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Outer-sphere Complexes in Analytical Chemistry

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Published data on the use of outer-sphere complexes, formed from coordinatively saturated inner-sphere complexes and ligands, cationic species, or molecules of organic solvents present in the outer sphere, in present-day analytical chemistry have been reviewed. The characteristic features of the outer-sphere complexes, namely their relatively low stability and low activation energy for reactions in the outer sphere, together with their variety, make these complexes effective for the separation, isolation, and more particularly determination of inorganic and organic substances. The consequent improvement in the sensitivity, selectivity, and speed of analytical determinations has been discussed.
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INTRODUCTION

In recent years there has been a considerable increase in interest in the practical application of outer-sphere complexes (OC) and the concepts of outer-sphere coordination in analytical chemistry. This is related to the need to solve a large number of urgent practical problems, which requires considerable improvement of traditional methods and techniques of analysis, based on non-trivial approaches and new theoretical concepts. Significant improvement of the sensitivity and selectivity, lowering of the detection limits, and decrease in the time taken for analysis can be achieved using the chemical-analytical properties of OC. There are practically no published reviews of the use of OC in analytical chemistry, however. The information in the published review[1] and monographs[2,3] deals mainly with the use of OC only in the photometric analysis of inorganic substances, whereas the role of OC in present-day analytical chemistry is much more significant and varied.[4] Progress in the chemistry of OC[5-11] makes it impossible to re-examine published data on the interesting analytical possibilities provided by this group of compounds.

Outer-sphere complex formation is used to obtain analytical information on the object of analysis not only in photometry[3,12-14] and fluorimetry,[3,13-17] but also in extraction methods,[13,18-20] ionometry,[21-24] and chromatography.[25-28] OC are also used in the trace analysis of elements,[29] in methods for concentrating micro-elements,[30-32] in the chemistry of organic reagents,[3] and in the analysis of various organic substances.[33-35] They are used as analytical forms in crystal-microscopy,[36] qualitative and gravimetric analysis,[37,38] titrimetry,[39,40] work in aqueous-organic solutions,[39-44] automatic analysis,[45-47] and in other situations.[48,49] The analytical use of OC therefore constitutes a fairly

extensive and independent field of application of complex compounds in analytical chemistry. The unique nature of the chemical-analytical properties of OC is determined by the characteristic features of coordination in the outer sphere and by the thermodynamic properties of these compounds. It is therefore appropriate to examine briefly those aspects of the chemistry of OC of greatest importance for analytical purposes.

II. THE CHARACTERISTIC FEATURES OF OUTER-SPHERE COMPLEXES—THE BASIS OF THEIR ANALYTICAL APPLICATIONS

Published definitions of OC are not unambiguous. Usually, OC are defined as compounds formed by the attachment of electrically neutral[2] or charged[3] ligands to a coordinatively saturated complex. The features emphasised range from the absence of a bond between the outer-sphere ligand and the central atom[5,10,50–53] to the identification of OC with ion pairs.[54–56] The ambiguity of the definition was eliminated in a paper[57] which reflects the many years' experience of the Leningrad school in the study of outer-sphere complex formation. The fundamentally important fact is that an OC is formed by an inner-sphere complex, saturated with respect to its coordination number, and *any* species in the outer sphere. A new direct chemical bond with the central atom of the original reagent is not formed, since the reaction in the outer sphere and the direct chemical bonding take place between the ligands of the inner sphere and the species in the outer sphere. The species of the outer sphere can be described in general terms as ligands—electron pair donors or acceptors[59]—possibly reflecting present-day concepts of the coordinate bond.[60] A characteristic feature of OC is their definite stability towards solvolytic dissociation in polar solvents, characteristic of complex compounds in general.[61]

Ion pairs differ from OC;[53,57–59] ion pairs are produced as a result of the Coulombic interaction of partly or completely solvated ions, whereas OC are formed by a donor–acceptor interaction and show appreciable signs of covalent bonding.[58] The change in the potential energy of the system with change in the distance between the ions in ion pairs is smooth. In the ionisation of OC, however, it is necessary to overcome a potential barrier, whose magnitude is determined by the activation energy,[62] which is low for reactions in the outer sphere.[8,56,57] Thus it is possible in principle for ion pairs and OC to coexist in solution.[53]

The coordinating centre of OC of interest for analytical chemistry are usually inner-sphere cationic or anionic complexes[7,8,10] or neutral chelates.[26,27] The variety of outer-sphere species, which may be anionic complexes[63] or the neutral molecules of organic reagents or solvents,[11] which have electron-donor properties, or the cations of organic bases,[57] which have electron-acceptor properties, is apparently responsible to a large extent for the fairly extensive occurrence of OC. The characteristic features of these compounds used in analysis cannot be attributed entirely to electrostatic interaction. OC also differ from anisotropic[2,10] and mixed-ligand[3] complexes, although this is not always taken into account in the examination of their analytical applications.[1] The anionic complexes of metals, forming the coordination centres of the corresponding OC, do not always contain the number of acido-ligands specified by the coordination number of the metal ion.[5,57] Outer-sphere complexes containing complex forms of the same metal in the inner and outer coordination spheres have been called polycomplexes.[64] The inclusion of OC among the so-called "super-complexes"[65] has been regarded as inappropriate.[10]

The problem of the nature of the chemical bond in the outer sphere is complex. Donor–acceptance interaction makes the most important contribution, and the electrostatic contribution constitutes only part of the outer-sphere forces.[8,11,53,56–59,66] In general, it is recommended that account be taken of ion–dipole interaction, hydrogen bonding, covalent bonding, forces of structure formation in the solvent, dispersion forces, and the influence of external electric fields.[56] Problems of outer-sphere coordination and its experimentally detectable effects in solutions and crystals have been examined.[8–11,14,56–59,66,67]

The three-dimensional delocalisation of one-electron states, a characteristic of the coordinate bond,[60] is revealed by the fact that the points of contact between the outer-sphere ligands and the inner-sphere complexes are usually the points with the highest effective charges of the interacting species.[10] The appearance of or a change in a charge-transfer band in the electronic spectra of OC are regarded as fairly clear signs of outer-sphere coordination.[8,10,57,58] Charge transfer is due to the mixing of the wavefunctions of closely situated excited and ground states, so that in the systems being considered it corresponds to a greater or lesser covalent contribution to the chemical bonding in the outer sphere. This phenomenon has been described, for example, for a large number of OC based on metal–phenanthroline complexes[3] and the OC of hexammineruthenium(III) with various substituted pentacyanoferrates.[68]

The stereoselectivity of outer-sphere complex formation by Λ-(+)- and Δ-(−)-tris(ethylenediamine)cobalt(III) with the Δ-(glycinato)bis(oxalato) cobaltate(III) anion,[69] the localised attachment of fluoride and chloride ions in the outer sphere of hexasolvates of aluminium in methanol and ethanol,[70] and the outer-sphere coordination of pyridine molecules to the hexasolvate of cobalt(II) in deuteriated methanol, established by spin–lattice relaxation,[71] can also be related to the appearance of covalent interaction in the outer sphere. The specific nature of the outer-sphere forces, associated with charge transfer to antibonding orbitals of the inner-sphere complex and with dispersion interaction, is also confirmed by the explanation for the increase in the stability of the OC of tris(2,2′-bipyridyl)cobalt(II) with ammonia, methylamine, and ethylamine with increase in the complexity of the ligand.[72] The three-dimensional oriented solvation of the molecules of coordinatively saturated transition metal chelates by organic solvents determines the energetically most favourable position of the ligands in the outer sphere of these OC.[11] The calculated effects of the redistribution of electron density in hexakis(dimethylformamide)iron(III) and hexakis(dimethylthioformamide)iron(III) perchlorates differ considerably.[73]

Among OC with an electron-acceptor species in the outer sphere, the compounds of greatest interest for analytical chemistry are those formed by metal acido-complexes with the outer-sphere cations of onium compounds and basic organic dyes, referred to in the literature as ionic associates. Recent papers[67,74–76] indicate that electrostatic theories cannot explain the properties of these compounds. The covalent contribution to the bonding in the outer sphere in these systems is indicated, in particular, by the interpretation of the charge-transfer bands in their electronic spectra.[67] Data of this kind have been published, for example, for the compounds formed by anionic halogeno-complexes of copper(II), iron(II), cobalt(II), mercury(II), palladium(II), and silver with the doubly-charged cation of N,N′-dimethyl-4,4′-bipyridyl,[74] for the OC of hexacyanoferrate(II) ions with the cations of various heterocyclic

amines,[75] for the OC of pentacyanoferrate with coordinated dimethyl sulphoxide and pyridine molecules[76] and for other similar complexes.[77] The outer-sphere coordination of electron-pair acceptors by hexacyanoferrate(II,III) ions is indicated by the displacement of the half-wave potential to more positive values.[53] The specific nature of the interionic interaction of 2-octylpyridine with various anions is revealed by the decrease in the polarisation of the π-electron cloud of the aromatic cation and the formation of hydrogen bonds with them, in particular with the tetrachlorogallate ion.[67]

There is practically no corresponding published information on compounds with the acceptor species of a basic dye in the outer sphere. It has been suggested that there are localised contacts between the cations of these dyes and anions as a result of the irregularity of the electron density distribution in the former and the increase in the contribution of ion–dipole interaction to the chemical bonding.[3] Other factors possibly of importance are the type of hybridisation of the atomic orbitals in the acido-complex, which determines its geometry; the difference in the electronegativities of the central metal atom and the donor atom of the inner-sphere ligand, which determines the distribution of the atomic charges in these anions;[78] and the increase in the stability of the OC as a result of the forces of structure formation in the solvent.[79] This is consistent with data on the stability of compounds of BF_4^- (calculated charge on the fluorine atom −0.63[78]) with the cations of basic dyes. The stability constants (lg β) of OC increase in the order Methyl Green, Fuchsine, Malachite Green, Brilliant Green, Crystal Violet: 1.8, 2.0, 2.0, 2.6, and 3.2 respectively.[80] The OC with the most symmetrical species in the outer sphere has the highest stability. The stability of the OC of $SbCl_6^-$ with the cation of Crystal Violet is noteworthy; this complex is decomposed completely only in concentrated ammonia.[13]

The stability constants of the outer-sphere compounds of cationic complexes of metal ions with various ligands have been systematised.[10] Most of the data relate to compounds based on inert inner-sphere complexes of Co^{III} and Cr^{III}. There is much less published information on the OC of iron(II,III), nickel(II), and the platinum metals,[10] and for OC formed by neutral chelates with the molecules of organic solvents in the outer sphere.[11] The literature on analytical chemistry contains no examples of the practical application of the tabulated stability constants of OC.

The concentration stability constants of various OC formed by the aquo-ions of the alkali and alkaline earth metals with polyatomic anions in aqueous-organic solutions[81] are provisional, since they were calculated without allowance for side reactions. In these systems, because of the lability of the coordination centre, it is particularly important to distinguish the effects of outer-sphere and inner-sphere complex formation; this is an extremely complex problem, which has not been fully resolved.[8]

The specific nature of the properties of OC as chemical compounds determines their practical importance in analytical chemistry.

III. THE CHEMICAL-ANALYTICAL PROPERTIES OF OUTER-SPHERE COMPLEXES

In analytical chemistry, outer-sphere complex formation reactions and OC themselves are used in various methods for the qualitative detection, quantitative determination, isolation, and separation of inorganic ions and organic substances.

1. Principal Fields of Application of Outer-Sphere Complexes

The analytical application of OC depends on processes in solution in which these complexes are reaction products or, less frequently, the starting materials. The use of OC in analysis is determined by their characteristic properties, which enable these compounds to be the material carriers of analytical signals. These characteristic properties are low solubility in water and higher solubility in organic solvents; characteristic crystal shape; the ability of OC, containing the element being determined, to be coprecipitated; intense absorption in the visible or ultraviolet ranges of the spectrum or bright fluorescence; and the ability of OC to undergo flotation at the interface between two immiscible solvents or extraction into an organic phase. Another form of application of OC involves the production of an indirect analytical signal by a change in the concentration of the ions forming the OC, or its fulfilment of a "transmitting" function with respect to this signal by the selective ionisation of the OC in the outer sphere, often in conjunction with a dynamic process. This becomes possible because of the low thermodynamic stability of OC and the low activation energy of ligand replacement processes in the outer sphere. OC and the reactions involved in their formation are therefore used to produce indirect analytical signals in titrimetric methods with different techniques for establishing the end point—photometric,[39–44,82] amperometric,[83,84] conductometric,[85] potentiometric,[82] and others.[86,87] These characteristic features of OC play an important role in their use as electrode-active materials in the membranes of liquid ion-selective electrodes, in extensively repeated sorption and desorption processes in chromatographic separation systems, and in the rapid formation of OC in flow-type automatic analysers.

An intense analytical signal resulting from the formation of OC, for example their strong absorption or bright fluorescence, makes it possible to achieve a fairly low detection limit.[12–17] The marked dependence of the properties of OC on the nature of the metal ion and the inner- and outer-sphere species often makes it possible to achieve a high selectivity in the determination. Examples can be found in various fields of application of OC—ionometry,[21–24] ligand-exchange[25,88] and other forms of liquid chromatography,[26–28,69,89,90] and titrimetry in aqueous-organic solutions.[39–44]

OC with inert and labile inner coordination spheres have different chemical-analytical properties, and this must be taken into account in analytical practice. The situation is simpler in the first case, since in the analytical determination the OC dissociates only in the outer sphere. In the second case, dissociation of the OC in the inner sphere is also possible, and to suppress this and to ensure the maximum yield of the analytical form, an excess of the inner-sphere ligand is added to the solution.

Dilute aqueous solutions of most salts of *s*-, *p*-, and *d*-block elements, in which the anions are most frequently singly charged, contain only OC at concentrations below the limit of complete solvation.[8] Many reactions, therefore, for example complex formation[2,8,57,91] and redox reactions,[92,93] pass through a stage involving the decomposition of the OC of the aquo-ions of the metals and (or) the formation of intermediate OC. The formation of these OC as sources of analytical signals has no practical value, so that the kinetic role of OC is not examined in the present review.

The analysis of published data on the analytical applications of OC makes possible their systematisation, apparently for the first time. The results are given in Table 1, which shows the great variety of types of OC finding practical applications, although their use is not equally important in different analytical methods. Specific examples are examined below.

2. The Precipitation of Sparingly Soluble Outer-Sphere Complexes

The inner-sphere complexes of metals have low hydration energies, so that they can react with fairly large outer-sphere counter-ions to form neutral OC which are relatively sparingly soluble in water. This characteristic feature of OC was apparently first used by Bjerrum to separate thiocyanate complexes of chromium(III) by precipitating with quinolinium sulphate.[94]

Table 1. Fields of application of outer-sphere complexes in analytical chemistry.[1-4,12-28,30-35]

Outer-sphere complex		outer-sphere species
Fields of application	coordinating centre	
ML_n^{x+}, $ML_{n-k}L_k^{*x+}$	A^{y-}, R^{y-}	ph, e.ph, fl, e.fl, p, g, e, c, i.ch
»	$M^*X_m^{y-}$, $M^*X_{m-k}A_k^{y-}$	ph, e.ph, p, g, lig.ch
MQ_q^{x+}	A^{y-}, R^{y-}, $M^*X_m^{y-}$, $M^*R_n^{y-}$	ph, e.ph, fl, e.fl, c, i, flot, p, g, i.ch
MQ_q	*m*Solv, HO—Si≡	e, liq.ch
$M(OH_8)_n^{x+}$	A^{y-}, $M^*X_m^{y-}$, $\mathscr{M}-A^{y-}$	aq-org, i.ch
$M^{x+}\cdot$Solv	A^{y-}, $M^*X_m^{y-}$	e, aq-org
MX_m^{y-}, $MX_{m-k}X_k^{*y-}$	D^{x+}	e.ph, e.fl, flot. c, i
»	B^{x+}, Z^{x+}	e, flot, c, i
»	$\mathscr{M}-B^{x+}$	i.ch, lig.ch

Notation: M = metal, L and Q = unidentate and multidentate ligands, A = outer-sphere ligand, R = anion of coloured reagent, X = acido-ligand, D^{x+}, B^{x+}, Z^{x+} = cations of a basic dye, an organic base, and an onium compound respectively, ≡ = ion-exchanger matrix, HO—Si = silica gel, Solv = organic solvent; ph = photometry, e.ph and e.fl = extraction photometry and extraction fluorimetry, fl = fluorimetry, p = precipitation, g = gravimetry, e = extraction, c = coprecipitation, flot = flotation, i = ionometry, aq-org = reactions in aqueous organic solvents, lig.ch, i.ch, and liq.ch = ligand-exchange, ion-exchange, and liquid chromatography.

Quantitative data on the solubility of sparingly soluble OC, usually in the range 10^{-3}–10^{-5} M, are rarely used as a basis for their analytical application. They are most frequently determined by studying the OC equilibrium by the solubility method,[95,96] or the thermodynamics of transfer.[97,98] The least soluble OC are important in analysis. The solubility of OC in water is lower, the larger their component fragments. For example, at 25° the solubility of hexamminecobalt(III) oxalate is 3.9×10^{-4} M,[99] and that of octammine-μ-aminohydroxodicobalt(III) chloride sulphate is 10^{-7} M.[100] The solubility of OC can be calculated from the solubility product;[95,96,101,102] more accurate determination requires allowance for the stability of the OC in solution and the contribution of side reactions of the coordinating centre and the outer-sphere ligands.[102] With increase in the ionic strength of the solution, the solubility of OC increases slightly.[95,96,102] The compounds of metal acido-complexes with outer-sphere organic cations, containing larger species, are less soluble. For example, the solubility of the OC of CdI_4^{2-} with Chromopyrazole is 0.87×10^{-3} M, and that with Chromopyrazole II is 7.2×10^{-6} M.[103] The more hydrophobic the inner- and (or) outer-sphere species, the greater the solubility of the OC in an aqueous-organic solvent.[98]

The precipitation of OC is widely used in the identification of ions[37,38] and pharmaceutical products,[33] crystal-microscopy,[36] gravimetric analysis, and different forms of precipitation titration, and to separate elements. A particular field of application is the concentration of micro-elements by coprecipitation and flotation.

The element being determined is most frequently present in OC in the inner-sphere complex, and less frequently as the outer-sphere species. Data on OC used as gravimetric forms are given in various sources, including a series of monographs.[49,82,84,86,104-124] The directed selection of the ligands or species of the outer and inner coordination spheres makes it possible to achieve the required analytical effect relatively easily. Thus hexamminecobalt(III) is used for the gravimetric determination of anionic forms of beryllium,[107] cobalt,[82] chromium(III),[110] indium,[111] phosphorus,[115] rhodium(III),[86] and uranium,[122] and the outer-sphere coordination of organic bases by the anionic complexes of elements makes it possible to determine silver,[104] gold,[105] cadmium,[109] mercury,[84] zinc,[124] and other metals.[86,117,121,123] The use of OC in gravimetric analysis extends the possibilities provided by the method and makes it possible to obtain gravimetric forms with a high molecular mass, decreasing the conversion factor and increasing the accuracy of the analysis, particularly in the determination of small quantities of elements. For example, it is possible to determine down to 5 mg of silver or molybdenum as $[Co(en)_2 \cdot (SCN)_2][Ag(SCN)_2]$ (en = ethylenediamine) and $[Cr(NH_3)_5 \cdot Cl](MoS_4)$ respectively[104,114] or down to 2 mg of palladium as $[Pd(SCN)_4][(C_4H_9)_4N]_2$.[116] In qualitative reactions the detection limit is fairly low, amounting to fractions of a microgram.[36-38]

The precipitation of OC is in general not very selective. It is possible to achieve selective precipitation by using different combinations of ligands in complex inner- and outer-sphere species. For example, nickel, copper, iron(III), zinc, and cobalt do not interfere in the determination of gold as bis(trimethyl)hexamethylenediammonium bromoaurate.[105] The gravimetric determination of uranium as $[Co(NH_3)_6]_2[UO_2(CO_3)_2](H_2O)_3(NO_3)_2$ is highly selective.[122] Selective precipitation is used to isolate and separate various elements; for example the precipitation of sulphates by octammine-μ-aminohydroxodicobalt(III) chloride for their indirect photometric determination,[100] the separation of tellurium from selenium as $[Te(phen)_3]X_4$ (phen = 1,10-phenanthroline, X = Cl^-, Br^-),[125] tantalum from niobium as $[Fe(phen)_3](TaF_7)$,[126] and niobium from tantalum by precipitating $[Fe(phen)_3][NbO_2(C_4H_5O_5)_2]$ from tartrate solution.[127]

Precipitation titration methods based on the formation of sparingly soluble OC, with different means of establishing the end point, are widely used, for example to determine cobalt,[82] silver,[85,104] platinum,[86] anionic complexes of cadmium,[109] tin,[119] mercury,[84] boron, iron(III), gold, and other elements using quaternary ammonium bases[87] and onium salts.[128] High sensitivity in the determination is achieved in the amperometric titration of BiI_4^- with the protonated 8-quinolinol cation[83] and of zinc with thiocyanate ions in the presence of diantipyrinylmethane and its analogues, and even in the visual titration of $Zn(SCN)_4^{2-}$ with Chromopyrazole.[124]

Indirect titrimetric methods based on the preliminary precipitation of OC[108,109,112] have now lost their importance. It is possible, however, to determine down to 15 μg bismuth by precipitating as $[Bi(SCN)_6][(C_4H_9)_4N]_3$ after treating

the precipitate with hydrogen carbonate and titrating thiocyanate ions in an amplification reaction which gives 114 moles of iodine per mole of metal.[129]

OC are effective for concentrating elements. The marked structural similarity between various sparingly soluble OC and the corresponding organic collectors[31] ensures a high degree of coprecipitation of elements in the outer or inner coordination spheres. For example, 90% plutonium(IV) is coprecipitated as the OC of $Pu(NO_3)_6^{2-}$ with the Butylrhodamine cation using Butylrhodamine nitrate as collector; the detection limit is 0.02 μg Pu in 200 ml of solution. The same degree of separation is achieved for silver as the OC formed by its dithizone chelate with azo-dye anions in the outer sphere, and also for other elements as various OC.[31] In the coprecipitation of cobalt, molybdenum, zinc, and lanthanides with salts of antipyrine dyes in the presence of thiocyanate ions, competition between the ligands for a place in the inner sphere, and the formation of two types of coprecipitated OC, are possible.[130,131] The OC of metal–phenanthroline complexes with singly-charged anions in the outer sphere are effectively coprecipitated with AgX (X = Cl^-, Br^-, I^-, SCN^-), making it possible to achieve an absolute concentration enrichment coefficient of 10^3.[132]

Various OC with hydrophobic species in the inner or outer spheres have amphiphilic properties, so that they can be concentrated by flotation, usually with photometric analysis in the final stage. The flotation of OC based on metal–phenanthroline complexes has been examined in a monograph.[3] By carrying out this process at the interface between water and a mixture of toluene and carbon tetrachloride, using the bismuth–Alizarin Red–Brilliant Green system, it is possible to determine down to 10^{-4}% bismuth in arsenic salts with a detection limit of 0.5 μg Bi in 25 ml of solution.[133]

Examples of the use of sparingly soluble OC in analytical chemistry are given in Table 2.[49,86,110,112,130–136]

3. Outer-Sphere Complexes in Photometry and Fluorimetry

The OC used in photometric and chemical luminescent analysis are extremely varied, because of the ready production, on the basis of these compounds, of analytical forms (see Table 1) showing strong absorption in the visible and ultraviolet ranges of the spectrum, or bright fluorescence. The absorbing centre in these OC may be the inner-sphere complexes (the coordination unit of the OC), the outer-sphere species, or both partners of the photometric reaction. Fluorescence is most frequently produced in outer-sphere cations. The element being determined is usually in the inner-sphere complex, and is less frequently a component of the outer-sphere species. Coloured and fluorescent OC are usually extracted by organic solvents, and this makes it possible to carry out multiple extraction-photometric and extraction-fluorimetric determinations.[1–3,12–17,33,34,137–142] The compounds formed are usually ionic associates. The inadequacy of traditional views of these compounds has been noted in an examination of the properties of the OC of metal–phenanthroline complexes with various outer-sphere ligands.[2,3] In recent years there has been a greater tendency to regard the production of the analytical forms being considered here as the result of the interaction of complex electronic systems, and not individual oppositely charged ions.

In photometry and fluorimetry, extensive use is made of OC with the molecules of heterocyclic polyamines in the inner sphere; the wide range of outer-sphere ligands in these complexes makes it possible to develop an extremely large number of methods for determining various elements.[3,14] The nature of the outer-sphere ligands in these OC is important, since it determines the ability of the analytical form to undergo extraction, and the selectivity of the determination. The high extractability of $[Fe(phen)_3]X_2$ (X = BF_4^-, ClO_4^-), which in the case of the perchlorate ion correlates with the stability of the OC,[143] has been used to determine these anions.[49,85] The detection limit for various elements, achieved using OC, is fairly low, for example 0.07 μg Co in 6 ml of solution in the determination of cobalt as the OC of its phenanthroline complex with hydroxyxanthene dyes[144] or 10^{-5} μg Ru in 1 ml of solution in the determination of ruthenium(II) as $[Ru(phen)_2]Cl_2$ by a luminescent method.[145] In the last case the covalent hydration of the inner-sphere ligand, leading to the formation of the carbinolamine, increases the fluorescence of this OC. The possibility of cooperation (that is outer-sphere coordination of ligands in the OC of metal–phenanthroline complexes with dye anions, which excludes the mutual displacement of ligands, has been examined.[146] The inner coordination sphere of a coloured OC may be more complex, as observed, for example, in the extraction-photometric determination of iron(III), bismuth, indium, gallium, and various other elements as $[M(PAR)(ANT)_3]ClO_4.nCHCl_3$ (PAR = pyridylazoresorcinol, ANT = antipyrine). The dependence of the extractability of these OC, the optical characteristics of the extract, and the solvation number on the nature of the anion of the outer sphere has been determined.[142] The outer-sphere complexes $[ReO(thur)_3Cl_2]Cl$ and $[ReO(thur)_4.Cl]Cl_2$ (thur = thiourea) have been used as analytical forms in the determination of rhenium;[117] the compound $[BiSO_4.(oxin)_3]X_4$ (oxin = 8-quinolinol; X = Cl^-, Br^-, I^-, ClO_4^-, etc.) in the precipitation-photometric determination of bismuth;[147] and $[Co(NH_3)_2(NO_2)_4][(C_6H_{13})_4N]$ in the indirect determination of perchlorates by exchange extraction (from the decrease in the intensity of the colour of the organic phase).[85]

In extraction photometry and fluorimetry, extensive use has been made of associates of anionic complexes of elements with outer-sphere coloured or fluorescent cations of aryl-, diaryl-, and triarylmethane, xanthene, acridine, arylamine, antipyrine, azo, cyanine, and other dyes.[12–17,137–142] The selectivity of the determination depends on the nature of the outer-sphere anionic complex of the element, and its sensitivity on the intensity of the colour of the outer-sphere species. For example, gallium in zinc was determined by converting the element being estimated into an anionic complex with pyrocatechol, followed by extraction as the OC with basic dyes.[148] The detection limits achieved in these methods are extremely low,[8,12–17] for example 0.03 μg ml^{-1} for uranium(VI),[149] 0.02 μg ml^{-1} for scandium,[150] 24 μg ml^{-1} for magnesium,[151] and 10^{-4} μg ml^{-1} for gallium (extraction-fluorimetric method).[160,161] Examples of the use of other OC which make it possible to improve considerably the analytical characteristics of reactions[149–167] are given in Table 2.

A correlation is observed between the stability constants of OC and the molecular refraction of the inner-sphere ligands, which is a function of their average polarisability. This confirms the possibility of the outer-sphere coordination of the cations of Rhodamine S by anionic complexes of the lanthanides with substituted salicylic acid and 8-quinolinol,[152] and also other basic dyes in similar systems.[148–153] The displacement of the absorption band in the spectra of these OC is attributed to the difference in their stabilities in the ground and excited states.[15] The hypsochromic shift of 10–20 nm in the spectra of the outer-sphere cations of antipyrine dyes in compounds with $AuCl_4^-$ [158] and of

Table 2. Principal fields of application of outer-sphere complexes in analytical chemistry.

Species being determined	Coordinating centre of the OC	Outer-sphere species	Method of determination*	Refs
P	$[Co(en)_3]^{3+}$	$HP_2O_7^{3-}$	g	[49]
Pt	$[Pt(thur)_4]^{2+}$	$[Cr(SCN)_4(NH_3)_2]^{2-}$	g	[86]
Cr	$[(NH_3)_5CoO_2 \cdot Co(NH_3)_5]^{5+}$	$Cr_2O_5^{2-}$	g	[110]
Ge	$[Cd(phen)_3]^{2+}$	$[Ge(C_6H_4O_2)_3]^{2-}$	g	[112]
Co, Mo, Zn, Ln	$[M(SCN)_n]^{x-}$	antipyrine dye	c, emis	[130]
Nd, Sm, La	$[Ln(diantipyrinylmethane)_3]^{3+}$	SCN^-		[131]
Tl	$TlBr_4^-$	acridine	flot, ph	[134]
Tl	$TlCl_4^-$	papaverine		[135]
Pt, Pd, Au	MCl_n^-	cetylpyridinium	flot	[136]
Hg	$[Hg(phen)_3]^{2+}$	Bromophenol Blue	e.ph	[146]
U	$[UO_2(oxin)_3]^-$	Butylrhodamine	e.ph	[149]
Sc	$[Sc((NO_2)_2oxin)_3]$	Rhodamine S	e.fl	[150]
B	$[B(mandelic\ acid)_n]^-$	Malachite Green	e.ph	[153]
Pt	$PtCl_4^{2-}$	Methyl Green	»	[154]
Au	$AuBr_4^-$	Chromopyrazole I	»	[157]
Au	$AuCl_4^-$	Antipyrine dye	»	[158]
Ga	$GaCl_4^-$	Rhodamine, Acridine Orange	e.fl	[160, 161]
Au	$AuCl_4^-$	Acridine Yellow	e.ph	[162]
Sb	$SbCl_6^-$	Acridine Orange	»	[163]
Bi	BiI_4^-	azomethine dye	»	[164]
Co	$Co(SCN)_4^{2-}$	Brilliant Green	ph	[166]
Bi	$BiO(S_2)_2^-$	cetyltrimethylammonium	e.ph	[167]
Ru	$[Ru(phen)_3]^{2+}$	SCN^-	»	[176]
Cu	$[Cu(biquinolyl)_2]^+$	ClO_4^-, nitroso-R-salt	»	[177]
Cu	$[Cu(phen)_3]^+$	dibromofluorescein	»	[174]
Fe	$[Fe(phen)_3]^{2+}$	pelargonic acid	»	[175]
Cu	$[Cu(SCN)_4]^{2-}$	$[(C_4H_9)_4N]^+$	e.ph	[179]
Ag	$[Ag(Cadion\ 2B)]^-$	Triton X-100	»	[181]
Hg	$[Hg_3(Xylenol\ Orange)_2]^{2-}$	Amberlite A-2	»	[182]
Ce	CeX_n^{3-} (X=Cl⁻, NO_3^-, SO_4^{2-})	cetyltrimethylammonium	e.ph	[189]
Tl	$TlCl_4^-$	Brilliant Green	e, at.abs	[197]
In, Tl ...	MCl_4^-	Aliquat	e	[200]
Be	$[(OH)_2Be(malonate)_n]^{2-}$	»	e.ph	[201]
Os, Ru	$M(SCN)_6^{3-}$	mesityl oxide	e, ph	[202]
ClO_4^-, NO_3^-	$[Cu((CH_3)_2phen)_3]^+$	ClO_4^-, NO_3^-	e, at.abs	[49]
Cu	»	SO_4^{2-}, picrate	i	[207]
Au, Ag	$[M(thur)_2]^+$	$[Co(NO_2)_4(NH_3)_2]^-$	»	[208]
»	$M(CN)_4^-$, MCl_2^-	Rhodamine B	»	[209]
Ag	$Ag(CN)_2^-$	tetradecylphosphonium	»	[210, 211]
Au	$AuCl_2^-$, $Au(CN)_4^-$	tetraphenylarsonium	»	[212]
Zn, SCN^-	$Zn(SCN)_4^{2-}$	tributyloctadecylammonium	»	[213]
Ag	$Ag(CN)_2^-$	hexadecyltrioctylammonium	»	[214]
Ga	$GaCl_4^-$	Ethyl Violet	»	[215]
Ta	TaF_6^-	cetylpyridinium	»	[216]
racemates of Co(III) complexes	Λ-(+)-,Δ-(−)-$[Co(en)_3]^{3+}$	Δ-(glycinato)-bis(oxalato)-cobalt(III)	lig.ch	[69]
racemates of organic acids	Λ-(+)-,$[Co(en)_2(NO_2)_2]^+$	Λ-(+)-, Δ-(−)-anions	»	[224]
racemates of complexes	»	Λ-(+), Δ-(−)-$[M(C_2O_4)_3]^{3-}$	»	[224]
dinucleotides, cephalosporins	≡SiA—R—[en $Co(en)_2]^{3+}$ ≡SiO—R—[en $Co(phen)_2]^{3+}$	anions of dinucleotides and cephalosporins	»	[225]
Au	$AuBr_4^-$, $Au(SCN)_4^-$	≡Si—O—Si$(CH_2)_3$ $(NHCH_2CH_2)NH_2$	liq.ch	[159]
acetylacetonates, etc.	chelate of Co(III), Cr(III)	di-isopropyl ether, HO–Si≡	»	[26, 27]
metal chelates	»	chloroform, HO–Si≡	»	[228]
Al, In, Ga...	$[M(Xylenol\ Orange)_n]^-$	anion-exchanger groups	i.ch	[232]
alkaloids	$[Cr(SCN)_4(NH_3)_2]^-$	alkaloids	e, at.abs	[35]
aminoacids	$[Ni(phen)_3]^{2+}$	aminoacids	e, at.abs	[35]
benzylpenicillin	$[Cd(phen)_3]^{2+}$	benzylpenicillin	»	[35]
polyhydroxyethylene surfactants	$[Fe(SCN)_6]^{3-}$	surfactants	e.ph	[185]
V, Ta, Nb, Sb, P	$[K((CH_3)_2SO)_n]^+$	$VO_2F_3^{2-}$, TaF_7^{2-}, $NbOF_5^{2-}$, SbF_6^-, PF_6^-	aq-org, ph.titr	[41]
Al, In, Ga, Tl, B	»	MF_4^-	»	[266]
Ti	»	TiF_6^{2-}	aq-org, ph.titr	[271]
Pd, Pt	»	$PdCl_4^{2-}$, $PtCl_6^{2-}$	»	[43]
benzenesulphonates	$[Ba(OH)_2)_6]^{2+}$	benzenesulphonates	»	[256]
naphthalenesulphonates	»	naphthalenesulphonates	»	[238]
hydroxynaphthalenesulphonates	»	hydroxynaphthalenesulphonates	»	[257]
aminonaphthalenesulphonates	»	aminonaphthalenesulphonates	»	[259]
anthraquinonesulphonates	»	anthraquinonesulphonates	»	[260]
alkyl sulphonates	»	alkyl sulphonates	»	[261]
alkyl sulphates	»	alkyl sulphates	»	[44]

*For notation see Table 1; emis = atomic emission, at.abs = atomic absorption, ph.titr = photometric titration.

acridine in compounds with $TeBr_6^{2-}$ [134] can then be regarded as proof of outer-sphere association.

The irregular distribution of electron density in dye cations,[3,165,168] which influences the stability of the corresponding OC by non-Coulombic interaction,[85,152] apparently opens up the possibility of a search for the optimum outer-sphere cations for use in the determination of metals as OC based on acido-complexes. For example, in the extraction-photometric determination of lead, best results were obtained using OC formed by the halogeno-complexes of this element with Brilliant Green and Malachite Green ($PbCl_3^-$) or Victoria Blue 4R ($PbBr_3^-$).[156] Examples of increase in the complexity of the outer-sphere species of OC used as analytical forms are provided by the compounds of BiI_4^- with the phenylhydrazone-1,3,3'-trimethyl-2-formylindolinium cation,[164] of $SbCl_6^-$ with Phenosafrazo Blue,[165] and other compounds.[141]

The anionic coordinating centre of OC, in addition to acido-ligands, may sometimes also contain other species contributing to its coordination saturation. Examples of such systems are the OC of $AuCl_3(OH)^-$ with Chromopyrazole,[158] of $SbCl_5(OH)^-$ with the cations of triarylmethane dyes,[3] of $PdX_3(H_2O)^-$ (X = SCN^-, I^-, Br^-, Cl^-) with the cation of Brilliant Green,[155] and of PbX_3^-.Solv (X = Cl^-, Br^-; Solv = benzene, toluene, pentyl acetate) with the cations of triphenylmethane dyes.[156] The OC of $AlF_2F_2^{3-}$ (R = Xylenol Orange) with tri-n-octylamine has been used for the extraction-photometric determination of fluorine.[169]

The difference in the stabilities of labile OC makes exchange of outer-sphere species possible. For example, exchange between the cation of Crystal Violet in its OC with $SbCl_6^-$ and the cations of antipyrine, diantipyrinylmethane, and its analogues, and also trioctylamine, has been used for their determination.[13]

An original type of coloured OC is represented by the compounds of anionic complexes of elements with organic reagents and with the outer-sphere cations of surface-active substances (SAS). In this case a marked improvement in the analytical characteristics of the reactions in aqueous solution is achieved by the complex effects of hydrophobic interaction.[170,171] The outer-sphere complexes formed by the anionic compounds of disulphodecylfluorene with molybdenum(VI), tungsten(VI), germanium, titanium(IV), and tin(IV) with outer-sphere cations of the N-cetylpyridinium type have been characterised as outer-sphere chelates.[172] The sensitivity and selectivity of the reactions in these systems are much better than in those examined above. For example, in nickel and its alloys it is possible to determine 3×10^{-5}% antimony as the OC of its trihydroxyfluoronate with the N-cetylpyridinium cation in the outer sphere.[173]

The stability of OC towards ultraviolet radiation has not been specially studied, but the ability of iron(III) as $[Fe(phen)_3X_n]$ (X = ClO_4^-, $C_2O_4^{2-}$) to undergo photochemical reduction has been used for its determination.[48] The photometric study of mercury-catalysed ligand exchange in $Fe(CN)_6^{4-}$ to give OC based on iron(II)–phenanthroline complexes has made it possible to determine down to 200 ng ml^{-1} of the catalyst element.[29]

Examples of the use of OC in photometry and fluorimetry[174–185] are given in Table 2.

4. Outer-Sphere Complexes in Extraction

The extraction of OC is used to isolate or separate elements and in mixed methods of analysis. In general it is possible to draw a parallel between the coordinative unsaturation of the compound extracted, the necessity of which is one of the basic postulates of extraction theory,[186] and the state of the metal ion in the coordinating centre of the OC, when the inner-sphere ligand occupies the energy gap between the central atom and the outer-sphere ligand. This makes it possible to formally compare the properties of the OC being considered in this section with the properties of other extractable compounds. The lack of data on the stability of extractable OC towards solvolytic dissociation in polar solvents creates certain difficulties in applying the concepts of outer-sphere coordination in extraction chemistry, but the available experimental data[67] indicate that this approach is promising.

The use of OC in extraction can be examined on the basis of the type of compound transferred to the organic phase[18,30,32] or on the basis of the characteristics of the extraction process.[19] In the first case, the OC may be various coordinatively non-solvated salts, that is compounds of the type $[Fe(phen)_3](ClO_4)_2$, $[Ca(TBP)_m](SCN)_2$, $[Tl(TBP)_3(H_2O)]Cl_4$ (TBP = tributyl phosphate); compounds of metal solvates, for example $(Mg.Solv)Cl_2$, $(Ca.Solv)(SCN)_2$; and the compounds of acidocomplexes with organic cations, examined above.[18,30,32] The significant covalent contribution to the chemical bond in the outer sphere is revealed by the anomalously high distribution coefficients, as for example in the extraction of tetrachlorogallate by 2-octylaminopyridine.[67] Many extractable compounds of anionic complexes of metals—halide and thiocyanate,[13,14,18,19,187] less frequently nitrate,[20] carbonate,[188] and others[14,110,113]—with the cations of organic bases, of considerable importance in analytical chemistry, are apparently OC.

In the second case it is possible to consider from the viewpoint of outer-sphere complex formation the processes involved in the cation- and anion-exchange extraction of cationic and anionic inner-sphere coordinatively saturated complexes respectively.[19] The outer-sphere coordination of the molecules of organic solvents by neutral metal chelates, distinguished by its orientational specificity and discrete character,[11] makes it possible to relate their extraction, and also the forms of various adducts used in analytical chemistry,[3] to these phenomena.

Synergic extraction in various systems can also be related to the formation of OC. Thus the formation of stable adducts, essentially OC, observed in the extraction of europium by thenoyltrifluoroacetone in the presence of quinolinium cations in cyclohexane, benzene, carbon tetrachloride, and chloroform, increased the extraction constant by a factor of about 10^5.[189] The formation of a compound containing the inner-sphere complex of uranyl ions with di-(2-ethylhexyl) phosphate and a molecule of a crown ether in the outer sphere made possible the synergic extraction of the element into nitrobenzene.[190]

Competing processes in the outer sphere can explain the suppression, usually interpreted in terms of the "common ion" mechanism, of the extraction of indium from bromide solutions containing the cations of Brilliant Green into benzene in the presence of thallium(III), or the decrease in the extraction of thallium(III) from chloride solutions into chloroform with Crystal Violet in the presence of mercury.[191]

The extraction of OC is used for the effective separation of elements,[30,32,192] including platinum metays with similar properties.[193,194] Various analytical methods are used to determine the elements after their separation or extraction, for example titrimetric (after the separation of zinc and cadmium by extraction from halide solutions by dipyrazolonylmethane[195]), atomic emission (after the extraction of gold(III) and thallium(III) by Chlorex[196]), flameless atomic absorption (in the determination of thallium(III) in sedimentary rocks[197]), and radiometrically (after concentrating iridium and rhodium

by 2-octylaminopyridine,[198] thallium(III) by alkyldiamines,[199] and other elements by methyltrioctylammonium chloride[200]). Small quantities of silver can be determined by an extraction-catalytic method based on the catalytic oxidation of Bromopyrogallol Red (BPR) by persulphate in the presence of 1,10-phenanthroline and extraction of the catalyst [Ag.$(phen)_2$]BPR by nitrobenzene.[29] Examples of the use of OC in extraction[49,195–202] are given in Table 2.

5. Outer-Sphere Complexes in Ionometry

The properties of various OC correspond effectively to the requirements to be satisfied by electrode-active materials in membrane liquid ion-selective electrodes (ISE). These requirements include low solubility in water, ready extractability into an organic solvent, ensuring that the OC is in the membrane phase of the liquid ISE, and the ability of the OC to undergo selective ionisation in the outer sphere, resulting from the low activation energy of this process.

These properties are shown by, for example, the OC, dissolved in nitrobenzene, of the phenanthroline complexes of iron(II), nickel, and various other metals with different anionic outer-sphere ligands. Depending on the nature of the outer-sphere ligand, it is possible to prepare ISE for determining NO_3^-, BF_4^-, ClO_3^-, ClO_4^-, IO_4^-, ReO_4^-, and various other anions.[21–24] Since the rate of exchange of a transition metal on a membrane surface is much lower than the rate of anion exchange, the potential of the ISE is determined by the activity of the corresponding outer-sphere ions in the solution. The selectivity of ISE of this type generally decreases in the order $PF_6^- > ClO_4^- > SCN^- > I^- > BF_4^- > NO_3^- > Br^- > Cl^-$, and this can be related to the change in the stability of the OC.[21] A large number of examples of ISE with membranes containing compounds of this type have been described.[203–206]

Electrode-active properties are shown by solutions of the dimethylphenanthroline complex of copper(I) with sulphate and picrate ions in the outer sphere in dibutyl phthalate. This made it possible to develop ISE for the determination of these cationic complexes of copper(I).[24,207] Similar properties are shown by solutions of OC based on thiourea complexes of silver and gold(I) in nitrobenzene, chlorobenzene, and 1,2-dichloroethane.[24,206,208] An electrode with a membrane based on a silver complex can also show an electrode function with respect to phosphate ions.[203]

Electrode-active properties are shown by various OC of anionic halide and pseudohalide complexes of metals with different organic anions in the outer sphere, capable of undergoing solvolytic dissociation in polar organic solvents such as *o*-dichlorobenzene, decan-1-ol, etc.[21,24,204,209–216] ISE of this type are used in flow injection methods in automatic chemical analysis.[46,47]

Additional information on the use of OC with different coordinating centres as electrode-active substances in membrane liquid ISE are given in Table 2.

6. Outer-sphere Complexes in Chromatography

The low activation energy of the replacement of outer-sphere ligands in OC makes it possible to carry out this process under the dynamic conditions of various forms of liquid chromatography with extensive repetition of sorption and desorption processes in new layers of sorbent. In different specific cases the stationary phase may be associated either with the coordinating centre of the OC (inner-sphere complex) or with the outer-sphere ligand. The concepts of outer-sphere coordination can be used in ion-exchange, ligand-exchange, and extraction chromatography and in the liquid chromatography of coordinatively saturated metal chelates. The possibility of carrying out "fine" separations of mixtures of substances and concentrating elements is of practical importance. An infrared spectroscopic study of the characteristic features of cation-exchange resins with sulphonate functional groups showed that during ion-exchange sorption on a sulphonic acid cation exchange resin, characteristic OC of the metal aquo-ions with the solid polyelectrolyte in the outer sphere are formed.[217] The formation of OC is also the first stage of the exchange of metal ions in complex-forming ion exchangers.[28] The anion exchange of halide, pseudohalide, nitrate, and other complexes of various metals on anion exchange resins involves the formation of OC.[218,219] In this case the anionic complexes react with the cationic groups of the quaternary ammonium bases of the ion exchange resin, that is with outer-sphere species fixed in the stationary phase. Ion-exchange processes have proved to be effective for the group concentration of micro-quantities of transition metals[220] as their phenanthroline complexes on a polyfunctional outer-sphere ligand (KU-2 cation exchange resin), and is also a convenient method for separating the phenanthroline complexes of nickel, iron(II), and ruthenium(II) on modified silica.[221]

The difference in the stability of OC based on $[Co(en)_3]^{3+}$ with anionic ligands leads to differences in their retention times in the anion exchanger phase, and this has made it possible to separate mixtures of oxalates and sulphates[222] and fumarate and maleate ions.[223]

An even finer chromatographic separation can be achieved by the highly selective method of ligand-exchange chromatography, based on outer-sphere ligand exchange.[25] This makes it possible to separate mixtures of compounds with very similar properties, for example the optical isomers of kinetically inert complexes of chromium(III) and cobalt(III) and various other metals by chromatography on dissymmetric sorbents, or racemates of the tris(oxalato)-compounds of cobalt(III) and chromium(III) as their OC with the cations of brucine, quinine, or cinchonine by electrophoresis.[25] Optically active metal complexes can be used for the enantioselective coordination of asymmetric species in the outer sphere, and this makes it possible, for example on silica gel modified by N-aminoethylaminopropyl groups and Λ-(+)-$[Co(en)_2(NO_2)_2]^+$, to separate respectively the racemates of organic acids and the tris(oxalato)-compounds of cobalt(III) and chromium(III).[224] The modification of silica gel by chloroamine complexes of cobalt(III) makes possible the chromatographic separation of dinucleotides and cephalosporins.[225] The stereoselectivity of outer-sphere complex formation on Sephadex A-25 has been used to separate the racemates of (glycinato)bis(oxalato)cobaltates(III).[69]

The concepts of outer-sphere coordination are actively used in the interpretation of the mechanism of the separation of neutral coordinatively saturated metal chelates by liquid adsorption chromatography in chloroform, di-isopropyl ether, and other solvents with medium polarity.[26,27,89,226–229] The chromatographic properties of the chelates of metals with acetylacetone, benzoylacetone, dibenzoylmethane, dibutyldithiophosphinate, and other multidentate ligands depend on the structure of the ligand fragment peripheral to the chelate unit. The difference in the mobility of these chelates is attributed to the formation of hydrogen bonds between a peripheral electronegative atom of the ligand and the surface

hydroxide groups of the sorbent,[26,27] that is outer-sphere coordination.

Since in organic solvents neutral metal chelates are present as OC,[11] the chromatographic process being considered can be regarded as a characteristic ligand exchange of the outer-sphere molecules of organic solvents with the surface groups of the sorbent.

The concepts of OC formation can also be used in the extraction chromatography of anionic metal complexes,[90,230] as in the case of anion-exchange extraction.[19] The formation of outer-sphere compounds of anionic chloro-complexes of iron(III), copper, cobalt, and other elements in the trioctylamine in toluene—Fluoroplast system has made possible the selective concentration of micro-quantities of these elements. They were determined with a detection limit of 10^{-6}–2×10^{-5}% by flame atomic absorption or emission spectroscopy.[231] The use of high-pressure liquid chromatography for complex analytical purposes has been examined.[232]

7. Outer-Sphere Complexes in Organic Analysis

The electron-donor or electron-acceptor properties of the molecules or ions of organic compounds make it possible to attach them as outer-sphere species to coordinatively saturated metal complexes to give OC used as analytical forms. Since the organic compounds considered here have an anionic or cationic function in solution, the pH must be selected to obtain OC. For analytical purposes, use is generally made of the low solubility of OC in water, or their ability to be extracted into an organic solvent. The actual determination is carried out by titrimetric, photometric, atomic absorption, radiometric, and other methods. An example is the determination of aliphatic and aromatic sulphonates.[233]

The outer-sphere compounds of iron(II) chelates with heterocyclic diamines and alkyl sulphates have been used for the sensitive determination of small quantities of these outer-sphere anions.[234] Even greater sensitivity and variety are shown by methods for the extraction-atomic absorption determination of organic substances with an anionic function, such as sulphonates, aminoacids, carboxylic acids, antibiotics, and other compounds from the atomic absorption by copper(II), cobalt(II), cadmium, and nickel[35] in the coordinating centre of the OC.

Various organic compounds with a cationic function can be determined as OC containing anionic inner-sphere metal complexes. OC of this kind are formed in the detection of xanthene dyes by precipitating their cations with $SbCl_6^-$, $AuBr_4^-$, and other anionic complexes; in the detection by extraction of higher aliphatic acids in paraffin wax and vaseline from the formation of coloured compounds of $[UO_2(RCOO)_3]^-$ with the cations of basic dyes;[235] and in the identification of biotin by the reaction with PtI_6^{2-}, of thiamine and Vitamin B with $HgCl_4^{2-}$, of the hexamethonium cation with CdI_4^{2-} and other similar compounds.[33] The low solubility of complexes of $[Cr(SCN)_4(NH_3)_2]^-$ with outer-sphere cations has been used to detect pyridostigmine and carbocholine,[33] and also in the photometric determination of aniline, betaine, brucine, caffeine, morphine, pilocarpine, and other compounds as the corresponding OC, dissolved in acetone after precipitation and filtration.[34] It is more convenient to carry out the extraction-photometric determination of various amines as their OC with $Co(SCN)_4^{2-}$.[34] The quantitative determination of alkaloids, aminoquinoline, cationic surfactants, and other organic compounds of similar character by atomic absorption after extraction of their OC with Reinecke's salt or $Co(SCN)_4^{2-}$ appears promising.[35]

In some specific cases the method of analysis in the final stage may be simpler, for example titrimetry in the determination of thiamine as its OC with BiI_4^-.[236] The outer-sphere coordination of alcohols by vanadium(V) 8-quinolinolate in chloroform or benzene has been used for their photometric determination.[34] Down to 2 μg of albumin can be determined by making use of its ability to lower the catalytic activity of $[Co(NH_3)_4(H_2O)_2]_2(SO_4)_3$ in the chemiluminescent reaction of luminol with hydrogen peroxide.[237]

8. Outer-Sphere Complexes in Aqueous-Organic Solutions

Aqueous-organic solvents are binary systems which have complex compositions and in which the influence on the solute is complex.[56] In aqueous-organic solutions, metal aquo-ions can hold various outer-sphere ligands more firmly than in water, as a result of hydrogen bonding, and this is of considerable importance for analytical practice.[39,40,44,238,239] In some cases the selection of the metal aquo-ions acting as the coordinating centre of the OC can be based on the concept of localised hydrolysis.[44,238,239] From general considerations,[8] superposition of the effects of outer-sphere and inner-sphere coordination is possible in this case, but this does not influence the analytical results achieved.

The formation of outer-sphere complexes by metal aquo-ions with anionic ligands in aqueous-organic solutions is used to mask interfering reactions, in the indirect photometric determination of sulphates,[239] sulphites, and hydrogen phosphates,[240] and, most effectively, in indicator spectrophotometric titration.[42,241,242]

The masking of the reaction of barium with bis(azo)-derivatives of chromotropic acid as a result of the formation of stable OC $[Ba(OH_2)_6]SO_4$ [239] in aqueous acetone and aqueous ethanol solutions can be used to improve the selectivity of the photometric determination of the alkaline earth metals.[243] The same method is used to mask barium in the photometric determination of strontium in barium salts.[244] The formation of OC of this type is particular widely used in methods for the indirect photometric determination of sulphates,[245,246] in their spectrophotometric titration,[247–249] and also in the indicator spectrophotometric titration of mixtures of microgram quantities of barium and strontium.[250] The high rate of formation of these OC makes the corresponding reactions suitable for the sensitive automatic determination of sulphates. The productivity of this analysis reaches 60 specimens per hour,[45] and the information efficiency is very high, 433 byte h^{-1}.[239]

Outer-sphere complexes of similar type, formed by barium aquo-ions in aqueous-organic solutions, can also apparently contain the structural analogues of sulphate ions—selenate, chromate, molybdate, fluoroberyllate, and other complex anions of elements of groups IV–VI. This makes possible the selective spectrophotometric titration of micro-quantities of these elements by barium salts in aqueous acetone and aqueous acetonitrile solutions.[241,251–255]

The formation of neutral OC by barium aquo-ions with the anions of various aromatic sulphonic acids, aliphatic sulphonates, and sulphates in aqueous acetone solutions opens up extensive possibilities for the determination of organic compounds containing the corresponding functional groups, by indicator spectrophotometric titration with barium salts.[39,42,44] Of particular interest are methods for the selective determination of various sulphonates of the benzene,[256] naphthalene,[238,257–259] and anthraquinone[260] series, which also make it possible to analyse mixtures of sulphates with any sulphonates, and the mixtures of isomeric products obtained in industrial processes, and this is of considerable

practical importance.[42] Sensitivity and selectivity are also shown by similar methods for determining alkyl and alkylaryl sulphonates and alkyl sulphates,[261,262] and also substances containing a thiol group, for example cystine, cysteine, Captax, and others, after their oxidation to sulphonates by hydrogen peroxide in an alkaline medium.[263] Aromatic sulphonates can be titrated without interference from sulphate ions using solutions of potassium salts in aqueous acetone,[264] where the formation of neutral OC by aquo-ions of potassium with the sulphonates is possible. The aquo-ions of other alkaline earth metals can be used to determine alkyl phosphates, aryl arsenates, and carboxylates by this method.[265]

The solvated potassium ion can undergo outer-sphere coordination with various polyatomic and complex anions in aqueous dimethyl sulphoxide solutions.[40,43,266] This has been shown by spectroscopic and polarographic studies of fluorocomplexes of group V elements.[41] In general, the formation of OC of this type is related to the characteristic features of the behaviour of the dimethyl sulphoxide molecule in the solvate layer of the potassium ion. The coordination of the dimethyl sulphoxide molecule to metal ions through the oxygen atom leads to an increase in the strength of the $S^+ \rightarrow O^-$ σ-bond and to slight polarisation of this bond. This increases the ability of the coordinated dimethyl sulphoxide molecules to undergo ion–dipole interaction with outer-sphere anionic ligands, and leads to the formation of relatively stable outer-sphere associates, suitable for titrimetric determinations.

The materials determined by spectrophotometric titration with potassium salts in aqueous dimethyl sulphoxide solutions are outer-sphere ligands consisting of the anionic fluorocomplexes of the elements of groups III,[266,268–270] IV,[271] and V[41,272–274] of the periodic system, perrhenates,[275] chlorates, perchlorates,[276] chloro-complexes of palladium(II), platinum(IV),[43,277] and ruthenium(IV),[267] and other polyatomic anions.[242]

The methods developed are highly selective in the analysis of mixtures of elements with similar properties, for example tantalum and niobium,[272,273] uranium and thorium,[270] and palladium and platinum,[43,277] for the determination of chlorates and perchlorates,[276] and in other cases.[242] The absence of interference from hydrolysis, hydrolytic polymerisation, and masking reagents makes these methods convenient in practice. These methods have found practical application in the analysis of minerals,[254] glasses,[253] alloys,[43,268,271] fertilisers,[269] electroplating bath electrolytes,[266] and other materials.[248,274]

The use of OC formation in spectrophotometric titration is illustrated in Table 2.

IV. SUMMARY

The material presented indicates the intensive development of the application of OC in various fields of present-day analytical chemistry, associated with their flexibility and variety in the production of appropriate analytical signals. The achievements have been most significant in the development of new sensitive and selective methods of analysis associated with the direct use of OC or the reactions involved in their formation. Examples are provided by interesting applications in analytical concentration, extraction-photometric and extraction-fluorimetric methods, ionometry, titrimetry in aqueous organic solutions, and ligand-exchange chromatography. The further development of the analytical applications of OC should lead to new methods for determining elements and organic compounds, showing a high selectivity combined with the necessary sensitivity. These may be, for example, original photometric and fluorimetric methods, ion-selective electrodes for doubly-charged anionic complexes of elements and organic ionophores, methods for the spectrophotometric titration of elements as anionic pseudohalide complexes, "fine" effects of separation in ligand-exchange chromatography, and new methods for the automatic analysis of solutions.

A characteristic feature of the present state of the analytical chemistry of OC is the practical absence of, and hence urgent need for, quantitative data on the stability of these compounds; this is to a considerable extent preventing the possible achievement of maximum pragmatic effects in the development of new methods. The problem of estimating the contribution of outer-sphere interaction to complex-formation equilibrium in labile analytical systems, particularly in aqueous-organic solutions, is most complex. Further studies in this field should apparently find an adequate solution.

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