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Features of the complexation of trivalent rare earths

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ABSTRACT. Reasons why chelates of rare earths (RE) do not obey the tetrad 'doublet' effect are discussed. The examination is based on the concept of an ionic metal–ligand bond in RE complexes. The mutual influence of ligands in lower, higher, polynuclear and mixed complexes formed by ligands of low, medium and high denticity is discussed from this viewpoint. Intermolecular interactions in complexes of various structure are examined relative to variations in the volatility of chelates and their selectivity in sublimation and deposition. Structural rearrangement occurring at different points in the RE series for different ligands is proven to be the reason behind the irregular change of properties of RE complexes as a function of RE ionic radius.

A bibliography with 42 citations is given.

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I. Introduction

The predominantly ionic nature of the RE^{III}–ligand bond has been cited as the main feature of RE (Sc, Y, La, Ce–Lu) complexes in previously published reviews.[1,2] The most important consequence of the ionic bonding is a high and variable coordination number (CN) for RE.[3] During the last decade, new evidence supporting such an approach for analysing the nature of the bonding in RE complexes has been gathered. The ionic bond, with a small covalent contribution, does occur. However, questions about the size of the covalent contribution to the metal–ligand bond in such compounds is still actively discussed. A consensus has not been reached. Therefore, in this review we direct special attention to this aspect of RE coordination chemistry.

Problems of RE^{III} complexation are discussed using complexes with organic ligands of various classes as examples (abbreviations for these ligands are given below):

a) Aminocarboxylic acids:

H_4EDTA—ethylenediaminetetraacetic acid
H_5DTPA—diethylenetriaminepentaacetic acid
H_2EDDA—ethylenediaminediacetic acid
H_3NTA—nitrilotriacetic acid
H_2IDA—iminodiacetic acid
Hal—α-alanine
Hgl—aminoacetic acid (glycine)

b) Carboxylic and hydroxycarboxylic acids:

HA—acetylacetone
HDPM—dipivaloylmethane
HPiv—pivalic acid

c) β-diketones:

HA—acetylacetone
HDPM—dipivaloylmethane
HPTFA—pivaloyltrifluoroacetone
HAcim—acetylacetoneimine

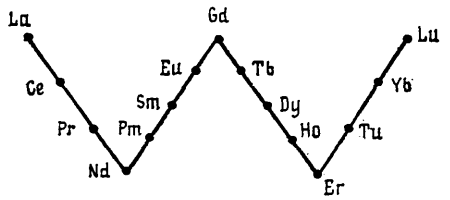
d) Neutral ligands with N and O donors:

phen—*o*-phenanthroline
bipy—α,α′-bipyridyl
py—pyridine
DMSO—dimethylsulphoxide
MESO—methylethylsulphoxide
DMF—dimethylformamide
THF—tetrahydrofuran
HMPA—hexamethylphosphortriamide
TPPO—triphenylphosphineoxide
TBP—tributylphosphate
3(4) – Pic—3(4)-picoline

II. The 'tetrad' effect and the nature of the chemical bond in RE coordination compounds

Let us recall that the tetrad effect consists of the periodic change of properties in the 15-membered RE series La, Ce–Lu.[4,5] This enables the series to be broken into four 'tetrads' corresponding to

the four straight lines in the letter 'W':



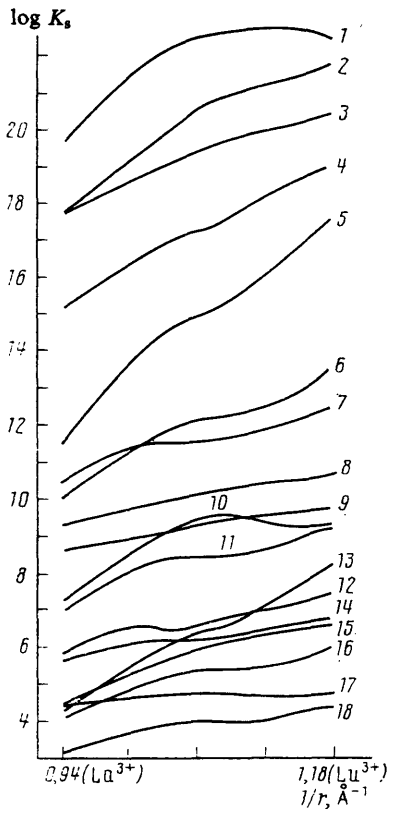


Figure 1. Dependence of lg K_s (K_1, K_2 or β_2) on RE^{III} ionic radius: M(DTPA)$^{2-}$(K_1) (*1*); M(NTA)$_2^{3-}$(β_2) (*2*); M(DPM)$_2^{+}$(β_2) (*3*); M(EDTA)$^{-}$(K_1) (*4*); M(EDDA)$_2^{-}$(β_2) (*5*); M(IDA)$_2^{-}$(β_2) (*6*); M(NTA)(K_1) (*7*); M(DPM)$^{2+}$(K_1) (*8*); M(DPM)$_2^{+}$(K_2) (*9*); M(NTA)$_2^{3-}$(K_2) (*10*); M(EDDA)$^{+}$(K_1) (*11*); M(EDDA)$_2^{-}$(K_2) (*12*); M(IDA)$^{+}$(K_1) (*13*); M(NTA)(OH)$^{-}$(K_2) (*14*); M(EDDA).(OH)(K_2) (*15*); M(IDA)$_2^{-}$(K_2) (*16*); M(al)$_2^{+}$(K_1) (*17*); M(gl)$_2^{+}$(K_1) (*18*)

Many articles published over the last few years on the chemistry of RE compounds, including complexes, have tried to prove that there is a tetrad effect [or double-u (W) or double–double effect]. It has been assumed that its detection is a direct indication of the reliability of new results obtained. However, such a position is incorrect since the change of properties in RE complexes, especially if their structure is complicated, frequently does not exhibit a W-shaped nature. We read, 'There are only a few ligands for which the rules are observed over the whole RE series and many for which such rules are observed for only a part of the series' (Ref. 6, p. 185).

It must also be noted that even if the dependence in coordinates of property–RE atomic number is W-shaped, in other coordinates, for example property–RE^{III} ionic radius, the dependence is not W-shaped but monotonic.

Let us examine as an example the dependence of lg K_s for RE complexes of polyaminocarboxylic acids on the inverse of the RE^{III} ionic radius. It is clear from Fig. 1 that the W-rule is not obeyed.[7,8] More often than not the curves are smooth and sometimes, for example for EDTA, the dependence of lg K_s on $1/r$ is practically a straight line.

In our opinion, the latter example is of prime importance. It indicates that the bonding in RE complexes is predominantly ionic since the coulombic force itself, which determines the strength of the complexes, is inversely proportional to the distance (its square) between the interacting centres of positive (RE cation) and negative (ligand) charge. This in turn depends on r.

The dependence of the properties of RE complexes not on $1/r$ but on atomic number is plotted in Fig. 2.[6] The similar W-shaped changes of average free energy of complexation ($\Delta\overline{G}$) and ionic radii are interesting. This indicates that the ionic radius itself is the principal factor determining the properties of RE compounds including $\Delta\overline{G}$ of complexation. Since both quantities exhibit a W-shaped change in the RE series, it is obvious that the dependence of $\Delta\overline{G}$ on r will not be W-shaped. In fact, this same conclusion was made before.[6] According to the previous report,[6] since all described properties reflect the lanthanoid† contraction, it follows that this contraction is not a smooth function of Z (atomic number).

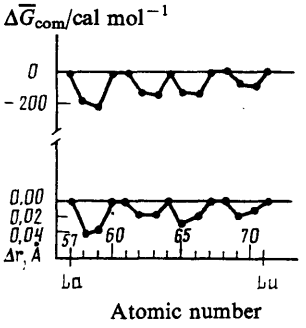


Figure 2. Dependence of average free energy of complexation $\Delta\overline{G}_{com} = \Delta G_{exp} - \Delta G_{int}$ (*a*) and RE ionic radii $\Delta r = r_{exp} - r_{int}$ (*b*) on atomic number.[6]

Therefore, the principal reason for the W-effect is taken to be the controlling influence of changes of radius (atomic, ionic) in the RE series on properties of the compounds. Consequently, the W-shaped dependence on atomic number is seen for those properties that depend on the RE^{III} ionic radius, i.e., have an ionic nature.

† Correctly stated 'lanthanide' and not 'lanthanoid' contraction (Ref. 9 p. 10) (author's note).

The W-shaped dependence can be converted into a smooth one (sometimes linear) by changing the 'atomic number' coordinates into 'ionic radius' (Fig. 1). This indicates that the ionic component predominates in the chemical bonding in RE complexes. Moreover, a deviation from linearity (ideality) in property–radius coordinates can be qualified as a result of the superposition of other factors, primarily, stereochemical hindrances, a covalent contribution and structural changes in the RE series.

In this sense, plotting graphs of any property of RE compounds in property–atomic number coordinates is uninformative since the dependence of the examined property on ionic radius taints all effects. If the plot is made in property–ionic radius coordinates, those factors that are specific for the given system and not for the RE series in general will be identified. Thus, the irregularities in the functions $\lg K_s = f(1/r)$ (Fig. 1) indicate[7,8] at what place in the RE series the structure of the RE complexes changes and how the covalent contribution influences the strength of the complexes if their structure is mainly determined by the ionic contribution.

The dependence of the properties of RE complexes, for example their stability, on ionic radius has a well interpreted physical meaning. It suggests that a decrease of metal ionic radius, makes the metal–ligand bond in the complex stronger. This follows from Fajans simple polarisation theory (for example, cf. Ref. 9, pp 25–40). According to this, the polarising effect exerted on the ligands by RE^{III} cations with a hard rare-gas outer electron shell ($5s^25p^6$) increases from La^{3+} to Lu^{3+} (and from La^{3+} to Sc^{3+}) owing to an increased positive charge density on these cations. As a result, the ligand unavoidably draws nearer to the metal. This increases the metal–ligand electrostatic interaction and simultaneously increases the covalent contribution to the chemical bond (especially if the ligand or its separate functional groups can be polarised).

It is noteworthy that RE^{III} ions, which have a rare-gas configuration, can present only energetically unfavourable vacant *5d*-, *6s*- and *6p*-orbitals and unfilled *4f*-orbitals, which are highly shielded by the $5s^25p^6$ electrons, to the ligands for formation of covalent donor–acceptor bonds. The small degree of participation of *4f*-orbitals in complex formation is well documented. For example, the small shifts of absorption bands in RE electronic spectra even on formation of very strong complexes with polydentate ligands provide evidence for this (Ref. 8, pp 5–23, 65–76). This is also supported by the low stability of RE complexes with monodentate ligands (including strong-field ligands such as CN^-, CO, etc.). Only the chelate effect arising on formation of RE complexes with polydentate ligands substantially increases the stability of the RE^{III} complexes. For example, K_s of Nd^{III} complexes with $EDTA^{4-}$ and $DTPA^{5-}$ are 10^{16} and 10^{22}, respectively.

Furthermore, since the ratio between the ionic and covalent contribution to the RE^{III}–ligand bond is often poorly defined, the choice of coordinates for examining the dependence of properties on position of the metal in the RE series is made arbitrarily in many instances.

For example, we learn (Ref. 10, p. 205) that *'additional effects* of stabilisation resulting from the influence of the ligand field and spin–orbit coupling are determined by the number of *f*-electrons. Therefore, the correct correlation for revealing *all effects that determine the bond energy* is the dependence on the number of *f*-electrons, i.e., on the RE atomic number'. The question arises, 'If the *4f*-electrons influence namely the *"additional"* effects of complex stabilisation (which can be agreed to), then why will it be correct to correlate the strength of *all chemical bonding* with the number of *f*-electrons and not the parameters determining the principal (ionic) contribution to the chemical bonding?' In our opinion, a mistake has been made here since the nature of the chemical bonding in RE complexes must be carefully discussed taking into account recently obtained data.

The semiquantitative nature of the simple polarisation approach based on Fajans rules (or the contemporary but also semiquantitative Pearson concept of hard and soft acids and bases[11]) usually yields the correct prediction of the principal tendencies in the change of properties of one or another series of chemical compounds, if the series is chosen legitimately. In our opinion, the RE series is an ideal subject for demonstrating the fruitfulness of such an approach. Therefore, the concept underlying further examination of the properties and structure of RE complexes can be formulated as follows:

1. Complexes of a given composition in the series La, Ce–Lu and La–Y–Sc are formed mainly by ionic interaction of the RE^{III} and ligands. The strength of the ionic bond increases in these series as the RE^{III} radius decreases.

2. The covalent contribution to the RE^{III}–ligand bond increases according to Fajans rules as the polarising action of the RE^{III} cations increases, i.e., from La^{3+} to Lu^{3+} and from La^{3+} to Sc^{3+}.

3. The presence of a W-effect in the dependence of any properties of RE compounds on atomic number is consistent with primarily ionic bonding in these compounds. The lack of a W-effect for the majority of RE^{III} complexes indicates the existence of effects that complicate the simple ionic model. These are a greater or lesser covalent contribution, a change of structure in one or another part of the RE series, the influence of steric hindrances that weaken the chemical bond, etc.

III. Evidence for a covalent contribution to the RE^{III}–ligand bond

The bonding in RE complexes is undoubtedly primarily ionic. However, it is important to estimate the amount of covalent interaction between the RE^{III} cation and the ligands. The simple polarisation model of Fajans predicts, as already indicated, an increase in the covalent (and ionic) contribution to the metal–ligand bond as the RE ionic radius decreases. However, compounds of the lighter lanthanides, i.e., RE with the maximal radius, are viewed as having the greatest covalent contribution in a number of reports.

Thus, Tananaev et al. (Ref. 6, p. 186) report that 'the *f*-orbitals contract faster in the first half of the series and slower in the second owing to the decrease of exchange interactions (a decrease in the number of unpaired electrons) in the f^7–f^{14} series.' Hence the conclusion was drawn that the *f*-orbitals more actively participate in chemical bonding in the first half of the RE series than in the second half.

This conclusion is supported[6] by data for the faster decrease of average molar volumes of the unit cells in the first half of the RE series than in the second. In our opinion, this conclusion is inaccurate since it is obvious that the rapid contraction of the *f*-orbitals in the beginning of the RE series controls the rapid decrease of molar volumes. This occurs because the ionic radius decreases quickly whereas the covalent contribution takes a different path.

Kostromina has come to the same, in our opinion, inaccurate conclusion.[10] A comparison of the enthalpic and entropic contributions to the thermodynamic stability of *f*- and *d*-element complexes (Ref. 10, p. 195 ff.) suggested that the enthalpic contribution to the formation energy of *d*-element complexes is large

and the entropic contribution to that of the *f*-elements with about the same K_s is large. Then, the conclusion was reached that 'for elements of the Ce subgroup the covalent component provides a substantial contribution to the bond energy' by carrying out multistepped calculations using data from methods of varying accuracy such as electronic spectroscopy, thermochemistry and pH measurements (Ref. 10, p. 216). Such a calculation was not carried out for RE of the Y subgroup. However, the whole discussion by Kostromina[10] leads one to believe that the covalent contribution to the bonding of later RE with polydentate ligands is relatively small.

We have already noted that the simple polarisation approach predicts a rule opposite to that accepted previously[6,10] New experimental data, as will be demonstrated below, confirm the correctness of the polarisation prediction.

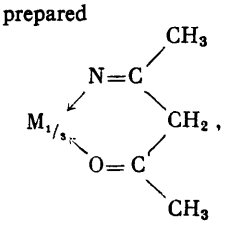
A large number of physical-chemical methods can detect the covalent contribution to the RE^{III}–ligand bond. We will discuss results obtained by photoelectron spectroscopy (PES), IR spectroscopy and kinetics studies.

1. Photoelectron spectroscopy

The principles of the PES method have been developed previously.[12,13] The study of RE β-diketonates by Vovna et al.[14] demonstrated a decrease of metal–ligand covalency as the metal radius increased in the following series of tris-acetylacetonates: $ScA_3 > LuA_3 > YA_3$. It was noted that an increase of the metal radius in tris-acetylacetonates of the iron subgroup (Fe^{III}–Ru^{III}–Os^{III}) caused the opposite effect, an increase of covalency. It is noteworthy that such a trend agrees completely with Fajans rules, according to which the polarising action of ions with a rare-gas electron configuration, for example RE^{III}, increases with decreasing radius. However, ions with an unfilled (as in the Fe subgroup) or completely filled 18-electron shell polarise (and are polarised) more strongly the greater their radius. Since the covalent bond can be viewed as a polarising perturbation of the ligands by the metal, the series cited above agree with predictions of simple polarisation theory.

The same result as for the RE^{III} tris-acetylacetonates was obtained by PES for RE^{III} tris-dipivaloylmethanates $M(DPM)_3$. The photoelectron spectra of $M(DPM)_3$ are consistent with a greater donor strength of DPM compared with acetylacetone. For $M(DPM)_3$, additional bonding molecular orbitals are detected in the valence band whereas the upper MOs are withdrawn from the valence band. Like for the RE^{III} tris-acetylacetonates, signals in the PES of the RE^{III} tris-dipivaloylmethanates shift by 0.2–0.3 eV to higher ionisation potentials owing to an increase of covalency and a change of $M(DPM)_3$ geometry as the RE^{III} ionic radius decreases (Ref. 14, p. 149). The smallest covalent contribution to the metal–ligand bond among the $RE(DPM)_3$ studied is found for $Pr(DPM)_3$. The MO in its spectrum is not split (splitting is a sign of covalency).

It is also very interesting to compare the PES of RE acetylacetonates and acetylacetoneiminates. As demonstrated previously,[15] where RE acetylacetoneiminates $M(Acim)_3$ with chelate rings were first prepared



substitution of one of the O atoms in the six-membered chelate rings in MA_3 by a N atom in $M(Acim)_3$ causes the PES to change. This is indicative of a relatively large covalent contribution to the M^{3+}–$Acim^-$ bond. It can be seen in Fig. 3 (Ref. 15, p. 87) that the splitting of PES signals of $Lu(Acim)_3$ is much greater than that of LuA_3.

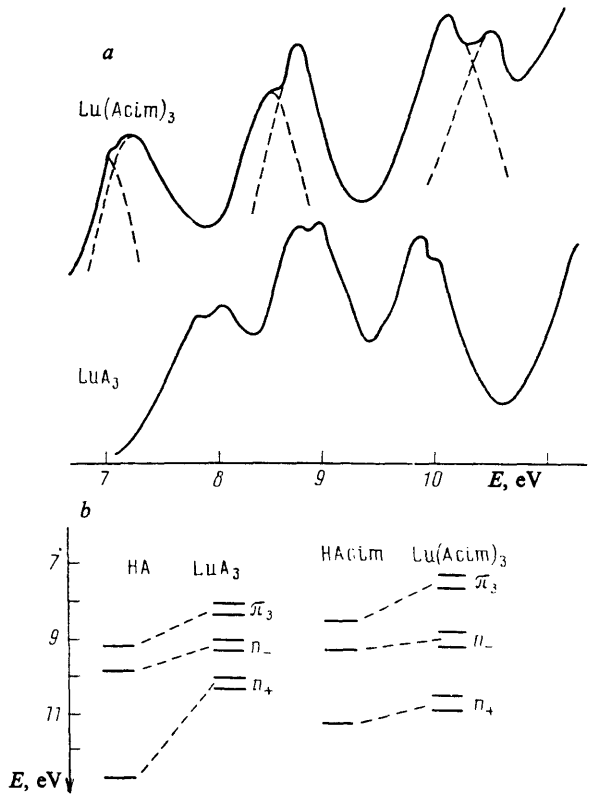


Figure 3. Photoelectron spectra of Lu acetylacetonate and acetylacetoneiminate (*a*); comparison of orbital energy of free ligands (HA, HAcim) and the same ligands in Lu complexes (PES data) (*b*).[15]

This fact agrees well with general concepts of polarisation theory, according to which the N atoms (one of the two donors in $Acim^-$) are more strongly polarising. Consequently, this forms a stronger covalent bond than the O atoms (in A^-) under otherwise equal conditions. However, it is noteworthy that the thermodynamic and, therefore, the chemical stability of $M(Acim)_3$ compounds is less than that of MA_3. Hence, $RE(A)_3$ are unstable in air, quickly hydrolyse, and lose volatility. However, $RE(Acim)_3$ of the Ce subgroup are difficult to isolate pure.[15] Apparently the large covalent contribution (due to substituting O by N) to the bonding in $M(Acim)_3$ is accompanied by a weakening of the metal–ligand coulombic interaction. As already stated, this is the principal component of the chemical bond in all RE^{III} compounds.

As is clear from the preceding, the PES method provides direct evidence for a covalent contribution to the bonding of RE^{III} to

ligands and also indicates that this contribution increases as the RE ionic radius decreases. In our opinion, these data are of prime significance in understanding the coordination chemistry of RE.

2. IR spectroscopy of RE complexes

The literature contains an enormous amount of information on the IR spectra of RE complexes. Unfortunately, the M–O and M–N stretching vibrations are located in the low-frequency IR region (<400 cm^{-1}). As a rule, they are insufficiently characterised due to the mixing of these vibrations with skeletal vibrations of the polydentate organic ligand. The broad contours of these bands make their assignment and analysis difficult. Therefore, the type of metal–ligand bond is usually evaluated by noting how coordination to M^{n+} affects the position of the absorption bands in the spectrum of the free ligand (Ref. 8, pp 76–102). Numerous investigations have demonstrated that the C–O stretches in spectra of RE^{III} complexes with O- and N-donor ligands, as a rule, do not shift compared with their position in the spectrum of the free ligand (for example, in the spectrum of the Na salts, which are usually taken as a model of the ligand with ionic bonds[8]). This is consistent with a RE^{III}–O ionic bond. On the other hand, absorption bands corresponding to the N–H and C–H bonds in the ligand shift in the spectra of chelates with a RE^{III}–N bond. This is consistent with a partially covalent M–N bond. Apparently the N atom is softer than the hard, strongly electronegative O donor and experiences a shift of electron density owing to polarisation by the RE^{III}. This shift extends to the ligand bonds conjugated with the RE^{III}–N bond. The importance of analysing the structure of complexes by IR spectroscopy is supported by the data in Table 1. It is clear that the ν(C–N) and ν(N–H) bands of a RE^{III} complex with IDA shift most in spectra of RE(IDA) compared with their position in ionic NaIDA, less in $RE(IDA)_2$ and least in $RE(IDA)_3$. In the last compounds, the polarising action of the RE^{III} is 'absorbed' by the three IDA ligands and, therefore, is weak.[16]

Hence, IR spectroscopy not only indicates partial covalency in the metal–ligand bond but also enables the relative strength of this bond in series of related compounds to be characterised.

Let us illustrate the capabilities of IR spectroscopy using RE^{III} β-diketonates as an example. As seen in Table 2, the shift of ν(C=O) to low frequencies in the spectra of RE^{III} tris-acetylacetonates is maximal for anhydrous MA_3.

The low-frequency position of the ν(C=O) band indicates that the C=O bond is weakened most where only acetylacetonates enter the RE^{III} coordination sphere. Introduction of additional neutral ligands such as H_2O, phen, DMSO, etc. into the inner sphere weakens the coordination of the principal ligand, acetylacetonate. This strengthens the C=O bond and increases ν(C=O). It is also shown in Table 2 that chelation of acetylacetoneiminate by RE^{III} greatly weakens the N–H bond in the ligand. The greatest weakening occurs in $M(Acim)_3$, the M^{3+} cations of which have the smallest ionic radius, i.e., are the strongest polarisers.

It is interesting that the sensitivity to the size of the RE^{III} polarising action in this instance also (like for RE complexes) is substantially greater for the M^{3+}–N bond than M^{3+}–O.

Structural data confirm the correctness of conclusions about RE chelate structures made on the basis of IR spectra. For example, the average Yb^{3+}–O distance in YbA_3,[17] for which ν(C=O) = 1585 cm^{-1}, is 2.211(8) Å, i.e., slightly less than in $Yb(Acim)_3$ (2.233 Å) and in $YbA_3 \cdot 3H_2O$ (2.23 Å).[19] This agrees with ν(C=O) = 1595 cm^{-1} (Table 2).

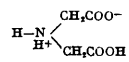
3. Kinetic studies

Systems of ionic compounds are known to be kinetically labile under appropriate conditions (solutions, melts, vapors). However, systems of covalent compounds (organic compounds, Pt complexes), as a rule, are kinetically slow. This can sometimes reach the point where equilibrium is not attained. For example, Pt complexes cannot be characterised by stability constants for this reason. Therefore, it can simply be said that rapid exchange reactions are a sign of ionic bonding whereas slow processes are typical of covalency.

Table 1. IR spectra of RE iminodiacetates[16].

Compound	ν(N–H), cm^{-1}	$\Delta\nu^*$(N–H), cm^{-1}	ν(N–C), cm^{-1}	$\Delta\nu^*$(N–C), cm^{-1}
Na_2Z	3340	–	1140, 1145	–
NdZCl	3250	90	1120	22
ErZCl	3255	85	1118	24
Nd_2Z_3	3270	70	1125	17
Er_2Z_3	3275	65	1125	17
$KNdZ_2$	3280	60	1128	14
$KErZ_2$	3280	60	1127	15
K_3NdZ_3	3290	50	1122, 1148, 1132	9
K_3ErZ_3	3290	50	1111, 1130, 1145	12

Note. Iminodiacetic acid (HIDA, H_2Z) has the structure



*$\Delta\nu$ = ν(RE^{III} complex) – ν(Na_2Z).

Table 2. IR spectra of RE^{III} acetylacetonates and acetylacetoneiminates.[15,17,18]

Compound	ν(C=O), cm^{-1}	ν(N–H), cm^{-1}
(Tb–Lu)$A_3 \cdot$HAcim	1600	3380, 3220
(La–Gd)$A_3 \cdot 2$HAcim	1605	3340, 3180
(La–Lu)$A_3 \cdot H_2O$	1615	–
(La–Lu)$A_3 \cdot 3H_2O$	1600	–
(Gd–Lu, Y, Sc)A_3	1585	–
HAcim	1625	3350, 3180
(Tu, Yb, Lu, Sc)$(Acim)_3$	1595	3265
(Dy, Er)$(Acim)_3$	1595	3275
$Gd(Acim)_3$	1595	3290
(Pr–Yb)$A_3 \cdot$DMSO	1600	–
(Pr–Yb)$A_3 \cdot$phen	1625	–

However, there usually is no simple and direct dependence between the kinetic parameters of exchange processes in systems with complexes and the type of metal–ligand bond that determines the

thermodynamic and structural characteristics. Comparison of kinetic, thermodynamic and structural parameters is most often complicated by the different mechanisms of the reactions being compared. However, if subjects with reactions described by identical kinetic equations can be found, such an examination can become valid.

We carried out a special investigation of the kinetic parameters of solutions of RE complexes and proved that the metal exchange in systems with light and heavy RE occurs by the same mechanism (identical kinetic equations) but with different rates. Such a conclusion suggests that the kinetic sluggishness typical of heavy RE complexes (RE of the Y subgroup) is due to a larger covalent contribution to the metal–ligand bond in these chelates compared with the same chelates of light RE (RE of the Ce subgroup).

Results of a study of the metal exchange in aqueous solutions containing RE^{III} and H_4EDTA are presented in Table 3.

Table 3. Metal exchange rate in aqueous solutions of EDTA complexes.[20]

M^{3+}_{leav}	M^{n+}_{ent}	$10^{-2}k'$, $dm^3 mol^{-1} sec^{-1}$	$10^{-2}k''$, $dm^3 mol^{-1} sec^{-1}$
Nd^{3+}	Yb^{3+}	4.67±0.33	18.0±0.20
Nd^{3+}	Tu^{3+}	4.50±0.50	17.6±0.17
Nd^{3+}	Er^{3+}	4.17±0.51	15.6±0.10
Nd^{3+}	Gd^{3+}	4.33±0.17	14.0±0.36
Nd^{3+}	Eu^{3+}	4.00±0.50	13.3±0.20
Nd^{3+}	Pr^{3+}	4.67±0.20	12.3±0.34
La^{3+}	Cu^{2+}	20.2±0.2	$(2.2\pm0.1)\cdot10^2$
Pr^{3+}	Cu^{2+}	6.6±0.1	$(0.92\pm0.09)\cdot10^2$
Nd^{3+}	Cu^{2+}	4.8±0.1	$(0.67\pm0.01)\cdot10^2$
Eu^{3+}	Cu^{2+}	2.3±0.3	$(0.22\pm0.01)\cdot10^2$
Gd^{3+}	Cu^{2+}	1.6±0.1	$(0.13\pm0.03)\cdot10^2$
Tb^{3+}	Cu^{2+}	0.82±0.04	3.17±0.02
Er^{3+}	Cu^{2+}	$(5.5\pm0.1)\cdot10^{-2}$	0.83±0.03
Yb^{3+}	Cu^{2+}	$(1.56\pm0.05)\cdot10^{-2}$	0.33±0.01

It was found[20] that the exchange

$$[M_{leav}(EDTA)]^- + M^{n+}_{ent} \rightleftharpoons [M_{ent}(EDTA)]^{4-n} + M^{3+}_{leav},$$

obeys the following kinetic equation:

$$V = V_I + V_{II} = k'[H^+][M_{leav}(EDTA)^-] + k''[M_{leav}(EDTA)^-][M^{n+}_{leav}],$$

where M^{3+}_{leav} and M^{n+}_{ent} are the leaving and entering cations, respectively, and k' and k'' are the exchange rate constants for the dissociative and associative mechanisms. The rate of the dissociative process (V_I), as previously demonstrated,[20] is limited by cleavage of the leaving cation–acetate ($EDTA^{4-}$) bond in the intermediate protonated complex whereas the rate of the associative process (V_{II}) is limited by cleavage of the leaving cation–$N(EDTA^{4-})$ bond in the intermediate binuclear complex. Table 3 clearly shows that V_I does not depend on the nature of the entering RE^{III} cation but decreases as the leaving cation shifts towards the heavy RE. The rate V_{II} also is minimal in complexes of heavy RE, which have the minimal ionic radius and, therefore, provide the greatest chance for covalency owing to the large polarising effect.

Fig. 4 shows that the slope of the dependences of rate constants on ionic radius of leaving RE^{III} changes in the middle of the RE series. This can be related[20] to the change of inner-sphere hydration on going through the RE series. Whereas inner-sphere dihydrates $[M(H_2O)_2(EDTA)]^-$ are typical of heavy RE, formation of di- and trihydrates is equally probable for RE in the middle of the series. Thus, the following equilibrium was studied for the system with Eu^{III}

$$[Eu(H_2O)_2(EDTA)]^- \rightleftharpoons [Eu(H_2O)_3(EDTA)]^-,$$

and it was demonstrated[21] that the reactivity of the inner-sphere dihydrate is less than that of the trihydrate $[Eu(H_2O)_3(EDTA)]^-$. Structural data indicate that inner-sphere trihydrates are more characteristic of the light RE. This was found, in particular, for Nd and Eu complexes of EDTA. The structural data suggest (Ref. 8, p. 10) that the RE^{III} draw closer to the ligand if the number of inner-sphere waters of hydration decreases in the RE^{III} complexes of EDTA. In particular, the average RE^{III}–O ($EDTA^{4-}$) and RE^{III}–N ($EDTA^{4-}$) bond lengths in $[Er(H_2O)_2(EDTA)]^-$ are substantially less (2.27 and 2.56 Å) than in $[Nd(H_2O)_3(EDTA)]^-$ (2.53 and 2.83 Å).[22,23] Such a decrease of the bond lengths should certainly increase the polarisation of metal–ligand interactions. This increases the covalent contribution to the bond and affects the rate of electrophilic and nucleophilic substitution in addition to the size of the change of k' and k'' with decreasing RE^{III} ionic radius, as can be seen in Fig. 4.

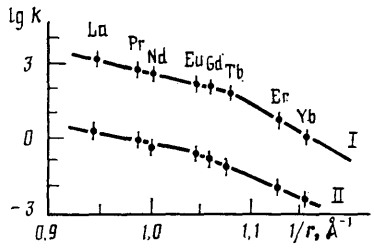


Figure 4. Change of metal-exchange rate constant in solution of RE^{III} EDTA complexes.[20] *I*, $\lg k'$; *II*, $\lg k''$.

Hence, the kinetic data and the PES and IR results confirm the correctness of the hypothesis ensuing from the simple polarisation model that the covalence in the metal–ligand bond increases as the RE^{III} radius decreases in the series La–Ce–Lu and La–Y–Sc.

IV. Mutual influence of ligands and metals in homoleptic and polynuclear RE^{III} complexes

If a complex contains several identical or different ligands in addition to several cations, all of these components of the coordination sphere affect each other. Obviously their mutual influence will be stronger the more labile their bonding in the complex. In our opinion, it is completely justified to assume that the mutual influence of coordination-sphere components is more easily transferred through an ionic metal–ligand bond than through a

covalent one. The reasons for this are the long range and sphericity of coulombic forces in contrast with the directionality and saturation (relatively short range) of covalent forces.

In our work[7,8] in addition to that of others,[6,10] it is possible to find numerous examples in support of the prediction just given, which invokes a strong and rapidly attained mutual influence of coordination-sphere components in RE^{III} complexes. In particular, the regular decrease of successive K_s for RE complexes formed by incorporation into the coordination sphere of one, two, three and more identical (cf. Table 1) or different ligands support the correctness of such an approach. The changes of successive K_s in the RE series of neutral mono-, bis- and tris-IDA complexes of RE [8,24] are plotted in Fig. 5 as an example. It can be seen that the first ligand (formation of the mono-complex) is bound most strongly in the coordination sphere (CS). The energy stored in one metal–ligand bond decreases smoothly on going to the bis- and tris-complexes. The anomalous path of $\lg K_3$ near the heavy RE is due to the generation of steric hindrances owing to the decrease of ionic radius and the approach of the cations and anions in the complex. In general, incorporation of each successive ligand decreases K_s by almost two orders of magnitude. This should be expected if the ionic model of the CS is accepted. According to this model, neutralisation of the positive charge of the RE^{III} cation by each negatively charged ligand should substantially weaken the metal–ligand bond in the CS.

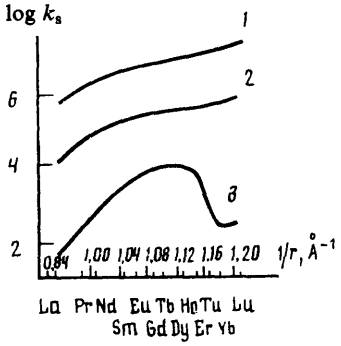


Figure 5. Change of stability of mono- (*1*), bis- (*2*), and tris-IDA complexes (*3*) of RE.[24]

The path shown in Fig. 5 for the successive K_s is normal for an ionic CS.[8] However, these data of themselves do not answer the question of whether the position of ligands in higher complexes is equivalent. For example, is each IDA ligand in bis- and tris-IDA complexes of RE bound with the same strength? In order to answer this question, data obtained by other methods can be used. For example, an IR study of solid RE complexes, as already mentioned above (cf. Table 1), indicates successive weakening of the RE^{III}–N bond on going from the mono- to bis- and tris-IDA complexes and equivalence for the two IDA residues in the bis-complex and three in the tris-complex. This conclusion agrees with PMR spectroscopic results.[11] However, this method detects equivalent ligands in higher RE complexes only for ligands of low denticity (in particular, including tridentate IDA). According to PMR, only one of the ligands remains highly dentate in complexes of ligands with high denticity for example, $[M(EDTA)_2]^{5-}$ with sexadentate H_4EDTA. The second only partially uses its donor atoms. This fact is explained in the monograph of Kostromina[11] by the large energy gained by retaining the configuration of the mono-complex $[M(EDTA)]^-$ in the bis-complex $\{[M(EDTA)](EDTA)\}^{5-}$ compared with the compound where some of the chelate rings of $[M(EDTA)]^-$ are broken and both $EDTA^{4-}$ residues are identically bound, i.e., exhibit decreased denticity of 4: $[(EDTA)\equiv M\equiv(EDTA)]^{5-}$. Apparently such a redistribution of donor atoms opens (breaks) the EDTA ring in the mono-complex. This sharply reduces the entropy of the system.

It is interesting that a similar nonequivalence of the structural components of the CS based on the polydentate complexants H_4EDTA and H_5DTPA is achieved not only in higher complexes (excess of ligand) but also in polynuclear complexes (excess of M^{3+}).

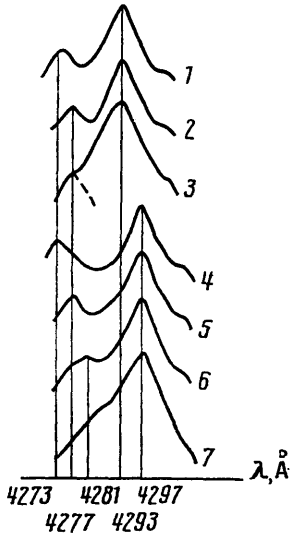


Figure 6. Electronic spectra of Nd complexes with $EDTA^{4-}$ (*1–3*) and $DTPA^{5-}$ (*4–7*).[25] Concentration, M: $[Nd_4(EDTA)_3]$ = 0.04 (*1*); 0.14 (*2*); $[Nd_5(DTPA)_3]$ = 0.02 (*4*); 0.15 (*5*); 0.40 (*6*). Solid complex (*3*, *7*).

As demonstrated in Fig. 6,[25] high-resolution electronic spectroscopy (Ref. 8, pp 65–76] detects nonequivalent positions for the two Nd atoms in the dinuclear complexes $[Nd_2(EDTA)]^{2+}$ and $[Nd_2(DTPA)]^+$. In dilute solutions, one of the two moles of Nd^{3+} used per one mole of complexant forms the mono-complex $[Nd(EDTA)]^-$ or $[Nd(DTPA)]^{2-}$ with absorption bands at 4292 and 4297 Å, respectively. The second mole of Nd^{3+} remains as the aqua-ion $[Nd:aq]^{3+}$ with an absorption band at 4273 Å. Polynuclear complexes form as these solutions are concentrated (Ref. 8, pp 15–18). This produces only a small shift to long wavelength of the absorption band of the aqua-ion (to 4277 and 4281 Å in the H_4EDTA and H_5DTPA systems, respectively). A shift

of this value corresponds to coordination of Nd^{3+} by only one or two of the acetato-groups of the ligand. Therefore, high-resolution spectrography reveals the nonequivalence of the two Nd^{3+} ions in dinuclear complexes. Consequently, here, like in the higher complexes, the ligands and RE ions remain different. Their positions are not averaged. The energy gain from this structure apparently determines the state of the system in polynuclear complexes based on $EDTA^{4-}$ and $DTPA^{5-}$. Such an unaveraged state for the metals and ligands does not contradict the postulated ionic bond in RE complexes. In fact, PMR [10] and kinetic studies[20] detect rapid exchange in such systems so that the discussion is not about the nonequivalence of polynuclear or polyligand CS that presumes metal–ligand covalency but about which arrangement of donors and RE ions is thermodynamically most favorable.

Results of mathematical modelling of equilibria in EDTA solutions of Nd^{III} and Yb^{III} using experimental pH measurements are presented in Tables 4 and 5.[26]

Table 4. Modelled pH-tritration of $2Nd^{3+}-EDTA^{4-}-KOH$ solutions.[26]

Model No.	Model	Sum of squares of experimental deviations
0	H^+; Nd^{3+}; $NdOH^{2+}$; $EDTA^{4-}$; $HEDTA^{3-}$; H_2EDTA^{2-}; H_4EDTA; H_5EDTA^+; $Nd(EDTA)^-$	2.07
1	{0}+HNd(EDTA)	0.12
2	{1}+$Nd_2(EDTA)^{2+}$	0.07

Table 5. Stability of Nd^{III} and Yb^{III} EDTA complexes by mathematical modelling[26].

Compound	ln β	log K_s	pK_a
$[Nd(TDTA)]^-$	36.02±0.08	15.66	–
$H[Nd(EDTA)]$	40.88±0.09	–	2.11
$[Nd_2(EDTA)]^{2+}$	38.46±0.16	1.06	–
$[Yb(EDTA)]^-$	43.01	18.70	–
$H[Yb(EDTA)]$	47.10±0.09	–	1.78
$[Yb_2(EDTA)]^{2+}$	44.04±0.52	0.45	–

Note. β is the overall formation constant. K_s is the step-wise stability constant. K_α is the acid dissociation constant.

The data suggest that the strength of the polynuclear complexes decreases from light RE (Nd) to heavy ones (Yb). The very large difference in successive K_s corresponding to binding of one or two RE^{III} by one $EDTA^{4-}$, respectively, is interesting. For Nd^{III} and Yb^{III} this difference is greater than 14 and 18 orders of magnitude, respectively. Therefore, the thermodynamic efficiency of removing part of the donors from the mono-complex to form the polynuclear compounds is small. The same can be said about the nonequivalence of identical ligands in a system with more EDTA ligands and other RE polyligand compounds based on high-denticity ligands.[7] However, the less stable the mono-complex is (achieved with a low-dentate complexant), the less the difference is in the state of the second and successive ligands in the RE CS and the greater their mutual influence.

V. Mutual influence of ligands in heteroleptic RE complexes

If the principal ligand, i.e., the ligand forming the stronger bond to the RE^{III} in a mixed coordination sphere has high denticity and high donor activity then, as a rule, additional weaker ligands enter the complex with a relatively small K_s. Let the additional ligand be citrate with a comparatively low denticity (equal to 4). Then, RE^{III} form heteroleptic complexes in addition to those with the principal ligand, for example, EDTA. However, these have low stability.[7,27] This agrees well with the low stability (consider the successive K_s) of higher homoleptic complexes of RE with H_4EDTA. However, if the principal and additional ligands are of comparable denticity and donor strength (for example, H_2IDA and H_3Cit), their state in the $RE^{III}CS$ is essentially the same and resembles the situation discussed above for formation of higher homoleptic IDA complexes (cf. Table 1 and Fig. 5).

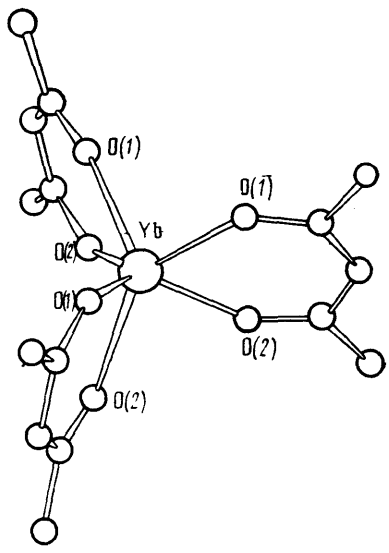


Figure 7. Crystal structure of anhydrous Yb tris-acetylacetonate.[28]

Mixed complexation in systems with principal and additional ligands of comparable strength have been studied by us in connection with adduct formation in RE^{III} tris-β-diketonates. Since RE^{III} characteristically have high and variable coordination number and the denticity of each β-diketonate is 2, only six donors surround the RE^{III} in monomeric tris-β-diketonates (Fig. 7).[28]

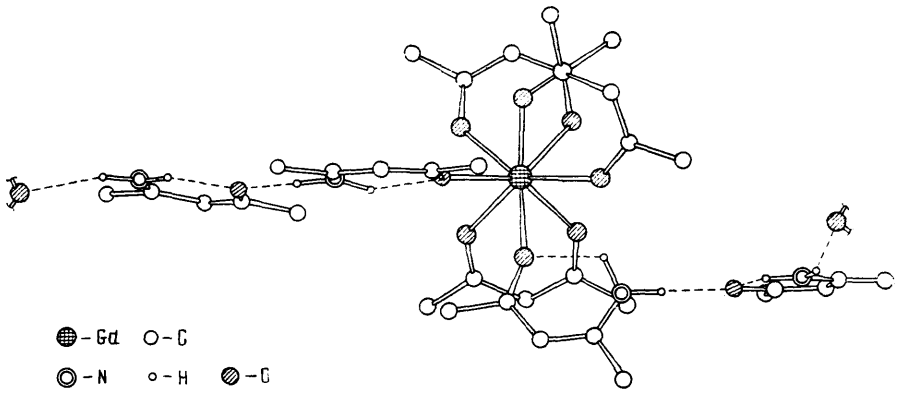


Figure 8. Structure of the adduct $GdA_3 \cdot 4HAcim$.[30]

In general this is clearly insufficient to saturate the $RE^{III}CS$. Therefore, tris-β-diketonates, including RE^{III} tris-acetylacetonates MA_3 and tris-dipivaloylmethanates $M(DPM)_3$, usually polymerise.[29] Polymerisation does not occur if an additional ligand capable of entering the inner CS of the RE^{III} tris-β-diketonate and increasing its CN to 7–9 is present. Mixed complexes based on tris-β-diketonates form. These are called adducts (i.e., addition products) although the additional ligands are inner-sphere and in this sense are equal to the principal ligands. The structure of the adduct of GdA_3 with HAcim of composition $GdA_3 \cdot 4Acim$ is shown in Fig. 8.[30] Of the four HAcim molecules, two are monodentate (through O) and increase the CN to 8. Two HAcim molecules are outer-sphere and bonded through H-bonds.

Incorporation of an additional neutral ligand into the CS of a RE tris-β-diketonate usually lengthens the $RE^{III}-O$ distance owing to partial neutralisation of the metal charge (ion–dipole interaction) and generation of steric hindrances. This can lead to competition with donor atoms of the principal ligand for the CS. This does not open the chelate rings formed by the principal ligand even if the additional neutral ligand is bidentate (bipy, phen, etc.). However, the $RE^{III}-O$ distance in adducts (including hydrates) is always slightly greater than in the monomeric tris-β-diketonates themselves (Table 6).

Apparently this difference in bond lengths would be much greater if data for the monomeric and not dimeric (as in Table 6) tris-β-diketonates were used for comparison in systems with $RE(DPM)_3$ of the Ce subgroup. Polymerisation has the same weakening effect on the $M^{3+}-O$ bond as adduct formation. However, data for the monomers exist only for RE of the Y subgroup where both polymerisation and adduct formation are sterically hindered. The influence of the additional ligand on the strength and length of the $M^{3+}-O$ bond is less than in these same systems with RE of the Ce subgroup. There are no structural data for anhydrous RE tris-β-diketonates (acetylacetonates) of the Ce subgroup. Even for the heavy RE only the one structure mentioned above, YbA_3, has been solved.[28]

Therefore, the mutual influence of identical and mixed ligands in the $RE^{III}CS$ is substantial. It is not determined by any one factor, for example, the nature of the metal, but by several parameters. First of all, a donor strength and steric characteristics must be assigned to the ligands interacting in the inner sphere of RE^{III} complexes.

Table 6. Influence of adduct formation on M–O bond length in chelate rings of RE^{III} tris-β-diketonates.[17,18]

tris-β-Diketonate	M–O bond length, Å	Adduct	M–O bond length, Å
$[Nd(DPM)_3]_2$	2.32	[Nd(DPM)$_3$.bipy]	
		[Eu(DPM)$_3$.py$_2$	2.35
		[Eu(DPM)$_3$.DMF]	2.36
$[Pr(DPM)_3]_2$	2.41	$[Pr(DPM)_3 \cdot TPPO]$	2.36
$[Er(DPM)_3]_1$	2.21	$[Dy(DPM)_3 \cdot H_2O]$	2.30
		$[Ho(DPM)_3 \cdot (4\text{-}Pic)_2]$	2.27
$[Lu(DPM)_3]_1$	2.19	$[Lu(DPM)_3 \cdot (3\text{-}Pic)_2]$	2.24
$[NdA_3]_1$		$[NdA_3 \cdot 2H_2O] \cdot H_2O$	2.44
		$[NdA_3 \cdot H_2O \cdot DMSO] \cdot DMSO$	2.43
		$[PrA_3 \cdot 2H_2O] \cdot H_2O$	2.44
		$[EuA_3 \cdot phen]$	2.40
		$[GdA_3 \cdot 2HAcim] \cdot 2HAcim$	2.38
		$[YbA_3 \cdot H_2O]$	2.233
$[YbA_3]_1$	2.211	$[YbA_3 \cdot HAcim]$	2.23

Our attempt to determine the stability of $M(\beta\text{-diket})_3 \cdot xQ$ adducts by gas–liquid chromatography (GLC) demonstrates just how complicated it is to predict the result of the mutual influence of ligands in heteroleptic RE complexes, for example, in the CS based on β-diketones. It is clear from Table 7 that the stability of the adducts changes differently in the RE^{III} series depending on the nature of the principal ligand, i.e., the β-diketone. Since HDPM creates steric hindrances in the $M(DPM)_3CS$ owing to the two tert-butyl radicals in each molecule, the probability of incorporating an additional ligand in it decreases as the RE ionic radius decreases. The adducts have minimal stability for the small Lu^{3+} and maximal

Table 7. Effective formation constants (K_{eff}) of RE tris-β-diketonate adducts $ML_3 \cdot Q$[31].

ML_3	Additional ligand, Q	Determination method	K_{eff}						
			Lu	Yb	Tu	Er	Ho	Gd	Nd
$M(DPM)_3$	TPPO	GLC, mathematical modelling	0.9±0.2	1.3±0.2	4.0±0.2	4.0±0.2	7.7±0.3		
$M(DPM)_3$	THF	GLC of additional ligands (Q) on stationary phase with $M(DPM)_3$	0.3±0.1	0.3±0.1		0.3±0.1		0.4±0.1	0.3±0.1
	DMFA		1.4±0.0	1.8±0.4		2.2±0.1		3.8±0.1	3.4±0.6
	DMSO		2.6±0.1	7.0±0.1		7.5±0.3		13.4±0.3	11.7±0.1
	MESO		4.2±0.1	3.9±0.1		7.1±0.3		11.4±0.4	10.4±0.3
$M(PTFA)_3$	THF	ditto		4.3±0.1		3.9±0.1	2.4±0.1	0.5±0.1	

for the large Nd^{3+}. Conversely, $M(PTFA)_3$ are less sterically hindered (Table 7) and add an additional ligand more strongly the smaller the RE^{III} ionic radius. In this instance, the normal relation predicted by Fajans simple polarisation theory is seen.

Table 8. Temperature of maximal thermolysis (T_s) of RE tris-dipivaloylmethanate adducts $M(DPM)_3 \cdot Q \rightarrow M(DPM)_3 + Q$.[18]

M	Q	T_s, °C	M	Q	T_s, °C
–	phen	340	–	DMSO	180
Nd	phen	385	Nd	DMSO	325
Tb	phen	380	Tb	DMSO	325
Yb	phen	380	Yb	DMSO	305
–	bipy	250	–	TBP	240
Nd	bipy	335	Pr	TBP	330
Sm	bipy	335	Sm	TBP	340
Tb	bipy	330	Tb	TBP	335
Yb	bipy	300	Ho	TBP	320

The reversal in the dependence of effective formation constants of the RE^{III} tris-β-diketonate adducts due to steric parameters of the principal ligand (Table 7) is confirmed by chromatography of $RE(DPM)_3$ and $RE(PTFA)_3$ with and without additional ligands. As demonstrated previously,[31] the difference between the retention times (Δt_{ret}) of the tris-β-diketonates and their adducts is greatest for DPM complexes of the light RE. This is consistent with maximal stability of the adducts $M(DPM)_3 \cdot Q$ for the light RE. For $M(PTFA)_3$, the greatest difference in retention time of the tris-β-diketonates and their adducts is seen in the middle of the RE series. At this point, the steric hindrances to adduct formation are still small and the complexing power of the metal (Ho^{3+}) is still significant, in contrast with the light RE^{III}, owing to the 'average' size of M^{3+}.[31]

A study of the thermal stability of the RE tris-β-diketonate adducts also demonstrates the complexity of the competition between the different ligands in the $RE^{III}Cs$. It is evident from Table 8, in agreement with the GLC data (Table 7), that the thermal stability of $M(DPM)_3 \cdot Q$ for all additional ligands studied[18] decreases as the RE ionic radius decreases, i.e., the steric effect of the DPM, the principal ligand, is unfavourable and here has the definitive effect.

The thermal stability changes in the opposite direction for adducts of less sterically hindered RE acetylacetonates. Table 9 shows that the temperature of maximal thermolysis of the adducts does not decrease with decreasing RE^{III} ionic radius [as for $RE(DPM)_3$]. It increases somewhat (Q = phen) or changes little (Q = bipy). The simple explanation is that acetylacetone is not a sterically hindered ligand. Therefore, the normal relation resulting from Fajans polarisation laws is in effect during adduct formation.

Table 9. Temperature of maximal thermolysis of RE tris-acetylacetonate adducts $MA_3 \cdot Q$.[18]

M	Q	T_s, °C	M	Q	T_s, °C
–	phen	340	–	bipy	250
Pr	phen	315	Nd	bipy	235
Eu	phen	357	Sm	bipy	230
Er	phen	383	Gd	bipy	235
Y	phen	385	Y	bipy	235
Yb	phen	388	Yb	bipy	240
Lu	phen	395			

It is interesting (Table 9) that the temperature dependence is much stronger for $MA_3 \cdot Q$ adducts with phen than bipy. This can be explained by the greater rigidity of phen compared with bipy. The latter can rotate fragments around the C–C bond and, therefore, more flexibly than phen fills the voids in the MA_3 structure. Hence, steric effects for systems with $RE(A)_3$ are determined mainly by the structure not of the principal but of the additional ligand.

It is noteworthy that Table 9 includes data for $RE(A)_3$ adducts $MA_3 \cdot Q$ only with bidentate additional ligands (phen, bipy) whereas Table 8 includes data for $RE(DPM)_3$ adducts with monodentate additional ligands. This is due to the fact that $RE(A)_3$ form not only mono- but also bis-adducts with monodentate ligands owing to the lack of steric hindrances on coordination of the principal ligand. As a rule, formation of $MA_3 \cdot 2Q$ is characteristic for light RE, which have a large ionic radius, whereas mono-adducts $MA_3 \cdot Q$ are typical of heavy RE, which have a small ionic radius. Solid $MA_3 \cdot 2Q$ and $MA_3 \cdot Q$ undergo thermolysis by different mechanisms. Therefore, the thermal stability of such adducts over the whole RE series cannot be compared, in contrast with $M(DPM)_3 \cdot Q$, where the RE adducts have a constant composition.

The change of composition of $RE(A)_3$ adducts is sometimes even more complicated. For example, adducts of MA_3 with monodentate (neutral) HAcim reportedly have the following composition:[17]

$MA_3 \cdot 2HAcim$ (M = La–Gd);

$MA_3 \cdot 4HAcim$ (M = Sm–Tu, Y);

$MA_3 \cdot HAcim$ (M = Tb–Lu).

Regions of stability of the different adducts in the RE series overlap. For example, Tb forms all three adducts: $TbA_3 \cdot HAcim$, $TbA_3 \cdot 2HAcim$ and $TbA_3 \cdot 4HAcim$. It is important to note that the mono-adduct is thermally more stable than the bis-adduct.[17]

$$TbA_3.HAcim \xrightarrow[-HAcim]{105\ ^\circ C} TbA_3(s.) + HAcim\uparrow \quad \xrightarrow[sublimation]{110\ ^\circ C} TbA_3(g.),$$

$$TbA_3.2HAcim \xrightarrow[-2HAcim]{95\ ^\circ C} TbA_3(s.) +$$

$$+2HAcim\uparrow \xrightarrow[melting]{105\ ^\circ C} TbA_3(l.) \xrightarrow{160\ ^\circ C} \text{thermolysis}.$$

Thermolysis of only the mono-adduct produces the monomeric sublimable TbA_3. Thermolysis of the bis-adduct leads to melting, polymerisation, and anhydrous $[TbA_3]_n$ that cannot be sublimed.

Therefore, practically each studied series of mixed RE complexes has its own specific type of complicated interaction of numerous factors that often have an equivalent influence on the properties of the complexes. However, it can be confirmed with certainty that such an array of structures and properties of RE^{III} complexes is a consequence of the predominantly ionic interaction in these compounds.

VI. Intermolecular interaction in RE complexes with polydentate organic ligands

The predominantly ionic metal–ligand bonding in RE^{III} complexes frequently leads to catenated structures where one polydentate ligand is shared between two or more RE^{III}. Such a structure is especially characteristic for compounds with a deficit of ligands (of moderate denticity). Therefore, it is very often found in 1 : 1 complexes. For example, monocitrates $[M(Cit)]_n$ monotartrates $[M_2(tart)_3]_m$ and mononitrilotriacetates $[M(NTA)]_p$ have extensively linked (by polymerisation) chain structures (Ref. 8, p. 11).

As a rule, such compounds are difficultly soluble. However, addition to the RE^{III} coordination sphere of another such ligand can form a monomeric structure with weak intermolecular contacts. This solubilises the initially poorly soluble 1 : 1 complex:

$$\underset{\text{ppt.}}{[M(Cit)]_n} + n Na_3Ci \rightarrow \underset{\text{solution}}{n Na_3[M(Cit)_2]};$$

$$\underset{\text{ppt.}}{[M(NTA)]_m} + m K_3(NTA) \rightarrow \underset{\text{solution}}{m K_3[M(NTA)_2]} \text{ etc.}$$

If the ligand forming the RE^{III} complex is highly dentate (denticity 6 and greater) and sufficiently flexible to surround the RE^{III} with a spherical (or hemispherical) shield that isolates it from other RE^{III}, the resultant structure is monomeric. As a rule, the intermolecular contacts in it are weak. Such a compound is very soluble in polar solvents, for example, water.[1,2,7,8]

Conversely, the number of donors in 1 : 1 complexes with ligands of low denticity (1, 2 and 3) is insufficient to saturate the inner CS of RE^{III} even if a bridging structure is formed. Therefore, other ligands must be added (or they are added during synthesis, for example, solvent) to the CS of such complexes to produce monomers. Such CS most often are mixed. Their properties and intermolecular contacts are determined by the stoichiometry of the complex and the relationship among properties of the system components. An example would be RE^{III} chloride–HAcim complexes synthesised and studied previously.[15] The properties of these $MCl_3 \cdot n$ HAcim are exceedingly varied:

$MCl_3 \cdot 3{,}5HAcim$ (M = Pr, Nd, Sm);

$MCl_3 \cdot 3HAcim$ (M = Gd–Yb);

$MCl_3 \cdot 4HAcim$ (M = Lu, Sc);

$MCl_3 \cdot 6HAcim$ (M = La, Pr, Nd, Sm, Gd–Er, Lu).

Among RE complexes with low-dentate ligands, the most completely studied are the β-diketonates. This is due to practical applications related to their ability to dissolve in low-polarity solvents and to sublime. Therefore, they are suitable for extraction, chromatography and sublimation.

We have already mentioned the coordinative saturation of RE^{III} tris-β-diketonates and their tendency to saturate the CS by adding ligands or by forming bridging O bonds. (This was first found structurally in $[Pr(DPM)_3]_2$.[32]) Intermolecular contacts in such compounds are controlled by the properties of the affected principal and additional ligands in addition to the degree of polymerisation (oligomerisation) of the tris-β-diketonates themselves. Somehow the majority of these compounds can be vaporised by heating under vacuum. They can be distilled or sublimed.

The discovery that RE^{III} complexes can be sublimed at first was surprising since it was generally accepted that ionic compounds were involatile. Attempts to find an appreciable covalent component in tris-β-diketonates and to explain their volatility by their covalent nature were unsuccessful.[33,34] However, it has now been established that the volatility and solubility of tris-β-diketonates in low-polarity solvents are due to their pseudoorganic properties. The hydrocarbon radicals of the β-diketonate ions form a hydrophobic sphere around the ionic core that has little tendency to form associates. This determines the behaviour of RE tris-β-diketonates, which is characteristic for ordinary molecules comprising the world of organic compounds.

The pseudoorganic nature of neutral RE tris-β-diketonates is responsible for the low selectivity in fractional sublimation, gas chromatography and extraction. However, the specific properties of different RE^{III}, no matter how subtle they may be, still cause substantial differences in the thermodynamic characteristics, for example, K_s (cf. Fig. 1). On the other hand, if the compounds do

not decompose or at least the RE CS does not open temporarily during sublimation and extraction, the selectivity leads to differences in the intermolecular interactions.[35] Therefore, fractional sublimation of tris-β-diketonates under ordinary conditions is suitable only for group separation of RE mixtures. For example, dimeric $[M(DPM)_3]_2$ of light RE can be separated by fractional sublimation from monomeric $[M(DPM)_3]$ of heavy RE,[33] whereas intragroup separation of RE^{III} without competing decomposition is ineffective.[35]

Intermolecular interaction of RE complexes explains the important loss of individual properties of complexes in the mixture to be separated. For RE β-diketonates, the mutual influence of individual RE complexes is accompanied by formation of heterometallic oligomers. Preliminary experiments demonstrated that these can be detected by mass spectrometry. However, reliable proof of their existence comes from preparative chemical studies. We will give some examples.

The pioneering work of Sievers and Eisentraut[36] demonstrated that group separation of RE^{III} mixtures by fractional sublimation of $RE(DPM)_3$ of the Ce and Yb subgroups was not complete. The separated components contained an approximately 3% impurity of the other RE subgroup elements even though an apparatus with a gradient heater was used. In our opinion, such a consistent mutual contamination that could not be eliminated by repeated sublimation is due to formation of oligomers that are stable in the vapour.

Another example. It has been found[17,18] that adducts of $RE(A)_3$ of the Ce subgroup with DMSO ($MA_3 \cdot 2DMSO \cdot H_2O$) and HAcim ($MA_3 \cdot 2HAcim$) do not give volatile products containing RE on heating in vacuum. Moreover, as we showed in collaboration with Dzyubenko and Kalinichenko,[37] these compounds in the presence of $RE(A)_3$ adducts of the Yb subgroup do appear in the sublimate. The percent transferred can be significant. Thus, heating in vacuum a 1 : 1 mixture of $[NdA_3 \cdot 2DMSO \cdot H_2O]$ and $[YA_3 \cdot DMSO]$ produced 40% of the starting Nd in the sublimate even though the starting complexes are involatile.

The amount of involatile $MA_3 \cdot nH_2O$ transferred to the vapour and then into the sublimate increases sharply if coordinatively saturated Zr^{IV} tetrakis-acetylacetonate is added to the starting compound, for example, $YA_3 \cdot 3H_2O$.[38]

In the preceding examples, the loss of identity of $RE(A)_3$ on mixing with each other can be linked to formation of oligomers that contain RE of different subgroups in one molecule. However, in our opinion, break-up of YA_3, which tends to oligomerise, by coordinatively saturated ZrA_4 is more probable in the example with ZrA_4. This prevents formation of $[YA_3]_x$ oligomers that are less volatile than YA_3.

Furthermore, the components in a subliming mixture of $RE(A)_3$ have practically no influence on each other if a stable adduct that does not decompose during sublimation is present. Since MA_3 adducts with strong donor ligands such as HMPA and TPPO only partially dissociate on heating in vacuum and partially lose the additional ligand (in contrast with adducts with weaker donors: H_2O, DMSO, HAcim), the coordinative saturation of the RE complexes is preserved during sublimation. This prevents oligomerisation of the individual chelates and interaction of the components with each other. In fact, as demonstrated in Table 10, the separation coefficients of RE mixtures determined experimentally and calculated from the sublimation parameters of the individual components are practically the same for such mixtures. Consequently, coordinatively saturated RE complexes exhibit independent behaviour, retain their integrity, and remain monomeric during separation.

It is noteworthy that multiple repetitions and intricate mathematical treatment of the experimental results is necessary to obtain reliable data for the fractional sublimation of partially dissociated adducts of RE β-diketonates. This happens since small changes in the experimental conditions have a large effect on the results.[39]

Table 10. Separation of RE mixtures by fractional sublimation of $MA_3 \cdot HMPA$.[37]

Sublimed mixture (M', M")A_3.HPMA	Separation coefficient $\alpha^{M'/M''}$	
	experimental data for the mixture	calculated data for individual adducts
(Nd, Pr)A_3.HMPA	1.2±0.1	1.2
(Gd, Nd)A_3.HMPA	6.0±0.1 *	1.2
(Er, Gd)A_3.HMPA	4.4±0.3	5.4
(Er, Nd)A_3.HMPA	35±5 *	6.5
(Er, Ho)A_3.HMPA	1.3±0.1	0.97

*Experimental $\alpha^{M'/M''}$ are greater than calculated since the mixture was separated in a gradient furnace.

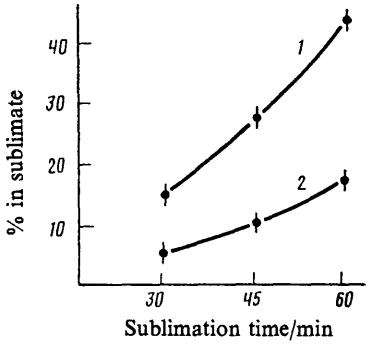


Figure 9. Sublimation of $Nd(Piv)_3 \cdot 3.5HPiv$ (*1*) and $Er(Piv)_3 \cdot 3HPiv$ (*2*) at 360 °C and 10^{-1} torr.

The RE carboxylate system is an example of a sublimation system where the mutual influence of the components is very strong.

The volatility of RE carboxylates was recently discovered by our co-workers at Moscow State University (Kuz'mina et al.[39,40]). Fig. 9 shows that RE pivalates $M(Piv)_3 \cdot nHPiv$ only partially vaporise. The individual RE^{III} pivalates of the Ce subgroup under our experimental conditions sublime more completely than those of the Yb subgroup. The separation coefficient for $Nd^{3+} - Er^{3+}$ from separate sublimation of Nd and Er pivalates is (heating at 360 °C and 10^{-1} torr for 75 min) $\alpha^{Er/Nd} = 68.7$. Such an α value promises

good group separation of RE mixtures. However, an experimental check of the separation gave $\alpha^{Er/Nd} \approx 1.0$, i.e., the sublimate had the composition of the starting mixture. The reason for the lack of separation was the loss of integrity of the components owing to polymerisation of the chelates during sublimation. It can be assumed that the carboxylates act as bridges to form strongly bonded oligomers that are stable in the vapour. Preliminary mass spectroscopic data[40,41] enabled detection of heterometallic RE oligomers that were stable even under the high vacuum of the mass spectrometer.

Instances where the properties of individual RE chelates are suppressed by another component of the mixture are quite common. However, let us recall that this is characteristic for systems in which the complex is not monomeric and oligomers and polymers form owing to coordinative unsaturation.

Such instances are characteristic not only for vapour processes but also for complexation in liquid solutions and solid-state mixtures of chelates. For example, it was found[17] that trihydrates of individual $RE(A)_3$ are isomorphous for the series Pr–Tm and Y whereas $YbA_3 \cdot 3H_2O$ has a different structure. However, coprecipitation from aqueous solutions of $MA_3 \cdot 3H_2O$ and the Yb^{III} complex causes the latter to lose its integrity and form the trihydrate $YbA_3 \cdot 3H_2O$, isomorphous with the other RE $MA_3 \cdot 3H_2O$. It is interesting that addition to the coordination sphere of $RE(A)_3$ of a ligand more bulky than H_2O, for example, HAcim,[17] leads to simultaneous precipitation of crystals of the separate noniso-morphous $NdA_3 \cdot 2HAcim$ and $YbA_3 \cdot HAcim$ with insignificant mutual contamination (2% Nd in $YbA_3 \cdot HAcim$ and 7% Yb in $NdA_3 \cdot 2HAcim$).

This fact suggests that $YbA_3.3H_2O$ in the presence of other RE $MA_3 \cdot 3H_2O$ loses its integrity owing to rather strong intermolecular interaction, possibly with conversion of monomeric structures into catenated ones. The greater bulk of the additional ligand in $MA_3 \cdot HAcim$ than in $MA_3 \cdot 3H_2O$ prevents such a process. The monomeric structure is preserved. The chelate does not lose its integrity.

The mutual influence of components in a precipitated mixture was detected by us[42] during attempted group separation of mixtures of protonated RE EDTA complexes. If $HM(EDTA) \cdot xH_2O$ are prepared separately for RE of the Ce and Yb subgroups, the solubility differs ($\alpha_{calc}^{M'/M''} = 10-1000$). However, coprecipitation under the same conditions gives separation coefficients close to unity. Such a result is consistent with coordinative unsaturation in the RE^{III} mono(EDTA) complexes and polymerisation of the CS.[8]

These data indicate that the behaviour in the presence of other RE can be changed by varying the composition of the complexes and thereby changing the stability of the CS and the degree of coordinative saturation in the RE^{III} chelates. An excess of ligands ensures coordinative saturation and prevents formation of polymers. On the other hand, a deficit of ligands generates polymers, i.e. strong intermolecular interaction.

However, this does not mean that preparation of coordinatively saturated RE chelates guarantees highly effective separation of RE mixtures. Results of sublimation of $RE(A)_3$ adducts with additional ligands of various donor strength are plotted in Fig. 10. It is quite clear that formation of the stable adducts $MA_3 \cdot phen$[18] completely averages the properties of the RE chelates. Conversely, thermolysis of the less thermodynamically and thermally stable chelates $MA_3 \cdot HMPA$[39] and $MA_3 \cdot HAcim$[17] reveals certain differences in the sublimation behaviour of RE chelates. Therefore, stable coordinatively saturated compounds are suitable for practical use where the composition of the RE mixture must be preserved without change.[29] Less stable compounds that partially dissociate are promising in separation and purification processes of RE mixtures.

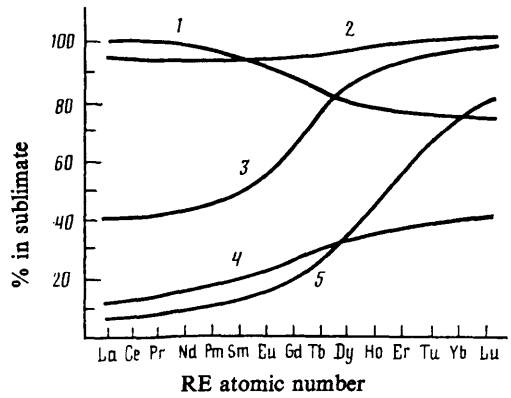


Figure 10. Sublimation of RE^{III} pivalates (*1*) and acetylacetonate adducts (*2–5*) (optimal temperature, 10^{-1} torr): $M(Piv)_3$ (*1*); $MA_3 \cdot phen$ (*2*); $MA_3 \cdot HMPA$ (*3*); $MA_3 \cdot 3H_2O$ (*4*); $MA_3 \cdot n HAcim$ (*5*).

VII. Reasons behind the variation in RE-chelate property changes across the series

One of the most interesting problems in RE chemistry is the variable nature of the change in structural and thermodynamic characteristics of their complexes with ligands of different structure and properties (for example, cf. Fig. 1). This has often been discussed in the literature.[1,2,7,8,10] At the start of this article we prove that the irregularity in the change of RE-chelate properties does not produce a W-effect. We confirm that the principal role in this is played by a ligand of one or another structure that can react flexibly as the ionic radius changes across the RE series. Owing to different flexibilities, each of the ligands has its own limit on permitted interatomic distances and angles for a given structure around the metal.

The greater the ligand geometry deviates from the optimal one in a given RE chelate, the less stable is the structure. In our opinion, it is obvious that the strain that accumulates in the chelate structure surfaces in the details of isostructural complexes across the RE series. When the flexibility of the complex reaches its limit as the RE^{III} radius changes, the chelate rearranges its structure. However, it would be incorrect to assume that the point where the slope changes on the curve of one or another property vs. RE ionic radius (cf. Figs. 1 and 5) corresponds to the place at which the 'old' structure can no longer exist and a new CS structure is formed. Numerous investigations carried out in our laboratory[8,9] and those of others[6,10] of the structure and properties of RE chelates confirm that the old, no longer stable structure continues to exist at one or another break in the RE series, although conditions are favourable for generation of a new structure.

Let us return to Fig. 1 and recall that the slower increase of K_s for RE complexes as the ionic radius decreases usually occurs due to

generation of steric hindrances that prevent a regular approach of the metal and ligand on moving across the RE series. That point for DTPA complexes occurs (cf. Fig. 1) near Sm. Apparently the RE^{III} and ligand in general do not come closer after the octadentate $DTPA^{5-}$ ligand forms a closed sphere around the RE^{III}. Therefore, the strength of the coulombic interaction between the RE^{III} and $DTPA^{5-}$ is practically constant in the series from Sm to Lu and K_s does not change. Ligands of lower denticity change their structural role several times in the RE series. This is reflected in the plots of the dependence of the Cs properties on RE^{III} ionic radius.

Unfortunately, data for isostructural chelates of the whole RE series or several of its members are usually lacking. These could indicate how the ligand strain in a chelate ring increases in an isostructural series and eventually leads to a CS structural change. Therefore, in our opinion, the data on polymorphic transformations in a series of anhydrous $RE(A)_3$ obtained by Trembovetskii[17] in our laboratory are interesting. It was found that anhydrous $RE(A)_3$ (volatile species[29]) synthesised by the reaction

$$MA_3 \cdot HAcim \xrightarrow{T^\circ C} MA_3 + HAcim$$

can exist in four modifications:

I. ScA_3—monomer, octahedron (X-ray structure).[17]

II. ErA_3, TmA_3—unknown structure.

III. YbA_3, LuA_3—monomer, trigonal prism (X-ray structure).[28]

IV. (Y, Tb, Dy, Ho, Er, Tm, Yb)A_3, oligomeric structure (NMR and IR spectroscopy).[17]

Only TmA_3 and YbA_3 are obtained simultaneously in two modifications by sublimation (metastable species are marked with an asterisk): TmA_3^{II}, TmA_3^{IV*}, YbA_3^{III}, YbA_3^{IV*}, respectively. On prolonged heating in vacuum, the following monotropic transitions occur: $TmA_3^{IV} \rightarrow TmA_3^{II}$, $YbA_3^{IV} \rightarrow YbA_3^{III}$. The species ErA_3^{IV} was also metastable. However, it is more stable than TmA_3^{IV*} and TbA_3^{IV*}. Only extended heating (for 23 h) produces the rearrangement $ErA_3^{IV} \rightarrow ErA_3^{II}$. Therefore, the type IV MA_3 structure is metastable for RE^{III} with a small radius. Apparently[17] this is due to steric hindrances to forming the oligomeric species $[MA_3]_n^{IV}$ that are generated by the shielding of the small ions of heavy RE^{III} by the chelate rings.

The metastability of ErA_3^{IV}, TmA_3^{IV} and YbA_3^{IV} is evident in the higher vapour pressure compared with the corresponding type II and III, which condense in the hotter zone of the sublimator. Direct proof of the metastability of (Er, Tm, Yb)A_3^{IV} was obtained by differential scanning calorimetry (DSC). It was demonstrated[17] that the monotropic transition $MA_3^{IV} \rightarrow MA_3^{II,III}$ is an exothermic process. It is clear from Fig. 11 that only the melting endotherm of the chelates is detected on heating all stable MA_3 from 80 to 200 °C. Metastable MA_3^* exhibit also a premelting endotherm and then an exotherm for the monotropic rearrangement (Ref. 17, pp. 99–105). Obviously the MA_3 molecules acquire the mobility (premelting) necessary to rearrange into the stable TmA_3^{II} and YbA_3^{III} near the melting points of the metastable modifications TmA_3^{IV} and YbA_3^{IV}.

The existence of metastable MA_3 for the heavy RE^{III} and their ability on heating to transform into more stable structures support the hypothesis that a new structure gradually replaces an old one on moving across the RE series. Therefore, it is as a rule impossible to find a single point in the RE series where one structure transforms into another. The regions of existence of two or more structures usually overlap.

We have already presented examples of the coexistence under actual experimental conditions of different compounds {for example, $TbA_3 \cdot HAcim$, $TbA_3 \cdot 2HAcim$ and $TbA_3 \cdot 4HAcim$[17] or $[Eu(H_2O)_3(EDTA)]^-$ and $[Eu(H_2O)_2(EDTA)]^-$ (Ref. 11, 26]}. This also supports the presence of a certain range in the RE series where the complex is changing from one structure to another.

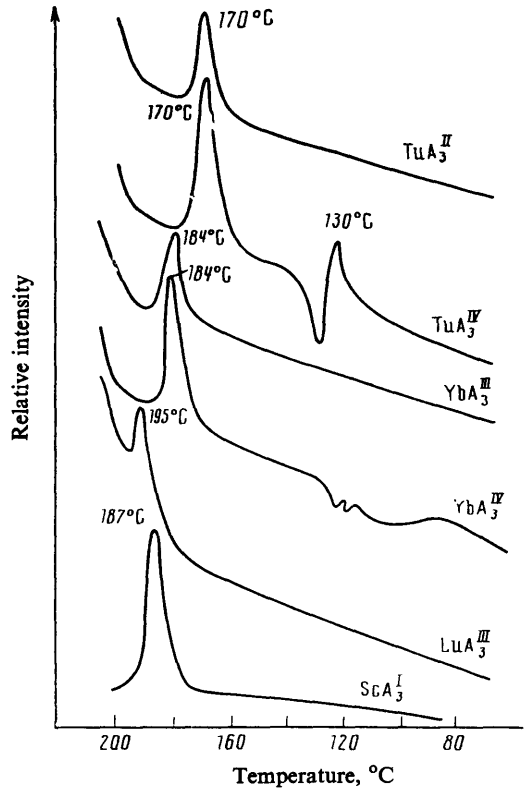


Figure 11. Scanning calorimetry of MA_3.[17]

VIII. Conclusion

The data presented demonstrate the complexity of RE^{III} complexes with organic polydentate ligands and reveal the unwarranted simplicity of the concept of a W-effect. Numerous facts indicate that the crystallographic instability of RE chelates due to small differences in ionic radii of neighbouring RE does not appear in any individual RE but in a more or less broad range of the RE series. Moreover, these ranges can considerably shift in the presence of several RE toward the light or heavy RE. This must be considered in developing industrial separations, purifications and applications of RE compounds since the RE^{III} characteristically lose their integrity in mixtures of coordinatively saturated and unsaturated compounds.

References

1. L I Martynenko *Zh. Vses. Khim. Ova im D I Mendeleeva*, 1984, **29**(3) 133–146
2. L I Martynenko, V I Spitsyn *Advances in Inorganic Chemistry* Pergamon Press, London, 1983, pp. 139–155
3. N K Davidenko *Doctoral Dissertation in Chemical Sciences*, Kiev, 1971
4. D F Peppard, C A A Bloomquist, E P Horwitz, et al. *J. Inorg. Nucl. Chem.*, 1970, **32** 339–343
5. C K Jørgensen *J. Inorg. Nucl. Chem.*, 1970, **32** 3127–3129
6. G A Bandurkin, B F Dzhurinskii, I V Tananaev *Osobennosti Kristallokhimii Soedinenii RZE* (Crystal Chemistry of Rare Earth Compounds), Izd. Nauka, Moscow, 1984, 228 pp
7. L I Martynenko *Doctoral Dissertation in Chemical Sciences*, Moscow State University, Moscow, 1973
8. V I Spitsyn, L I Martynenko (Editors) *Koordinatsionnaya Khimiya* (Coordination Chemistry), Izd. Mosk. Gos. Univ., Moscow, 1974, 168 pp; 1979, 250 pp
9. L I Martynenko, V I Spitsyn *Methodicheskie Aspekty Kursa Neorganicheskoi Khimii* (Methodological Aspects of the Inorganic Chemistry Course), Izd. Mosk. Gos. Univ., Moscow, 1983, 164 pp
10. N A Kostromina *Kompleksonaty RZE* (Rare Earth Complexants), Izd. Nauka, Moscow, 1980, 216 pp
11. J E Huheey *Inorganic Chemistry, 3rd Edn.* (Translated into Russian), Izd. Khimiya, Moscow, 1987, 696 pp
12. V I Vovna, V A Andreev, A I Cherednichenko *β-Diketonaty Metallov* (Metal β-Diketonates), Izd. Daln. Vost. Gos. Univ., Vladivostok, 1990, pp. 7–31
13. V I Nefedov, V I Vovna *Elektronnaya Struktura Khimicheskikh Soedinenii* (Electronic Structure of Chemical Compounds), Izd. Nauka, Moscow, 1987, 347 pp
14. A I Cherednichenko, V I Vovna, L I Martynenko *β-Diketonaty Metallov* (Metal β-Diketonates), Izd. Daln. Vost. Univ., Vladivostok, 1990, pp. 143–156
15. I V Andrienko *Candidate Dissertation in Chemical Sciences*, Mosk. Gos. Univ., Moscow, 1987
16. R Badalova *Candidate Dissertation in Chemical Sciences*, Mosk. Gos. Univ., Moscow, 1973
17. G V Trembovetskii *Candidate Dissertation in Chemical Sciences*, Mosk. Gos. Univ., Moscow, 1985
18. N G Dzyubenko *Candidate Dissertation in Chemical Sciences*, Mosk. Gos. Univ., Moscow, 1984
19. M F Richardson, P W R Corfield, D E Sands, R E Sievers *Inorg. Chem.*, 1970, **9**(7) 1632–1638
20. S I Nikitenko *Candidate Dissertation in Chemical Sciences*, Mosk. Gos. Univ., Moscow, 1985
21. G Gaier, U Karlen, A V Zelensky *Helv. Chim. Acta*, 1969, **55** 1967
22. L M Nesterova, S G Zbryskaya, T N Polynova, M A Porai-Koshits *Zh. Strukt. Khim.*, 1972, **13** 739
23. T V Filippova, T N Polynova, A L Il'inskii, et al. *Zh. Strukt. Khim.*, 1977, **18**(6) 1127–1128
24. G N Kupriyanova, L I Martynenko, V I Spitsyn *Dokl. Akad. Nauk SSSR*, 1974, **216** 912–913
25. Le Ba Thuan, G N Kupriyanova, L I Martynenko *Zh. Neorg. Khim.*, 1988, **33**(6) 1423–1428 [English translation in *Russ. J. Inorg. Chem.*, 1988(6)]
26. Le Ba Thuan, G N Kupriyanova, N S Smirnova, et al. *Vestn. Mosk. Gos. Univ., Ser. Khim.*, 1987, **28**(6) 560–563
27. M A Tokmadzhyan, N A Dobrynina, L I Martynenko, A A Alchudzhyan *Zh. Neorg. Khim.*, 1974, **19**(10) 2888–2889 [English translation in *Russ. J. Inorg. Chem.*, 1974(10)]
28. A S Batsanov, Yu T Struchkov, G V Trembovetskii, et al. *Dokl. Akad. Nauk SSSR*, 1986, **280** 903–906
29. L I Martynenko *Vysokochist. Veshchestva*, 1987, (1) 88–93
30. A S Batsanov, Yu T Struchkov, G V Trembovetskii, et al. *Zh. Neorg. Khim.*, 1986, **31**(2) 345–350 [English translation in *Russ. J. Inorg. Chem.*, 1986(2)]
31. N V Magazeeva, L I Martynenko, I A Murav'eva *β-Diketonaty Metallov* (Metal β-Diketonates), Izd. Daln. Vost. Gos. Univ., Vladivostok, 1990, pp. 39–50
32. C S Erasmus, J C A Boeyens *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1970, **26**(11) 1843–1854
33. R W Moshier, R E Sievers *Gas Chromatography of Metal Chelates* (Translated into Russian), Izd. Mir, Moscow, 1967, 173 pp
34. A S Berlyand, L I Martynenko, V I Spitsyn *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1971, 1100
35. N P Kuz'mina, L I Martynenko, V I Spitsyn *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 504–508
36. K J Eisentraut, R E Sievers *J. Inorg. Nucl. Chem.*, 1967 **29** 1923–1936
37. N G Dzyubenko, Yu V Kalinichenko, L I Martynenko *Zh. Neorg. Khim.* (in press)
38. N Ya Zharkova, N G Dzyubenko, L I Martynenko *Zh. Neorg. Khim.* (in press)
39. N P Kuz'mina, T N Chieu, L I Martynenko *Vysokochist. Veshchestva*, 1988, (2) 103–109
40. N P Kuz'mina, L I Martynenko *Tezisy Dokladov XVII Vsesoyuznogo Chygaevskogo Soveshchaniya po Khimii Kompleksnykh Soedinenii* (Abstracts of Papers of the XVIIth All-Union Chugaevskii Conference on the Chemistry of Complex Compounds), Minsk, 1990, Part 1, p. 76
41. L Y Martynenko, N P Kuzmina, N D Mitrophanova *Abstracts of Posters of the XXVIIIth Int. Conf. Coord. Chem.*, DDR, Vol. 2, p. 695
42. USSR P. 861 310; *Byull. Izobret.*, 1981, (33)