C and zero ionic strength of the aqueous solution. This series suggests that an increase of the charge and a decrease of the dimensions of the outer-sphere ligands almost always entail an increase of the stability of the outer-sphere complex. There are only a few deviations from this rule—for example, the position in the series of the hydroxide ion. The charge and dimensions of this ion suggest a higher stability of the hydroxo-complex than is indicated by the literature data [137]. The reason for this discrepancy may be the specific features of the hydration or the association of the OH^- ion or it may be due to experimental error. The results of quantitative studies on the stability of sulphate, sulphite, and thiosulphate complexes of hexamminecobalt(III) are extremely contradictory [10].

Deviations from the expected position in the stability series of single-ligand hexamminecobalt(III) association complexes may be caused by hydrogen bonds between the outer-sphere ligands and the inner-sphere ammonia molecules, the effect of which is superimposed on that of the charge and ligand radius. However, the study of infrared spectra and in particular the vibration frequencies of the N–H bond indicates [177] the absence of an appreciable contribution of hydrogen bonding even in the formation of the fluoride complexes of hexamminecobalt(III). This finding may be related to the non-linearity of the Co–N–H group. A strong hydrogen bond formed in the presence of a linear N–M–A structure, where A is an outer-sphere ligand leads [178,179] to the maximum distance between A and cobalt and is clearly reflected in the N–H frequency, but the latter may not in fact change when a non-linear N–H–A group is formed. Consequently the conclusion [177] that there is no hydrogen bond in hexamminecobalt(III) complexes requires further confirmation, particularly since in outer-sphere trisethylenediamine-, diamminebisethylenediamine-, and dichlorobisethylenediaminecobalt(III) complexes a hydrogen bond has been detected [44] by proton magnetic resonance.

A steady decrease of the enthalpy and entropy is observed in the interaction of the following series of outer-sphere ligands with the hexamminecobalt(III) cation: chloride > bromide > iodide > azide.

The formation of chloride [97] and probably fluoride [30] complexes of hexamminecobalt(III) complexes involve an increase of entropy. The enthalpy change prevents the formation of monohalide complexes of this cation in solutions at low ionic strengths. The magnitude of the hindering enthalpy effect diminishes with increase in the size of the halide ion, but the entropy contribution diminishes still further. This results in a decrease of the stability of the outer-sphere complexes in the ligand series fluoride > chloride > bromide > iodide and the logarithms of the stability constants vary in inverse proportion to the crystallographic radii of the halide ions [180]. In contrast to the monohalide complexes, the monoazide complex of hexamminecobalt(III) is formed by virtue of the decrease of the enthalpy with an insignificant effect of the entropy factor [97]. The sulphate and thiosulphate complexes are formed because of the increase of entropy in the presence of only a slightly unfavourable enthalpy effect [95,174].

Far-reaching conclusions concerning the enthalpies and entropies of formation of hexamminecobalt(III) complexes are impossible at present, since these quantities are not accurate, having been determined from the association constants found at only two or three temperatures. Direct thermochemical studies [30,100] confirm this.

The errors in the determination of the stability constants of the outer-sphere complexes of hexamminecobalt(III) and related ions may be estimated on the basis of nine investigations [95,119,125,134,157,159,165,181,182] carried out during the period between 1930 and 1967. The constant for the association of $Co(NH_3)_6^{3+}$ with sulphate ions in aqueous solutions at zero ionic strengths and 25°C was calculated in these investigations. The average value of the logarithm of the constant is 3.30 and the error in its determination amounts to approximately 6%. However, a decrease in the association constant usually entails an increase in the error of its determination.

The formation of polyligand complexes of hexamminecobalt(III) has been demonstrated by Brintzinger [38,39,68] and has been confirmed in recent years for sulphate [40], halide [40,100], thiocyanate [110], thiosulphate [40], carbonate [110], salicylate [40], ammine [108], and aquo-compounds [173]. The majority of the data on the polyligand complexes have been obtained by ion-exchange [40], extraction [34], solubility [100,108], and spectrophotometric [110] methods and by studying the adiabatic compressibility of solutions with the aid of an ultrasonic interferometer [173]. Almost all these data are qualitative or semi-quantitative. Rigorously quantitative studies have not so far been made on the polyligand complexes. However, one may note that hexamminecobalt(III) forms complex anions with an outer-sphere coordination number of 3. [38,39] Judging from anion-exchange data, the stability of these complexes decreases [40] in the following series of outer-sphere ligands: iodide > bromide > > chloride > fluoride thiosulphate > sulphate. This series is the reverse of the series corresponding to the variation of the stability of the single-ligand association complexes [10]. The reversal of the stability series of the cobalt(III) association complexes for high degrees of coordination is a consequence of the large contribution of the entropy term to the addition of the first outer-sphere ligand [95]. It is reasonable to suppose that the enthalpy term varies little with the number of the successive outer-sphere ligands, while the entropy term may decrease. Hence the reversal of the stability series for higher cobalt(III) outer-sphere complexes may be understood.

The inverse stability series of the outer-sphere complexes is also the opposite of that expected from a purely electrostatic interaction. The extent of the formation of higher outer-sphere complexes increases with the polarisibility of the ligands, which has been attributed [35] to charge transfer from the complex ion to the outer-sphere ligand. This is in good agreement with electronic spectroscopic data [110].

Experimental determination of the limiting coordination number of outer-sphere complexes is difficult because of their low stability, although extraction with non-aqueous solvents helps solve this problem. Thus in the study of

extraction by cyclohexanone it was shown [41] that hexamminecobalt(III) probably coordinates eight salicylate ions. This finding is consistent with theoretical postulates concerning outer-sphere coordination [6].

It has been established [183] that the fourth chloride ion adds to hexamminecobalt(III) in 7 M aqueous hydrogen chloride solutions because under these conditions the solubility curve for hexamminecobalt(III) chloride passes through a minimum. Hence the constant for the addition of the fourth chloride ion is about 0.1.

It is interesting to note that the hexamminecobalt(III) ion combines in aqueous solutions with as many water molecules as CoL_3^{3+} ions, where L is ethylenediamine, propylenediamine, trimethylenediamine, and diethylenetriamine. Consequently all the above complexes have an outer sphere of the same composition.

The determination of the change in the volume of the solution on association of hexamminecobalt(III) with the first sulphate ion [184] showed that the volume change is almost the same as in the conversion of aquopentamminecobalt(III) into sulphatopentamminecobalt(III). Hence it follows that it is not always possible to distinguish inner- and outer-sphere complexes by dilatometric measurements.

Several studies have been devoted to the effect of pressure on the formation of chloride and sulphate complexes of hexamminecobalt(III). [117,118] The investigations were carried out conductimetrically. It has been found for the chloride complexes that the formation constant of the complex with one ligand passes through a minimum at a pressure of about 400 kg cm^{-2} and 25°C. Calculations by the van't Hoff equation showed that at pressures of 300 and 500 kg cm^{-2} the volume changes are 17 and 13 cm^3 $mole^{-1}$. These values consist of the volume change of the ions themselves and of the solvating solvent. The first type of change predominates at low pressures and the second at high pressures, where the dielectric constant of water increases with pressure.

The association of hexamminecobalt(III) has been investigated [118] in sulphate solutions at 25–40°C and pressures in the range 1–600 atm. It was found that the association is accompanied by a small positive enthalpy change at pressures below 200 atm and an enthalpy effect of the opposite sign at pressures in excess of 400 atm. The interaction is accompanied by an increase in the volume and entropy of the system, an increase of pressure and temperature reducing appreciably the contribution of the entropy component to the free energy. This has been attributed [118] to the decrease in the dielectric constant of water.

The study of the infrared spectra of freshly prepared aqueous solutions of hexamminecobalt(III) salts in the presence of an excess of sodium sulphate showed [12] the occurrence of slight outer-sphere interaction: the sulphate ion is probably coordinated as a monodentate ligand.

Interesting data on outer-sphere interactions were obtained [172] by comparing the results of conductimetric and ultraviolet spectroscopic measurements. It was found that the formation constants of single-ligand hexamminecobalt(III) complexes with chloride, bromide, iodide, and sulphate ions calculated from conductimetric data are much higher than the values obtained by ultraviolet spectroscopy. The constants were calculated on the assumption that association complexes with one ligand species only are formed. The neglect of the formation of complexes with two ligands or association complexes involving the third solvation shell of the species represented by formula (1) accounts for the observed difference. The involvement of the third shell is indicated by the virtual equality of the constants for the addition of hexammine cobalt(III) of perchlorate, chloride, and iodide ions [172], although perchlorate ions do not affect the ultraviolet spectra.

Solubility measurements led to the conclusion [108] that the hexamminecobalt(III) ion forms complexes with acetone in aqueous solutions. These compounds are probably similar to the ketone complexes of actinides [185]. It is not known whether such complexes can be regarded as products of outer-sphere coordination, because it is difficult to distinguish typical outer-sphere complex formation and solvation leading to the formation of the second solvation shell. Additional studies on the interaction between cobalt(III) complexes and various molecules are necessary.

8. TRISETHYLENEDIAMINECOBALT(III) COMPLEXES

The results of studies on the outer-sphere interaction of the trisethylenediaminecobalt(III) ion with various anions by potentiometric [30], calorimetric [30], and spectroscopic [31–36,40–46] methods constitute the main bulk of the experimental data on trisdiaminecobalt(III) outer-sphere complexes.

The circular dichroism spectra of (+)-trisethylenediaminecobalt(III) hardly change in the presence of perchlorate, chlorate, nitrite, nitrate, borate, and tetraborate ions [32,43,113]. This fact indicates the absence of measureable amounts of outer-sphere complexes. The ions enumerated above interact with trisethylenediaminecobalt(III), occupying the third coordination sphere.

Halide, pseudohalide, sulphate, sulphite, thiosulphate, selenite, tellurite, phosphate, phosphite, hypophosphite, arsenate, arsenite, hexafluoroarsenate, hexacyanoferrate(II), carbonate, oxalate, malonate, succinate, maleate, fumarate, tartrate, lactate, formate, acetate, propionate, diethyldithiocarbamate, and benzenehexacarboxylate ions have a significant influence on the circular dichroism spectrum of an aqueous solution of (+)-trisethylenediaminecobalt(III) perchlorate. Their effect is reflected [32,45] in a change in the rotatory powers R determined from the area of the corresponding circular dichroism bands—E_a at 4900 Å and A_2 at 4300 Å. All the ions which influence the circular dichroism spectrum form typical outer-sphere complexes.

The rotatory power of the low-frequency component E_a decreases and that of the high-frequency component A_2 increases at low concentrations of the anion. At high concentrations the opposite changes are observed, which suggests [31,32,35–37,45,46] that outer-sphere complexes of different compositions with different circular dichroisms spectra are formed when the concentration of the outer-sphere ligands is varied. The validity of this hypothesis is confirmed by careful potentiometric and thermochemical studies [30]. The e.m.f. of cobalt(III)–cobalt(II) electrodes was measured in the potentiometric experiments. The diffusion potentials of the cells were determined experimentally [28,30]. Some experiments were performed by the familiar method [4,5,186–188] for the determination of the changes in activity coefficients due to the replacement of the inert ClO_4^- ions by anionic ligands in solutions with high and constant ionic strengths maintained with lithium or sodium perchlorate. The corrections for the observed changes in activity coefficients were applied to the experimental data. The heats of formation were calculated from the thermochemical measurements and the stability constants found potentiometrically and from the solubility of

trisethylenediaminecobalt(III) perchlorate. Part of the results of these investigations are compiled in Table 1, which shows that sulphate, carbonate, thiosulphate, sulphite, selenite, and tellurite ions form a series of outer-sphere complexes in which the trisethylenediaminecobalt(III) cation behaves as the central ion. The formation constants for the outer sphere complexes found by solubility, potentiometric, and calorimetric methods agree with one another for all degrees of outer-sphere coordination. The errors in the determination of the constants listed in Table 1 increase with increasing n, as for inner-sphere complexes.

Table 1. Stepwise thermodynamic functions of formation of outer-sphere complexes of the type $[Coen_3]A_n^{3-2n}$ in 3 N solutions of $Na(ClO_4$, A) at 25°C.

Ionic ligand	n	κ_n	ΔH_n, kcal g-ion^{-1}	ΔS_n, e.u.
Sulphate	1	3.6	1.7	8.5
	2	1.4	0.80	3.5
	3	0.40	0.40	−0.5
Carbonate	1	2.9	1.2	6.0
	2	1.4	0.30	2.0
	3	0.40	0	−2.0
Thiosulphate	1	5.3	0.80	6.0
	2	1.7	0.40	2.5
	3	1.0	0.20	1.0
	4	0.50	0	−1.5
Sulphite	1	4.1	1.9	9.0
	2	1.5	1.0	4.0
	3	0.85	0.50	2.0
	4	0.40	0	−2.0
Selenite	1	3.6	1.4	7.0
	2	1.4	0.40	2.0
	3	0.70	−0.20	0
	4	0.30	0	−2.0
Tellurite	1	2.0	1.1	5.0
	2	1.1	0.50	1.0
	3	0.50	0	−2.0

The systems which were investigated up to high concentrations of the anionic ligands may be characterised, to within the experimental error, by four outer-sphere complexes. This agrees well with the data examined earlier in this review and also indicates a characteristic coordination number of four. The stepwise stability constants, and the enthalpy and entropy changes at all stages of outer-sphere coordination for all the complexes investigated decrease steadily with increasing coordination number or, more precisely, with increasing number of the successive ligands added to the complex (Table 1).

The substitution of outer-sphere ligands in the series sulphate, sulphite, and thiosulphate and tellurite, selenite, and sulphite increases the stability of the outer-sphere complexes at all coordination stages (Table 1). The enthalpies and entropies of formation in the first of the above two series change less regularly than the stability constants but in the second series the components of the free energy vary almost as regularly as the stability constants. The existence of these series indicates an important role of electrostatic interactions in the formation of outer-sphere complexes.

Sulphate ions exhibit a lower capacity for outer-sphere association than sulphite ions. This fact is associated with the presence of lone-pair electrons in sulphite ions [32]. Similar relative stabilities have been observed for selenate and selenite complexes of trisethylenediaminecobalt(III). [32]

The majority of outer-sphere complexes are formed by virtue of the increase of entropy, while the enthalpy change hinders their formation (Table 1). An increase of the number of the successive ligand combined reduces the entropy component. The addition of a third doubly charged ligand to trisethylenediaminecobalt(III) involves a negative or a small positive entropy change. The fourth ligand always adds a negative entropy change. This finding can be explained by the absence from the third coordination sphere of the association complex, the composition of which is represented by formula (1), of perchlorate anions when the outer sphere contains two anionic ligands of the type listed in Table 1.

For the outer-sphere complex series with the (+)-trisethylenediaminecobalt(III) central ion as an example, it has been established [30,35,45] that the circular dichroism spectra are characterised by changes in rotatory powers of alternating sign at even and odd stages of outer sphere coordination. Relative to the rotatory powers of the free complex ion, $R[A_2]$ increased and $R[E_a]$ decreased on formation of outer-sphere complexes with odd n. On the other hand, these changes were of the opposite sign at even stages of outer-sphere coordination. Thus for $n = 2$, $R[A_2]$ and $R[E_a]$ did not differ from the analogous characteristic for the free (+)-trisethylenediaminecobalt(III) ion. The facts considered show that symmetry elements are lost at odd stages of outer-sphere coordination and are fully (for $n = 2$) or partially (for $n = 4$) recovered in outer-sphere complexes with an even value of n. This finding constitutes unambiguous evidence that outer-sphere complexes are formed as a result of forces directed to fixed positions in space.

Electronic transitions of the d–d type in octahedral cobalt(III) complexes are forbidden by the selection rule. Deviations from this rule are shown [31] by (+)-trisdiaminecobalt(III) complexes as a result of the loss of a centre of symmetry. The deviations increase on formation of an asymmetric outer coordination sphere.

Electrostatic forces favour a centrosymmetric linear environment of the inner-sphere complexes on formation of outer-sphere complexes with two ligands. A tetrahedral configuration of outer-sphere complexes with four ligands is more favourable from the electrostatic standpoint than a planar square outer-sphere ligand environment of the inner sphere. An increase of the polaribility of the ions may also influence the structure of the outer sphere. Further studies are necessary to solve the problem of the geometrical configuration of the outer sphere.

The much smaller frequency shifts in the circular dichroism spectra of trisdiaminecobalt(III) as a result of the formation of outer-sphere complexes than the shifts caused by inner-sphere interaction suggest that outer-sphere coordination has only a slight direct effect on the d orbitals of cobalt(III). This effect is not shown at all in the visible part of the usual spectra [189].

The appearance of bands in the circular dichroism spectra as a result of an interionic electronic transition from an outer sphere ligand to the complex ion confirmed that the ions forming the outer-sphere complex exhibit mutual orientation. The closest and most probable approach of the outer sphere ligands to their coordination centre is determined by many factors, including steric factors [32,43]. The problem of the configuration of the monophosphate complex of trisethylenediaminecobalt(III) was examined from these standpoints. Interesting conclusions were arrived at also from a study of the interaction between this central ion in outer-sphere complexes with polyanions [112]. The latter have a very strong effect

on the circular dichroism spectra of trisethylenediaminecobalt(III).

Numerous data have been published [96,116,120,161,190,191] on the stability of single-ligand complexes of trisethylenediamine- and, more rarely, trispropylenediaminecobalt(III). The majority of them refer to highly dilute aqueous solutions. Under such conditions, an increase in the size of the trisdiaminecobalt(III) and outer sphere ions and a decrease of the charge of the latter reduces the stability of the outer-sphere complexes. The variation of the stability is largely consistent with the series quoted in Section 7 of this review for hexamminecobalt(III) association complexes [30,192].

It has been shown [191] that the addition of dioxan to water sharply increases the stability of trisdiaminecobalt complexes with OH^- ions, while the addition of heavy water does not have a significant effect.

Proton magnetic resonance data [44] unambiguously indicate the formation of a second coordination sphere around trisethylenediaminecobalt(III) in various solvents. Outer-sphere coordination sharply increases the activation energy for conformational transformations in the inner sphere.

The problem of the stability of CoL_3^{3+} complexes, where L = 2,2′-dipyridyl and 1,10-phenanthroline, with various ligands can be solved only qualitatively on the basis of data at present available. The study of these outer-sphere complexes by electrophoretic [103,104] and potentiometric [193] methods suggests that the replacement of 2,2′-dipyridyl by 1,10-phenanthroline reduces the stability of the cobalt(III) outer-sphere complexes.

Thermochemical study of trisethylenediaminecobalt(III) association complexes with halide ions shows that for the series of the outer-sphere ligands fluoride, chloride, bromide, and iodide the formation of outer-sphere complexes entails a sharp decrease of the entropy contribution and a decrease of the enthalpy term hindering complex formation. Since the enthalpy changes less and the formation of the outer-sphere complexes involves an increase of entropy, the stability of the association complexes with one ligand species diminishes in the above series [30].

9. ACIDO- AND AQUO-PENTAMMINECOBALT(III) COMPLEXES

The interaction of acido- and aquo-pentamminecobalt(III) complexes with various anions has been investigated by solubility [102,194], spectrophotometric [95,123,127,195], pH titration [135,195], kinetic [102], and isopiestic methods [87–91]. The formation of chloropentamminecobalt(III) complexes has been investigated most thoroughly. The association constants were determined from the solubility of the iodate of this complex, by pH titration, and by kinetic methods [102,135], the result agreeing to within 5–30%. The stability of the single-ligand complexes of chloropentamminecobalt(III) increases for the following series of outer-sphere anions: acetate < chloride < nitrate < azide < perchlorate < < glycolate < succinate < malate < tartrate < malonate < < sulphate < maleate < phthalate. This series is not consistent with the electrostatic characteristics of the outer-sphere ligands, but the available data show [102,135] that the stability of outer-sphere complexes with doubly-charged anions is higher than that of the complexes with singly-charged anions. The constants for the addition of sulphate and succinate ions to chloropentamminecobalt(III) agree with the analogous characteristics of the divalent nickel, zinc, cobalt, manganese, cadmium, and copper complexes [196]. All the above metals probably form with these ligand complexes which are largely of the outer-sphere type. This has been confirmed by other investigations [17,18].

The data in Table 2 shows that the stability of the monosulphate complexes of the acidopentamminecobalt(III) ion falls with decrease of the charge, but the stability of the outer-sphere complex remains high when $L = F^-$, the fluoride ion being small. The nature of ligands with the same charge also has an appreciable influence on the stability of the outer-sphere complexes. This problem should be the subject of a detailed investigation.

Table 2. Logarithms of the stability constants of outer-sphere complexes of the type $[Co(NH_3)_5L]SO_4^{Z-2}$ at 25°C in 0.1 M $NaClO_4$ solutions according to polarographic data [157].

L	lg ω_1	L	lg ω_1	L	lg ω_1	L	lg ω_1
NH_3	2.1	NO_2^-	1.7	N_3^-	1.2	F^-	1.85
H_2O	1.9	CH_3COO^-	1.65	SO_4^{2-}	1.0	—	—

Measurements have shown [87–91] that the activity coefficients of acidopentamminecobalt(III) nitrates, halides, and perchlorates are almost equal in solutions at concentrations less than 0.1 M but at higher concentrations decrease for the following series of outer-sphere ligands: chloride > bromide > iodide > nitrate and change little when the inner-sphere anions are substituted. It has been suggested [88] that, judging from the activity coefficients, the stability of the outer-sphere complexes cannot be accounted for by Coloumbic interaction.

The stability constants of single-ligand complexes of acidopentamminecobalt(III) complexes were calculated from the activity coefficients of their various salts [88,90]. The constants remained invariant when the salt concentrations were altered by a factor of 10–20. The stabilities of the outer-sphere complexes were compared on the basis of the constants referred to solutions at an ionic strength of 0.1 as standards. This comparison showed that the stability of the nitrate, iodide, and bromide complexes of acidopentamminecobalt III) increases with the size of the complex ion, while the stability of the chloride complexes varies in the opposite sense. The replacement of the *trans*-isomer of bisethylenediaminenitroamminecobalt(III) by the *cis*-isomer resulted in an increase of the stability of the halide outer-sphere complexes. This is because the *cis*-isomer has a higher dipole moment than the symmetrical *trans*-isomer. Nitrate ions, which show little tendency towards polarisation, interact to an equal degree with the *cis*- and *trans*-isomers.

The substitution in acidopentamminecobalt(III) of four ammonia molecules by two ethylenediamine molecules reduced appreciably the stability of the outer-sphere complexes. This is probably due to the contribution of dispersion forces to outer-sphere interaction [92].

A spectrophotometric method has been used to investigate the aquation of pentamminecobalt(III) containing the sulphate ion in the inner sphere and the formation of the

monosulphate complex of aquopentamminecobalt(III).[95, 122,123] It was established that the aquation equilibrium involving the formation of an outer-sphere complex is displaced towards the latter. This is favoured by the enthalpy change with a small antagonistic entropy effect. Similar equilibrium with phosphate ions is strongly displaced towards the inner-sphere complex[197].

Equations have been derived for the effect of ionic strength on the stability of monosulphate complexes of aquopentammine- and hexammine-cobalt(III) complexes[95]. The form of these equations shows that the cratic contribution to the stability constants is probably represented by the coefficient of the square root of the ionic strength of the test solution in the denominator.

The chromate complex of aquopentamminecobalt(III) was studied spectrophotometrically and by pH titration[198]. Both enthalpy and entropy changes favour the formation of this outer-sphere complex, which results in a high formation constant (3.07×10^5).

10. DIACIDOTETRAMMINECOBALT(III) COMPLEXES

Diacidotetramminecobalt(III) complexes have been the subject of a large number of studies[41,93,105,128,129,131,150,198–211]. The halide, thiocyanate, and sulphate association complexes of dichloro-, bromochloro-, and dithiocyanatobisethylenediaminecobalt were mainly investigated. A considerable proportion of these studies on outer-sphere complexes were performed in non-aqueous solvents. Stepwise outer-sphere coordination by diacidotetramminecobalt(III) ions has been demonstrated in only a few studies[41,140], but recently its occurrence has been unambiguously proved[47].

Combination of anion-exchange and extraction data led to the suggestion that three thiocyanate complexes are formed by the dithiocyanatobisethylenediaminecobalt(III) cation in 3.0 M aqueous solutions of a mixture of sodium perchlorate and thiocyanate. The results of a study of the kinetics of the substitution of the inner-sphere ions in diacidobisethylenediaminecobalt(III) complexes, could be explained only by stepwise outer-sphere coordination[47].

A spectrophotometric study[198,199] of the interaction of *cis*- and *trans*-dichlorobisethylenediaminecobalt(III) complexes with chloride and acetate ions in methanol solutions led the authors to the conclusion[71] that only the *cis*-isomer forms outer-sphere association complexes. Recent work[203] demonstrated that this is erroneous. It proved possible to show that the *trans*-isomer also forms outer-sphere complexes, but less stable than the *cis*-compound which has a high dipole moment. The low association constant for the *trans*-isomer calculated from the experimental data is also due to the neglect of the association of the chloride ion and the cation with which the ligand was introduced into the solution[207].

Thermochemical[93,105] and spectrophotometric[128,137,202] methods have been used to investigate the association of *cis*- and *trans*-dichloro-, bromochloro-, and chlorodimethylformamidecobalt(III) complexes with halide ions in *NN*-dimethylformamide (DMF), dimethyl sulphoxide (DMSO) and *NN*-dimethylacetamide (DMA). Earlier, such association was investigated by a semiquantitative kinetic method[138,140]. It was found that an increase of the size of the halide ions usually reduces the formation constant of the outer-sphere complex, but the constant is not a linear function of the crystallographic radius of the halide ion. Thus the constants for the addition of bromide and iodide ions to *cis*-dichlorobisethylenediaminecobalt(III) are almost equal. This indicates a considerable contribution to the formation of the outer-sphere complex by charge transfer from the ligand to the central group[199].

The enthalpy change in outer-sphere association is due to the formation of the outer-sphere complex and the desolvation of the interacting species. The small enthalpy of formation of chlorodimethylformamidebisethylenediaminecobalt(III) chloride shows[202] that the desolvation energy is a little higher than the association energy.

Bromide ions are solvated by dimethylformamide to a greater extent than chloride ions[212] and therefore the formation of outer-sphere complexes with bromide ions entails a greater increase of entropy than the formation of the chloride complexes[202].

The addition of the second chloride ion to *cis*-dichlorobisethylene diaminecobalt(III) takes place owing to the decrease of enthalpy and is accompanied by a decrease of entropy[202], in contrast to the addition of the first chloride ion.

An increase of the charge, a decrease of the dimensions, and conversion of the *trans*- into the *cis*-isomers of the complexes under consideration almost always increases the stability of the outer-sphere complex. A change of solvent reduces the stability of the majority of the outer-sphere complexes in the following series: DMF > DMA > DMSO. This lowering is correlated with the dielectric constants of the solvents[213,214].

The distances of average approach of the ions in outer-sphere complexes were calculated[93,199] from the stability constants in DMA, DMF, and DMSO, and were found to be smaller than the dimensions of the free complex ion. This has been explained[93,105] by postulating that the outer-sphere complexes are not formed solely by electrostatic forces. The absence of a contribution by the Coloumbic interaction to the formation of outer-sphere complexes of diacidotetramminecobalt(III) with two ligands is confirmed also by the stepwise thermodynamic functions[202] of formation of the complexes[215]. The presence of hydrogen bonds between the Werner complex and the outer-sphere ions or molecules has been confirmed by studies on proton magnetic resonance in systems containing dichlorobisethylenediaminecobalt(III) ions[44,150].

Outer-sphere complexes with a cation of the diacidotetrammine type have been assigned (on the basis of kinetic studies) a tetragonal-pyramidal structure[204], but this hypothesis requires confirmation.

11. OUTER-SPHERE INTERACTION OF COBALT(III) ACIDO-COMPLEXES

Cobalt(III) acido-complexes usually behave as ligands like any simple or complex anions. The species produced by the outer-sphere association of acido-complexes of cobalt(III) with cations showing a tendency towards the formation of covalent bonds are frequently converted into heteromononuclear complexes[164,216] or are intermediate between the latter and ion pairs. Only the interactions of the hexacyanocobalt(III) ion with alkali metals[217], lanthanides[219], cadmium[218], and hexammine- and trisethylenediaminecobalt(III)[218] cations have so far been investigated in detail in aqueous[217], mixed[219], and non-aqueous solvents.

A detailed examination of outer-sphere association complexes of cobalt(III) acido-complexes does not come within the scope of the present review, since the formation of such compounds does not characterise the capacity of cobalt(III) to form an outer coordination sphere.

12. SOME HYPOTHESES CONCERNING THE BOND IN COBALT(III) OUTER-SPHERE COMPLEXES

The numerous literature data examined in this review show that the formation of cobalt(III) outer-sphere complexes, like that of the outer-sphere complexes of other transition metals, cannot be accounted for solely by electrostatic forces. The contribution of hydrogen bonds [44] is hardly ever sufficient to prevent the mutual repulsion of the complex and outer-sphere ions bearing similar and high charges.

The type of bond in cobalt(III) outer-sphere complexes frequently depends on the structure of the inner sphere [32,220]. The presence of charge-transfer bands in the ultraviolet spectra of cobalt(III) outer-sphere complexes indicates [109-110] the occurrence of donor–acceptor electronic interaction as in the molecular complexes of benzene with iodine and other similar compounds [221,222]. It has been shown [223] that the electron is transferred from the readily oxidisable outer-sphere ligand to the central cobalt(III) ion in the complex converting it into an almost typical divalent state. This is evidence of possible formation of a dative bond in which the electron from the outer-sphere ligand is transferred to a lower free orbital of the inner-sphere complex. This mechanism of addition of outer sphere ions is denoted by the symbol *a* and is represented by the formula $M + A = M^{\delta-}A^{\delta+}$, where the symbol M denotes an inner-sphere complex with any charge, A denotes an outer-sphere ligand and the charge symbols $\delta-$ and $\delta+$ of the reaction products characterise the redistribution of electrons in the course of the formation of the outer-sphere complex. A typical example of mechanism *a* is the formation of hexamminecobalt monoiodide [109].

The stability of the bond linking the fourth (and succeeding) outer-sphere halide ions to the hexamminecobalt(III) cation increases with the dimensions of the outer-sphere ligand [5]. This phenomenon is attributed to the "hardness" (in Pearson's terminology [224]) of the central group of the outer-sphere complex and is interpreted [225] as evidence for d_π–d_π interaction. It may be supposed that in this type of bond the electrons are displaced from the filled orbitals of hexamminecobalt(III) to the large halide ions or other outer-sphere ligands. This type of bond in outer-sphere complexes is denoted by the symbol *b* and is represented by the formula $M + A = M^{\delta+}A^{\delta-}$.

Mechanism *a* increases the number of electrons in the antibonding orbitals of the inner-sphere complexes and makes the inner-sphere bonds more labile [226], which is reflected in an enhanced reactivity of cobalt(III) complexes.

The outer-sphere bond types represented by mechanisms *a* and *b* are extreme. There is no doubt about the existence of intermediate bond types. This is confirmed by data on the solubility of non-electrolytic cobalt(III) complexes in aqueous salt solutions [227]. These data were explained within the framework of the formation of outer-sphere complexes [30]. In addition, the stability of the solvation shells of the reactant and product ions and molecules may play a decisive role in the formation of outer-sphere complexes.

Aquo-complexes of cobalt(III) and chromium(III) are known [4,228] to show a smaller tendency towards outer-sphere interaction with small singly-charged anions than the analogous compounds with ammonia and ethylenediamine. This difference has been explained [71] by the high positive charge on the periphery of the inner-sphere complexes the ligands of which have a large number of protons. However, one should remember [88] that hydrated cations may enter into the structure formed by water molecules. Such incorporation hinders a close contact with the anions. Ammine complexes of cobalt(III) combine with water in the second coordination sphere more slowly and less strongly, which facilitates their outer-sphere interaction with other ligands. Moreover, large complex ions enter into the structure of the solvent, forming cavities [229], the dimensions of which are sufficient to accomodate small outer-sphere ligands. Large and highly charged ligands form more stable associated species with aquo-complexes than with ammine compounds because the bonds between the water protons and the oxygen atoms of the oxy-anions are stronger than the analogous bonds with the ammine protons [230].

Dispersion forces may play a definite role in the formation of outer-sphere complexes. Forces of this type in fact lead [88] to enhanced stability of hexamminecobalt(III) complexes when ethylenediamine is gradually replaced by ammonia.

Hydrogen bonds are also important for the formation of outer-sphere complexes [44]. As a result of these forces, inner-sphere ligands combine with hydrogen and many metal ions [231] and sometimes also anions and solvent molecules.

Further expansion of work on cobalt(III) outer-sphere complexes constitutes an important task. The concept of additional specific forces must be developed or rejected. The necessity for a thorough investigation of outer-sphere complexes was pointed out also in one of the latest papers by Bjerrum [232].

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