ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2019, Vol. 45, No. 11, pp. 749–758. © Pleiades Publishing, Ltd., 2019.
Russian Text © The Author(s), 2019, published in Koordinatsionnaya Khimiya, 2019, Vol. 45, No. 11, pp. 644–653.

Dedicated to blessed memory of Academician Yu.A. Buslaev (1929–2001)

Inner- and Outer-Sphere Coordination of Acido and Neutral N,O-Donor Ligands in the Rare-Earth Metal Complexes

S. P. Petrosyants*

Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, 119991 Russia
**e-mail: petros@igic.ras.ru*

Received January 25, 2019; revised March 19, 2019; accepted May 25, 2019

Abstract—The data on the rare-earth metal complexes with the anionic (halides, NCS) and neutral N,O-donor ligands are systematized and generalized. The influence of the ionic radius of the complexing agent and the ligand nature (donor characteristics, steric features, nonvalent interactions) on the formation of the coordination sphere with the inner- or outer-sphere position of the ligands is monitored. The transitions of the ligands from the outer-sphere position to the first coordination sphere are considered.

Keywords: rare-earth metals, halides, NCS, neutral N,O-donor ligands, inner- and outer-sphere coordination

DOI: 10.1134/S1070328419100051

INTRODUCTION

The concepts about the first and second coordination spheres have been developed by A. Werner more than 100 years ago. The first coordination sphere is formed by the direct interaction (covalent, electrostatic) of the ligands with the complexing agent (metal cation). At present, the following synonyms are used most frequently for the first coordination sphere: inner-sphere or endo coordination. The second coordination sphere defined as the outer-sphere or exo coordination is formed when the ligands of the first sphere interact with additional molecules or ions and can also be formed due to the almost whole range of secondary interactions, such as electrostatic interactions, hydrogen bonding, halide bond, charge transfer, and van der Waals interactions. Coordination chemistry was developed for a long time as the chemistry of *d* elements. In the 1980s, Yu.A. Buslaev advanced an approach defining the formation of the second coordination sphere in the complexes of *p*-element halides on the basis of hydrogen bonding. The studies of coordination compounds of rare-earth metals (REM) became primary in the recent decades. The coordination compounds of REM have characteristic photophysical and magnetic properties, which predetermines their promising use in magnetic and optical devices, sensor systems, biological assay, and medical diagnostic apparatus [1]. The compounds are synthesized either by self-assembling from REM salts (these are almost always hydrated samples) and the chosen ligands in appropriate solvents, or by the hydro(solvo)thermal method from the REM salts and ligands as well. The final products also contain solvent molecules, whose inner- or outer-sphere position can determine the coordination number of the complexing agent, nonvalent interactions, and topology of the product. If complex formation occurs in a donor solvent (water, alcohols, etc.), then the solvent acts as a ligand. Many REM salts are hydrates, for example, in $MX_3 \cdot 6H_2O$ (X = Cl, Br, NCS) the coordination sphere is formed of molecules of water and acido ligand: yttrium chloride hexahydrate consists of the cationic complex $[YCl_2(H_2O)_6]^+$ [2], whose charge is compensated by the outer-sphere Cl^- anion. The whole coordination sphere in yttrium bromide hydrate is occupied by water molecules, and the complex has the composition $[Y(H_2O)_8]Br_3$ [3]. Yttrium thiocyanate hydrate forms the $[Y(NCS)_3(H_2O)_5] \cdot H_2O$ complex [4]. The coordination number of the metal in these hydrates is 8 but takes place due to the redistribution of molecules of water (ligand) and acido ligand between the contact (in the coordination sphere of the complex) and outer-sphere position, which is determined by the high donor number of H_2O and an increase in the ionic radius of the anion in the series N < Cl < Br.

Rare-earth elements (Sc, Y, La, and lanthanides) are characterized by the stable oxidation state +3, and the ionic radius of three-charge cations in the octahedral environment is 0.83, 1.06, and 1.22 Å for Sc, Y, and La, respectively, and then varies within a value lower than 1 Å in the lanthanide series. Cations of REM are arranged in the series of hard acids according to the HSAB (hard and soft acid and bases) concept and prefer ligands with rigid donor atoms (N, O) or acido ligands (halides, pseudohalides). The large ionic radius of REM cations in combination with the predominantly electrostatic nature of the metal–ligand binding results in the formation of the compounds with the coordination number of REM to 9 and higher and in a stereochemical diversity of the formed species.

The present review is not a detailed and comprehensive compilation of the modern data on the REM halide complexes with the N,O-donor ligands. We considered the main tendencies and regularities of the formation of coordination compounds of three-charge REM cations with the mono- and polydentate ligands (*N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMA), phosphine oxide, crown ethers, 2,2'-bipyridine (Bipy), 1,10-phenanthroline (Phen), and their derivatives (triazines)), the use of which made it possible to monitor the formation of the mononuclear complexes and the related outer-sphere associates and supramolecular ensembles. The ligands, whose coordination is accompanied by deprotonation (carboxylic acids, amino acids, β-diketones, and others), were excluded from consideration. Our attention was focused on the influence of the complexing agent cation and ligand environment on the compositions and stereochemical regularities of the inner- and outer-sphere compounds and supramolecular associates. The works published within three recent decades are analyzed.

The review can be helpful for post-graduate students and researchers, whose interests are related to the coordination and supramolecular chemistry of REM.

COMPLEXES WITH NEUTRAL ACIDO O-DONOR LIGANDS

Solvents DMF and DMA are good O-donor ligands [5]. The thermodynamic and structural aspects of complexation of the REM salts (Cl, Br, ClO_4) with DMF and DMA were reviewed [6]. The solvated REM cations in these solvents are characterized by the formation of the complexes with the outer-sphere arrangement of the halide ligands in DMF and by the incorporation of the halide ions into the first coordination sphere of the solvates in DMA, whereas the transition from the exo to endo coordination takes place in a mixture of these solvents. When DMF is coordinated via compact formyl group (–CHO), the coordination sphere of REM is saturated with the O-donor ligand and the exo coordination of the acido ligand is observed. In the case of DMA, the more bulky acetyl group $-C(CH_3)O$ creates steric hindrances for the formation of the homoleptic coordination sphere of REM and, as a result, the anions (Cl, Br) participate in the endo coordination.

Phosphine oxides are monodentate ligands frequently used in extraction processes, and upon interacting with REM they give, as a rule, compounds with the inner-sphere coordination of the O-donor ligands. Bulky tricyclohexylphosphine oxide (Cy_3PO) reacts in ethanol with lanthanide chlorides to form complexes $[Ln(Cy_3PO)_2(H_2O)_5](Cy_3PO)Cl_3$, and in these compounds phosphine oxide occupies the sites in the first and second coordination spheres [7]. The complexes of two types (neutral and cationic forms) are formed with the bulky halide ion in the reactions of lanthanide bromides with Cy_3PO. The coordination number of the cation is 6 in the *mer*-$LnBr_3(Cy_3PO)_3$ complexes (Ln = La, Pr, Nd, Gd, Ho). In the compounds with the $[Ln(Cy_3PO)_n(H_2O)_5]^{3+}$ complex cation, the acido ligands are localized in the external sphere of the pentagonal bipyramid. At $n = 2$, both phosphine ligands are bound to the metal cation. At $n = 4$, two ligands are localized in the first coordination sphere, and two other phosphines are bound by hydrogen bonds to the coordinated water molecules. The isolation of the anhydrous neutral species for lighter lanthanides (La–Ho) and the formation of the hydrated cationic complexes for the whole Ln series can be associated with the fact that the initial hydrates of lighter Ln (La–Ho) contain the contact pair Ln–X (Cl, Br), while in the heavier Ln cations the first coordination sphere consists of water molecules only [8].

The coordinated water molecules in the REM salts are easily substituted by molecules of aliphatic alcohols. For example, ensembles $Eu_3(H_2O)_{12}(EtOH)_3(NCS)_9$ [9] and $Dy_3(H_2O)_{12}(EtOH)_3(NCS)_9$ [10] containing coordinated water and alcohol molecules were isolated from $Ln(NCS)_3(H_2O)_5 + H_2O + EtOH$ solutions. The structures of these associates are formed by the neutral $[Ln(H_2O)_4(EtOH)(NCS)_3]$ species, $[Ln(H_2O)_4(EtOH)_2(NCS)_2]^+$ cation, and $[Ln(H_2O)_4(NCS)_4]^-$ anion. All polyhedra (tetragonal antiprism with different degrees of distortion) are joined by hydrogen bonds of 27 hydrogen atoms of the coordinated water and alcohol molecules into the 3D framework.

Crown ethers are polydentate O-donor ligands and can serve as efficient ligands for the coordination of REM cations. Anhydrous scandium(III) salts (scandium is the lightest element of the REM series) with cyclic ethers form the complexes in which the cation directly contacts with the donor atoms of the ligand to form the endo complexes. However, even trace amounts of water or the use of hydrated salts as the initial reagents result in the formation of the exo complexes in which crown ethers are fixed only in the external sphere of scandium [11, 12]. Depending on

Table 1. Complexes of REM chlorides with 18C6

Compound	Coordination number	Literature
$[Y(H_2O)_8]Cl_3 \cdot (18C6) \cdot 4H_2O$	8	[15]
$[Dy(H_2O)_8]Cl_3 \cdot (18C6) \cdot 4H_2O$	8	[16]
$[Y(H_2O)_7(MeOH)][YCl(18C6)(H_2O)_2]_2Cl_7 \cdot 2H_2O$	8, 9	[17]
$[Dy(H_2O)_7(MeOH)][DyCl(18C6)(H_2O)_2]_2Cl_7 \cdot 2H_2O$	8, 9	[17]
$[Y(H_2O)_3(18C6)]Cl_3 \cdot 1.25H_2O$	9	[15]
$[PrCl(18C6)(H_2O)_2]Cl_2 \cdot 2H_2O$	9	[18]
$[NdCl(18C6)(H_2O)_2]Cl_2 \cdot 2H_2O$	9	[19]
$[SmCl(18C6)(H_2O)_2]Cl_2 \cdot 2H_2O$	9	[20]
$[EuCl(18C6)(H_2O)_2]Cl_2 \cdot 2H_2O$	9	[18]
$[GdCl(18C6)(H_2O)_2]Cl_2 \cdot 2H_2O$	9	[20]
$[TbCl(18C6)(H_2O)_2]Cl_2 \cdot 2H_2O$	9	[20]
$[H_3O][EuCl(18C6)(H_2O)_2]Cl_3$	9	[21]
$[GdCl_2(18C6)(H_2O)][GdCl(18C6)(H_2O)_2] [GdCl_6] \cdot 2MeOH$	6, 9	[18]
$[H_9O_4][LaCl_2(18C6)(H_2O)]Cl_2$	9	[21]
$[LaCl_2(18C6)(Y)]Cl \cdot 1.5H_2O$	9	[18]
$[CeCl_2(18C6)(H_2O)]Cl \cdot 2H_2O$	9	[18]
$[GdCl_2(18C6)(EtOH)]Cl$	9	[22]
$[LaCl_2(18C6)(H_2O)]Cl$	9	[18]
$[LaCl_3(18C6)]$	9	[18]

the reaction conditions, the reaction of yttrium(III) chloride with crown ether (18C6) can afford the outer-sphere [13] or inner-sphere complexes [14]. In solutions of aliphatic alcohols, the $[YCl_2(H_2O)_6]Cl$ complex reacts with 18C6 to form $[Y(H_2O)_3(18C6)]Cl_3 \cdot 1.25H_2O$ and $[Y(H_2O)_8]Cl_3 \cdot (18C6) \cdot 4H_2O$ with the endo and exo coordination of the macrocycle and chloride ions in the external sphere. In these complexes, the internal coordination sphere of yttrium consists of nine and eight oxygen atoms, respectively, yttrium does not directly interact with the chloride ions, and the acido ligands are localized in the external sphere only. The coordination environment of the yttrium cation is rearranged during solid-phase thermolysis: the chloride ions are inserted into the coordination sphere of yttrium [15]. The structurally characterized complexes of REM chlorides with 18C6 are presented in Table 1.

The complexing agents in the complexes with the intra-sphere coordination of 18C6 have the coordination number 9, which is formed of six oxygen atoms of the crown ether and three coordinated water molecules (yttrium complex), whereas other REM are characterized by the substitution of one or two inner-sphere water molecules by the chloride ion. The dependence of the outer- and inner-sphere coordination of crown ether on the solvent is especially pronounced for the REM thiocyanate complexes. Yttrium thiocyanate with 18C6 in a methanol solution forms an outer-sphere associate, whose crystal structure contains the centrosymmetric ensemble $[Y(H_2O)_4(NCS)_3]_2 \cdot 3(18C6)$ (Fig. 1a) formed due to hydrogen bonds and, as a result, the coordination number of Y decreases to 7 [4].

The reactions of $[Y(NCS)_3(H_2O)_5] \cdot H_2O$ with 18C6 in solutions of MeCN, THF (tetrahydrofuran), EtOAc, CH_2Cl_2, and *iso*-PrOH at room temperature in air afford dehydrated compounds $[Y(18C6)(NCS)_3]$ and $[Y(18C6)(NCS)_3] \cdot n$A (A is the solvent molecule) (Fig. 1b) in which all inner-sphere water molecules in the initial thiocyanate are replaced by the crown ether molecules, and the coordination number of the complexing agent increases to 9 involving six crown ether molecules and three NCS^- anions. The transformation of crown ether from the endo to exo coordination (and backward) occurs easily when the withdrawing solvent is replaced by the donating one [23]. Unlike yttrium, the reactions of Eu(III) and Tb(III) aquathiocyanates with the 18C6 macrocycle in solutions of aliphatic alcohols (methanol, ethanol) afford two polymorphous modifications (monoclinic and triclinic) of the anhydrous $[Ln(18C6)(NCS)_3]$ complexes [9]. The structures of the complexes are the same in all phases, the conformation of the coordinated macrocycle molecule is also similar, and the

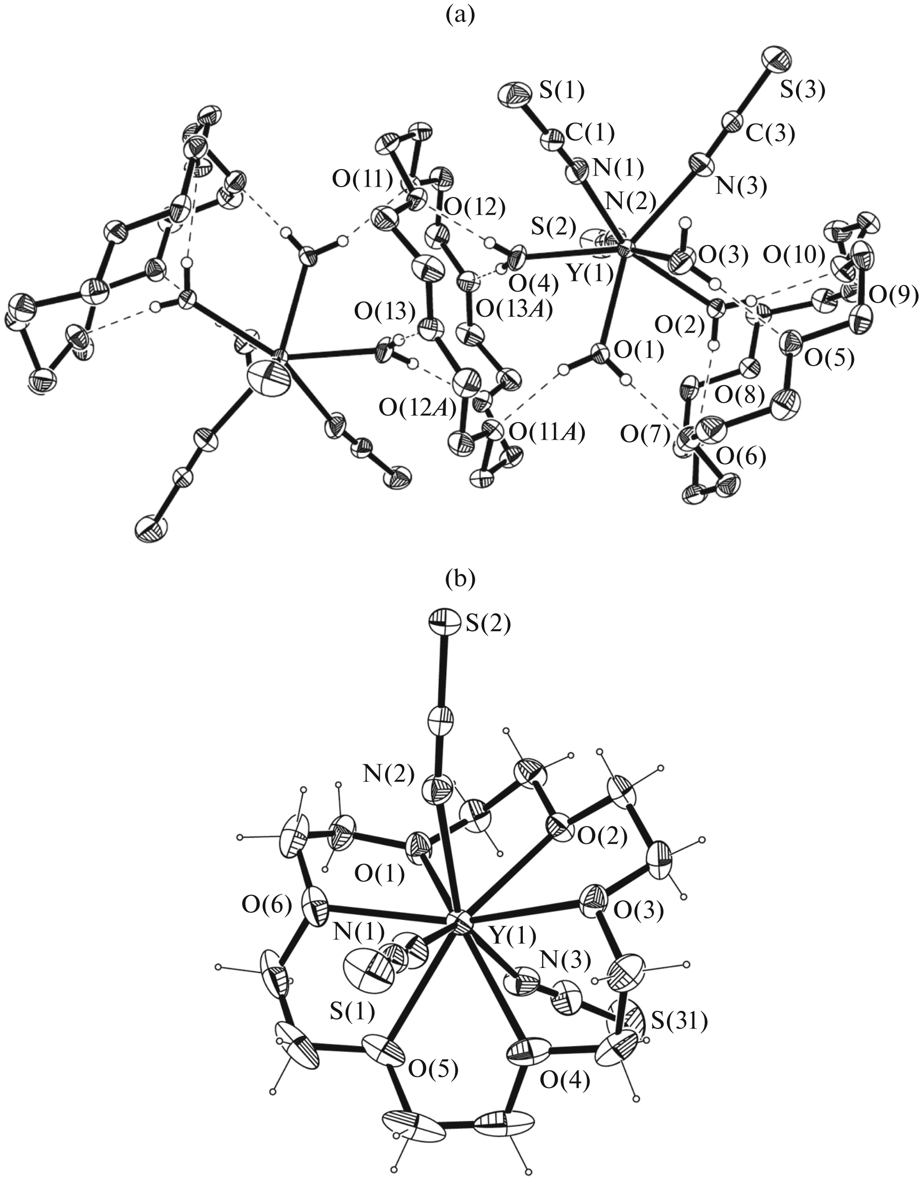

Fig. 1. Fragments of the structures of (a) $[Y(H_2O)_4(NCS)_3]_2 \cdot (18C6)_3$ [4] and (b) $[Y(18C6)(NCS)_3] \cdot 0.5(18C6)$ [23].

coordination number of Ln is 9 in all complexes. The solvated $[Eu(18C6)(NCS)_3] \cdot 0.5(18C6)$ complex obtained as an impurity is isostructural to the Y analog [23]. The formation of solvates in solutions of europium salts is a reason for a low (~50%) yield of two phases of $[Eu(18C6)(NCS)_3]$. In the case of terbium thiocyanate, no solvates are formed and, hence, the yield of two forms of terbium (monoclinic and triclinic) is nearly quantitative. In the complexes with the inner-sphere coordination of 18C6, the coordination number of the cations is 9, which is formed of six oxygen atoms of the crown ether and three coordinated NCS anions, resulting in the formation of neutral complexes in all cases. The structural diversity of the REM thiocyanate complexes with the 18C6 macrocycle (Table 2) is related, most likely, to the fact that these crystals contain no significant secondary interactions, which could determine the mutual orientation of the adjacent molecules during crystallization.

Acyclic polyethylene glycols (EO), unlike macrocyclic molecules of the 18C6 type, are more flexible polydentate ligands, which allow them to form inner-sphere complexes more frequently upon the coordination with the REM salts [24, 25]. The reactions of a series of REM nitrates with hexadentate polyglycol EO5 was studied [25], and the dependence of the formation of a certain structural type on the complexing agent size was revealed. In the cases of La and Ce, the inner-sphere species $[M(NO_3)_3(EO5)]$ are formed in which the coordination number of the cation is 12.

Table 2. Complexes of REM thiocyanates with 18C6

Compound	Coordination number	Literature
$[Y(H_2O)_4(NCS)_3] \cdot 1.5(18C6)$	7	[4]
$[Y(18C6)(NCS)_3]$	9	[23]
$[Y(18C6)(NCS)_3] \cdot n$A (A = CH_3CN, THF, 18C6)	9	[23]
$[Eu(18C6)(NCS)_3]$, two modifications	9	[9]
$[Tb(18C6)(NCS)_3]$, two modifications	9	[9]
$[Eu(18C6)(NCS)_3] \cdot 0.5(18C6)$	9	[9]

The complexes with the coordination number 10 and general formula $[M(NO_3)_2(EO5)][NO_3]$ with the nitrate anion in the external sphere are formed in the series from Pr to Dy. Lanthanides with the shortest radii of the cations from Ho to Lu, as well as Y, are characterized by the formation of the outer-sphere complexes $[M(H_2O)_3(NO_3)_3] \cdot EO5$.

COMPLEXES WITH NEUTRAL N-DONOR LIGANDS

Neutral bidentate N-donor ligands Bipy and Phen form the traditional pair for studying specific features of the complex formation of REM salts. The reactions of hydrated REM chlorides with Bipy in aqueous solutions at the 1 : 1 reactant ratio afford crystalline samples of $[(Bipy)Ln(H_2O)_6]Cl_3$ for Ln = Ho, Er, Yb, and Y, and a similar Lu complex was obtained from an ethanol solution [26]. In these mononuclear cationic complexes, the coordination number of the complexing agent is 8 and all chloride ions are displaced to the external sphere. In the case of Eu, the cationic complex with the coordination number 8 but with the different composition $[(Bipy)Eu(H_2O)_4Cl_2]Cl \cdot H_2O$ was obtained from an aqueous solution, and its external sphere contains the anion and also the water molecule [26]. As the Bipy : Ln molar ratio increases to 2 the $[(Bipy)Ln(H_2O)_6]Cl_3 \cdot 0.5Bipy \cdot 2H_2O$ complexes containing one molecule of the coordinated ligand (another molecule is fixed in the external sphere) were obtained from ethanol solutions.

The inner-sphere coordination of two bidentate ligands with the formation of the cationic complexes $[(Bipy)_2Ln(H_2O)_2Cl_2]Cl$ (Ln = Pr, Er) and $[(Bipy)_2La(H_2O)_4Cl]Cl_2 \cdot 2H_2O$ and the neutral complex $[(Bipy)_2Ln(H_2O)Cl_3] \cdot n$EtOH (Ln = Pr, Nd, Eu [27] was established when the ratio Bipy : Ln = 2 is retained in the reaction solution. In the case of Phen, solvates $[(Phen)_2Ln(H_2O)_3Cl_3] \cdot MeOH$ (for Ln = La, Pr, Nd, and Eu) and cationic complexes $[(Phen)_2Ln(H_2O)Cl] \cdot Cl_2 \cdot H_2O$ (for Ln = Dy, Er, and Y) in which the first coordination sphere of REM contains two bidentate ligands [27] were identified by the X-ray diffraction analysis data. Three chloride ions are in the external coordination sphere of the supramolecular ensemble $[Pr(Phen)_2(H_2O)_5]Cl_3 \cdot H_2O \cdot MeOH$ [28]. The coordination sphere is rearranged on heating (117°C), when the outer-sphere methanol and water molecules are removed, due to the transition Cl exo → Cl endo to form $[Pr(Phen)_2(H_2O)Cl_3]$ [28].

The possibility of formation of the compounds with different amounts of the bidentate ligand, chloride ions, and water molecules in the internal and external coordination spheres can be associated with the fact that the nonvalent interactions in the second coordination sphere of REM (hydrogen bonds, π-stacking) are comparable with the interactions determining the Ln–ligand bonds. The influence of the exo and endo binding of lanthanide chlorides with Bipy and Phen on the photophysical characteristics was studied in [29] and [30], respectively. Specific interionic interactions play an important role in the sensitization of luminescence of Tb and Eu, for example, the $[TbCl(H_2O)_3([(Bipy)_2]Cl_2(H_2O)$ complex demonstrates the unexpectedly high quantum yield (37%) due to the intermolecular interactions (Cl···π and π-stacking) in spite of the presence of three H_2O molecules in the internal coordination sphere [30].

The experimental data indicate that the compositions of the inner- and outer-sphere complexes formed by the coordination of Bipy or Phen by the neutral REM thiocyanate complexes depend, to a high extent, on the synthesis conditions. Although the ionic radii of the three-charge REM cations allow each of them to coordinate three Bipy or Phen molecules, the third molecule of the bidentate ligand is localized in the external sphere at the N-donor ligand to REM molar ratios from 1 to 3 (Fig. 2, Table 3).

Perhaps, the coordination of the bidentate ligand by the neutral REM thiocyanate complexes (unlike the cationic chloride precursors) competes with the stacking interactions of these ligands in the lattice, which results in the formation of the outer-sphere associates. It should be emphasized that all thiocyanate complexes with the outer-sphere coordination of the chelate ligands presented in Table 3 were synthesized using individual $Ln(NCS)_3 \cdot 6H_2O$ salts. If the thiocyanate precursor was obtained in the solution by the reaction of $Ln(NO_3)_3$–KNCS redistribution, then

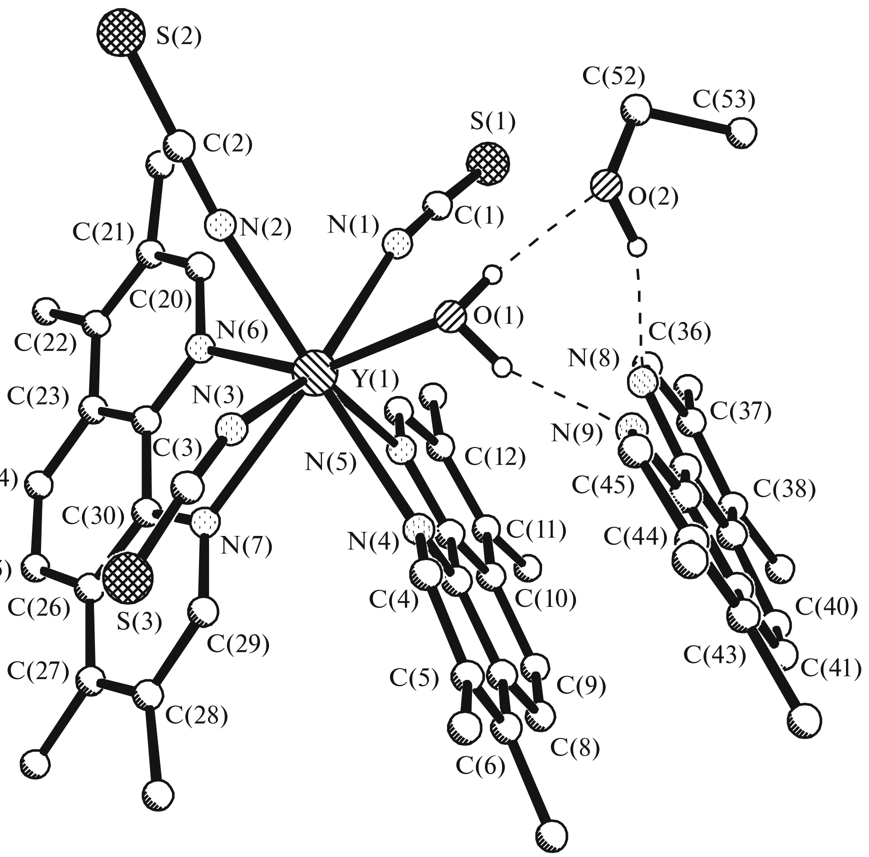

Fig. 2. Fragment of the structure of $[Y(NCS)_3(H_2O)(Me_4Phen)_2] \cdot (Me_4Phen) \cdot 0.75EtOH$ [32].

the tris(chelate) complexes, $[Pr(NCS)_3(Bipy)_3]$ with the coordination number of Pr equal to 9 [35] or $[Ln(NCS)_3(Phen)_3] \cdot EtOH$ (Ln = Pr, Nd) [36], are formed.

The study of the solid-phase thermolysis of the complexes with the outer-sphere Phen and Me_4Phen molecules showed that the outer-sphere molecules of N-donor ligands can enter into the internal sphere of the metal [31, 32]. A sufficiently distinct dependence of the temperature of entering of the solvate N-donor ligand into the internal sphere of the metal on the ionic radius of Ln^{3+} was observed (Fig. 3). The data presented in Fig. 3 make it possible to reveal a noticeable role of the steric factor determining the thermodynamics of insertion of the Phen and Me_4Phen ligands into the coordination sphere of REM. For more bulky Me_4Phen, the temperature of insertion increases by 30–60°C depending on the complexing agent (Fig. 3). The incorporation of the third molecule of the bidentate ligand into endo coordination increases the coordination number of the complexing agent to 9 and changes the coordination environment $LnN_7O \rightarrow LnN_9$, which is accompanied by the sensitization of luminescence of Tb and Eu and by an increase in the quantum yield [31].

In the case of the ditopic ligands (4,4'-bipyridine (4,4'-Bipy) and 4,7-phenanthroline (4,7-Phen)), specific interactions, which are characteristic of heterocyclic molecules, play a special role in the stabilization of supramolecular forms. In the structurally characterized compounds $[Y(H_2O)_3EtOH(4,4'\text{-}Bipy)(NCS)_3] \cdot 4,4'\text{-}Bipy$,$\{(\mu\text{-}4,4'\text{-}Bipy)[Y(H_2O)_3(NCS)_3]_2\} \cdot 3(4,4'\text{-}Bipy) \cdot 2(iso\text{-}PrOH)$, and $[H(4,4'\text{-}Bipy)]_2\{(\mu\text{-}4,4'\text{-}Bipy)[Y\text{-}(H_2O)_3(NCS)_4]_2\} \cdot 4,4'\text{-}Bipy$, the ditopic ligand acts as a mono- (Fig. 4a) or ditopic (Figs. 4b, 4c) ligand. In each case, 4,4'-Bipy is also present in the external sphere, and supramolecular ensembles are stabilized due to the hydrogen bonds $OH\cdots N(S)$ [33]. In aprotic solvents (and partially in a solution of *iso*-PrOH), ditopic 4,4'-Bipy induces the redistribution of the acido ligands, which leads to the formation of the anionic dimer (Fig. 4c). A similar situation was observed for ditopic 4,7-Phen. The mononuclear complexes (in which from 1 to 3 acido ligands are coordinated) were isolated from the reaction of $Y(NCS)_3 \cdot 6H_2O$ with 4,7-Phen and structurally characterized. There is no contact of yttrium with the ditopic ligand. The NCS^- anions and heterocyclic ligand are in the exo coordination, and the stacking interaction joins the 4,7-Phen molecules into piles (Table 3) [34].

Table 3. Complexes of REM with the outer-sphere N-bidentate ligands

Compound	Coordination number of Ln	Literature
$[(Bipy)Ln(H_2O)_6]Cl_3 \cdot 0.5Bipy \cdot 2H_2O$ (Ln = Er, Lu, Y)	8	[26]
$[Y(NCS)_3(H_2O)(Bipy)_2] \cdot 0.5(Bipy) \cdot H_2O$	8	[31]
$[Eu(NCS)_3(H_2O)(Bipy)_2] \cdot 0.5(Bipy) \cdot H_2O$	8	[31]
$[Dy(NCS)_3(H_2O)(Bipy)_2] \cdot 0.5(Bipy) \cdot H_2O$	8	[10]
$[Y(NCS)_3(H_2O)(Phen)_2] \cdot Phen \cdot 0.5H_2O$	8	[31]
$[Eu(NCS)_3(H_2O)(Phen)_2] \cdot Phen \cdot 0.5H_2O$	8	[31]
$[TbNCS)_3(H_2O)(Phen)_2] \cdot Phen \cdot 0.5H_2O$	8	[31]
$[Dy(NCS)_3(H_2O)(Phen)_2] \cdot Phen \cdot 0.5H_2O$	8	[10]
$[M(NCS)_3(H_2O)(Me_4Phen)_2] \cdot (Me_4Phen) \cdot 0.75EtOH$ (M = Y, Eu, Tb)	8	[32]
$[Y(H_2O)_3EtOH(4,4'\text{-}Bipy)(NCS)_3] \cdot 4,4'\text{-}Bipy$	8	[33]
$\{(\mu\text{-}4,4'\text{-}Bipy)[Y(H_2O)_3(NCS)_3]_2\} \cdot 3(4,4'\text{-}Bipy) \cdot 2(iso\text{-}PrOH)$	7	[33]
$[H(4,4'\text{-}Bipy)]_2\{(\mu\text{-}4,4'\text{-}Bipy)[Y(H_2O)_3(NCS)_4]_2\} \cdot 4,4'\text{-}Bipy$	8	[33]
$[Y(H_2O)_7(NCS)](NCS)_2 \cdot 5(4,7\text{-}Phen) \cdot 5(H_2O)$	8	[34]
$[Y(H_2O)_5(NCS)_3] \cdot 2(4,7\text{-}Phen) \cdot 2(H_2O)$	8	[34]
$\{H(4,7\text{-}Phen)\}_2[Y(H_2O)_7(NCS)](NCS)_4 \cdot 2(4,7\text{-}Phen) \cdot 5(H_2O)$	8	[34]

Tridentate terpyridine (Terpy) and its numerous derivatives compose one of the most studied classes of chelating ligands. The influence of the acido ligand on the compositions and structures of the complexes was revealed for the reactions of Terpy with the REM salts. According to the X-ray diffraction data, REM perchlorate salts form the tris(chelate) species, and the solvated $[Ln(Terpy)_3](ClO_4)_3 \cdot MeCN$ (Ln = Ce, Pr, Sm, Eu) complexes and neutral nonsolvated $[Ln(Terpy)_3](ClO_4)_3$ forms were isolated from acetonitrile solutions for Ln = Eu–Lu and Y in which the coordination number of REM was 9 [37].

The cationic complexes with the coordinated chloride ion and one molecule of the tridentate ligand, $[Ln(H_2O)_4(Terpy)Cl]Cl_2 \cdot nH_2O$ with the coordination number 8 containing the anions and water molecules in the external sphere, were isolated at the stoichiometric ratio REM trichloride : Terpy = 1 from water-alcohol solutions for almost the whole series of REM [38]. Hydrated REM bromides with Terpy form a series of the cationic complexes $[Ln(H_2O)_x\text{-}(Terpy)]Br_3 \cdot yH_2O$ without coordination of the bromide ion by the metal cation, where only Terpy molecule is coordinated and all three bromide ions are localized in the external sphere [39]. In the case of NCS^-, two Terpy molecules enter into the coordination sphere to form the mononuclear neutral $[Ln(NCS)_3(Terpy)_2]$ (Ln = Pr, Nd) species and solvates $[Ln(NCS)_3(Terpy)_2] \cdot EtOH$ (Ln = Pr, Nd) in which the coordination number of the complexing agent is 9 [36].

The influence of acido ligands on the composition and charge of the formed complexes is observed in the

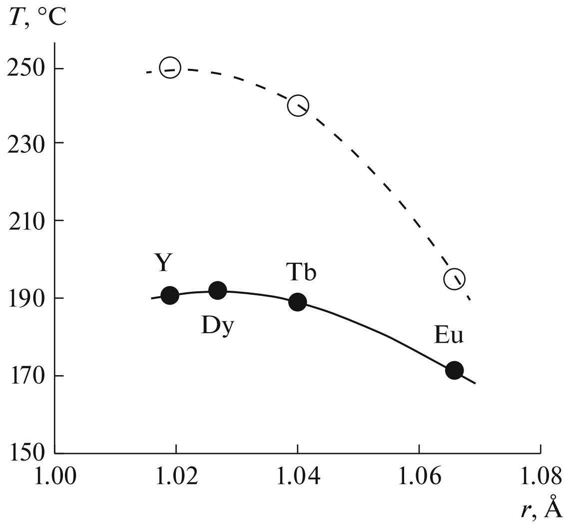

Fig. 3. Dependences of the temperature of the transition of N-donor ligand from the external to internal sphere on the ionic radius of Ln^{3+} for (solid line) $[Ln(NCS)_3(H_2O)(Phen)_2] \cdot Phen \cdot 0.5H_2O$ and (dashed line) $[Ln(NCS)_3(H_2O)(Me_4Phen)_2] \cdot (Me_4Phen) \cdot 0.75EtOH$.

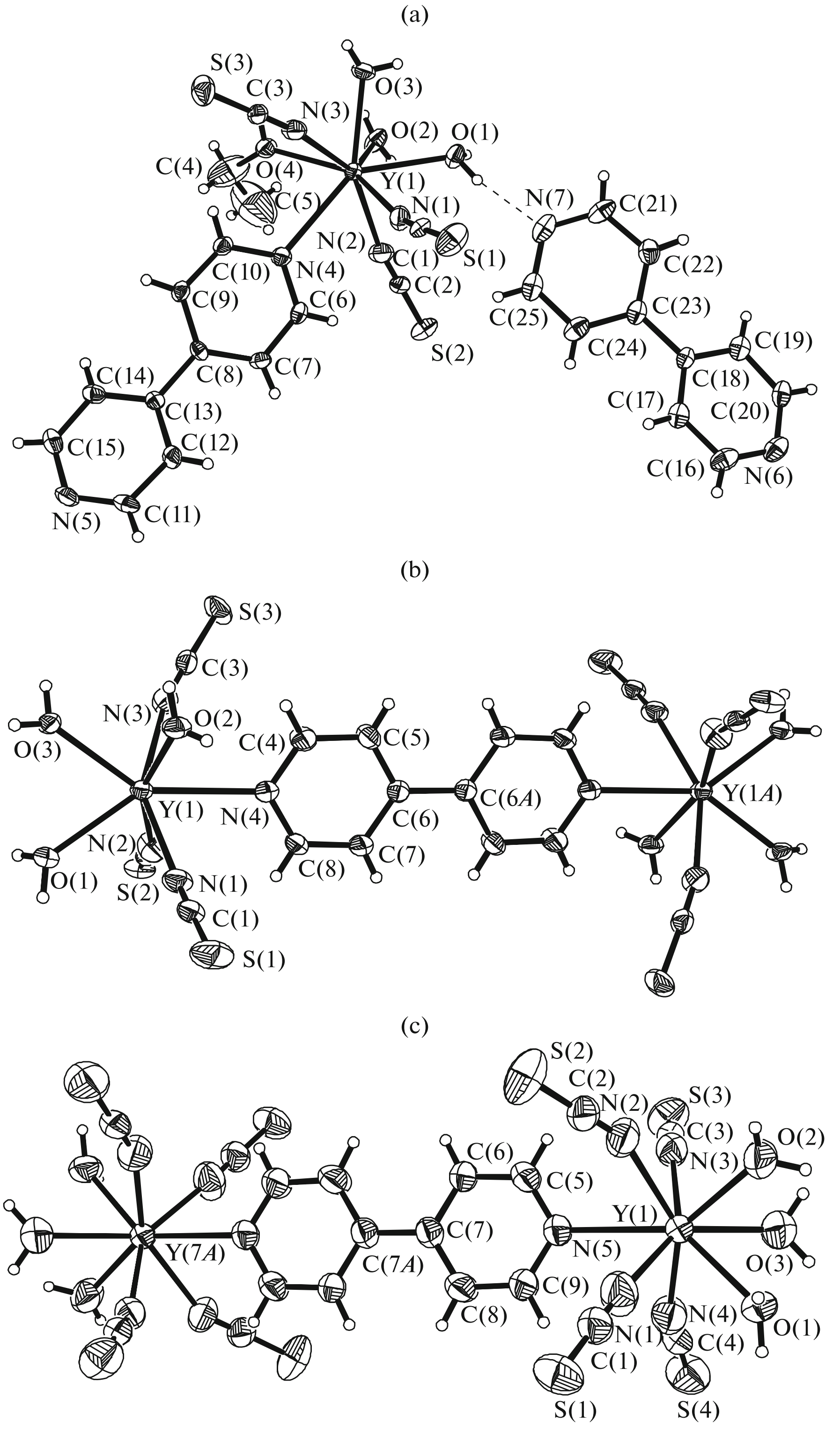

Fig. 4. Fragmenta of the structures of (a) $[Y(H_2O)_3EtOH(4,4'\text{-Bipy})(NCS)_3] \cdot 4,4'\text{-Bipy}$, (b) $\{(\mu\text{-}4,4'\text{-Bipy})[Y(H_2O)_3(NCS)_3]_2\} \cdot 3(4,4'\text{-Bipy}) \cdot 2(\textit{iso}\text{-PrOH})$, and (c) $[H(4,4'\text{-Bipy})]_2\{(\mu\text{-}4,4'\text{-Bipy})[Y(H_2O)_3(NCS)_4]_2\} \cdot 4,4'\text{-Bipy}$.

reactions with Terpy. Three-charge cationic complexes of various compositions with one or three molecules of coordinated Terpy are formed with the bulky anions (Br^-, ClO_4^-). Only one Terpy molecule and one chloride anion are coordinated in chlorides, and the neutral mononuclear complexes with three NCS^-

groups and two Terpy molecules in the first coordination sphere are formed with thiocyanates. The formation of the complexes solvated by the solvent was observed in almost all cases.

Published data on polydentate N-donor *s*-triazine, 2,4,6-tris(2-pyridyl)-*s*-triazine (Tptz), in compounds with REM are restricted. According to the known data, Tptz with REM accomplishes the tridentate position with the formation of the monomeric complexes with the coordination number of the complexing agent equal to 9: $[EuL_3(Tptz)]$ (L is dibenzoylmethane) [40], $[Ln(Tptz)(NCS)_3(H_2O)(CH_3OH)_2]$ (Ln = Gd, Eu), and $[Tb(Tptz)(NCS)_3(H_2O)_3]$ [41]. The external sphere of these compounds contains no Tptz molecules. The study of the reactions of hydrated thiocyanates $Ln(NCS)_3 \cdot 6H_2O$ (Ln = Y, Eu, Tb) with Tptz in MeOH, MeCN, and H_2O showed the formation of the neutral or ionic thiocyanate complexes with one coordinated Tptz molecule and the coordination number of Ln equal to 8. A specific feature of these complexes is the presence of the second Tptz molecule in the exo coordination. The recrystallization from the aprotic solvent (MeCN) induces the transition of Tptz to the endo coordination to form $[Ln(Tptz)_2(NCS)_3] \cdot MeCN$ [42]. Two Tptz molecules in the first coordination sphere increase the coordination number of Ln to 9. The transition of Tptz from the exo to endo coordination is also possible due to thermolysis [43], which occurred in the cases of the complexes with Phen [31] and Me_4Phen [32].

The tris(heterocyclic) ligands based on 2,6-di(pyrazolyl)pyridines were intensively used as chelating ligands in the coordination chemistry [44–46]. The reactions of $Ln(NO_3)_3 \cdot nH_2O$ (Ln = Pr, Eu, Dy, Yb) in methanol with a series of 2,6-di(pyrazolyl)pyridines (L) afforded the solvated complexes $[Eu(L\text{-}2)(NO_3)_3](MeOH)(H_2O)$, $[Dy(L\text{-}4)(NO_3)_3](H_2O)$, and $[Ln(L\text{-}5)(NO_3)_3](H_2O)$ (Ln = Eu, Pr) with one chelating ligand in the first coordination sphere. The recrystallization of these solvates from CH_2Cl_2 or a CH_2Cl_2–MeOH mixture gives single-crystal samples with the L to La ratio equal to 2 : 1 containing no solvate molecules of water and methanol. The use of the aprotic solvent CH_2Cl_2 changes the compositions of the complexes. The water and methanol molecules leave the coordination sphere. Two L ligands are involved in the endo coordination, and the coordination number of Ln, which is equal to 10 in the single-crystal complexes, changes.

The date presented show that the variance of the compositions and stereochemical features of the inner- and outer-sphere REM compounds depend, to a high extent, on the donor ability of the ligands and solvents used. The ionic character of the formed REM–ligand bonds and their lability affect the formation of various species: neutral, ionic monomeric, or oligomeric complexes. The stability of the M–X contact pair and the ionic radius of the acido ligand are especially significant for the halide and pseudohalide ligands involved in the inner-sphere coordination [6–8, 27–30, 37–39, Table 3].

The formation of the first and second (external) coordination spheres and supramolecular association depend on the secondary interactions (and other factors) caused by the ligands and solvents. The effect of the medium on the ligand transitions exo ↔ endo is especially distinct for the coordination of polydentate ligands, crown ethers [33, 34], and triazine [42, 46] and was clearly demonstrated for the influence of the aprotic solvent on the compositions of the complexes and coordination numbers of the complexing agents [23, 42, 46]. The transition of the ligands from the exo to endo coordination can also be initiated by thermolysis [15, 28, 31, 32, 43]. The changes in the ligand composition of the endo coordination and secondary interactions in the external sphere modify the physical properties of the REM compounds with the polydentate ligands [29–31]. The formation of the outer-sphere complexes with the polydentate ligands depends on the used precursors, and the compounds with the molecule of the N-donor ligand in the external sphere are formed in the reactions with the heterocyclic polydentate ligands in the case of hydrated REM thiocyanates (Table 3). The transition of the polydentate N-donor ligand from the exo to endo coordination is observed during solid-phase thermolysis, and the temperature of the coordination transition exo → endo is related to the ionic radius of the REM cation and steric features of the organic ligand.

FUNDING

This work was supported by the Russian Science Foundation, project no. 16-13-10407.

REFERENCES

1. Petrosyants, S.P., *Russ. J. Coord. Chem.,* 2015, vol. 41, no. 11, p. 715. https://doi.org/10.1134/S107032841511007X
2. Bell, A.M.T. and Smith, A.J., *Acta Crystallogr., Sect. C:, Cryst. Struct. Commun.*, 1990, vol. 46, p. 960.
3. Semenova, L.I., Junk, PC., Skelton, B.W., and White, A.H., *Aust. J. Chem.*, 1999, vol. 52, p. 531.
4. Ilyukhin, A.B., Dobrokhotova, Zh.V., Petrosyants, S.P., and Novotortsev, V.M., *Polyhedron*, 2011, vol. 30, no. 16, p. 2654.
5. Gutmann, V., *Coordination Chemistry in Non-Aqueous Solutions*, New York: Springer, 1968.
6. Ishiguro, S., Umebayashi, Y., and Komiya, M., *Coord. Chem. Rev.*, 2002, vol. 226, p. 103.
7. Lees, A.M.J. and Platt, A.W.G., *Polyhedron*, 2014, vol. 67, p. 368.
8. Bowden, A., Lees, A.M.J., and Platt, A.W.G., *Polyhedron*, 2015, vol. 91, p. 110.

9. Petrosyants, S.P., Dobrokhotova, Zh.V., Ilyukhin, A.B., et al., *Inorg. Chim. Acta*, 2015, vol. 434, p. 41.
10. Petrosyants, S.P., Dobrokhotova, Zh.V., Ilyukhin, A.B., et al., *Eur. J. Inorg. Chem.*, 2017, vol. 2017, p. 3561.
11. Brown, M.D., Lewason, W., Murray, D.C., et al*., Dalton Trans.,* 2003, vol. 32, no. 5, p. 857.
12. Petrosyants, S.P. and Ilyukhin, A.B., *Russ. J. Coord. Chem.*, 2010, vol. 36, no. 2, p. 97. https://doi.org/10.1134/S1070328410020028
13. Mishra, S., *Coord. Chem. Rev.*, 2008, vol. 252, p. 1996.
14. Rogers, R.D., Rollins, A.N., Etzenhouser, R.D., et al., *Inorg. Chem.*, 1993, vol. 32, p. 3451.
15. Dobrokhotova, Zh.V., Petrosyants, S.P., Ilyukhin, A.B., and Novotortsev, V.M., *Russ. Chem. Bull. Int. Ed.*, 2012, vol. 61, no. 11, p. 2056.
16. Rogers, R.D., *Inorg. Chim. Acta*, 1987, vol. 133, p. 347.
17. Rogers, R.D., Kurihara, L.K., and Voss, E.J., *Inorg. Chem.*, 1987, vol. 26, p. 2360.
18. Rogers, R.D., Rollins, A.N., Etzenhouser, R.D., et al., *Inorg. Chem.*, 1993, vol. 32, p. 3451.
19. Rogers, R.D., Rollins, A.N., Henry, R.F., et al., *Inorg. Chem.*, 1991, vol. 30, p. 4946.
20. Rogers, R.D. and Kurihara, L.K., *Inorg. Chem.*, 1987, vol. 26, p. 1498.
21. Hassaballa, H., Steed, J.W., Junk, P.C., and Elsegood, M.R.J., *Inorg. Chem.*, 1998, vol. 37, p. 4666.
22. Forsellini, E., Benetollo, F., Bombieri, G., et al., *Inorg. Chim. Acta*, 1985, vol. 109, p. 167.
23. Petrosyants, S., Dobrokhotova, Zh., Ilyukhin, A., and Novotortsev, V., *Inorg. Chim. Acta*, 2013, vol. 408, p. 39.
24. Rogers, R.D., Zhang, J., and Bauer, C.B., *J. Alloys Compd.*, 1997, vol. 249, no. 1, p. 671.
25. Hines, C.C., Bauer, C.B., and Rogers, R.D., *New J. Chem.*, 2007, vol. 31, p. 762.
26. Semenova, L.I., Skelton, B.W., and White, A.H., *Aust. J. Chem.*, 1999, vol. 52, p. 551.
27. Semenova, L.I. and White, A.H., *Aust. J. Chem.*, 1999, vol. 52, p. 571.
28. Saha, R., Goswami, S., Biswas, S., et al., *Inorg. Chim. Acta*, 2014, vol. 423, p. 123.
29. Puntus, L.N., Lyssenko, K.A., Antipin, M.Yu., and Bunzli, J.-C.G., *Inorg. Chem.*, 2008, vol. 47, no. 23, p. 11095.
30. Puntus, L.N., Lyssenko, K.A., Pekareva, I.S., and Bünzli, J.-C.G., *J. Phys. Chem. B*, 2009, vol. 113, no. 27, p. 9265.
31. Dobrokhotova, Zh.V., Petrosyants, S.P., Ilyukhin, A.B., et al., *Inorg. Chim. Acta*, 2017, vol. 456, p. 76.
32. Petrosyants, S.P., Ilyukhin, A.B., Dobrokhotova, Zh.V., et al., *Russ. J. Coord. Chem.*, 2017, vol. 43, no. 6, p. 352. https://doi.org/10.1134/S1070328417060057
33. Petrosyants, S., Dobrokhotova, Zh., Ilyukhin, A., and Novotortsev, V., *New J. Chem.*, 2014, vol. 38, p. 3803.
34. Petrosyants, S.P. and Ilyukhin, A.B., *Russ. J. Coord. Chem.*, 2014, vol. 40, no. 6, p. 401. https://doi.org/10.1134/S1070328414060050
35. Bower, J.F., Cotton, S.A., Fawcett, J., et al., *Polyhedron*, 2003, vol. 22, p. 347.
36. Cotton, S.A., Franckevicius, V., How, R.E., et al., *Polyhedron*, 2003, vol. 22, p. 1489.
37. Semenova, L.I., Sobolev, A.N., Skelton, B.W., and White, A.H., *Aust. J. Chem.*, 1999, vol. 52, p. 519.
38. Kepert, C.J., Weimin, L., Scelton, B.W., and White, A.H., *Aust. J. Chem.*, 1994, vol. 47, p. 365.
39. Semenova, L.I. and White, A.H., *Aust. J. Chem.*, 1999, vol. 52, p. 539.
40. De Silva, C.R., Wang, J., Carducci, M.D., et al., *Inorg. Chim. Acta*, 2004, vol. 357, no. 2, p. 630.
41. Goel, N., *J. Coord. Chem.*, 2015, vol. 68, no. 3, p. 529.
42. Petrosyants, S.P., Ilyukhin, A.B., Gavrikov, A.V., and Efimov, N.N., *Russ. J. Coord. Chem.*, 2018, vol. 44, no. 12, p. 733. https://doi.org/10.1134/S1070328418120060
43. Petrosyants, S.P., Ilyukhin, A.B., Belova, E.V., et al., *Russ. J. Coord. Chem.*, 2019, vol. 45, no. 8, p. 692. https://doi.org/10.1134/S1070328419080062
44. Mukherjee, R., *Coord. Chem. Rev.*, 2000, vol. 203, p. 151.
45. Halcrow, M.A., *Coord. Chem. Rev.*, 2005, vol. 249, p. 2880.
46. Ouizem, S., Rosario-Amorin, D., Dickie, D.A., et al., *Polyhedron*, 2015, vol. 101, p. 37.

Translated by E. Yablonskaya