RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

December 1977

Translated from *Uspekhi Khimii*, **46**, 2105-2138 (1977)

U.D.C. 546.6:546.65

Some Aspects of the Coordination Chemistry of the Lanthanides

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A systematic account is given of data (mainly for the period 1965-1975) on the coordination chemistry of the lanthanides: the synthetic, phsysicochemical, and structural aspects of lanthanide complexes, mainly with organic oxygen- and nitrogen-containing ligands are examined. Attention has been concentrated on the application of the physical and physicochemical research techniques in the chemistry of lanthanide complexes.
The bibliography includes 484 references.

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I. INTRODUCTION

Since the publication of the monograph of Yatsimirskii et al.[1], extensive data have accumulated on the coordination chemistry of the lanthanides, their publication being associated not only with theoretical research but also and mainly with the significant expansion of the applications of the lanthanides and their complexes. During the last 10–12 years, reliable methods have been developed for the isolation of all the lanthanides in a pure state[2,3], which extended the possibility of their practical applications in technology in those cases where the purity of the lanthanides is the main requirement (laser and semiconducting materials, glasses of different kinds, ceramics, etc.)[2]. Coordination compounds of lanthanides in general and chelate complexes in particular are used in liquid media lasers (europium and terbium chelates)[4,5]. Lanthanide complexes are used successfully as chemotherapeutic preparations, including anticancer agents[6], although lanthanides (Ln) are not "metals of life"[7]. The use of lanthanide compounds as paramagnetic shift reagents (PSR) assisted the development of NMR spectroscopy[8-11]. Coordination compounds of the lanthanides are also used in Mössbauer spectroscopy[12-13].

Even a brief list of the advances in the employment of lanthanide complexes in various branches of science and engineering demonstrates the necessity for an account of the achievements of the coordination chemistry of the lanthanides during the last 10 years. At the same time the reviews on PSR already published (see, for example, Refs. 8–11) are concerned to only a very limited extent with this field, which is closely related to lanthanide

complexes. This review is virtually not concerned with the problems of complex formation and extraction of the lanthanides and their analytical chemistry. Despite their urgency, these are too broad for inclusion in this review, which is devoted to advances in the synthesis and the study of the physicochemical properties and structure of lanthanide complexes achieved during the 1965–1975 decade.

II. CHARACTERISTICS OF THE COMPLEX FORMATION REACTIONS

Whereas in the 1950's it was believed that the ability to form complexes is not a characteristic property of the lanthanides, the data which have accumulated during the last two decades created a new chapter in coordination chemistry—the chemistry of lanthanide complexes[14-17].

Certain features of the coordination chemistry of the lanthanides were examined previously by Yatsimirskii[1], Muller[2], Spitsyn and Martynenko[17], and Forsberg[16]. The majority of experimental data on the splitting of the energy levels of the 4*f* electrons of lanthanide ions on complex formation are nowadays interpreted in terms of the parameters of the semiempirical crystal field theory (CFT). The distinctive features of the states of *f* electrons in lanthanide complexes are associated primarily with the fact that they are to a large extent shielded from the ligand theory by the outer *s*, *p*, and *d* electrons and are therefore less subject to its perturbing influence. In those cases the spin–orbital interaction is much more pronounced than for *d* electrons. An unusual version of a weak crystal field therefore arises for *f* electrons, being weaker than the interelectron and spin–orbital interactions[18].

In order to determine the energy states of the lanthanide ion in the crystal field, it is necessary to begin by considering its states with allowance for interelectron and spin–orbital interactions, which are characterised for each state with the given orbital (L) and spin (S) quantum numbers by the additional quantum numbers J of the total momentum operator. The distribution of the electron cloud in compounds with a total momentum J and the splitting of the levels of the latter under the influence of the electrostatic effect of the ligand field must be calculated by methods of perturbation theory or determined qualitatively by methods of group theory[18]. Quantitative calculations of the splittings of the energy states of *f* electrons are performed similarly to those for *d* electrons[19], but attempts to calculate the CFT parameters for lanthanide compounds with a known structure[20] have demonstrated the impossibility of achieving a satisfactory agreement between the non-empirical values of the CFT parameters and the experimental data.

In the 1960's an attempt was made to describe more realistically the nature of the chemical bonds between lanthanide ions and ligands on the basis of the molecular orbital (MC) theory, which makes it possible to take into account the degree of covalence of the bonds under consideration. It is noteworthy that the accuracy of the calculations performed hitherto is low. Nevertheless it is believed to be an established fact[18,21] that a considerable (if not the major) component of the splitting of the energy levels of the 4*f* shell is due to the influence of the overlapping of the 4*f* orbitals of the lanthanide and the ligand orbitals. The overlap integral between the 4*f* orbital of the lanthanide ion and the valence np, ns ligand orbital is an order of magnitude smaller than the overlap integral between the outer vacant orbitals[21]. One may therefore expect that the influence of the overlap of the wave functions of the lanthanide ion and the ligands on the structure of the 4*f* shell is slight.

The influences of the external electrostatic field and the overlap of the 4*f* orbitals with ligand orbitals on the splitting of the energy levels of the 4*f* shell have been compared[20-24]. The *f* electrons shielded by *d* electrons in the lanthanide complexes have been shown to form weak covalent bonds with the ligands. The covalent bonds between lanthanide ions and ligands are formed mainly as a result of the mixing of the occupied ligand orbitals with partially occupied 4*f* orbitals and vacant 6*s*, 6*p*, and 5*d* orbitals of the lanthanide ions. The vacant 6*s*, 6*p*, and 5*d* orbitals are located outside the occupied $5s^2$ and $5p^6$ shells; the pair integrals for the overlap of the orbitals considered with the ligand orbitals are approximately 0.1. Calculations by the MO method in terms of the Wolfsberg–Helmholtz approximation (MWH), for example, for the tetra-acetatoeuropate anion[25], make it possible to infer the properties of the valence shell of the lanthanide. Calculations have been made[25] on the two complex ions $[EuO_8]^-$ and $[EuO_8]^{5-}$ and it was found that the excess charge is concentrated mainly at the oxygen atoms without altering significantly the orbital population of the europium atom. The MO method usually yields a somewhat high covalent contribution to the chemical bond, "equalising" the charges on the atom; nevertheless it can be regarded as established that the charge of the valence shell is quite capable of influencing appreciably the splitting of the energy levels of the 4*f* shell[26].

When the influence of the overlap of the 4*f* orbitals and the valence shell orbitals of the ligand on the splitting of the energy levels of the 4*f* shell is considered within the framework of the LCAO-MO method, it is believed useful[21] to distinguish two effects: the covalent mixing of a partially occupied *f* orbital of the lanthanide ion (f_α) with a fully occupied group orbital of the ligand (Φ_α) and the change in the energy of the molecular orbital of the complex (ψ_α) owing to the overlap of the f_α and Φ_α orbitals. Calculation[26] of the energy of the antibonding orbital taking into account both effects yields values in agreement with the observed experimental splitting.

In terms of the MWH approximation, it is also possible to estimate the relative positions of the energy levels of the 4*f* orbitals as a function of the structure of the coordination polyhedron. In conformity with theory[26], an admixture of covalent bonding in an ionic bond should favour the formation of coordination polyhedra with vertices distributed in the direction of the maxima of the hybrid sp^3d^n orbitals. This requirement is satisfied primarily by the nine-coordination polyhedron with D_{3h} symmetry. Among the polyhedra with a coordination number (C.N.) of 8, the dodecahedron with D_{2d} symmetry, in which the σ bonds are formed via the sp^3d^4 hybrid orbitals, and the square antiprism (D_{4d} symmetry), where the sp^3d^4 or p^3d^5 valence orbitals are hybridised, are preferred. There is also the possibility of a nine-coordination polyhedron with C_{4v} symmetry[27].

Calculations[28] have shown that the contribution of the *f* orbital to a coordinate bond is sometimes very high (between 34.8 and 46.2%) and the difference between the contributions of the *f* and *d* orbitals to the structure of the polyhedra diminishes with increasing atomic number of the element in the series of lanthanides. The relation between the existence of three regions of crystal-chemical instability in the series of lanthanides and the extrema on the energy curves of 4*f* orbitals has been discussed[29]. The first region usually corresponds to Pr, Nd, and Sm, the

second to Gd, and the third to Dy, Ho, and Er. The change in structure in the first region of crystal-chemical instability can be accounted for by a sharp decrease of the energies and effective radii of the 4*f* orbitals, calculated [30] by the Thomas–Fermi method. The possibility of the involvement of heavier lanthanides in bonds formed via *f* orbitals is also postulated [29].

It can be regarded as established that the symmetry of the coordination spheres of lanthanide ions sometimes deviates significantly from that predicted for the purely electrostatic model. The characteristics of the geometry of the ligand the capacity of the coordination sphere for mixing play an important role under these conditions: for example, when solvent molecules or those of some other inorganic or organic ligand are coordinated simultaneously in addition to the primary organic ligand.

The study of the relative geometries of lanthanide complexes has also proved convenient in the application of the MO method in terms of the angular overlap approximation [31]. The method is based on the assertion that the destabilisation of the central atom owing to the formation of covalent bonds is proportional to the square of the angular component of the overlap integral, which depends strongly on the geometry of the complex. Since the bonding orbitals in lanthanide complexes are located mainly at the ligands and the antibonding orbitals at the central atom (c.a.), the antibonding effects assume principal importance in the formation of covalent bonds in lanthanide complexes. Thus there is a possibility of estimating the influence of the antibonding effects on the symmetry of the complex. For lanthanide complexes with the f^0, f^7, and f^{14} electronic configurations, the antibonding effects do not influence the symmetry of the complex, which depends only on the electrostatic metal–ligand interaction.

When the bond between the central atom and the ligand is predominantly ionic, higher coordination numbers, permitted by the relative dimensions of the central atom and the ligand, are preferable (depending on the size of the ligand, coordination numbers of 8–12 and sometimes [14–16] higher are possible for lanthanide compounds); for a given coordination number, the polyhedron with triangular faces is preferable, since it constitutes a closer approximation to the sphere. Thus, whereas for the lanthanides with the f^0, f^7, and f^{14} configurations the symmetry of the complexes depends only on the ion–dipole electrostatic interaction, for the remaining lanthanides complexes having the composition LnL_6, for example, where L is the ligand, are formed comparatively rarely and have the structure of an octahedron and not a trigonal prism (in the latter case, the antibonding effect is a minimum [31]). A detailed consideration [32] has also shown that the antibonding effects for lanthanide complexes with different coordination numbers may determine the fine structure of their coordination polyhedra.

The partly covalent nature of the bond in lanthanide complexes is also to some extent demonstrated by the results of physical measurements: the study of luminescence spectra, absorption spectra in different wavelength ranges [31], Mössbauer spectra [12,22], and the deviation of the symmetry of the complexes revealed by X-ray diffraction analysis from the predictions based on the electrostatic model [18]. The partly covalent nature of the chemical bond in the coordination compounds necessitates the classification of the latter as labile and not as inert complexes. The lability of the lanthanide complexes and the ability of lanthanide ions to form complexes with variable and high coordination numbers create difficulties in the study of coordination compounds of the lanthanides in both the solid state and in solution.

In conclusion yet another interesting feature of the coordination chemistry of the lanthanides must be pointed out. Although the most characteristic oxidation state of the lanthanides is 3+, certain lanthanide ions, namely those of europium(III), ytterbium(III), and samarium(III), exhibit a tendency towards reduction to the bivalent state [33], the europium(III) ion showing the highest electron affinity and being most readily reduced to europium(II). It is thus not fortuitous [34] that europium(II) complexes of *NN*-bis-(1-acetonylethylidene)ethylenediamine have been isolated on a preparative scale.

All the foregoing factors illustrate the complexity and wide variety of the problems involved in the study of the coordination compounds of the lanthanides and demonstrate the necessity for the employment of many methods in the synthesis and physicochemical study of such complexes.

III. SYNTHESIS OF COORDINATION COMPOUNDS

The isolation of individual lanthanide complexes requires a careful selection of solvents and appropriate variation of the molar ratios of the reactants and the pH of the medium. In water, one of the commonest solvents [4,16,17] for the synthesis of coordination compounds of the lanthanides, complexes are formed mainly with weakly basic chelating organic ligands. This conclusion has been confirmed by numerous examples: chelate lanthanide complexes have been formed with complexones [1, 14,35–38], β-diketones [39,40], pyrazolones and their derivatives [41], 8-hydroxyquinoline *N*-oxide [42], as well as complexes of certain monodentate ligands (urea [43], thiourea [44], guanidinium hydrogen carbonates [45]), etc. [1,14,46,47]. As a rule, in addition to the organic ligand, solvent (water) molecules are coordinated at the same time, but complexes without solvent molecules can be isolated from an aqueous medium [48,49].

Similar results can be obtained also in aqueous organic media, since the sequence of solvents in terms of their electron-donating properties relative to the lanthanides ("hard acids") [48] indicates an appreciable stability of the hydrates of lanthanide compounds [50,51]. At the same time anhydrous lanthanide complexes or complexes with a mixed ligand environment can be isolated from aqueous organic media prepared on the basis of oxygen-containing solvents with a higher electron-donating activity than that of water [for example, dimethyl sulphoxide (DMSO) or dimethylformamide (DMF)] [49]. The atomic number of the lanthanide, the nature of the organic solvent, and the component ratio in the water–organic solvent mixture used as a medium for the synthesis of the complexes have a significant influence under these conditions on the composition of the coordination sphere. One of the most suitable media for the synthesis of lanthanide complexes is a water–ethanol mixture in which complexes of lanthanides with complexones [1,6,17] and oxygen-, nitrogen-, and phosphorus-containing ligands [1,14–17,52–55], including tetramethyl sulphoxide [52], salicylidenehydrazine [56], *N*-salicylideneanthranilic acid [54], hexafluoroacetylacetone, 4-methylpyridine [55], chloro-derivatives of *o*-hydroxyacetophenone [58], etc. [1,16,17,49], have been obtained. Crystalline holmium bisdipivaloylmethanate [57] and trisdipivaloylmethanate [58,59], whose existence in solution had been

postulated in an earlier study[60], were synthesised in the same solvent mixture in an alkaline medium from holmium nitrate and dipivaloylmethane.

Table 1. Compositions of lanthanide coordination compounds[72-219].

Formula	L	X, n	References
LnL_nX_3	Pyridine, 1,2-propylenediamine, 2,4,6-tri-α-pyridyl-1,3,5-triazine, thioxane oxide, tetramethylene sulphoxide	X = Cl, NO_3, ClO_4; n = 2—9	72—78
$LnL_6X_3 \cdot nH_2O$	Antipyrine, o-phenanthroline, *NN'*-ethyleneurea, tetramethylurea, 1,3-, and 1,1-dimethylurea	X = Cl, Br, I, ClO_4, NO_3, NCS; n = 0—3	79—84
LnL_6X_3	Urea, *NN*-dialkylamide	X = I, NCS	85—88
$LnL_4X_3 \cdot nH_2O$	Hydrazine, 1,10-phenanthroline, urea, alkylthiourea, dimethylformamide, dimethylacetoacetamide, *NNN'N'*-tetramethylmalonamide	X = Cl, NO_3, SO_4, ReO_4, NCS, ClO_4, C_2O_4; n = 0—2	89—104
LnL_3X_n	Hydrazine, pyridine, glycolate, acetylacetonate, benzoate, propionate, alkylphosphonothioate, dipivaloylmethanate, α-aminoacids, β-diketones, Schiff bases, cyclopentadiene	X = H_2O, EtOH, MeOH; n = 0—4	65—67, 105—141
$LnL_2X_3 \cdot n$Solv	1,10-phenanthroline, 2,2'-bipyridyl, hydrazine, uropropine, antipyrine, α-aminoacids, α-furoin oxime, alkyldiantipyrylmethane, tributyl phosphate, isocyanate	X = Cl, F, I, SO_4, C_2O_4, ClO_4, NO_3, SCN, SeCN; Solv = H_2O, EtOH, MeOH, n = = 0—5	142—154
$LnL_2X \cdot nH_2O$	Dipivaloylmethanate, phthalocyanine, diphthalocyanine	X = Cl, Br; n = 0—2	57—155
$Ln(L)X_m \cdot nH_2O$	4,4'-diamino,3,3'-dimethylbiphenyl, 4,4'-di-pyridylbenzimidazole, α-aminoacids, malonate, butyrate, tartrate, hydroxyethyl iminodiacetate	X = Cl, NO_3; m = = 0—3, n = 1—6	156—169
$LnL \cdot nH_2O$	Ethylenediaminetetra-acetate, nitrilotriacetate, citrate, alkylphosphonate, trimellitate	n = 0—8	170—183
$LnL_3L'_n$	L = β-diketone, chlorosalicylate, 2-hydroxy-3-naphthoate, 2,2,6,6-tetramethylheptane-3,5-dionate; L' = picoline, pyridine, 1,10-phenanthroline, quinoline, triphenylarsine oxide	n = 1,2	184—194
$LnL_3(NO_3)_2(ClO_4)_2$	2,2'-bipyridyl	—	195
$LnL_2X_3 \cdot nH_2O$	1,10-phenanthroline, 4,4'-bipyridyl, 2,2'-bi-pyridyl, tetrahydrofuran, thiourea, triglycine	X = Cl, NO_3, SCN, SeCN, $C_2H_3O_2$; n = = 0—6	196—216
$Ln_2L_3 \cdot nH_2O$	Malonate, picolinate, quinolinate, diethylmalonate, dihydroxymalonate	n = 1—8	217—219

Absolute benzene, which exhibits a weak solvating capacity, is frequently used to synthesise anhydrous lanthanide complexes. However, the low solubility of lanthanide salts in benzene makes it necessary to carry out the synthesis using lanthanide alkoxides. Sparingly soluble chelate complexes of the lanthanides with *o*-hydroxyazomethines have been synthesised in the same solvent[61-64]. Complexes of the lanthanides with Schiff bases can be obtained from the lanthanide chlorides in methanol[65-67].

The method whereby lanthanide complexes are obtained in the absence of solvents is extremely convenient. Comparatively unstable complexes of a series of lanthanides with monodentate acids[1,68-71] and nitrogen-containing ligands[16], for example with organic acids[68-70] and aliphatic heterocyclic amines[1,16], are synthesised by this procedure. However, although we believe it is extremely promising as a method for the preparation of non-solvated lanthanide complexes, it has not so far been adequately used in the coordination chemistry of the lanthanides.

When the molar ratio of the reactants (lanthanide salts and ligands) is varied, it is possible to obtain complexes having different compositions and coordination numbers ranging from 6 to 12 (Table 1).[79-219] It has been shown[220] that, for different reactant ratios (1 : 4, 1 : 5, and 1 : 7), the same ligand (antipyrine) in methanol can give rise to the complexes $Y(Ant)_n(NCS)_3$, where $n = 4-6$, and, when the ratio is 1 : 3, the complex is $Y(Ant)_3(NCS).2CH_3OH$. The composition of lanthanide complexes of hydrazine also depends significantly on the reactant ratio[221].

Control of the pH of the medium in which the complexes are obtained is important for the synthesis of lanthanide complexes. Allowance for this factor is particularly necessary when the synthesis is carried out in an aqueous medium: the ligands must be weakly basic compounds incapable of precipitating the lanthanide hydroxide or hydroxo-salt[222-226]. This is why it is impossible to isolate from aqueous and aqueous organic solutions lanthanide complexes with amines which have high pK_a values[16].

The influence of pK_a on the formation of lanthanide complexes with nitrogen-containing ligands was noted by the present authors[169]: $LnCl_3$ (Ln = Sm or Eu) reacts with benzimidazole (pK_a = 5.53) to form the complexes $LnCl_3.L.6H_2O$ in aqueous methanol, while the reaction with imidazole (pK_a = 7.05) results in the formation of lanthanide hydroxides. This is apparently why it is comparatively easy to synthesise lanthanide complexes of weakly basic[227] and oxygen-containing ligands[200-226] in water-containing media. Strict control of the pH of the medium is necessary not only to prevent the possible formation of lanthanide hydroxides but also for the specific synthesis of lanthanide complexes of a particular type. Metal chelates are usually synthesised in weakly alkaline media[1,35,36,42,56,71,228,229], the required pH values being attained by the addition of ammonia or alkali; molecular lanthanide complexes of the type $LnX_3.mL.pSolv$ (Table 1) are isolated from nearly neutral solutions; together with adducts of the above type, protonated lanthanide complexes are formed in acid media[230-233].

Reliable synthetic procedures and comprehensive study of the physicochemical properties of a wide variety of lanthanide salts[234-237] made it possible to obtain various coordination compounds of the lanthanides with oxygen- and nitrogen-containing ligands (Table 1) and to determine the influence of many factors on the composition of the complexes and the coordination number of the lanthanide. The highest coordination numbers are attained in lanthanide complexes with neutral ligands when the lanthanide salt anion is a pseudohalide species[108,152,202] or perchlorate[238]. For example, $Ln(phen)_4(ClO_4)_3$ and $Ln(terpy)_3.(ClO_4)_3$ with coordination numbers of 8 and 9 respectively have been synthesised[72,74]. Tris-complexes with bipyridyl and phenanthroline[152,202] have been obtained using the anions NCS^- and $SeCN^-$: according to infrared spectroscopic data[108], the coordination number in such complexes is 9. On the other hand, when the anion is Cl^- or NO_3^-, bis-complexes are formed and a coordination number greater than 6 is attained as a result of the binding of solvent molecules[89]. Analysis of X-ray diffraction data for lanthanide complexes with isoelectronic and tetrahedral (ClO_4^-, SO_4^{2-}, PO_4^{3-}, and SiO_4^{4-}) and triangular (NO_3^-, CO_3^{2-}, and BO_3^{3-}) anions demonstrated[238] a decrease of the coordination number of the lanthanide with increase of the formal charge of the oxo-anion. At the same time

the coordination number in the series of lanthanide complexes with EO_4^- anions decreases from 9 to 6, while in the case of EO_3^- the decrease is from 12 to 8.

The influence of the nature of the lanthanide on the coordination numbers of the complexes has been discussed in detail by Aslanov and Porai-Koshits[238]. The tendency towards a decrease of the coordination numbers of the lanthanides from lanthanum to lutetium has been known for a long time[1,14,16,17]. The authors[238] note that the coordination numbers of the lanthanides in compounds belonging to the same series (sulphates, phosphates, hypophosphites, and silicates) are higher for the lighter lanthanides than for the heavier lanthanides. This tendency has also been observed for lanthanide complexes with nitrate, carbonate, carboxylate, and also borate anions and with organic acid amides. Having explained these trends, Aslanov and Porai-Koshits, emphasised justifiably that the coordination numbers of the lanthanides and the composition of their complexes depend significantly on the nature of the ligand.

Chelating ligands stabilise complexes with a constant coordination number of the lanthanide regardless of the atomic number of the latter. In this case the coordination number is determined primarily by the geometrical characteristics of the ligand system: the number of members in the metal-containing rings and the number of such rings, the rigidity of their configuration, and other factors resulting from the stability of the metal chelates [239]. Among the factors enumerated, the number of members in the metal-containing rings assumes a particularly important role[238]: four-membered rings promote the formation of lanthanide complexes with coordination numbers of 8–12; five-membered rings lead to complexes with constant coordination numbers (9 for light lanthanides and 8 for heavy lanthanides); six-membered rings give rise to complexes with coordination numbers of 8 (light lanthanides) or 7 (heavy lanthanides).

A constant composition of the complexes over the entire series of lanthanides can arise also for compounds with bulky monodentate ligands (for example a coordination number of 6 is obtained for lanthanide complexes with *NNN'N'*-tetramethylurea)[238]. Extensive reviews of the formation of crystalline lanthanide complexes have been published in monographs[240,241]. Methods of synthesis characteristic of π-complexes of transition metals predominate in the chemistry of π-complexes of the lanthanides[242,243].

IV. THERMODYNAMICS OF COMPLEX COMPOUNDS

After the publication of the monograph of Yatsimirskii et al.[1], numerous studies demonstrating the validity of the approach of these workers to the interpretation of the thermodynamics of lanthanide complexes with a wide variety of ligands were carried out; this makes it possible to take into account, in estimating the stability of lanthanide complexes, the fine structure of the ligand system and the influence of a number of factors on the complex formation process (i.e. on the number and types of reactions) namely the composition of the complex and other factors[244–250].

Calorimetric measurements of the enthalpies of stepwise complex formation, which have many advantages compared with the usual methods for estimating formation constants[244], have recently become important. The calorimetric titration method[245], whereby it is possible to obtain information in many cases about the number and type of reactions occurring simultaneously in the system and also about the concentrations of various reactants involved, is of particular interest. Furthermore, the method permits the determination of the values of ΔH, ΔS, and ΔG solely on the basis of calorimetric data. For example, a linear correlation between ΔH and ΔS has been observed for lanthanide fluoride complexes[247], which makes it possible to regard LnF^{2+} complexes as compounds with predominantly ionic bonds. Positive and fairly high entropies of formation (18–20 e.u.) lead to the conclusion[246–248] that lanthanide fluoride and sulphate complexes have an inner-sphere structure.

All the thermodynamic characteristics of the complex formation reactions of the lanthanides (except promethium) with various organic ligands are now known, namely for propionate, isobutyrate[251], α-hydroxyisobutyrate[252], acetate[39], lactate[252], glycolate[251], mercaptopropionate[253], diglycolate[39], ethylenediaminetetra-acetate (EDTA), ethyl sulphate[253,254], nitrilotriacetate (NTA),[255] diethylenetriaminetetra-acetate (DTRA),[256,257] triethylenetetramine[16], triaminotriethyleneamine[258], threonine and hydroxyproline[259], and thioglycolic acid[260], and others.

Examination of the above studies reveals certain general characteristics in the variation of the thermodynamic functions of the complex formation reactions of the lanthanides. The higher values of ΔH for lanthanide glycolates compared with the acetates, propionates, and isobutyrates can probably be accounted for by the formation of an additional bond with the hydroxy-group of the glycolate anion. Replacement of the oxygen atom by a sulphur atom reduces the stability of the complexes and the ΔH and ΔS for the lanthanum, samarium, and erbium thioglycolates, which have been investigated, are very close to those for the lanthanide acetates[252]. The thermodynamic parameters of the lactates and α-hydroxyisobutyrates are close to the corresponding parameters of the glycolates:

	ΔH, kcal mole^{-1}	
	La	Lu
Lactates (Ref.252)	—1.58	—2.19
α-Hydroxyisobutyrates (Ref.252)	—1.96	—1.11
Glycolates (Ref.252)	—0.85	—0.65
Glycolates (Ref.24)	—0.63	—0.29 (Yb)

Assuming that diglycolate complexes are formed mainly as a result of the disruption of the hydration shell of the hydrated lanthanide ion, the authors[253] showed that a sharp change in the entropy and hence the disruption of the hydration shell begin approximately in the middle of the lanthanide series.

The heat of the reaction $Ln^{3+} + L^{3-} \rightarrow LnL$, where H_3L = NTA, has been measured for the lanthanides except lanthanum[254]. The heat of formation of LaNTA has been measured by Milyukov and Polenova[255]. In the lanthanum, gadolinium, and lutetium series, there is a maximum (or minimum) in the absolute heat of formation corresponding to gadolinium, as for simpler organic ligands. ΔS is constant for lanthanides of the cerium group, while in the yttrium group it increases.

The ΔH for lanthanide complexes of EDTA increase from lanthanum to neodymium, decrease on going to terbium, then increase again, i.e. the overall variation is the same as for other complexes[256,257]. However, there is a significant difference: the dependence of the heat of formation and ΔS on the atomic number of the lanthanide in LnEDTA has a minimum corresponding to gadolinium (as for LnCDTA complexes[258]). This is most probably associated with the different structures of the complexes

formed by the lanthanides of the cerium and yttrium groups. Data for the variation of entropy in the series of these complexes are consistent with the above hypothesis[259]. The maximum entropy change is observed for the LnCDTA complexes (up to 80–105 e.u.)[258]. The deviation of the ΔH for the complexes in the lanthanum, gadolinium, and lutetium series from the monotonic variation shows that the complexes LnEDTA are stabilised when the lanthanide belongs to the cerium group and are destabilised when it belongs to the yttrium group.

The available data[249,250,258] show that the variation of the thermodynamic functions with the atomic number of the lanthanide is non-monotonic for all the complexes. There is a definite parallelism in the variation of both thermodynamic functions (ΔH and ΔS) of lanthanide complexes with the same ligand, but the ΔH and ΔS for ligands having different structures and different numbers of binding sites can vary similarly in the given series. Consequently the nature of the variation of the thermodynamic functions is determined by the variation of the properties of the central atoms and not the ligands. The non-monotonic S-shape of the curve relating the enthalpy to the atomic number of the lanthanide is evidence against the view that the interaction between lanthanide ions and ligands is predominantly electrostatic. According to some data[244–246], the variation of the thermodynamic functions in the series of lanthanides may be determined by the variation of the structure of the complex, particularly by the variation of the coordination number and probably the contribution of the *f* orbitals to the formation of the coordinate bond[260].

In the formation of lanthanide complexes with valine (an α-aminoacid)[261] in an aqueous medium, the stability constant K_1 varies at temperatures from 15° to 55°C in the range from lanthanum to lutetium with a break corresponding to gadolinium. The dependence of $\lg K_1$ on the atomic number of the lanthanide is represented by a convex curve with a maximum in the cerium group, which can be explained by the partial formation of a covalent bond, when account is taken of the extra stabilisation energy, and by the variation of the coordination number in the series of lanthanides. Inner-sphere coordination of the metal and ligand with disruption of the hydration shell of the former has been suggested for lanthanide complexes of glycine and histidine[262,263]. However, these studies[262,263] were performed at high ionic strengths (2 and 3.0 M $NaClO_4$ respectively). One may therefore presume that an increase of the overall concentration in the medium ($NaClO_4$ + ligand) entails a greater degree of disruption of the hydration shell of the metal ion with displacement of solvent molecules from its inner sphere. At an ionic strength of 0.1 (KCl), the hydration shells of the metal ions are not disrupted for cerium-group elements but are involved in the reaction to some extent for the yttrium-group elements, which entails a rapid increase of ΔS with the atomic number of the lanthanide.

A steady increase of stability from lanthanum to lutetium has been observed for lanthanide complexes of β-phenyl-α-alanine, tyrosine, and tryptophan[264], *NN*-biscarboxymethyl-2-aminoalkanoic acids[265], 1,3-diamino-5,5-dimethylcyclohexane[266], methyl 3-mercaptopropionate[267], and ethylene-*NN'*-diaminediglutaric acid[268]. The observed steady increase of stability from lanthanum to lutetium can be accounted for by the fact that the ionic radius decreases in the La–Lu series and there is a corresponding increase in the electron affinity of the element, which increases in its turn the degree of coordination of the lanthanide to the nitrogen atom (in the NH_2 group of the aminoacid).

The stability of the complex is known to be inversely proportional to the dissociation constant of the ligand (K_d). This rule is valid also for lanthanide complexes. The stability constants of lanthanide acetates are higher than those of the monochloroacetates, while the K_d of acetic acids increase with increase of the number of chlorine atoms[269]. The same rule has been noted for lanthanide salicylates, anthranilates, acetylacetonates, and 8-hydroxyquinolinates[210,270–286], as well as a wide variety of lanthanide complexonates. For complexes with certain carboxylic acids (for example lanthanide malonates, succinates, and fumarates[286–293]), a linear relation has been observed between $\lg K_1$ and pK_1 (for monocarboxylates) and pK_2 (for dicarboxylates) of the ligands. This behaviour can break down: thus lanthanide complexes of dinitrosalicylic acid (DNS) are more stable than the lanthanide chloroacetates (CA), although $K_d(\text{DNS}) > K_d(\text{CA})$. The anomaly has been explained[269] by the formation of chelate rings in the lanthanide complexes of DNS. The replacement of carboxy-groups (lanthanide nitrilotriacetates) by the less acidic alcoholic groups (lanthanide hydroxyethyliminoacetates) leads to a decrease rather than an increase of the stability constants of the complexes, which has been attributed[294] to a change in the number of members in the chelate ring.

The number of members and the lack of steric rigidity of the chelate ring are important factors influencing the stability of lanthanide coordination compounds. The stability of complexes of ethylenediamine-*NN'*-disuccinic and ethylenediamine-*NN'*-dimalonic acids is higher than that of ethylenediamine-*NN'*-diglutarates, since the former two complexones form with the lanthanides stable five- and six-membered chelate rings respectively, while ethylenediamine-*NN'*-diglutarates give rise to comparatively unstable seven-membered chelate rings[268]. Europium(III) complexes of cyclohexylenediaminetetraacetic acid (CDTA)[295–298] are formed in the presence of a larger excess of the ligand than, for example, the analogous complexes with ethylenediaminetetra-acetate, which has been attributed to the rigidity of the CDTA structure, hindering the incorporation of the second ligand in the inner sphere of the metal. Because of this, $\lg K_2 \simeq$ const. in the Gd–Lu series for the 1 : 1 complexes with salicylhydroxamic acid[247], 8-hydroxyquinoline, and some of its 5,7-disubstituted derivatives[248], while the variation of $\lg K_1$ exhibits the usual regularities: an increase from La to Sm and from Gd to Lu, $\lg K_1$ for Gd being lower than for Sm.

The values of K for the complexes of 5-sulphosalicylic acid (SSA) with the compositions Ln(Y)$(SSA)_2$, where Y = EDTA–OH, EDTA, or CDTA (*trans*-1,2-cyclohexylenediamine-*NNN'N'*-tetra-acetate), and Ln(Y)$(SSA)_2$, where Y = IMDA (iminodiacetate) or NTA in alcoholic solutions (pH 10.7–11.0) indicate an enhancement of the chelating effect in the EDTA–CDTA–OH (1 : 1 : 1 complexes) and the NTA–HIMDA (hydroxyethyliminodiacetate)–IMDA (1 : 1 : 2 complexes) series[299].

It is of interest to compare the enthalpies ΔH_1 of formation of the 1 : 1 chelate lanthanide complexes of EDTA with the enthalpies of formation ΔH_2 of the 1 : 1 : 1 lanthanide chelates incorporating mixed ligands, namely, EDTA–TP (triphosphate) or ATP (adenosine triphosphate)[300]. The ΔH_2 for the formation of complexes of the Gd–Tm heavy lanthanides are more exothermic than the

values for the corresponding 1 : 1 lanthanide complexes of EDTA; on the other hand, the ΔH_2 for the complexes of light lanthanides, with the exception of lanthanum(III), are less exothermic than the ΔH_1, which can be accounted for by the formation of supercoordinate bonds when heavy lanthanides interact with EDTA (1 : 1 complexes), ATP, or TP. The formation of complexes with mixed ligands by the lighter lanthanides should also be accompanied by a more exothermic ΔH_2, but the energy evolved on abstraction of strongly bound coordinated water and ligand groups diminishes ΔH_2 in this instance. The entropies of formation ΔS_2^0 of 1 : 1 : 1 chelates are relatively small and more negative than the entropies of formation ΔS_1^0 of 1 : 1 chelate lanthanide complexes of EDTA, evidently owing to the repulsive interaction between the negatively charged mixed chelate lanthanide–EDTA complexes formed with the ATP or TP anions, bearing four or five charges. The entropies of formation of the latter increase from La to Pr and then decrease to Tb, increasing subsequently to Er and decreasing again to Tm, which has also been attributed to differences in the degrees of hydration of the lanthanide ion in the above series. As was to be expected, the entropies of formation of the lanthanide complexes with mixed ligands, EDTA–ATP or TP, in the gas phase are much more positive than in solution.

There is relatively little information on the influence of the nature of the electron-donating centre in the ligand molecule on the stability of lanthanide complexes. It is known [13], however, that in terms of their tendency to form complexes with the lanthanides, which are hard acids, electron-donating atoms can be arranged in the sequence O > N > S. This sequence has been confirmed by the difficulty of synthesising lanthanide complexes of nitrogen-containing ligands [16] compared with oxygen-containing donors [1,17,39] and by the virtual absence of reports of lanthanide complexes with ligand systems in which the electron-donating atoms are those of "soft" sulphur, tellurium, phosphorus, and arsenic. The above factor precludes the estimation of the relative "hardness" of lanthanide ions from the standpoint of the concept of hard and soft acids and bases [48]. In order to solve this problem as well as the problems of competitive coordination [301], it is necessary to have information about the stability of lanthanide complexes for a series of ligands containing variable electron-donating centres: O > S > Se and N > P > As, and quantitative estimates of the Lewis acidities of lanthanide salts must be made [302].

The determination of the stepwise complex formation constants for the lanthanides in mixed aqueous organic solutions and non-aqueous media has been attracting increasing attention of investigators: the results of studies of the stability of lanthanide acetate complexes in aqueous ethanol solutions, dioxan, and aqueous dioxan solutions [281–283], of lanthanide salicylate and anthranilate complexes in methanol [270,280], of lanthanide complexes of acetylacetone in methanol and dioxan solutions [281,284], and of the complexes of 8-hydroxyquinoline in 50% n-propyl alcohol [274] are available. These data permit inferences about the variation of the dissociation constants when both the ionic strength of the solution and the composition of the mixed solvent are varied.

Computer calculations of the stepwise stability constants have shown [276] that, with increase of the atomic number of the lanthanide, the stability of its complexes increases monotonically. However, there is no simple relation between the overall stability constant and the stepwise stability constant: in lanthanide solvato-complexes, the complex-formation effect can be divided into the contributions of the inner-sphere and outer-sphere interactions [270–274]. The contribution of the inner-sphere complex formation process depends on the composition of the mixed solvent [271] and the overall complex-formation effect also depends on the nature of the lanthanide salt anion. There exist fairly well developed methods whereby one can calculate the stability constants for the stepwise formation of acid (protonated) lanthanide complexes [295–297, 303–314].

In the presence of an equimolar ratio of neodymium and ethylenediaminediacetic acid (EDDA), there exist in the pH range 5.19–6.01 the aquo-ion and the protonated and normal 1 : 1 complexes, while in the presence of a fivefold excess of the ligand the 1 : 2 complex is present [304]. For comparison with potentiometric pH measurements [315], the stability constants of NdL^+ and NdL^- were adjusted to an ionic strength of 0.1. The values $\lg K^{NdL^+} = 6.8 \pm 0.15$ and $\lg K^{NdL_2^-} = 4.97 \pm 0.08$, found by Bertha and Choppin [314], are lower than those quoted by Thompson [315] (8.06 and 5.63 respectively), possibly because no account was taken in the calculation of the formation of protonated complex. The latter has also been confirmed by a comparison of other data [316,317]. The calculated stability constants of the protonated complexes of hexamethylenediaminetetraacetic and iminodiacetic acids were compared with the stability constants calculated as the arithmetical mean values from three titration curves (the confidence limits of the $\lg K$ did not exceed 0.1) [303]. The similarity of the stabilities of the lanthanide complexes of the above acids shows that the ligands have the same numbers of binding sites; comparison of the data of Kurkina et al. [303] with those of Galaktionov and Astakhov [318] and Kornev and Konyukhov [319] is difficult, because the ionic strengths are not known and because of the different pH values and [Ln] : [L] ratios employed.

The values of $\lg K$ increase, while those of $\lg K_p$ (the logarithms of the protonation constants) steadily decrease in the series of lanthanides from La to Lu. Both effects have been attributed [320,321] to the changes in the effective ionic potential in the same series. The arrest of the increase of stability in this series at gadolinium, which is usual for lanthanide complexes, has also been observed, although the break is not very marked.

Certain general characteristics of the formation of lanthanide complexes have been interpreted [322,323] from the standpoint of the so called tetrad effect.

In conclusion mention must be made of the attempts to employ modern microwave spectroscopic (NMR) and quantum-chemical methods in the determination of the stability constants of lanthanide complexes, the lanthanide–EDTA–Cit (citrate) system has been investigated by ^1H NMR. [324] The value $\lg K = 1.2 \pm 0.1$ has been determined from the shift of the signal due to the ethylene protons of EDTA on formation of the mixed complex Lu(EDTA)Cit in the pH range 4–7. This is smaller by two orders of magnitude than the logarithm of the stability constant of the analogous neodymium complex and smaller by an order of magnitude than the logarithm of the stability constant of the complex Lu(EDTA)IMDA ($\lg K = 2.5 \pm 0.4$).

Comparison of the values measured by a potentiometric method at an ionic strength of 0.1(KCl), at 25° ± 0.1°C, and for the ratios [Ln] : [L] = 1 : 2 and 1 : 4 with the values calculated [325] from quantum-chemical data for the charge distribution on the ligand atoms and the mutual polarisability of the lanthanide ion and the ligand atoms [326,327] revealed a satisfactory correlation (Table 2).

V. INVESTIGATION OF THE MOLECULAR STRUCTURES OF THE COMPLEXES

1. X-Ray Diffraction Analysis

Many lanthanide complexes have different types of crystal lattices and transitions from one type to another are observed in different parts of the lanthanide series: for neodymium and gadolinium [328], ytterbium and terbium [329], etc. The lanthanides form a less perfect coordination polyhedron than in the complexes of *d* transition elements with the same ligand: an octahedral configuration, which is extremely characteristic of *d* element complexes, cannot be as a rule achieved in lanthanide complexes (particularly for polydentate ligands [17]), since the large size of the lanthanide ion makes the structure of the inner coordination sphere extremely strained. It has been established that the formation of the crystal structure is influenced by the duration of storage of specimens. Certain coordination compounds of lanthanides are amorphous to X-rays, for example protonated, neutral, and polynuclear species, as well as the dehydration products of many lanthanide complexes [166,218,329]. The hydroxyethyliminodiacetates of yttrium-subgroup lanthanides [329] are amorphous to X-rays with the exception of the europium complexes which has a crystal structure similar to that of other compounds of the cerium-subgroup elements [163].

Table 2. The measured and calculated values of $\lg K_1$ (Feige et al. [325]).

Ln	Dipeptide (expt.)	Diglycine (calc.)	Tripeptide		L-Pro-Gly (expt.)
			expt.	calc.	
Nd(III)	2.32	2.36	1.95	2.16	2.75
Er(III)	2.57	2.46	2.50	2.26	3.10
Gd(III)	2.39	2.50	2.10	2.30	3.00
Ho(III)	2.46	2.63	2.20	2.43	3.25
Yb(III)	2.80	2.70	2.40	2.50	3.50

Comparison of diffractometer traces has shown that the lanthanides form groups having the same structures, whose number depends on the nature of the ligand. Thus X-ray diffraction analysis of the thiourea complexes of the lanthanides [168] $Ln(C_2H_3C_2)_3.CS(NH_2)_2.nH_2O$, where Ln = La or Ce ($n$ = 2), Pr, Nd, or Eu–Yb (n = 1), and Sm or Lu (n = 0.5), has shown that the complexes can be divided into two series with identical structures: La–Pr and Nd–Eu or Y, each of which gives rise to characteristic diffractometer traces. The thiourea complexes of the yttrium sub-group lanthanides [329] $Ln(C_3H_5C_2)_3.CS(NH_2)_2.nH_2O$, where Ln = Tb, Dy, Ho, Er, or Y (n = 3.5), Tm or Yb (n = 3), and Lu (n = 1), form two groups with the same structures: Tb–Tm or Y and Yb–Lu. Starting with Yb, the crystal lattice of the complexes changes, while the crystal structure of the yttrium compound is close to that of the complexes formed by the elements of the Tb–Tm series.

The nonahydrates of lanthanide benzenesulphonates [223] can be divided into three groups with the same structures: one includes complexes of the elements ranging from La to Nd, the other Sm and Eu complexes, and the third the complexes of the elements ranging from Gd to Lu, including yttrium benzenesulphonate. Four groups with the same structures can be distinguished among the hydrated complexes with a low water content: the first includes La, Ce, Pr, and Nd salts, the second Sm, Eu, Gd, and Tb salts, the third Dy, Ho, Tm, and Y salts, and the fourth Er, Yb, and Lu salts. Comparison of the diffractometer traces for different hydrated benzenesulphonates of the same lanthanide has shown that they are identical for the free ion and the dihydrates of lutetium, cerium, and praseodymium benzenesulphonates and for the free ion and the trihydrate of neodymium benzenesulphonates[223]. Seven molecules (six in the case of neodymium) of the water of crystallisation are apparently not involved in the formation of the crystal structure. On the other hand, the diffractometer traces for the hydrated benzenesulphonates of the lanthanides ranging from Sm to Lu, including yttrium benzenesulphonate, with different water contents, are sharply different, which indicates the involvement of the entire water of crystallisation in the formation of the structure.

In solid lanthanide complexes, there are usually intermolecular hydrogen bonds, which decrease the flexibility of the metal-containing rings. The structure of the hydrates of the protonated complexes changes in the series of lanthanides [107], while the structure of the neutral complexes remains constant. This phenomenon has been attributed [330,331] to the polarising action of the outer-sphere cations.

Calculation of the crystallographic parameters of lanthanide complexonates makes it possible to isolate groups having the same structures in the La–Lu series [331].

2. X-Ray Diffraction Analysis

The amorphous behaviour in relation to X-rays or polycrystallinity as well as the extremely low solubility of lanthanide complexes frequently prevent the formation of single-crystal specimens. Nevertheless Porai-Koshits and Aslanov [240,331] have now examined series of compounds with the same structures belonging to 100 structural types: studies have been made of the problems of the relative roles of the Coulombic and covalent components in the stereochemistry of lanthanide complexes, statistical data have been published on their coordination numbers and their coordination polyhedra, a relation has been demonstrated between the latter and the nature of the lanthanide and the ligand, the stereochemistry of lanthanide complexes with six- (β-diketonates) and four-membered rings (nitrates, carbonates, and sulphates) has been investigated, and a comparative analysis of the stereochemistry of the lanthanides and *d*-transition metals in β-diketonates, carboxylates, and many other chelate complexes has been carried out.

The structural aspects of six-membered metal-containing lanthanide rings have been elucidated in X-ray diffraction studies on lanthanide diketones [332–340]. Lanthanide tetra-β-diketonates can exist in two forms: as complex acids and as salts of organic bases [332,334]. The unit cell parameters of the crystals of the α-form of piperidinium tetrabenzoylacetonatoeuropate [335] agree satisfactorily with the results of Il'inskii et al. [332] This form may be called a salt, since it contains the cation $Hpip^+$ (pip = piperidine) and the anion $[Eu(BA)_4]^-$. The second compound, described [336] as a solvate, is an acid, in agreement with a number of facts described in the literature [336,337]. In β-diketonates with electron-donating substituents, the

coordination polyhedron is as a rule a tetragonal antiprism, while in β-diketonates with electron-accepting groups it is a dodecahedron. The conversion of one polyhedron into another is difficult, which conflicts with the view [338] that the solvent plays a decisive role in the formation of the coordination polyhedra of lanthanide tetra-β-diketonates.

Comparison of the structures of tetra-β-diketonates has led to the conclusion [334] that the symmetry of the immediate environment of lanthanide ions depends on the electronic properties of the ligands: in the presence of non-fluorinated ligands [332,339], the characteristic coordination polyhedron of the lanthanide is a tetragonal antiprism, while in the case of fluorinated ligands [339,340] the polyhedron is a dodecahedron. It has been suggested [334] that this type of dependence of the form of the coordination polyhedron on the nature of the ligand can be accounted for by the degree of overlap of the orbitals of the lanthanide atoms and ions.

There have been so far few data concerning the absolute configurations of organic compounds coordinated to lanthanide ions. The study of Porai-Koshits et al. [341], who analysed the geometry of the EDTA anion in complexes and simple salts, merits most attention in this connection. Analysis reveals three configurational possibilities for the ligand: two with the *cis*-disposition of the nitrogen atoms of ethylenediamine (en) (the *gauche*-configuration of the en-ring) and one with the *trans*-configuration of ethylenediamine (planar en-ring). The first group (*E*, *G/R* conformation) with the non-planar structure of the en-ring (C.N. = 6–8) has the following polyhedra: octahedron, pentagonal bipyramid, and Chord's dodecahedron. Complexes with the configuration of a single-cap trigonal prism (C.N. = 7) are characteristic of the second group (*E*, *R/G* conformation). One of the consequences of the transition *E*, *G/R* → *E*, *R/G* is the flattening of the $O_RO_GO_GO_R$ tetragon. The *E*, *R/G* configuration obtains in the lanthanide complexes of EDTA; the transition to coordination numbers of 9 and 10 entails a further decrease of the endocyclic angles at the metal atom.

The results of X-ray diffraction analysis of lanthanide complexes permits the conclusion that lanthanide(III) ions in the compounds have high and variable coordination numbers. In lanthanide complexes, the coordination number is usually 9 (Table 3). [342–356] Amongst the factors influencing the coordination number, the strength of the Ln–ligand bond and the steric characteristics of the ligand systems have been noted. In particular, it has been suggested [343] that the Ln–O interaction in the hexamethanol complexes of lanthanide nitrates is so pronounced that the coordination number is ≤ 8. However, for the majority of lanthanide complexes of dimethyl sulphoxide [342–344,357,358], where a very strong interaction can also be postulated, no changes have been observed in the coordination number of the metal, contrary to the view of Ramalingam and Saundararajan [359].

X-Ray diffraction data have been used to solve the problem of the location of the coordinate bond in ambident bi- and poly-dentate ligands. As expected [301], only a "hard–hard" interaction takes place with O- and N-donors (in lanthanide nicotinates) [345,360,361], in contrast to the complexes of *d*-transition elements [301,362], and the Ln–C bond is formed. The latter has also been detected in the infrared spectra of lanthanide nicotinates [363].

Analysis of the X-ray diffraction data has shown that chain and isolated group ("island") structures are characteristic of lanthanide complexes. It has been shown that the chains of the complexes are frequently linked together by hydrogen bonds, formed both between coordinated water molecules and with participation of the donor (N, O, and S) atoms of the anions [346,360,364].

Certain regularities in the Ln–A interatomic distances (A is a donor atom) as a function of the nature of Ln–A and the ligand system are known (see Table 3 and the data analysed in the literature [240,331]). The average $Ln-O_{NC_3}$ interatomic distances in the hydrates (2.65 Å) and the dimethyl sulphoxide complexes of lanthanide nitrates (2.64 Å) are approximately equal [357]. However, the $Ln-O_{DMSO}$ distances are much shorter than $Ln-O_{H_2O}$, which cannot be accounted for solely by the lanthanide contraction, which is very slight on passing from Pr to Nd.

The large (compared with the water molecule) negative charge on the oxygen atom in the DMSO molecule apparently enhances the $Ln-O_{DMSO}$ interaction, which leads to a shortening of the bond. The $Ln-O_{DMSO}$ interatomic distances in the $Nd(NO_3)_2.(DMSO)_4$, [343] $Er(NO_3)_3.(DMSO)_3$, [344] and $Lu(NO_3)_3.(DMSO)_3$ structures are on average 2.26 Å, which is significantly less than the $Ln-C_{NC_2}$ bond length

Table 3. The structures of coordination compounds of the lanthanides (the interatomic distances are quoted for the compounds of the underlined lanthanide).

Composition of complex	Ln(III)	C.N.	Symmetry	Average interatomic distance, Å				References
				$Ln-O_{lig}$	$Ln-O_{NO_3}$	$Ln-O_{H_2O}$	$Ln\,N_{lig}$	
$Ln(NO_3)_3(DMSO)_3$	Nd, Er, Lu	9	C_3	2.26	2.50	—	—	342–344
$Ln(OOCC_5H_4N)_3\cdot 2H_2O$	Pr, Er	8	C_2	2.29 (bridge)	—	2.33	—	345–346
				2.42 (ring)	—	—	—	—
$Ln(NO_3)(NCS)_2\cdot 2[N_4(CH_2)_6]\cdot 8H_2O$	Nd, Er	9	—	2.65	—	—	2.40	346
$Eu(terpy)_3(ClO_4)_3$	—	8	D_3	2.40	—	—	2.64	347
$Ho(thd)_3(4\text{-}pic)_2$	—	9	C_2	2.27	—	—	2.53	348
$La(NO_3)_3(2,2\text{-}dipy)_2$	—	8	D_2	—	2.61	—	2.66	349
$HLn(BA)_4\cdot Pip$	La—Gd	8	D_2	2.36	—	—	—	—
$HLn(BA)_4NHEt_2$	La—Gd			2.38	—	—	—	332
$HPip[Ln(BA)_4]$	La—Lu	8	D_2	2.38	—	—	—	332
$Ln_3mal_3\cdot 8H_2O$	Nd, Eu	9	—	2.47	—	—	—	350,351
$Ln(HOCH_2COO)_3\cdot 2H_2O$	La, Gd, Er	8	—	2.31	—	—	—	352
$Ln(C_4H_5O_4N)(H_2O)_3Cl$	Pr—Lu	8	—	—	—	—	—	353
$Na_3[Ln(C_7H_3NO_4)_3]\cdot 13H_2O$	Nd, Yb	9	—	2.39	—	—	2.52	354,355
$Na_3[Ln(C_7H_3NO_4)_3]NaClO_4\cdot 10H_2O$	Nd, Yb	9	—	2.38	—	—	2.43	356

(2.50 Å), suggesting that the Ln–O_{DMSO} bond in compounds of this class is stronger than the Ln–O_{NO_3} bond. The Ln–O interatomic distances in lanthanide carboxylate complexes [361,365-367] obey the same rule: the lengths of the bonds between the oxygen atoms of the cyclic bidentate carboxy-group and the lanthanide atoms are longer than the distances between the lanthanide atom and the oxygen atoms of the bidentate bridging carboxy-group.

VI. SPECTROSCOPIC STUDIES

1. Fluorescence Spectra

The coordination compounds of the lanthanides are classified into three groups according to the nature of their fluorescence. The first group includes lanthanum(III), gadolinium(III), and lutetium(III) complexes, which exhibit the fluorescence of the non-metallic ions. The second group comprises dysprosium(III), samarium(III), europium(III), and terbium(III) complexes, which exhibit the characteristic intense fluorescence of the metal ions; each ion has an excited state whose energy is close to that of the triplet level of the ligands. Praseodymium(III), neodymium(III), holmium(III), erbium(III), ytterbium(III), and thulium(III) complexes, which exhibit a weak fluorescence of the metal atoms, constitute the third group; each [metal?] ion in this group has closely spaced energy levels.

Since the electrons of the 4*f* orbitals of the lanthanides are shielded from the action of the ligand field by the $5s^2 5p^6$ electron cloud, the following regularity is observed as regards the intensity of the influence on the lanthanide ion: crystal field < spin–orbital coupling < interelectron repulsion [18].

Theoretical analysis of the symmetry in the lanthanide complexes makes it possible to interpret their fluorescence spectra [368-371]. Europium(III) chelate complexes are most frequently investigated, because in this case the low value of the quantum number J for the most intense lines in the emission spectrum ($^5D_j \rightarrow {}^5F_j$; $J = 0, 1$; $J' = 0, 1, 2$) gives rise to a smaller number of energy levels than the number observed for the majority of other lanthanide ions. The transitions from the $^5D_0$ state are used to investigate the symmetry of the coordination compounds because this energy-emitting state ($J = 0$) cannot be split by the ligand field. Thus the transitions from $^5D_0$ to various F_j states are usually well separated and the transitions to the J states are frequently satisfactorily resolved. The interpretation of the fluorescence spectra of the europium complexes from the standpoint of symmetry agrees with the molecular structure of the complexes [338-349].

The study of the fluorescence spectra of 33 chelate complexes (pyridine derivatives of lanthanide tetrakis-1,3-diketonates) [331] showed that all eight oxygen atoms in the 1,3-diketone are directly linked to the lanthanide, which is confirmed by the analysis of the observed fluorescence spectra from the standpoint of the possible symmetry of the ion in complexes of different compositions which have been investigated. Analysis of the fluorescence spectra yields valuable information about the nature of the interaction of the lanthanide with organic ligands [372-379], the nature of the bond in lanthanide complexes [369-372,380-382], the symmetry of the complexes, and the conformation of the ligands [382-386].

A relation has been established between the probability of the energy transfer (k_t) and the degree of overlap of the electron clouds of aromatic ketones and lanthanide ions (Table 4). [387] The probability of energy transfer in the case of benzophenone, acetophenone, and benzoylpyridine (Table 4) reflects the similar changes in their capacity for complex formation, the differences being due to the differences in the donor–acceptor properties of the ketones and the overlap integrals for the spectra. The distinct increase of k_t for ketones having the $^3\Gamma(n,\pi^*)$ state compared with the analogous ligands with the $^3\Gamma(\pi,\pi^*)$ levels constitutes clear confirmation of the role of the overlap of the electron clouds of the excited ketone and the lanthanide ion in energy transfer. Energy transfer with participation of lanthanide ions to the triplet level of organic molecules and away from the latter proceeds via an exchange-resonance mechanism [388].

Table 4. The probabilities of energy transfer from aromatic ketones to lanthanide ions [387] (T = 383 K, acetone, air).

Ketone	$10^{-3}k$, M^{-1} s^{-1}									
	Ce^{3+}	Pr^{3+}	Nd^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}	Tb^{3+}	Dy^{3+}	Ho^{3+}	Yb^{3+}
Acetophenone	4	3	8	0.5	2	0.10	0.66	0.6	0.6	0.8
Benzophenone	—	5	17	1.0	6	0.01	0.1	0 8	0.8	0.76
Benzoylpyridine	—	4.5	5.4	0.6	3	—	0.26	0.6	0.6	0.5

The luminescence spectra of more than one hundred europium, terbium, and gadolinium complexes with different ligands have now been investigated [373-377]: $Eu(TTA)_4P$, $Eu(BTFA)_4P$, $Eu(o\text{-Cl-5-BTFA})_4Pyrr$, $Eu(DBM)_4P$, $Eu(BTFA)_4DMA$, $Tb(A)_4P$, $Eu(DFDBM)_3$, $Eu(DFDBM)_4P$, etc., where TTA = thenoyltrifluoroacetone, BTFA = benzoyltrifluoroacetone, DBM = dibenzoylmethane, P = piperidine, I = imidazole, Pyrr = pyrrolidine, DMA = dimethylamine, and DFDBM = decafluorodibenzoylmethane. Analysis of the splitting of the lines in the spectra has led to certain conclusions about the symmetry of the crystal field of the lanthanide complexes. If the crystal field has a threefold symmetry axis, three lines correspond to the $^5D_0 \leftarrow {}^7F_2$ transition and two components with the intensity ratio 2 : 1 (the inner coordination sphere is an octahedron with a D_3 symmetry axis) correspond to the $^5D_0 \rightarrow {}^5F_1$ transition. For a lower symmetry, the line due to the $^5D_0 \rightarrow {}^7F_1$ transition is split into three components with approximately equal intensities, and there is a weak $^5D_0 \rightarrow {}^7F_0$ transition. Solvent (water) molecules are not linked to the central atom, which is surrounded by six oxygen atoms. On the other hand, in the spectra of the di- and tri-hydrates of europium(III) tri- and tetra-acetylacetonates the line of the $^5D_0 \rightarrow {}^7F_1$ transition is split into three components and that due to the $^5D_0 \rightarrow {}^7F_2$ transition, into five components: the cubic environment, comprising eight oxygen atoms, is distorted to a tetragonal antiprism with a C_2 symmetry axis. The degree of hydration has a significant influence on the intensity, width, and Stark splitting of the luminescence bands of the ion in the chelate complexes.

Comparison of the results of the analysis of the luminescence spectra of europium nitrates combined with aromatic amines [358] with X-ray diffraction data showed that the luminescence spectra yield an average pattern of

the charge distribution, so that the real pattern in the structure of the complexes can be obtained solely with the aid of additional data.

The luminescence spectra of europium complexes of aromatic acids [389], complexones [390], and β-diketones [391] have been investigated in very great detail. Analysis of the luminescence spectra of europium β-diketonates using CFT led to the conclusion [391] that the vacant (*in vacuo*) 5*d*-orbitals of the lanthanides are involved in the Eu(III)–L bond.

The use of europium as a luminescence probe is of particular interest [390]. Several types of complexes of Schiff bases, in which covalent bonds are formed between europium and the ligands, were isolated by this method.

The formation of lanthanide complexes with various electron-donating solvents has been studied by the taumetric method based on the phenomenon of the radiationless energy transfer in the fluorescence spectra. It was shown [388] that, when inner-sphere lanthanide complexes are formed, the decisive factors are the relative electron-donating properties of the solvent and the competing ligand, and in outer-sphere complex formation the dielectric constant of the medium is of decisive importance.

2. The Absorption Spectra of Lanthanide Complexes

The absorption spectra of lanthanide ions have been investigated in fair detail in solutions of complexes [392-427]. Studies have been made on the intensities and positions of the absorption bands as a function of the nature of the lanthanide, the ligand environment, and the solvent.

In the far ultraviolet (210–300 nm), the ions of certain lanthanides have absorption bands corresponding to the allowed $4f-5d$ transitions; in the visible region, absorption bands associated with the $4f-4f$ transitions of the electrons are observed [392]. In conformity with theory [392, 393], the oscillator strengths P of the $4f-4f$ absorption bands are small, but the intensity of certain bands may increase as a function of the environment.

When the environment of the Ln^{3+} ion is altered, appreciable oscillator strengths are observed only for certain absorption bands, corresponding to the $4f-4f$ electron transitions—the so called hypersensitive transitions (HST). The absorption bands of lanthanide(III) ions corresponding to HST have been listed [392,394,398-415]. The appearance of HST has been explained [385,393] by the influence of the covalent nature of the Ln^{3+}–ligand bond (nephelauxetic shift [415-419]) and may be characterised by the CFT parameters.

In the spectra of many complexes of aromatic acids [405], the intensity of the $^7F_0 \rightarrow {}^5D_2$ and $^7F_1 \rightarrow {}^5D_1$ HST bands increases to the same extent (by factors of 1.8 and 1.62 respectively). The oscillator strength P_{exp} of the $^7F_0 \rightarrow {}^5D_2$ transition has been frequently determined as a function of the solvent (water, methanol) [405,406], the lanthanide ion [395,401-405], and the nature of the anion and the ligand [395,404]. Thus $P_{exp} = 0.0004$ for the $^7F_0 \rightarrow {}^5D_2$ transition in an aqueous $Eu(NO_3)_3$ solution, which is smaller by a factor of six than for a $Eu(NO_3)_3$ solution in methanol. The intensity of the $^7F_0 \rightarrow {}^5D_2$ transition increases even more in europium salicylate: P_{exp} is sixty times greater than for the aquo-ion. Consequently the field strength in methanol is greater than in water, and among all the complexes investigated [402-405] it is a maximum for europium salicylate [405].

It has been established that the intensity of the HST absorption bands and the oscillator strengths of lanthanide ions involved in complex formation depend on the chemical nature [395,406-410] and the molecular weight [406] of the ligand. Thus they increase for neodymium(III) and erbium(III) complexes of 8-hydroxyquinoline and its dihalogeno-derivatives (5-chloro-7-iodo-8-hydroxyquinoline and 5,7-di-iodo-8-hydroxyquinoline) with increase of the molecular weight of the ligand [405]. The same behaviour is characteristic of mixed lanthanide complexes formed as a result of the additional coordination of organic ligands [407-410].

Analysis of the intensities of the HST absorption bands of lanthanide ions is an effective means of determining the symmetry [415-421]. A general trend towards a decrease of the symmetry of the solvated lanthanide ions on passing from methanol to 1-propanol has been established [413,419] and the symmetries of many lanthanide complexes in different solvents [420,421] and the changes in the latter on passing from the crystalline phase to the solution [421] have been determined. Comparison [414] of the changes in the HST intensities in the luminescence spectra with the changes observed in the absorption spectra shows that the two sets of quantities are proportional. Thus the influence of the ligand field, which determines the HST intensities, is manifested to approximately the same extent in both absorption and luminescence spectra.

Not only the intensities but also the positions of the bands in the electronic absorption spectra of lanthanide complexes depend significantly on the nature of the ligand (the electron-donating atom) and the nature of the lanthanide cation and anion. The shift of the bands in the spectra of lanthanide complexes is determined by the immediate ligand environment of the central ion. A linear relation between the positions of the spectral bands and the average R_{Ln-O} distance has been observed for lanthanide complexes with ligands coordinated via oxygen atoms [420,422,423]. The positions of the bands in the electronic spectra of lanthanide complexes have been investigated as a function of the nature of the complexones and aminoacids [424-426]. The presence of a single band ($^4I_{9/2} \rightarrow P_{1/2}$ transition) in the spectra of the neodymium complexes with the above ligands [424] and of two bands in those of the erbium complexes [425] permitted the conclusion that the lanthanides are bound in different ways in the complexonates: rigid incorporation of neodymium(III) in the chelating unit of the complexones, which is always of the same type, and different types of binding of erbium(III) to different electron-donating groups of the ligand system. The same data combined with NMR data have been used [426] to determine the location of coordinate bonds in the complexonates.

The influence of the anion of the lanthanide salt on the spectra of the complexes has been investigated in relation to the behaviour of LnX_3 (Ln = Nd, Ho, or Er; X = Cl, Br, or NO_3) in *NN*-dimethylacetamide [420] and of the solvato-complexes of $EuCl_3$ and $Eu(NO_3)_3$ in water, ethanol, and acetic acid [427]. It was found [427,428] that, when the anion is altered in the sequence $Cl \rightarrow Br \rightarrow NO_3$, a bathochromic shift of the HST bands is observed.

In conclusion we may note that a correlation has been found between the results derived from the electronic and ^1H NMR spectra of the lanthanide–complexone complexes investigated [424,425]: the shift of the absorption bands ($\Delta\lambda$) in the electronic spectra and the chemical shift ($\Delta\delta$) of the protons in the ^1H NMR spectra increase on formation of a bond between the lanthanide and a nitrogen atom and

diminish from La to Lu when the lanthanide is coordinated to an oxygen atom. This observation may be used to characterise the bonds in lanthanide complexes with ON-ligands and to determine the distance between the lanthanide and the donor centre.

3. Infared Spectroscopy of Lanthanide Complexes

The infrared spectra of lanthanide complexes have been studied over a wide wavelength range (40–4000 cm^{-1}), mainly in the crystalline phase [422-446]. The long-wavelength region (40–600 cm^{-1}) has been studied in order to assign the frequencies, to determine the spectroscopic parameters of the Ln–X bonds (X = Cl, Br, I, O, N, or S), and to discover the location of the coordinate bond. Since lanthanide chlorides belong to the L_{3h} symmetry point group [115], the unit cell may be defined as a double trigonal antiprism. Consequently, four fundamental frequencies, $\nu_1(A_1')$, $\nu_2(A_2'')$, $\nu_3(E_1')$, and $\nu_4(E')$, may be expected for the vibrations of the Ln–Cl bond, the first of which should be inactive in the infrared spectra, since it is the frequency ν_S of the stretching vibration of the Ln–Cl bond. The observed vibration frequencies and calculation [115] led to the isolation of the following bands active in infrared spectra: A_2' (237 cm^{-1}); E_1' (318 cm^{-1}); E' (285 cm^{-1}). The vibrations of the Ln–Cl bond in bipyridyl and phenanthroline complexes are active in the range 200–260 cm^{-1}, while the frequencies of the vibrations of the Ln–Br bond are significantly lower (140–155 cm^{-1}).[429]

The vibrational spectra of the complex anions LnX_6^{3-} (Ln = Nd, Eu, Gd, Dy, Er, or Yb; X = Cl or Br) have been investigated in detail using calculated data [430]. In the calculation, the force fields of the molecules were analysed; among these, a modified valence-force field proved to be the most effective and, in the region of stretching vibrations, also a modified Urey–Bradley field. The LnX_6^{3-} anion has six vibrations active in the range 50–260 cm^{-1}; the experimental and calculated data have been tabulated in a review [430]. It has been established that (a) the strength of the $LnCl_6^{3-}$ bonds is greater than that of the $LnBr_6^{3-}$ bonds and that (b) the force constant K_{Ln-Cl} of the chlorides decrease in the sequence Yb > Er > Dy > Gd > Nd as the ionic radius of the lanthanide increases; in the case of the bromides, two groups were isolated in terms of the K_{Ln-Br}, namely Yb < Er < Dy < Gd and Eu < Nd; finally, (c) the force constant f, characterising the repulsion between non-bonded atoms, increases from Cl to Br as the ionic radius of the lanthanide increases.

The vibrations of the Ln–N bonds are active in the range 200–500 cm^{-1} for bipyridyl and phenanthroline [198], 350–380 cm^{-1} for ethylenediamine chelates [450], and 270 to 350 cm^{-1} for isocyanate complexes of the type $[Et_4N]_3.[M(NCO)_6]$. [431] There are so far relatively few data for the vibrations of the Ln–O bonds [129]: in the spectra of praseodymium, neodymium, europium, gadolinium, dysprosium, and erbium acetylacetonates, they are active in the vicinity of 420–432, 304–322, and 620–650 cm^{-1}. The bond force constants f_{Ln-O} increase with decrease of the Ln–O bond length. Although the Ln(III)–O bond is believed to be ionic, it has been suggested [129] that the increase of the Ln–O stretching frequencies is due to a slight increase of the degree of covalence in the acetylacetonate complexes as a result of π-bonding and the increase of the mass of the central ion.

The values of f_{Ln-O} calculated by an empirical method [130] (for example, f_{Pr-O} = 2.98–2.41 mdyn $Å^{-1}$) differ from those (f_{Pr-O} = 2.10) obtained [129] by the more rigorous Urey–Bradley method. It is very likely that the vibrations active at 268–296 and 353 cm^{-1} in the spectra of the tetraethylammonium isocyanate complexes mentioned above [431] are due to the Ln–O bond of the M–OCN group. The "hard–hard" interaction of lanthanides with ambident pseudohalide ions usually leads to the same conclusion [48,301].

The infrared spectra of lanthanide complexes in the range 600–4000 cm^{-1} have been investigated mainly in order to discover the donor centre in the molecules of bi- and poly-dentate ligands (competitive coordination [301]). Infrared spectroscopic data were used to determine its location in lanthanide complexes with many ambident organic ligands: tetramethylene sulphoxide (oxygen atom of the S=O group) [52], salicyl hydrazide (secondary amide nitrogen atom) [53], salicylidene- [54] and naphthylidene-anthranilic acids [228] (O–O rings), $\alpha\beta$-unsaturated β-ketoimines (NC-chelates) [434], 1,2-ethylenebisdiphenylphosphine and arsine oxides (bridging groups involving the phosphoryl and arsenyl oxygen atoms) [435], *N*-oxides of quinaldinic acid (NO linkage) [436] and of *o*-hydroxyquinoline (the oxygen atom in the hydroxy- and N → O groups) [437], *o*-hydroxyacetophenone [56], and salicylaldehyde (metal-containing OC-ring [437,438], thiourea (S atom) [44], 2,2′-bipyridyl *N*-monoxide (Ln–O bond absorbing at 324 cm^{-1}), [439] urea [439] and diphenylformamide [103,441,442] (oxygen atom), butyl phosphate (phosphoryl and ester oxygen atoms) [356, 443-445], protonated methyl iminodiacetates (oxygen atom of the acetyl group and possibly of the non-protonated carboxy-group) [446], various nitrogen-containing six- [16] and five-membered [169] heterocycles (nitrogen atoms of the pyridine type), and aliphatic and aromatic amines (nitrogen atoms of the amino-groups) [16].

With increased interest in the lanthanide complexes of aminoacids and complexones, numerous studies have been made in order to assign the vibrations of the carboxy-group [218,447-452] and to determine the amount of its ionic and covalent character [447,449] as well as the possibility of employing the different $\Delta\nu = \nu^{as}_{CCO} - \nu^{s}_{CCO}$ in order to characterise the relative strength of the Ln–O bond [128,449, 450]. The study of the infrared spectra also proved to be extremely useful in the solution of the problem of the formation of acid or neutral lanthanide salts of aminoacids and complexones [448-452].

4. Microwave Spectroscopic Studies

The NMR method is widely used in the coordination chemistry of the lanthanides in order to investigate the composition of the complexes, the mode of coordination, [453-463] the exchange kinetics, and the fine structure of the ligands [459-464]. NMR data have shown that [456] the interaction of the lanthanides with complexones is accompanied by the formation of 1 : 1 and 1 : 2 (La, Lu) complexes; hydroxo-complexes are formed in the alkaline region [451] and protonated complexes are formed in the acid region. The kinetic data obtained in NMR investigations of ligand exchange in lanthanide complexes of a number of nitrogen-containing donors [16] [4,4′-di-n-butylpyridine [462] and tri-(β-aminoethyl)amine [463]] made it possible to determine the parameters of the transition state, the order of the exchange reaction, and structural isomers of the ligands. It was established that the reaction with di-n-butylpyridine [462] is of second order: $\Delta H^{\neq}$ = 10.6 ± 1.3 kcal $mole^{-1}$ and $\Delta G^{\neq}$ = 17.6 kcal $mole^{-1}$.

The kinetics of ligand exchange, including transsolvation, have been studied in detail [457,458]. For ratios $SmCl_3$: EDTA ≥ 1 : 2, slow exchange is observed between

the free and bound ligand species:

$$SmL + H_nL_1 \rightleftarrows SmL_1 + H_nL \quad (1)$$

$$HSmL + H_nL_1 \rightleftarrows HSmL_1 + H_nL \quad (2)$$

where n is the degree of protonation of EDTA. The entropies, activation energies, and rate constants K for exchange for a ligand containing between two and four protons were determined for reactions of type (1). It was shown that K increases in the sequence $HL < H_2L < H_3L < H_4L$.[464]

It was established[54] that lanthanides are coordinated to the water molecule and the chloride ion in the complexes $[Ln(LH)_2(H_2C)Cl]$, where Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, or Lu and L = *N*-salicylideneanthranilic acid.

Polycrystalline hydrates having the composition $MLnEDTA.nH_2O$, where M = Na(I), K(I), Rb(I), or Cs(I), Ln = La(III), Lu(III), Nd(III), Eu(III), Gd(III), Dy(III), Er(III), or Yb(III), and $n = 3-9$, were investigated by the low-resolution ^1H NMR method[465] at temperatures between $-100°$ and 250°C. In all the cerium-subgroup lanthanide compounds in the range from 0° to 60°C, two groups of water molecules, differing in their mobility in the crystal lattice, were detected; a group of three water molecules is in a rigidly fixed state, while the proton–proton vectors of the remaining molecules are distinguished by a fairly considerable mobility in the crystals. Comparison of the ^1H NMR and optical absorption spectroscopic data in the visible region indicates the incorporation of three water molecules in the inner coordination sphere of the lanthanide, which agrees well with X-ray diffraction data. The structure of the hydrates of lanthanide complexonates has also been discussed in other studies[466,467]. The ^1H NMR, optical spectroscopic, and X-ray diffraction data led to the conclusion that the number of inner-sphere water molecules in the solid hydrated lanthanide–EDTA complexes decreases in the La–Lu series: whereas three water molecules are incorporated in the inner coordination sphere in the complexes of light lanthanides, ytterbium(III) forms a complexonate with a single molecule of inner-sphere water.

The ^1H NMR spectra of europium complexes as well as measurements of magnetic circular dichroism of the praseodymium and neodymium complexes of azomethines obtained from aspartic acid and aromatic aldehydes (pyridoxal, *o*-vanillin, 5-nitro-*o*-vanillin, and 5-bromosalicylaldehyde)[468] are different when optically active aspartic acid and the racemate are used, which shows that each lanthanide ion is linked to more than one ligand molecule.

The employment of NMR data makes it possible to determine the configuration of the coordinated ligand[469,470] and also the geometry of the complexes in solution. Ln^{3+} ions forms complexes and induce in NMR spectra both positive and negative paramagnetic shifts, yielding information about the structure of the ligands and about the contact and pseudocontact mechanism of the shifts. One of the methods developed for the separation of the pseudocontact and contact contributions to the overall shift of the signal in the NMR spectrum makes it possible to investigate the geometry of the complex (in accordance with McConnell's equation[471]). In particular, a conformation has been proposed[472] for the Ln(III) complexes of indoline-3-acetate (Ln = Pr, Nd, Eu, Gd, Tb, Dy, or Ho), in which the carboxylate behaves as a bidentate ligand and the Ln^{3+} ion is located on the bisector of the OCO angle; the calculated Ln–O distance varied in the range 2.2–2.5 Å.

The possibilities of the above method in the determination of the ligand configurations were illustrated by data[473] obtained in the determination of the configurations of the isomers of 2-methoxycarbonyl-4-methyl-5-phenylpenta-2,4-dienecarboxylic acid with melting points of 117°C (I) and 153°C (II), which could not be done by analysing the infrared and ultraviolet spectra recorded under the usual conditions. Analysis of the pseudocontact shifts induced by Ln^{3+} ions in NMR spectra showed that isomer (I) has the *E*,*E* configuration while isomer (II) has the *Z*,*E* configuration. Similar studies involving the analysis of NMR spectra of solutions (in D_2O) of α-azetidine-2-carboxylic acid in the presence of praseodymium(III), neodymium(III), and europium(III) nitrates established[474] that the four-membered ring of the azetidinecarboxylic acid has a folded configuration with a dihedral angle of 25°, the carboxy-group occupying the equatorial position. The fact that the above investigations were undertaken is evidence for a considerable interest in the study of the structures of the ligands and the geometry of lanthanide complexes in solutions by analysing NMR spectra. The method[471] based on the analysis of NMR spectra in terms of McConnell's equation is simpler and its accuracy is comparable to that of X-ray diffraction analysis.

Apart from NMR spectra, ESR and Mössbauer spectroscopic data have been used to investigate lanthanide complexes. ESR signals of europium(II) have been detected at frequencies of 9 and 35 GHz in solutions at 25°C; a hyperfine structure due to the europium nuclei appears in the spectra of frozen solutions[475]. The *g*-factors and the temperature variation of the line width in the ESR spectra of gadolinium(III) ions introduced into $Ln(C_2H_5SO_4)_3.9H_2O$ single crystals, where Ln = La, Pr, Nd, Sm, Tb, Dy, Ho, Er, Yb, or Lu, have been discussed[476]. The introduction of Gd^{3+} ions into the above single crystals as well as $Nd_2(SO_4)_3(NH_4)_2.8H_2O$ single crystals[477] makes it possible to observe at room temperature the ESR spectra of two magnetically non-equivalent gadolinium(III) complexes, the symmetry of these centres being tetragonal with unusually low values of the crystal field parameters. A decrease of temperature to 77 K results in the resolution of the gadolinium(III) spectra either owing to a stronger crystal field, leading to a greater zero-point splitting, or owing to a crystallographic phase transition in the above temperature range. As a result of the maximum splitting of the states characterised by the quantum number J, the magnetic susceptibilities of the majority of lanthanides in crystals and in solutions differ little from the values in the free state.

Relatively few instances are known in which magnetic resonance was observed in an excited state[478]. Such observations are possible if the difference between the energies of the excited and ground states is less than kT. For lanthanides with an odd number of electrons, the Kramers doublet occupies the lowest energy level owing to the presence of an axial crystal field and the spin–orbital interaction. However, the intense spin–orbital interaction in the excited states implies a strong interaction with the environment. For this reason, even in this case the recording of the ESR signal usually requires a temperature of 20 K or less. In lanthanides with an even number of electrons, the crystal field with C_{3v} or C_{3h} symmetry splits each state into singlets and doublets. The splitting associated with the Jahn–Teller effect is usually slight and does not remove the residual degeneracy. It is therefore postulated that the system symmetry is still C_{3h} or C_{3v}.

ESR studies of relatively simple systems provide a satisfactory answer to the question of the symmetry of the ion and its distortion. In complex systems, an unambiguous result may require much effort[478].

The spectra of europium[139] in weak, moderate, and strong external magnetic fields have been investigated by the Mössbauer method[479,480] at temperatures in the range 1.2–77 K. The form of the lineas in the Mössbauer spectra (MS) has been discussed on the basis of the relaxation theory and comparisons with calculation have been made: the MS parameters and the properties of the complexes are interrelated. The absence of a magnetic hyperfine structure in MS at temperatures in the range 1.2–77 K indicates the absence of magnetic ordering in $[Eu(NH_3)_6]^{3+}$ even at 1.2 K. The calculated rate of spin–lattice relaxation (50×10^6 s^{-1}) and other experimental data confirm the $4f^7$ configuration of europium(III). In the europium chelates EuL_4X, where L = PhC(O)CH(O)Ph and X = Et_4N (III), Et_2NH_2 (IV), or piperidine (V), and in the mixed chelate EuL_3Phen, where L = PhC(O)CHC(O)Me (VI), an appreciable Mössbauer effect was not observed at room temperature[22]. The isomeric shifts relative to Eu_2O_3 in compounds (III)–(VI) are respectively −0.58, −0.60, −0.50, and −0.58 mm s^{-1} and are independent of temperature. The shifts confirm that $5d$, $6s$, and $6p$ europium orbitals participate in the formation of partly covalent bonds in compounds (III)–(VI). The isomeric shifts in the Mössbauer spectra of europium(III) complexes with nitrogen- and oxygen-containing ligands[12] reveal the following regularity: coordination compounds with N-donors are characterised by lower shifts than compounds with O-donors.

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The data which have accumulated during the last decade and which have been discussed in this review, indicate a significant progress in the coordination chemistry of the lanthanides.

At the same time there is still little information about lanthanide complexes in which the oxidation state of the lanthanide is other than three and lanthanide oxide halide and dioxide halide complexes, while the methods of preparation of these halogen-containing compounds are fairly well known[234]. Polydentate macrocyclic ligands (porphyrins[481–483] and crown-ethers[484]) have begun to be used comparatively recently in the synthesis of lanthanide coordination compounds and their promise is evident.

The problems of "competitive coordination"[301] and of the Lewis acidity of lanthanide salts[302] have been inadequately investigated in the coordination chemistry of the lanthanides.

It is of interest to study the equilibria involved in the formation of lanthanide complexes of different types, particularly mixed and polynuclear complexes, to carry out quantum-chemical calculations, and to investigate further the physicochemical properties of lanthanide coordination compounds. The development of research on these and other fields traditional for the chemistry of complexes is the task for the immediate future.

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