THE ANALYTICAL CHEMISTRY OF MIXED LIGAND COMPLEXES

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ABSTRACT

Mixed ligand complexes are characterized by their extreme stability. The chemical individuality of the central atom displays itself clearly, and peculiarities in extractions with organic solvents may be observed. Such properties open new routes to the solution of various theoretical and practical problems in analytical chemistry; true mechanisms and kinetics of analytical reactions can be elucidated and the selectivity and sensitivity of analytical methods can be improved.

The process of complex formation and the properties of mixed complex compounds containing inorganic ligands are considered with reference to the platinum group elements. The formation of mixed complexes containing organic and inorganic ligands sometimes determines the mechanism of the analytical reaction and the composition of the end product; examples of such interaction are given. The sensitivity and selectivity of analytical methods can be improved by means of the formation of complex compounds of the ion-associate type, and unusual methods of separation and group concentration can be achieved. The study of mixed chelates has developed in two directions: (a) studies of improved extractability (synergy), and coextraction of elements as mixed chelates; and (b) studies of changes in the physicochemical properties of systems, *e.g.* absorbance and fluorescence. Various new analytical procedures are discussed.

INTRODUCTION

Developments in the field of coordination chemistry, which is closely bound up with the study of mixed and mixed polynuclear complexes, have been very extensive in recent years. A study of mixed ligand complex formation is of extreme interest to analytical chemists for the following reasons.

1. Mixed ligand complexes are the most general and probable form of existence of the elements in solution. 2. Studies of mixed ligand complex formation make it possible to estimate the characteristics of the intermediate and final forms of the complexes, and therefore to comprehend the mechanism and kinetics of analytical reactions. 3. Certain peculiarities of elements, which are most pronounced in mixed ligand complexes, as well as the physical phenomena accompanying the process of mixed ligand complex formation, open new prospects for the development of selective and sensitive methods for the determination, separation and concentration of elements. The quantitative

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evaluation of these physical phenomena enables solution of the problems of the composition and stability of mixed ligand complexes. 4. The processes of mixed ligand complex formation are closely bound up with one of the most challenging problems in modern analytical chemistry—the problem of extraction.

Hence it becomes clear why the number of publications on the experimental study, theoretical generalization and practical use of mixed ligand complexes increases at such speed.

At the present time there is a large number of physicochemical methods for the identification of mixed ligand complexes in solutions. These are spectroscopic methods, such as electron absorption spectra, Raman spectra, electron paramagnetic resonance spectra, Mössbauer spectra and fluorescence spectra. In addition, electrochemical methods, such as potentiometric, conductometric and high-frequency titrations, polarography and high-voltage ionic electrophoresis find general application; refractometry and measurements of the solution viscosity are also used. The absorption spectroscopic and electron paramagnetic resonance methods should be considered as the most reliable. These methods are used not only for the qualitative detection of mixed ligand complexes in solution, but also for the quantitative study of their formation, composition and stability.

Many of the factors that control the processes of mixed ligand complex formation, and determine the composition and stability of mixed ligand complexes, have already been established. Such factors as the electronic structure of the central atom and its coordination number, the donor nature of ligands and the mutual effect of ligands in a mixed ligand complex, the geometric structure of the complex and the coordination equilibria in solutions of mixed ligand complexes, have been studied for a large number of examples. The theoretical studies of these factors and their generalization from the viewpoints of polarization theory[1, 2], charge neutralization[3] and asymmetry of the ligand field[4], have made it possible to choose the most suitable ligands and to predict the probability of formation and the properties of mixed ligand complexes.

However, the complexity of this field of coordination chemistry still perplexes many chemists, and various theoretical problems, as well as practical problems closely connected with them, have not yet been solved. For example, investigations in the thermodynamics of mixed ligand complexes have been limited to data on the values of isobaric potential, which shows only the general direction of the mixed ligand complex formation. There are practically no data on the change of entropy and enthalpy values during the formation of mixed ligand complexes and these are the values that reflect changes in the nature of the metal–ligand bond when one turns from simple to mixed compounds (ΔH), as well as various structural changes in solutions and various configuration equilibria (ΔS). The reasons for the extreme stability of mixed ligand complexes as compared with simple complexes would be much more readily explained if every step of the mixed ligand complex formation could be characterized by the complete thermodynamic functions. Unfortunately, at present this question is being solved only by the ratio of stepwise stability constants. It is not yet possible to describe with sufficient certainty, the mechanism of extraction of metal chelates with neutral donors, or to elucidate fully their composition, because reliable data on the interaction of a chelating

agent (HA) with neutral donors (B) (HAB, HAB_2, H_2A_2B, etc.) or with the solvent molecules are not always available. The extraction of a metal with two chelating agents or with the participation of two neutral donors seems to be a very interesting but not sufficiently studied problem, as well as the problem of metal coextraction as mixed polynuclear complexes. Little is as yet known about the thermal stability of mixed chelates, etc.

In this paper, attention is drawn to a number of questions in analytical chemistry which are directly connected with the problem of mixed ligand complex formation in solutions.

PRINCIPAL PROPERTIES OF MIXED LIGAND COMPLEXES

The properties of mixed ligand complexes which determine their use in analytical chemistry are the cause of many phenomena which are of particular importance in analytical chemistry.

Enhancement of chemical individuality of similar elements

The coordination number of the central atom displays itself most perfectly in mixed ligand complexes, and thus the chemical individuality of the central atom is revealed most strikingly. New and selective methods for separating elements of similar properties, such as rare-earth and transuranium elements, metals of the platinum group, zirconium and hafnium and others, have been based on the formation of mixed ligand complexes.

The tendency of the rare-earth elements to show higher coordination numbers, and the nature of the splitting of the $4f$ level in the fields of symmetry created by different ligands, favour the enhancement of the chemical individuality of elements of this group in mixed ligand complexes. Of a large number of the rare earth elements in the mixed ligand Me—1, 10-phenanthroline—dibenzoylmethane complex, only europium and samarium exhibit
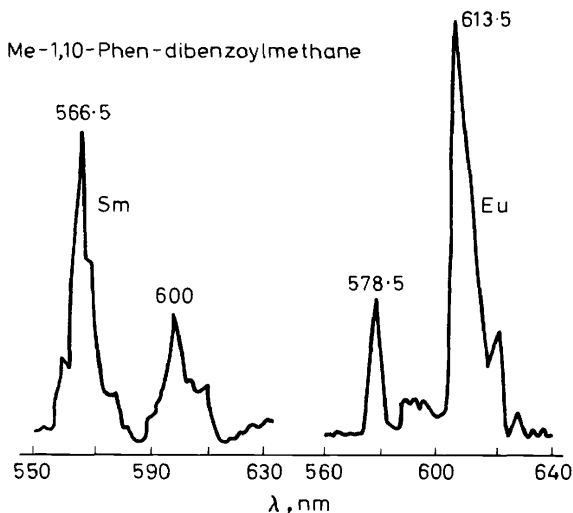

Figure 1. Fluorescence spectra of the mixed ligand Me—1,10-phenanthroline—dibenzoylmethane complexes[5]

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fluorescence when they are excited by ultraviolet radiation of long wavelength from a mercury tube at 365 nm; and their fluorescence spectra (*Figure 1*) are essentially different[5]. Insofar as the central atom in the complexes of the rare-earth elements is excited because of migration of energy absorbed by the organic part of the molecule, the correct choice of ligands in mixed complexes contributes to an increase in the reaction sensitivity. Mixed complexes of europium and samarium with β-diketones and heterocyclic nitrogen-containing bases (thenoyltrifluoroacetone and collidine) exhibit the brightest fluorescence and have been used for the determination of europium(III) oxide and samarium-(III) oxide (with a sensitivity of 10^{-4} and 10^{-3}% respectively) in a mixture of the rare-earth oxides[6].

Elimination of interfering side-reactions

Hydrolysis and polymerization reactions can be eliminated or considerably hampered by the influence of secondary ligands on the vacant coordination sites of the central atom and by the formation of mixed complexes. A large number of examples is known where the formation of a mixed ligand complex shifts the hydrolysis of an element to a more alkaline area. Moreover, the very shift of the hydrolysis into the alkaline area can be used in a number of cases for identification of the formation of a mixed ligand complex[7, 8].
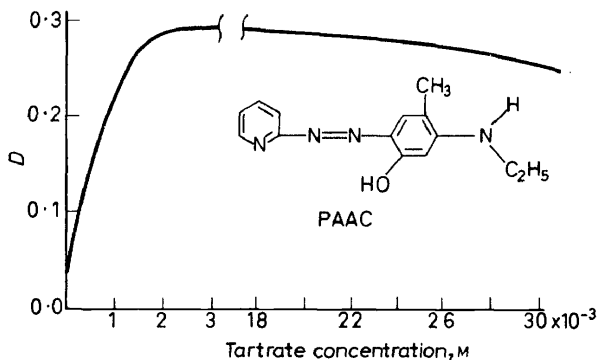

Figure 2. Dependence of the optical density of a solution of the niobium—5-(2-pyridylazo)-2-monoethylamino-*p*-cresol complex on the ammonium tartrate concentration[9]

The properties of many transition metals in solution are determined by the kinetic inertness of their aquo-complexes and by the stability of their poly-nuclear compounds. The reaction capacity of such elements increases in the presence of complexing ligands: the nature of the complexing reagent and its concentration determine the yield of the analytical reaction, and the complex-ing reagent may itself appear in the reaction end-product which then has the nature of a mixed ligand complex. Thus, for example, it has been shown[9] that niobium interacts with 5-(2-pyridylazo)-2-monoethylamino-*p*-cresol to form a coloured compound only in the presence of tartrate ions and that the absorb-ance of the complex depends on the tartrate concentration (*Figure 2*).

The end-product of the reaction of niobium with 5-[2-(3,5-dibromopyr-idyl)azo]-2-monoethylamino-*p*-cresol in the presence of tartrate ions, which
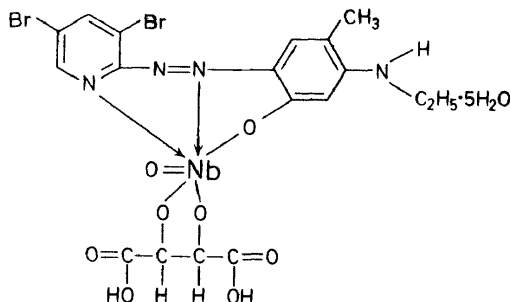
Figure 3. Product of the reaction between niobium and 5-[2-(3,5-dibromopyridyl)azo]-2-monoethylamino-p-cresol in the presence of tartrate ions[9]

has been separated in the solid state, is a mixed ligand complex with the structure shown in *Figure 3*. The interaction of niobium and tantalum with 1-(2-pyridylazo)-resorcinol (PAR) depends on the nature of the complexing reagent; the tantalum—PAR compound formed in the presence of citrate ions is extracted most readily (*Figure 4*)[10].
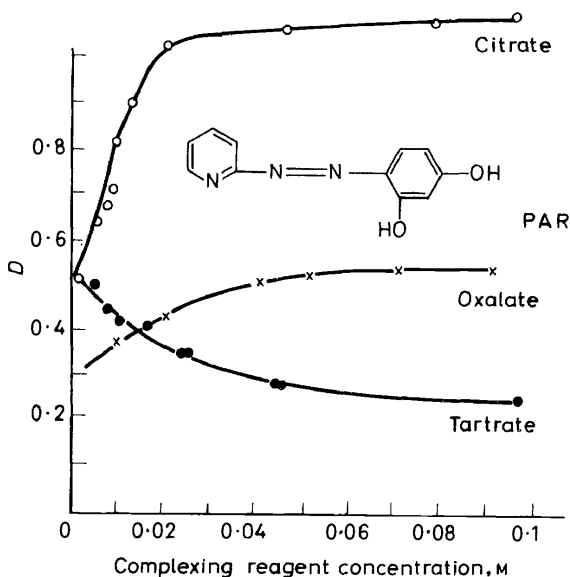

Figure 4. Effect of the salts of organic acids on the formation of the tantalum complex with 1-(2-pyridylazo)-resorcinol[10]

A similar phenomenon is observed in the extraction of the indium compound with 1-(2-pyridylazo)-naphthol in the presence of acetate ions, which form a part of the extracted compound (*Figure 5*).

There are several other examples in which an anion from the electrolyte of the medium enters into the composition of the end-product of the analytical
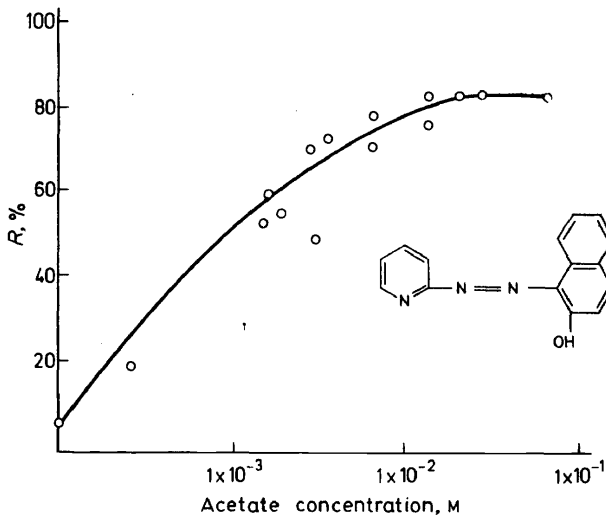
Figure 5. Dependence of the extraction of indium with 1-(2-pyridylazo)-naphthol on the acetate concentration[11]

reaction: the interaction of palladium(II) with ethylenediaminetetraacetic acid (EDTA) in a chloride medium with the formation of a mixed palladium— EDTA–chloride complex; the interaction of palladium(II) with thiourea in the presence of chloride, bromide or thiocyanate ions with the formation of mixed $[PdX_{4-n}Thio_n]^{2-n}$ (X = Cl⁻, Br⁻, SCN⁻) complexes[12, 13]; and the interaction of germanium(IV) with eriochrome or lumogallion in the presence of phosphoric acid[14] with the formation of a mixed ligand complex of the structure shown in *Figure 6*.
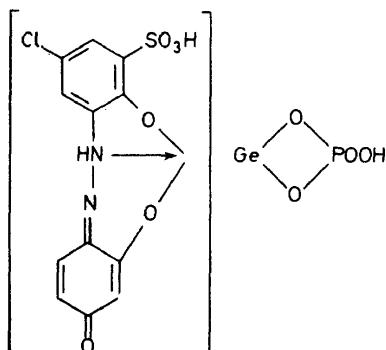

Figure 6. Mixed ligand complex of germanium(IV) with lumogallion in the presence of phosphoric acid[14]

It should be noted that such reactions as masking, or producing certain pH and ionic strength values by means of various buffer solutions and salts, which are widely used in analytical chemistry, may be followed by the formation of mixed ligand complexes. Analytical chemists rarely pay proper attention to

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this aspect when the mechanism of analytical reactions is discussed. It has been suggested that during the spectrophotometric determination of niobium with 1-(2-pyridylazo)-resorcinol in the presence of EDTA as a masking agent a mixed niobium–1-(2-pyridylazo)-resorcinol–EDTA complex is formed[54].

Mixed ligands as intermediates in analytical processes

Many intermediate forms of various chemical processes and active transition states in catalytic and oxidation–reduction reactions are connected with the formation of mixed ligand complexes.

It has been suggested[15] that an intermediate mixed electrochemically active $[Co (NH_3)_5Fe(CN)_6]$ complex is formed on the reduction of cobalt(III) in the presence of large amounts of hexacyanoferrate(III). The reduction of $(NH_3)_5CoSCN^+$ by hexaaquochromium(II) proceeds with the formation of an intermediate active binuclear mixed complex (*Figure 7*)[16].
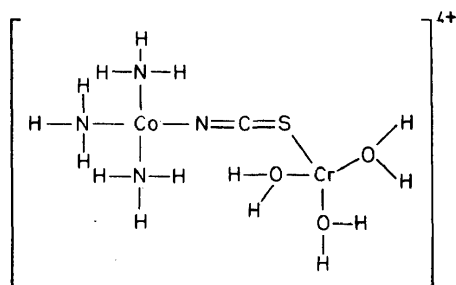

Figure 7. Intermediate active binuclear complex of cobalt and chromium[16]

Mixed complexes also play an important part in ligand exchange[17] and dissociation processes. The formation of mixed ligand complexes in catalytic reactions is probably a much more general phenomenon than is at present supposed.

Stabilization of oxidation states

The ability of mixed ligand complexes to stabilize the oxidation state of a central atom which is unstable under certain conditions is well known. For example, in compounds of the structure shown in *Figure 8*[18, 19] the unstable cobalt(III) and manganese(III) states are stabilized. The complex compound of
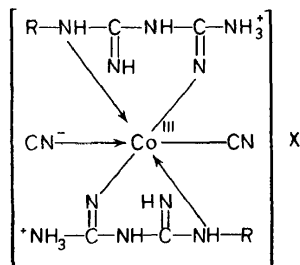

Figure 8. Mixed ligand cobalt(III) complex with diguanidine and cyanide ions[18]

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iron(II) with dimethylglyoxime, [Fe(DMG)$_2$], is unstable even in the absence of oxygen, but it is stable for a long time in the mixed ligand complex Fe(DMG)$_2$(base)$_2$[20].

In addition mixed ligand complex formation sometimes produces the most favourable conditions for a change in valence state of an element. For example, cobalt(II) is stable to oxidation in the bis-(dimethylglyoxime)thiocyanate complex, [Co(DMG)$_2$ (SCN)$_2$]$^{2-}$, in the hydroxo-bis-(dimethylglyoxime)-cobalt complex it is readily oxidized to cobalt(III)[21].

Synergy with mixed ligand complexes

An increased extraction of elements (positive synergy) is observed in mixed ligand complexes formed by unsaturated chelates with neutral donors. This phenomenon is at present successfully used in analytical chemistry for solving important practical problems in the isolation and separation of elements. Recently, new data have been described[22] on the synergic extraction of scandium 2-thenoyltrifluoroacetonate in the presence of tributyl phosphate (*Figure 9*), which is due to the formation of a mixed ligand complex.
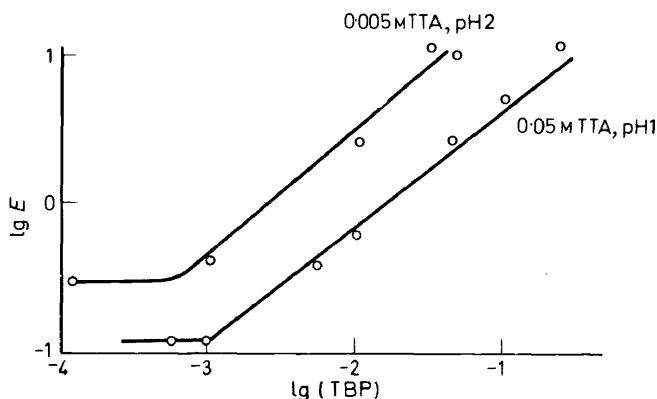

Figure 9. Extraction of scandium 2-thenoyltrifluoroacetonate as a function of the tributyl phosphate concentration in benzene[22]

USE OF MIXED LIGAND COMPLEXES IN ANALYTICAL CHEMISTRY

The specific characteristics of elements in mixed ligand complexes have led to the development of a number of trends in analytical chemistry.

The use of triple complexes

The use of ion associates (triple complexes) in analytical chemistry has become much more frequent in recent years. There are wide possibilities of forming compounds of the ion associate type of various compositions, and the possibilities for their practical application are numerous. A large number of studies on ion associates has been made by Belcher, West, Zigler, Spacu, Babko, Tananaiko, Zhivopistsev, Busev and others.

The reactions in which ion associates are formed may exhibit higher sensitivity than those with the most sensitive organic reagents. This can be seen from a comparison of the molar extinction coefficients of the solutions of Me— 1,10-phenanthroline—Rose Bengal Extra (where Me = Mn, Cu, Cd, Ni, etc) ion associates with the respective metal dithizonates (*Figure 10*)[23].
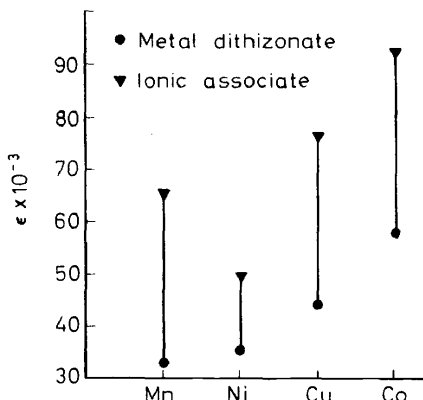

Figure 10. Molar extinction coefficients of solutions of Me—1,10-phenanthroline—Rose Bengal Extra ion associates with metal dithizonates[23]

The sharp increase of the molar extinction coefficient on the formation of the mixed ligand complex of niobium with pyrrolidinedithiocarbamate (PDTC) and pyrocatechol (PC)[24] is shown in *Figure 11*.

Solvent extraction methods should be considered the most suitable for the determination of small and ultra-small amounts of impurities in highly pure
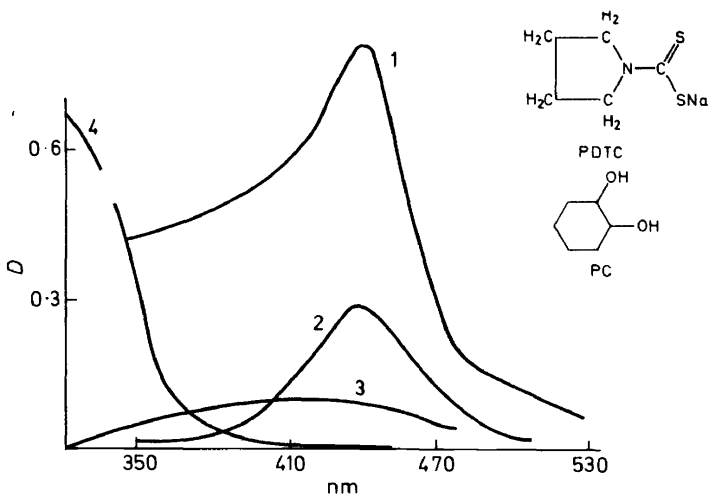

Figure 11. Absorption spectra of niobium complexes[24]. 1: Nb–PDTC–PC (chloroform); 2: Nb–PDTC (chloroform); 3: Nb–PC (water); 4: reference solution (a solution of the reagent mixture in chloroform)

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substances; these methods permit the simultaneous separation and concentration of large groups of elements for their subsequent physicochemical determination. The extraction separation of elements as mixed ligand complexes of the ion associate type formed by the anions of acido complexes and the cations of organic bases, depends on the difference in the complexing capacity of elements with respect to acido ligands (Cl^-, Br^-, I^-, SNC^-, CN^-). These differences are observed even for elements of similar properties and form the basis of selective methods for their separation. From this point of view the reagents of the pyrazolone class seem to be most promising. Thus, microamounts of about 20 elements such as iron, cobalt, copper, zinc, molybdenum, tungsten, tin, titanium, zirconium, hafnium, scandium, uranium, mercury, gallium, indium and others, can be extracted with diantipyrinylmethane in the presence of thiocyanate ions from highly pure salts of elements which are not extracted under appropriate conditions (salts of aluminium, nickel, chromium, beryllium, manganese, alkali and alkaline-earth metals). Microamounts of tin, zinc, cadmium, bismuth and antimony can be extracted from chloride media, and microamounts of scandium, hafnium and bismuth from nitrate media[25]. Hexyldiantipyrinylmethane permits a rapid separation of zirconium from thorium, uranium, scandium, yttrium and the rare-earth elements; in 8–10 M hydrochloric acid, zirconium and hafnium are extracted with this reagent into dichloroethane and chloroform and many other elements including elements of the scandium subgroup and the rare-earth elements remain in the aqueous phase[26]. The most selective method for the determination of thorium of those known at present has been developed with the use of methyldiantipyrinylmethane[27], etc.

In the formation of mixed complexes of the ion associate type, very interesting properties are exhibited by the thiocyanate complexes $[Me(SCN)_n]^{(m-n)}\delta$. The absorption bands of such mixed ligand complexes are charge transfer bands and have very high molar extinction coefficients. For example, the niobium—pyrrolidinedithiocarbamate—thiocyanate complex has $\varepsilon_M = 36000$ (ref. 28). The variety of compounds used for the separation and extraction-photometric determination of elements as mixed ligand complexes of the ion associate type is continuously widening. Among recent systems, the extraction of metals as ion associates of their positively charged chelates (with 1,10-phenanthroline or 2,2′-bipyridine) with anions of organic acids[29] should be mentioned. The use of coloured positively charged iron(II) complexes or 1,10-phenanthroline makes it possible[30] to carry out the extraction and photometric determination of colourless anions such as CdI_4^{2-}. A large number of dyes, in particular anabasine dyes, luminescent dyes and others, can be used for similar purposes[31, 32]. Several papers have dealt with the study of aliphatic and heterocyclic amines as organic bases[33, 34]. The variety of the available so-called 'onium' bases has been widened, and bases such as $R(CH_3)_4^+$ (ammonium, phosphonium, arsonium, stibonium), $R(CH_3)_3^+$ (sulphonium, telluronium), $[(C_6H_5)_4M]^+$ (tetraphenylarsonium, tetraphenylstibonium), etc., have been examined[35]. The determination of 10^{-6} per cent of tantalum in a sample of niobium pentoxide irradiated by neutrons has been carried out in our laboratory by the extraction of the $[(C_6H_5)_4As]\, TaF_6$ ion associate complex[36].

Studies of the behaviour of ion associates in non-aqueous media are being carried out at present. Such investigations, which have been recently begun by

Busev, will undoubtedly lead to results of considerable theoretical and practical interest[37, 38].

Mixed complexes containing three different ligands are now also known, e.g., the vanadium (V)—salicylate—fluoride—quinine complex[39]. However the number of such complexes is still small, and little is known about their analytical use.

Mixed ligand formation involving new compounds

In some cases, the formation of the mixed ligand complex is accompanied by the formation of a qualitatively new compound in the solution and by changes in the physicochemical properties of the system; these changes can be used for the detection and determination of one of the reacting components. The change in the optical characteristics of solutions on the interaction of such anions as fluoride, cyanide, phosphate, arsenate, sulphate, etc., with the so-called indicator systems, e.g. the iron complexes of thiocyanate, the titanium complexes of hydrogen peroxide, and the complexes of zirconium, thorium, cerium(III), lanthanum and praseodymium with a number of organic reagents, is due to the inhibiting action of the above anions and the formation of mixed complexes[40].

In this connection, the studies made by Belcher and West in 1959 should be noted. They found that on the interaction of fluorine ions with solutions containing the chelate of cerium(III), lanthanum or praseodymium with alizarin-complexan (alizarin fluorine blue), a mixed compound containing fluoride (*Figure 12*), with individual optical characteristics, is formed. The reaction is highly sensitive and selective for fluoride[41].
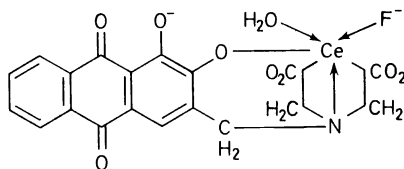

Figure 12. Suggested composition of cerium(III)—alizarin fluorine blue—fluoride[41]

The reaction of fluoride ions with the iron complex of xylenol orange proceeds similarly at pH 4. The optical density of the solution does not decrease, as is usually observed at pH 1, but increases because of the formation of the iron–xylenol orange–fluoride mixed complex[42].

Synergic phenomena with mixed complexes

A particularly interesting trend which has been broadly reflected in analytical chemistry, is the study of mixed complexes formed by coordinately unsaturated chelates with donor molecules (phosphorus-containing organic compounds, heterocyclic bases, carboxylic acids of the fatty series, etc.) The synergy phenomenon, which was first observed by Blake et al.[43] for uranium, has been widely examined by English and Scandinavian chemists (Dyrssen, Irving and others), whose work has laid the foundation of profound theoretical generalizations and also bears a direct relation to the problems of analytical chemistry.

As has been suggested by Irving, synergy is inherent in many elements in different oxidation states; this offers new possibilities of enhancing the chemical individuality of elements and new means of isolation and separation of various elements.

Many synergic phenomena have been observed in solvent extraction. Factors determining the positive and negative effects of synergy have been studied: the nature of the central atom, the nature of the ligands taking part in the formation of the adduct, the mutual effect of chelating and donor ligands, spatial effects, etc. But the complexity of this problem should be particularly emphasized. It should be recognized that many questions remain to be solved, and that the generalizations that have been suggested are not without exceptions[44, 45].

The formation of mixed polynuclear complexes

Another interesting trend is the use of mixed polynuclear compounds in analytical chemistry. The formation of such compounds is a fact which has both advantages and disadvantages in analytical work. The possibility of the formation of this type of compound has been demonstrated for a large number of examples. Polynuclear chelates can be formed by interaction of copper, tiron and triethylenetetraminehexaacetic acid (*Figure 13*). A polynuclear chelate is also formed when titanium(IV) and iron(II) are precipitated by pyridine from sulphuric acid media[47] (*Figure 14*). The possibility of forming a
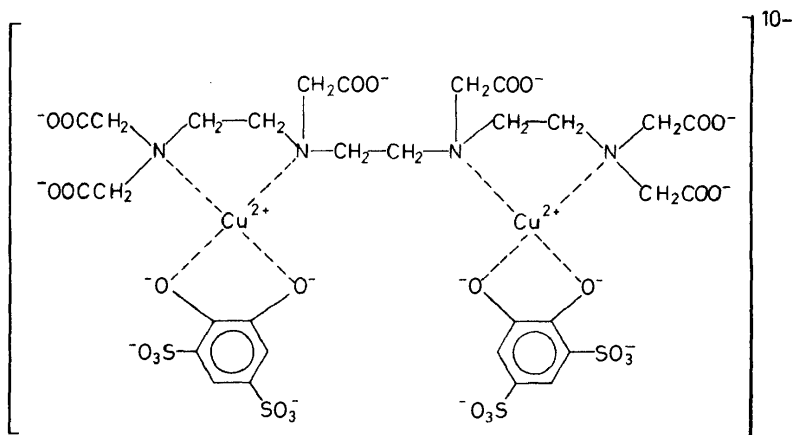

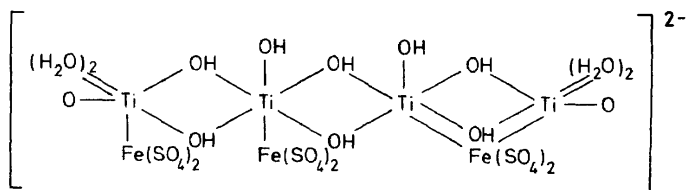*Figure 13.* Mixed polynuclear chelate of copper with triethylene-tetraminehexaacetic acid and tiron[46]

Figure 14. Mixed polynuclear complex of titanium(IV) and iron(II) [47]

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mixed polynuclear complex of the structure shown in *Figure 15* has been demonstrated[48] and many other examples are to be found in the literature.

There is a term 'complex ligand' in modern chemical literature; this signifies a complex particle containing an element which is capable of interacting with the same or another element. For example, complex compounds of salicylaldimine can be considered as bidentate chelating ligands[49] (*Figure 16*). Similarly, the boroalizarin complex (*Figure 17*) may be regarded as a complex ligand; this complex is used for the determination of many elements, as it masks the colour of alizarin S (ref. 17).
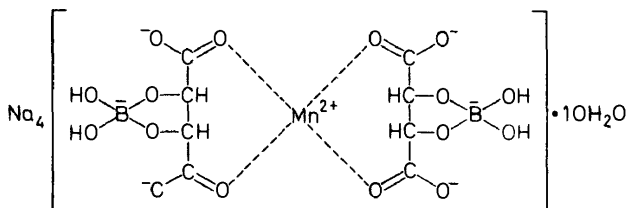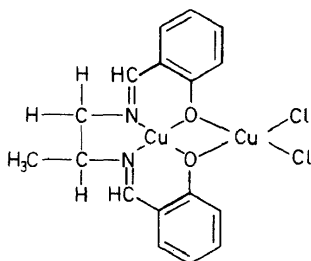

Figure 15. Sodium manganoborotartrate[48]

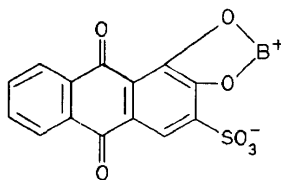Figure 16. Compound containing a bidentate complex ligand–copper(II) salicylaldimine[49]

Figure 17. 'Complex ligand'—a boroalizarin complex[50]

The mechanism and kinetics of the analytical reaction may be determined by the formation of mixed polynuclear forms. Many obscure interferences in analytical processes could be explained by establishing the formation of mixed polynuclear complexes. To such phenomena belongs the formation of inert tartrate polynuclear complexes containing copper and aluminium during the titration of copper by triethylenetetramine in tartrate solutions in the presence of aluminium, which causes low results[51]. A theoretical basis, involving the formation of a mixed polynuclear complex, has recently been provided for the

fact that low results are obtained in the determination of copper(I) as bis-(2,2'-biquinoline)-copper when chromium(III) is present; this is explained by the formation of an inert polynuclear mixed complex containing chromium(III), copper(II) and citrate ion [52]. The structure of such a mixed complex may be represented[52] as shown in *Figure 18*.
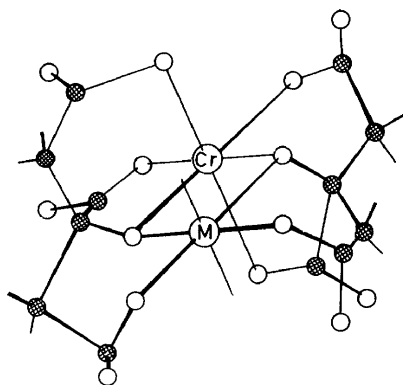

Figure 18. Structure of the mixed polynuclear chromium(III) Me–citrate complex (Me=Cu, Zn, Co, Ni, Fe)[52]

Coextraction phenomena

To all appearance, the phenomenon of coextraction is connected with the problem of mixed ligand complex formation; the nature of the compounds formed on coextraction is not always clear. This phenomenon has now been confirmed by many experiments and is of great practical importance in the chemistry of traces of elements.

Many new data have recently been obtained on the coextraction of chelates, and some of the most interesting of this information is summarized in the following paragraphs.
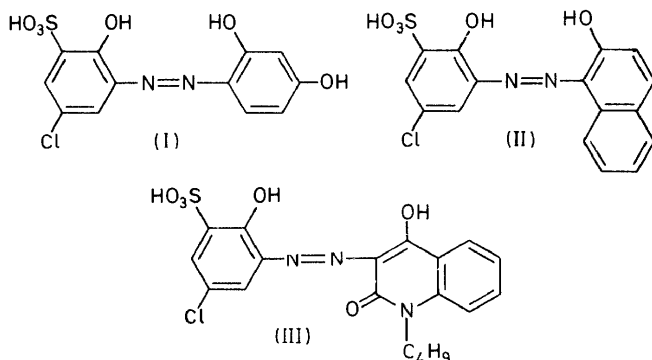

Figure 19. Lumogallion IREA; II: magneson IREA; III: acid monochrome Bordeaux S

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A study has been made in our laboratories, in collaboration with Shakhova, of the coextraction of calcium and strontium with scandium, neodymium and thorium 8-hydroxyquinolinates. The data obtained by electrophoresis of solutions containing calcium, scandium and 8-hydroxyquinoline have proved that calcium enters the cation part of the extracted compound, and scandium the anion part; on this basis the extracted compound can be represented[53] as $CA[Sc(Ox)_4]_2$.
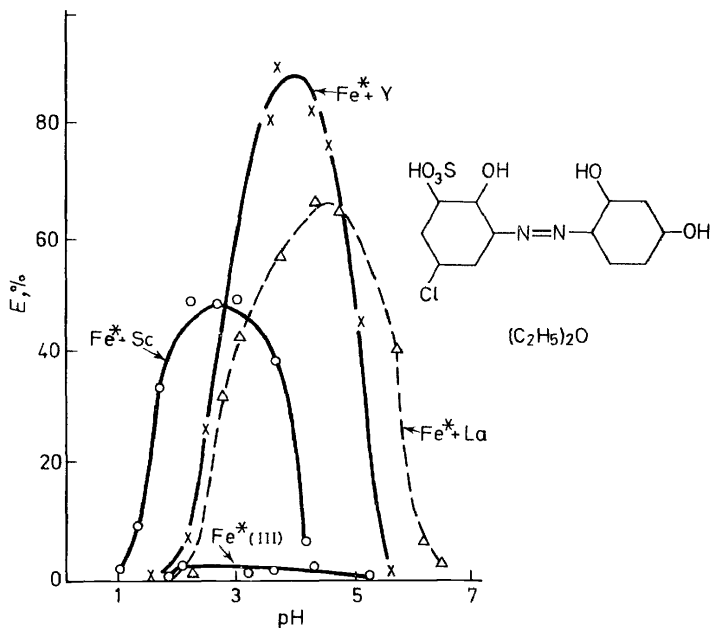

Figure 20. Coextraction of $^{55}Fe(III)$, Sc, Y and La complexes with lumogallion by diethyl ether[55]

The coextraction of scandium with yttrium, the rare-earth elements and iron(III), as well as the coextraction of iron(III) with scandium, yttrium and the rare-earth elements, has recently been observed for the first time during a study of the extraction of the scandium, yttrium, the rare earths and iron(III) chelate compounds with certain o,o'-dihydroxyazo compounds containing the sulpho group. The following o,o'-dihydroxyazo compounds have been applied in studies of the coextraction with the use of radioactive isotopes of elements: lumogallion IREA(I), magneson IREA(II), acid monochrome Bordeaux S(III) (Figure 19). Coextraction is much greater when ethers, in particular diethyl ether, are used as ectracting agents; (Figure 20, 21); it is less pronounced with butanol. Some of the mixed ligand complexes studied have been obtained in a crystalline state; the ratio of Me:Me':R in the mixed complexes has been found to be 1:1:2. It has been established that calcium, beryllium, thorium(IV), gallium, indium, thallium(III) and aluminium do not increase the scandium extraction, probably because of the absence of the mixed ligand complex formation[55].
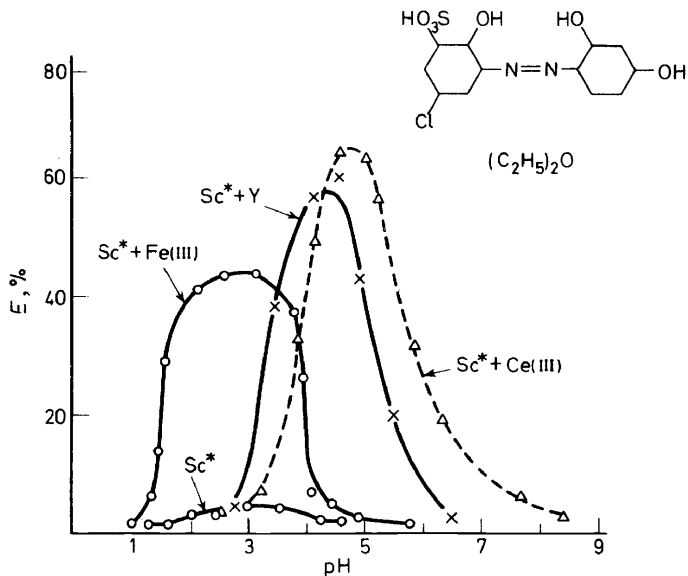
475

Figure 21. Coextraction of ^{46}Sc, Y, Ce and Fe complexes with lumogallion by diethyl ether[55]

CONCLUSION

Only some aspects of the problems of the analytical chemistry of mixed ligand complexes have been outlined. The problem is very wide and complicated, and developments on a large scale are to be expected in the future. Both in the theory and practical application of mixed ligand complexes, there are many questions that still require solution: as the answers are obtained, further interesting facts of the chemistry of mixed ligand complexes will undoubtedly be revealed.

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References

1 T. G. Spiro and D. N. Hume. *J. Am. Chem, Soc.* **83**, 4305 (1961).
2 Y. Marcus and L. Elizer. *J. Phys. Chem.* **66**, 1661 (1962).
3 W. B. Shaap and D. L. McMasters. *J. Am. Chem. Soc.* **83**, 4699 (1961).
4 Ya. D. Fridman and R. A. Veresova. *Zh. Neorg. Khim.* **8**, 344 (1963).
5 E. V. Melentieva, L. I. Kononenko and N. S. Poluektov. *Zh. Neorg. Khim.* **II**, 369 (1966).
6 E. V. Melentieva, N. S. Poluektov, and L. I. Kononenko. *Zh. Analit. Khim.* **22**, 187 (1967).
7 L. C. Thompson and J. A. Loraas, *Inorg. Chem.* **2**, 89 (1963).
8 G. H. Garey and A. E. Martell. *J. Am. Chem. Soc.* **89**, 2859 (1967).
9 S. V. Elinson and L. S. Maltseva. *Zh. Analit. Khim.*, **22**, 79 (1967).
10 I. P. Alimarin and Khan Si-i. *Zh. Analit. Khim.* **18**, 182 (1963).
11 Yu, A. Zolotov, I. V. Seryakova and G. A. Vorobieva. *Talanta* **14**, 737 (1967).
12 V. I. Shlenskaya, A. A. Biryukov and N. G. Shumkova. *Zh. Analit. Khim.* **21**, 702 (1966).

[13] V. I. Shlenskaya, A. A. Biryukov and E. M. Moskovkina. *Zh. Neorg. Khim.* **II**, 600 (1966).
[14] V. A. Nazarenko and G. V. Flyantikova. *Zh. Analit. Khim.* **24**, 1595 (1969).
[15] B. S. Bruk and E. I. Rozenfeld. Zavodsk. Lab. **33**, 395 (1967).
[16] H. Taube. *J. Chem. Educ.* **45**, 452 (1968).
[17] J. D. Carr, K. Torrana, C. J. Cruz and C. N. Reilley. *Analyt. Chem.* **39**, 1358 (1967).
[18] N. R. Sen Gupta and Pr. Ray. *Proceedings of the Symposium on the chemistry of Coordination Compounds*, 1959, p. 162.
[19] M. M. Ray and Pr. Ray. *ibid.* p. 188.
[20] A. K. Babko, P. B. Mikhelson and S. A. Romanenko. *Zh. Neorg. Khim.* **13**, 731 (1968).
[21] K. Burger and I. Ruff. *Acta chem. Acad. sci. Hung.* **41**, 75 (1964); **45**, 77 (1964).
[22] Yu. A. Zolotov, N. V. Shakhova and I. P. Alimarin. *Zh. Analit. Khim.* **23**, 1321 (1968).
[23] B. W. Bailey, R. M. Dagnall and T. S. West. *Talanta* **13**, 753 (1966).
[24] I. M. Gibalo, I. P. Alimarin and G. V. Eremina. *Zh. Analit. Khim.* **23**, 1822 (1968).
[25] V. P. Zhivopistsev, B. I. Petrov, E. A. Selezneva and I. F. Sibiryakov. *Proceedings of the Commission for Analytical Chemistry, USSR Academy of Sciences* **16**, 80 (1968).
[26] V. P. Zhivopistsev and B. I. Petrov. *Transactions of the Perm. State University* **159**, 248 (1966).
[27] V. P. Zhivopistsev and L. P. Pyatosin. *Zh. Analit. Khim.* **22**, 70 (1967).
[28] I. M. Gibalo, I. P. Alimarin and G. V. Eremina. *Doklady Akad. Nauk SSSR* **176**, 1300 (1967).
[29] V. I. Kuznetsov. *The Chemical Foundations of Extraction-Photometric Methods of Analysis.* Gosgeol-tekhizdat, Moscow, 1963.
[30] Kotsuji Keija. *Bull. Chem. Soc. Japan* **38**, 988 (1965).
[31] Sh. T. Talipov and R. Kh. Dzhijanbaeva. *Summary of the report at the All-Union Conference on the use of Organic Reagents in Analytical Chemistry*, Saratov, 1966, p. 60.
[32] I. A. Blyum and N. N. Pavlova. *Zavodsk. Lab.* **29**, 1407 (1963).
[33] S. I. Ivanova, L. M. Gindin and L. Ya. Mironova. *Izv. Akad. Nauk SSSR*, No. 7, vypusk 2, 35 (1964).
[34] V. F. Borbat, P. I. Bobikov and E. F. Kouba. *Zh Analit. Khim.* **20**, 192 (1965).
[35] I. P. Alimarin and S. V. Makarova. *Zh. Analit Khim.* **19**, 90, 564, 847 (1964).
[36] I. P. Alimarin, G. N. Bilimovich and Yu. V. Yakovlev. *Zavodsk. Lab.* **33**, 145 (1967).
[37] V. K. Akimov, A. I. Busev and I. A. Emelianova. *Summaries of the Reports at the Second All-Union Conference on the Analytical Chemistry of Non-Aqueous Solvents and Their Physico-Chemical Properties*, Kharkov, 1968, p. 55.
[38] S. I. Bragina, V. K. Akimov and A. I. Busev, *ibid.*, p. 59.
[39] A. K. Babko, A. I. Volkova and E. Getman. *Doklady Akad. Nauk Ukrainskoi SSR* **5**, 610 (1964).
[40] R. M. Dagnall, M. T. El-Ghamry and T. S. West. *Talanta* **15**, 107 (1968).
[41] R. Belcher, M. A. Leonard and T. S. West, *Talanta* **2**, 92 (1959).
[42] A. K. Babko and M. I. Shtokalo. *Doklady Akad. Nauk Ukrainskoi SSR* **5**, 1077 (1964).
[43] C. A. Blake, C. F. Baes, K. B. Brown, C. F. Coleman and J. C. White, *Proc. Int. Conf. peaceful Uses of Atomic Energy, Geneva*, Vol. 28, 289 (1958).
[44] O. Narvatil and J. Kotas. *Coll. Czech. Chem. Comm.* **30**, 1824 (1965).
[45] L. Genov and G. Georgiev. *Mh. Chem.* **98**, 2214 (1967).
[46] T. A. Bohigian, Jr. and A. E. Martell. *J. Inorg. Nucl. Chem.* **29**, 453 (1967).
[47] Z. Jerman. *Coll. Czech. Chem. Comm.* **32**, 260 (1967).
[48] E. M. Shwarts, A. A. Bernans and A. F. Ievinsh. *Zh. Neorg. Khim.,* **13**, 178 (1968).
[49] S. J. Gruber, C. M. Harris and E. Sinn. *J. Inorg. Nucl. Chem.* **30**, 1805 (1968).
[50] L. S. Serdyuk and L. I. Khatnyuk. *Ukrainskii Khim. Zh.* **28**, 226 (1962).
[51] H. Flaschka, J. Butcher and R. Speights. *Talanta* **8**, 400 (1961).
[52] H. M. N. H. Irving and W. R. Tomlinson. *Talanta* **15**, 1267 (1968).
[53] Yu. A. Zolotov, *Extraction of Chelate Compounds*, Nauka, Moscow, 1968, p. 179.
[54] T. S. West. *Zh. Analit. Khim.* **21**, 913 (1966).
[55] I. P. Alimarin, I. M. Gibalo and A. K. Pigaga. *Doklady Akad. Nauk SSSR* **186**, 1323 (1969).