ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2015, Vol. 41, No. 4, pp. 230–239. © Pleiades Publishing, Ltd., 2015.
Original Russian Text © I.V. Taidakov, Yu.A. Strelenko, R.S. Borisov, A.Z. Temerdashev, N.P. Datskevich, A.G. Vitukhnovskii, 2015, published in Koordinatsionnaya Khimiya, 2015, Vol. 41, No. 4, pp. 203–212.

Yttrium(III) and Lanthanum(III) Tris(1,3-Bis(1,3-Dimethyl-1*H*-Pyrazol-4-yl)propane-1,3-Dionato)(1,10-Phenanthroline): Synthesis and Study by Mass Spectrometry, X-ray Diffraction Analysis, and ^{89}Y and ^{139}La NMR Spectroscopy

I. V. Taidakov[a, *], Yu. A. Strelenko[b], R. S. Borisov[c], A. Z. Temerdashev[d], N. P. Datskevich[a], and A. G. Vitukhnovskii[a]

[a] *Lebedev Physical Institute, Russian Academy of Sciences, Leninskii pr. 53, Moscow, 119991 Russia*
[b] *Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences, Leninskii pr. 47, Moscow, 119991 Russia*
[c] *Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Leninskii pr. 29, Moscow, 119992 Russia*
[d] *Kuban State University, ul. Karla Libknekhta 9, Krasnodar, 350640 Russia*
**e-mail: taidakov@gmail.com*

Received October 26, 2014

Abstract—The reactions of $LaCl_3$ and YCl_3 with 1,3-bis(1,3-dimethyl-1*H*-pyrazol-4-yl)propane-1,3-dione (HL) and 1,10-phenanthroline (Phen) in the presence of a base afford complexes $[La(L)_3(Phen)]$ (**I**) and $[Y(L)_3(Phen)]$ (**II**). Unstable solvates **I** · *iso*-PrOH (**III**) and **II** · *iso*-PrOH (**IV**) are obtained from solutions of the complexes in 2-propanol, and their structures are determined by X-ray diffraction analysis (CIF files CCDC 1026802 (**III**) and 1026808 (**IV**)). The compositions of the complexes are additionally studied by ^{1}H, ^{13}C, ^{89}Y, and ^{139}La NMR methods. Fragmentation is studied by laser desorption/ionization (LDI) and electrospray ionization (ESI) mass spectrometry.

DOI: 10.1134/S1070328415040089

INTRODUCTION

Complexes of rare-earth metals, first of all, those capable of luminescing (for example, Eu, Tb, Sm, Nd, and others) are objects of intense studies in recent decades due to their wide use in various optical electronic devices and for biomedical purposes [1]. Nevertheless, the derivatives of non-luminescing rare-earth metals (Sc, La, Y, and Gd) also find use as precursors for the synthesis of oxide materials by the chemical vapor deposition (CVD) method (chemical deposition from the gas phase) [2]. In addition, some of these complexes are diamagnetic, which makes it possible to use NMR methods for studying their structures [3].

In this work, we describe the synthesis of two diamagnetic lanthanum(III) and yttrium(III) complexes with 1,3-diketone of the pyrazole series (1,3-bis(1,3-dimethyl-1*H*-pyrazol-4-yl)propane-1,3-dione) (HL) and 1,10-phenanthroline (Phen) and their structures determined by methods of NMR on various nuclei and mass spectrometry.

EXPERIMENTAL

Ligand HL was synthesized according to a known procedure [4]. Lanthanum and yttrium oxides (99.9%) and solvents ("for synthesis" grade) purchased from Aldrich (United States) were used without additional purification.

NMR spectra were recorded on a Bruker DRX-500 instrument (working frequencies were 500.12, 125.76, 70.65, and 24.51 MHz for ^{1}H, ^{13}C, ^{139}La, and ^{89}Y, respectively) in solutions of deuterated solvents (D_2O, DMSO-d_6, and $CDCl_3$) at 300 K. Chemical shifts were presented in ppm. For ^{1}H and ^{13}C, Me_4Si (δ = 0.00 ppm) was used as an internal standard. External standards, a 0.1 M solution of $La(NO_3)_3$ in D_2O at pH 1 and a 2 M solution of YCl_3 in D_2O at pH 1 (δ = 0.0 ppm) [5], were used for ^{139}La and ^{89}Y, respectively.

The mass spectra of the studied compounds were obtained on a Bruker Autoflex Speed mass spectrometer with LDI (337 nm) in the positive ion mode using a reflectron. The highest ionization efficiency was observed for the mass spectra without matrix compounds (LDI method) and on a Bruker MSP 96 NALDI nanostructured target for the nanostructure-assisted laser desorption/ionization (NALDI). A solution of the studied compounds in ethanol (2 mg/mL) was deposited on steel (LDI) or nanostructured (NALDI) targets.

ESI mass spectra were recorded on an Ultimate-3000 liquid chromatograph (Thermo Scientific) connected to a TSQ Quantum Access MAX triple quadrupole mass spectrometer through an ESI source in the

positive ion mode controlled by the XCalibur 2.2 software. Samples were examined in the full ionic current mode. The temperature of the ion source was 200°C, the pressure of the spraying gas was 20 arbitrary units, the pressure of the auxiliary gas was 5 arbitrary units, the temperature of the capillary was 250°C, and the voltage on the capillary was 2 kV. Scanning was carried out in the range from 400 to 1400 Da. The samples were analyzed using direct sample injection in the mobile phase flow. A 0.1% solution of HCOOH in a water–acetonitrile (20 : 80 vol/vol) mixture served as a mobile phase. The volume of the injected sample was 5 μL, and the flow rate was 0.3 mL/min.

The starting 0.5 M solutions of lanthanum(III) and yttrium(III) chlorides were prepared as follows: a weighed sample of La_2O_3 (2.036 g) or Y_2O_3 (1.411 g) calcined at 500°C was dissolved in a minimum amount of concentrated HCl (special purity grade), evaporated to dryness, and dissolved in distilled water bringing the volume to 25 mL.

Synthesis of [La(L)$_3$(Phen)] (I). Ligand HL (0.390 g, 1.5 mmol) and Phen (0.09 g, 0.5 mmol) were dissolved in ethanol (15 mL), after which a solution of $LaCl_3$ (1 mL) and a 1 M solution of NaOH (1.5 mL) were successively added dropwise with stirring. A yellowish solution that formed was filtered, kept at 60°C for 10 min, and then left for 24 h at room temperature. Then the solvent was evaporated to dryness, and the residue was extracted on heating with CH_2Cl_2 (40 mL). The organic phase was filtered, evaporated to a volume of 5 mL, and precipitated with hexane. An oily partially crystallized precipitate was recrystallized from 2-propanol. Colorless crystals were filtered off, washed with cold 2-propanol and hexane, and dried in vacuo (10^{-2} Torr) at 45°C to a constant weight. The yield of complex **I** as a white finely crystalline powder was 0.12 g (22%).

For $C_{51}H_{53}N_{14}O_6La$

anal. calcd., %:	C, 55.84;	H, 4.87;	N, 17.88;	La, 12.66.
Found, %:	C, 55.99;	H, 4.73;	N, 18.02;	La, 12.70.

^{1}H NMR ($CDCl_3$, c = 0.1 mol/L, 300 K), δ, ppm: 9.45 (s, 6H, CH–Pyr (pyrazole)), 8.01 (s, 2H,CH–Phen), 7.66 (s, 2H,CH–Phen), 7.58 (s, 2H, CH–Phen), 7.20 (s, 2H, CH–Phen), 5.77 (s, 3H, CH), 3.69 (s, 18H, N–CH_3), 2.24 (s, 18H, CH_3). ^{13}C NMR ($CDCl_3$, c = 0.1 mol/L, 300 K), δ, ppm: 178.38 (C=O), 151.85, 150.50, 148.96, 145.57, 136.87, 136.17, 132.64, 131.77, 128.78, 126.38, 123.28, 122.37, 119.84, 96.54 (CH=), 38.96 (N–CH_3), 14.08 (CH_3).

Synthesis of [La(L)$_3$(Phen)$_2$] was unsuccessful. The synthesis was carried out under the same conditions as that for compound **I** but in the presence of 2.2 equivalents of 1,10-phenanthroline (0.198 g, 1.1 mmol). The yield of complex **I** was 0.16 g (29%).

Synthesis of [Y(L)$_3$(Phen)] (II) was similar to that described for compound **I**. An organic solution after the extraction of the residue with CH_2Cl_2 (50 mL) was dried with $MgSO_4$, filtered, and concentrated in vacuo to a volume of 5 mL. Then hexane (2.5 mL) was added very slowly with vigorous stirring, after which crystallization occurred. The precipitate was filtered off, washed with hexane, and dried in vacuo (10^{-2} Torr) at 45°C to a constant weight. The yield of complex **II** as a white finely crystalline powder was 0.29 g (55%).

For $C_{51}H_{53}N_{14}O_6Y$

anal. calcd., %:	C, 58.51;	H, 5.10;	N, 18.73;	Y, 8.49.
Found, %:	C, 58.63;	H, 5.17;	N, 18.61;	Y, 8.53.

^{1}H NMR ($CDCl_3$, c = 0.2 mol/L, 300 K), δ, ppm: 9.50 (s, 6H, CH–Pyr), 8.21 (s, 2H, CH–Phen), 7.70 (s, 2H,CH–Phen), 7.61 (s, 2H, CH–Phen), 7.26 (s, 2H, CH–Phen), 5.80 (s, 3H, CH), 3.71 (s, 18H, N–CH_3), 2.20 (s, 18H, CH_3). ^{13}C NMR ($CDCl_3$, c = 0.1 mol/L, 300 K), δ, ppm: 178.28 (C=O), 151.08, 148.80, 136.78, 136.19, 132.65, 131.89, 128.55, 126.15, 123.28, 122.44, 96.30 (CH=), 38.90 (N–CH_3), 13.93 (CH_3). ^{89}Y NMR ($CDCl_3$, c = 0.1 mol/L, 300 K), δ, ppm: 52.02.

The slow evaporation of saturated solutions of complexes **I** and **II** in 2-propanol at room temperature gave crystals of compounds **I** · *iso*-PrOH (**III**) and **II** · *iso*-PrOH (**IV**) suitable for X-ray diffraction analysis.

Synthesis of $C_{27}H_{32}N_8O_4 \cdot 3H_2O$ (V). We attempted to synthesize [La(L)$_3$(Phen)] in the presence of an urotropine buffer. The synthesis was carried out under the same conditions as those for compound **I**; however, after the addition of a solution of NaOH (pH 6.5), solid hexamethylenetetramine (urotropine) (0.3 g, 2.1 mmol) was introduced. After heating to 60°C and keeping for 24 h at room temperature, a crystalline precipitate was formed, filtered off, and recrystallized from 50% aqueous ethanol. As a result, colorless crystals of compound **V** (1,5-bis(1,3-dimethyl-1*H*-pyrazol-4-yl)-2,4-bis[(1,3-dimethyl-1*H*-pyrazol-4-yl)carbonyl]pentane-1,5-dione trihydrate) suitable for X-ray diffraction analysis were obtained. The yield of compound **V** was 0.17 g (39%).

For $C_{27}H_{32}N_8O_4 \cdot 3H_2O$ ($C_{27}H_{38}N_8O_7$) (**V**)

anal. calcd., %:	C, 55.28;	H, 6.53;	N, 19.10.
Found, %:	C, 55.34;	H, 6.57;	N, 19.19.

High-resolution mass spectrum (m/z): M^+ 532.5949 (calculated for $C_{27}H_{32}N_8O_4$ (**V** · $3H_2O$) M^+ 532.5945).

^{1}H NMR (DMSO-d_6, 300 K), δ, ppm: 7.40 (s, 4H, CH–Pyr), 6.91 (t, 2H,CH), 3.71 (s, 12H, N–CH_3), 3.06 (t, 2H, CO_2), 2.25 (s, 12H, CH_3).

Main crystallographic data and refinement parameters for compounds **III–V**

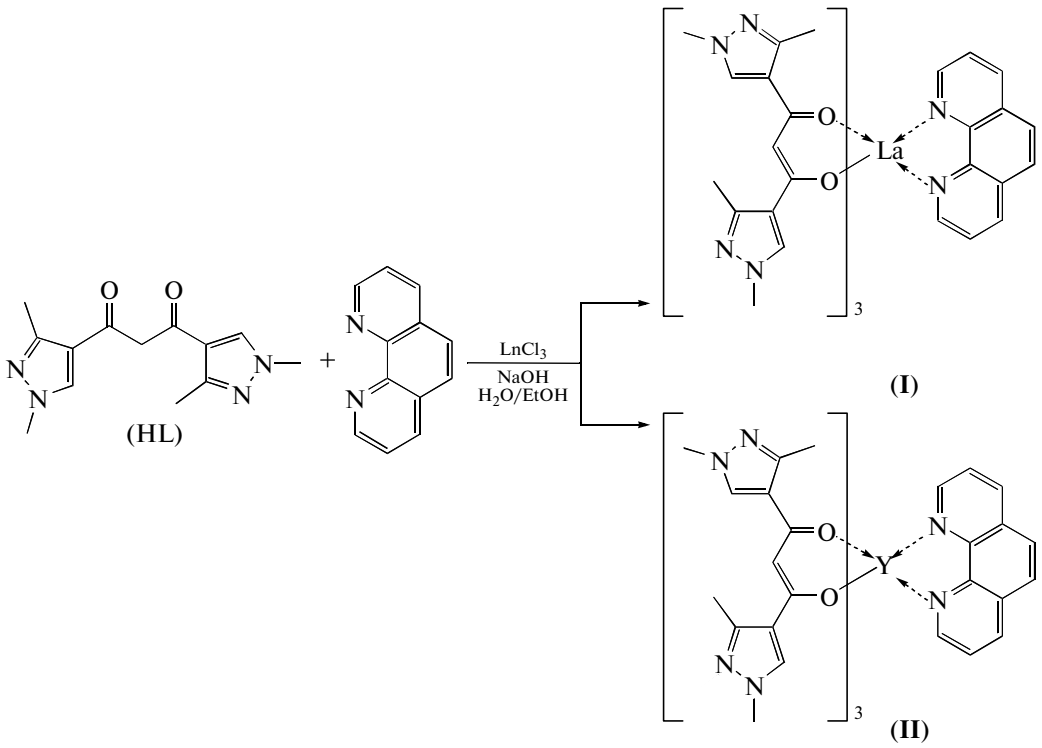
Parameter	Value		
	III	**IV**	**V**
Empirical formula	$C_{54}H_{61}N_{14}O_7La$	$C_{57}H_{69}N_{14}O_8Y$	$C_{27}H_{38}N_8O_7$
FW	1157.08	1167.17	586.65
T, K	150	150	120
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
Z	2	4	4
a, Å	11.2714(6)	12.1938(15)	8.4133(9)
b, Å	11.4929(6)	20.148(3)	17.646(2)
c, Å	22.7843(12)	26.225(3)	20.255(2)
α, deg	97.2190(10)	90.00	90.00
β, deg	90.1930(10)	102.448(2)	93.037(2)
γ, deg	109.0790(10)	90.00	90.00
V, Å^3	2764.1(3)	6291.5(14)	3002.9(6)
ρ_{calcd}, g/cm^3	1.390	1.232	1.298
μ, cm^{-1}	8.36	9.88	0.96
F(000)	1192	2448	1248
$2\theta_{max}$, deg	58	56	58
Reflection index ranges (*hkl*)	$-15 \le h \le 15$, $-15 \le k \le 15$, $-30 \le l \le 30$	$-15 \le h \le 15$, $-26 \le k \le 26$, $-34 \le l \le 34$	$-11 \le h \le 11$, $-24 \le k \le 24$, $-27 \le l \le 27$
Number of measured reflections	30589	49335	34601
Number of independent reflections (R_{int})	14573 (0.0231)	15080 (0.1782)	7985 (0.0820)
Number of reflections with $I > 2\sigma(I)$	13202	6366	4495
Number of refined parameters	699	731	384
R-factors with $I > 2\sigma(I)$	$R_1 = 0.0286$ $wR_2 = 0.0714$	$R_1 = 0.0795$ $wR_2 = 0.1758$	$R_1 = 0.0493$ $wR_2 = 0.1125$
R factors (all reflections)	$R_1 = 0.0332$ $wR_2 = 0.0742$	$R_1 = 0.2090$ $wR_2 = 0.2341$	$R_1 = 0.1118$ $wR_2 = 0.1387$
Goodness-of-fit	0.976	0.951	0.974
Residual electron density (ρ_{min}/ρ_{max}), *e* Å^{-3}	1.408/–0.412	1.124/–0.524	0.278/–0.280

X-ray diffraction analyses for compounds III, IV, and V were carried out on a SMART APEXII CCD diffractometer (MoK_α radiation, graphite monochromator, ω scan mode). The structures were solved by a direct method and refined by least squares in the anisotropic full-matrix approximation for F^2_{hkl}. The hydrogen atoms of the solvate PrOH molecules in structures **IV** and **V** were localized from difference electron density Fourier syntheses. The positions of other hydrogen atoms were calculated geometrically. All hydrogen atoms were refined in the isotropic approximation by the riding model, whereas for complexes **III** and **IV** the refinement was performed with the fixed O–H bond length (0.85 Å). The main crystallographic data and refinement parameters for structures **III–V** are listed in the table. All calculations were performed using the SHELXTL PLUS program package [5].

The atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Centre (CCDC 1026802 (**IV**), 1026808 (**V**), and 1026809 (**VI**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

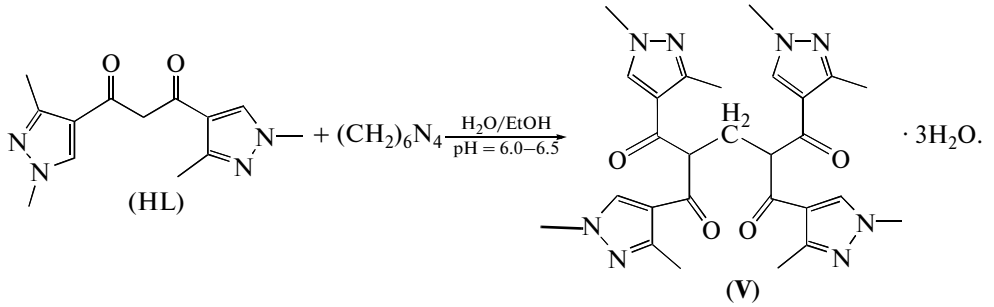
RESULTS AND DISCUSSION

Compounds **I** and **II** were synthesized according to the following scheme:



The best results were obtained when using yttrium(III) and lanthanum(III) chlorides as the starting compounds and a solution of NaOH as a base with the simultaneous control of the pH of the medium (pH 7.0–7.5).

We also attempted to synthesize complex La(III) in the presence of an urotropine buffer, which would make it possible to maintain a necessary acidity level. However, it turned out that the crystalline reaction product (**V**) contained no metal and represented the addition product of one formaldehyde molecule to two diketone molecules (formaldehyde is evidently formed upon the hydrolysis of urotropine).



Compound **V** was isolated as a solvate with three water molecules per molecule of the product, whose structure was proved by X-ray diffraction analysis (Fig. 1).

Similar products of addition to some diketones, for example, dibenzoylmethane, are known [6]; however, they are obtained, as a rule, by the interaction of stoichiometric amounts of formaldehyde taken as an aqueous solution and the dicarbonyl compound.

Although the urotropine buffer is recommended [7] as a medium for the complexonometric determination of rare-earth metals, it is evident that this method is inappropriate for the synthesis of complexes with 1,3-bis(1,3-dimethyl-1*H*-pyrazol-4-yl)propane-1,3-dione.

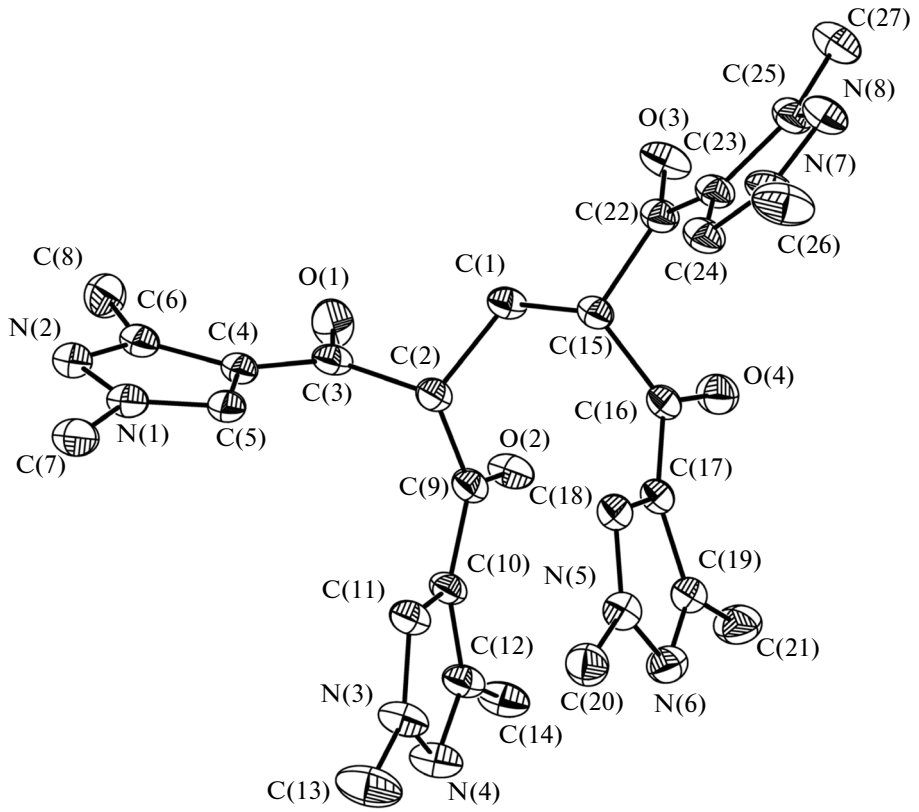


Fig. 1. General view of the dimeric molecule in structure **V** in the representation of atoms by thermal ellipsoids (with 50% probability). Hydrogen atoms and solvate water molecules are omitted.

The structures of molecules **I** and **II** in crystals **III** and **IV** are presented in Fig. 2. The coordination polyhedra $\{LaO_6N_2\}$ and $\{YO_6N_2\}$ are distorted square antiprisms. The average distances La–O (2.447 Å) and La–N (2.743 Å) slightly differ from those determined for other lanthanum(III) complexes of similar structure. For example, in complex $[La(dpm)_3(Phen)]$ (**VII**) (Hdpm is dipivaloylmethane), the average La–O and Ln–N bond lengths are 2.440 and 2.743 Å, respectively [8]. The planar pyrazole cycles are turned relatively to the plane passing through the atoms of the diketone fragment by angles ranging from 3.09° to 11.95°. The average OLnO angles and the NLaN angle are 69.4° and 59.68°, respectively (68.77° and 59.17°, respectively, for compound **VII**).

Yttrium compound **IV** also crystallizes in the monoclinic system as lanthanum complex **III**, but they are not completely isostructural. The unit cell parameters of compounds **III** and **IV** somewhat differ (table). The average distances in structure **V** (Y–O 2.297, Y–N 2.580 Å) are comparable to those in complex $[Y(tta)_3(Phen)]$ (**VIII**), where Htta is 2-thenoyltrifluoroacetone (2.307 and 2.546 Å, respectively) [9]. A significantly larger turn of the pyrazole cycles relatively to the plane of the diketone fragments (from 8.61° to 26.54°) is observed in structure **IV** compared to the molecule of lanthanum analog **III**, which can be due to a smaller ion radius of Y^{3+} compared to that of La^{3+} and, correspondingly, to increasing steric strain in the molecule. Interestingly, almost no turn of the thiophene cycles (the average deviation from the plane does not exceed 2°) is observed in complex **VIII**. The average OYO angles and NYN angle are 73.64° and 63.51°, respectively (73.10° and 64.05° for compound **VIII**).

It is known that the coordination number of La(III) atoms in complexes is often more than eight. In particular, it is shown [10] that complex $[La(tfac)_3(Phen)_2]$ (Htfac is trifluoroacetylacetone), in which the coordination number of La(III) atoms is ten, is formed as the single product even for a 1,10-phenanthroline deficient. Nevertheless, we failed to obtain complexes of similar composition in the presence of a phenanthroline excess. Probably, the formation of these complexes with 1,3-bis(1,3-dimethyl-1*H*-pyrazol-4-yl)propane-1,3-dione is difficult, because this ligand contains bulky substituents (which follows from the X-ray diffraction data) and the complexes with high coordination numbers become sterically overloaded.

The yttrium(III) (**II**) and lanthanum(III) (**I**) complexes are diamagnetic, which makes it possible to apply ^1H and ^{13}C NMR spectroscopy for their investigation. The position and multiplicity of the signals in

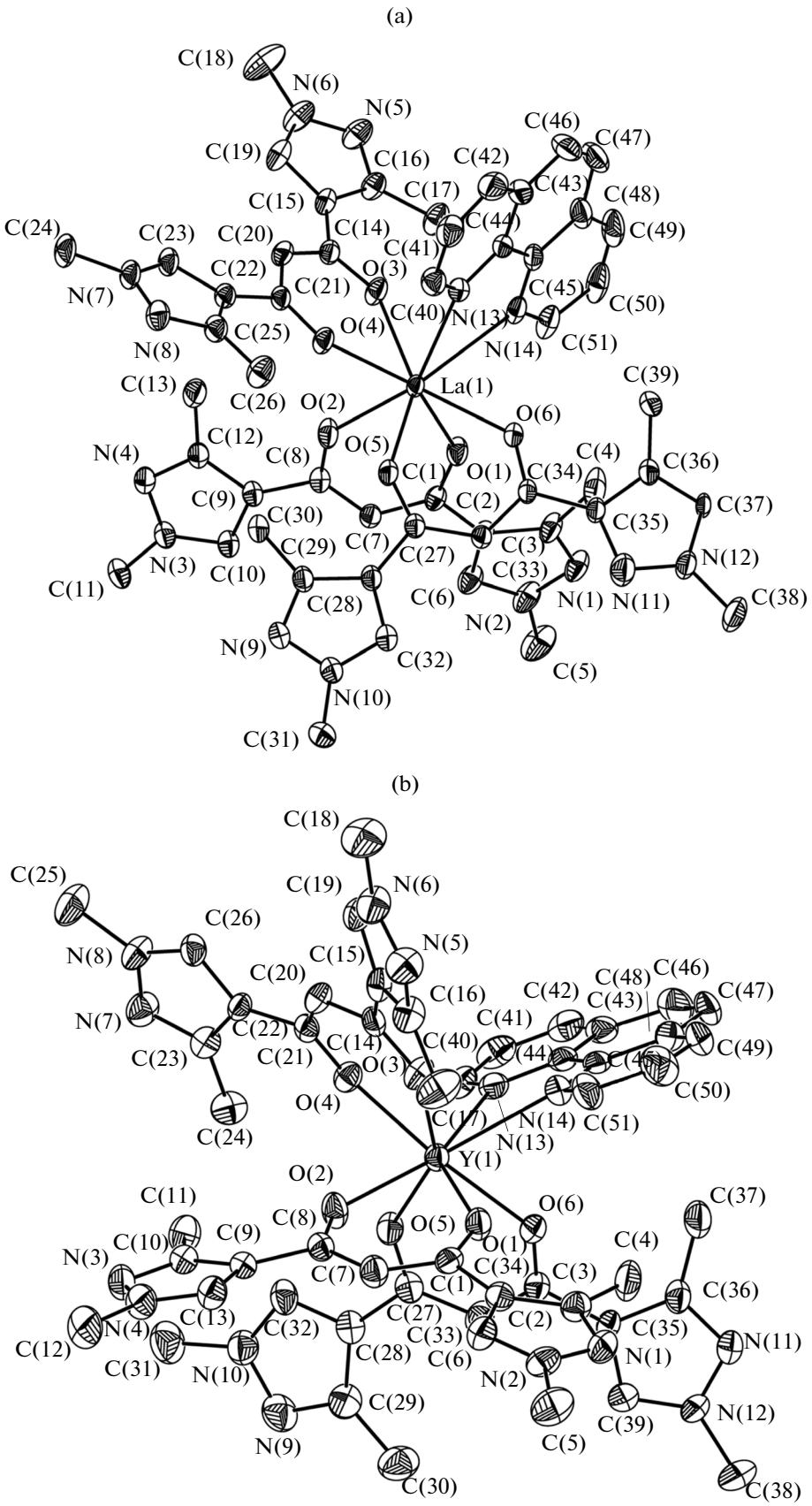


Fig. 2. General view of complexes (a) **I** and (b) **II** in structures **III** and **IV**, respectively, in the representation of atoms by thermal ellipsoids (with 50% probability). Hydrogen atoms and solvate water molecules are omitted.

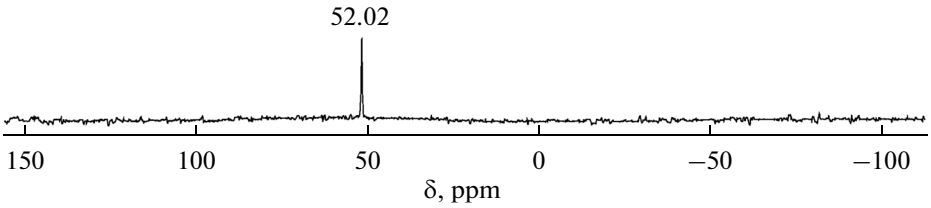


Fig. 3. ^{89}Y NMR spectrum of complex **II** in solution.

the NMR spectra completely correspond to the structures.

Let us consider in more detail the NMR data on the "exotic" nuclei ^{89}Y and ^{139}La. The content of the magnetic isotope ^{89}Y in natural yttrium is 100%. Its nuclear spin is 1/2, which theoretically makes it possible to detect rather easily the corresponding NMR spectra for this nucleus. In practice, resonance observation is difficult because of two factors: a very low resonance frequency at which the resonance is observed (4.899 MHz at 2.3488 T) and a low sensitivity of the nucleus itself (1.18×10^{-4} relatively to the sensitivity of ^{1}H). As a consequence, the relaxation times are prolonged [11]. The first factor results in the necessity to use broad-band sensors, and the second factor requires significant times of signal acquisition and the use of high concentrations of the sample.

Nevertheless, we obtained the spectrum of appropriate quality using a 0.2 M solution of the complex for an acquisition time of ~8 h (Fig. 3). The presence of only one signal indicates that the complex in solution is mononuclear.

Since published data on the ^{89}Y chemical shifts in complexes of similar structure are lacking, it is difficult to perform any comparison. However, the shift is close to that observed [12] for $Y(CH_3COO)_3$ (+37 ppm), which possibly indicates the absence of a significant influence of the ligand on the central atom. The shift of the resonance signal to a weaker field should be observed for strong electron-acceptor ligands, whereas electron-donor ligands should exhibit shifts to a higher field, which is not observed in practice.

A more complicated situation is observed for lanthanum [12]. The natural mixture contains two magnetic isotopes (0.09%) and ^{139}La (99.91%). However, the nuclear spin of ^{138}La (+5), the low content in the mixture, and a higher quadrupole moment make it lowly significant for NMR observation. The predominant isotope ^{139}La has a spin of 7/2 and a fairly high quadrupole moment (0.21×10^{-28} m^2) and is characterized by a low relative sensitivity (5.92×10^{-2} compared to the relative sensitivity of ^{1}H). The most part of NMR observations was carried out for this isotope. However, since the ^{139}La nucleus has a quadrupole moment, the resonance linewidth will depend strongly on the symmetry of the central atom environment. For a nonsymmetric environment, the linewidth can be so large because of quadrupole relaxation that it would be difficult to isolate it from noise. In particular, it was reported that the half-width of the line in the ^{139}La NMR spectrum observed for aqueous solutions of the lanthanum complexes with cyclic polyaminoacetic acids can attain 17 kHz and more [13].

Indeed, no ^{139}La NMR observations were reported for the lanthanum diketonate complexes. In our experiments, we also failed to detect an NMR signal for complex **I** even at very prolonged signal acquisition times (~12 h).

The experiments with the earlier described [14] complex $Et_3NH^+[La(bzac)_4]^-$ (Hbzac is benzoylacetone) with a higher symmetry than that of compound **I** were additionally carried out. However, we could not isolate an individual ^{139}La NMR spectrum in this case.

Thus, the method of ^{139}La NMR is not a convenient tool, most likely, for studying the structure of the La diketonate complexes in solutions but can find use for the study of the complex formation kinetics, because the starting aqua or halide complexes give distinct signals in the ^{139}La NMR spectra.

Mass spectrometry is a convenient method for establishing the composition of various organic and inorganic compounds, but its application in the area of studying complexes has some specific features.

Methods of laser desorption/ionization (LDI or MALDI if an additional substance (so-called matrix) providing better ionization is used) or the electrospray ionization (ESI) method are most appropriate for comparatively lowly volatile compounds with the average molecular weight about 1000–1500 Da.

The primary experiments on obtaining the mass spectra of compounds **I** and **II** were carried out using matrices. The following compounds were used as the matrices: 2,4-dihydroxybenzoic acid, 3-indolacrylic acid, 1,8,9-anthracenetriol (Dithranol), and 2-(4'-hydroxyphenylazo)benzoic acid. However, the quality of the spectra was unsatisfactory in all cases.

The best results were attained for the direct laser ionization of the complexes supported on the metallic targets. The obtained mass spectra are shown in Fig. 4.

The mass spectrum of compound **I** contains almost no signal from the molecular ion M^+ ($m/z = 1097$), and all major peaks are caused by fragmentation ions and products of ligand exchange. The heaviest ion with $m/z = 1574.4$ can be ascribed to cluster $[La_2(L)_5]^+$, the ion with $m/z = 939.9$ is attributed to

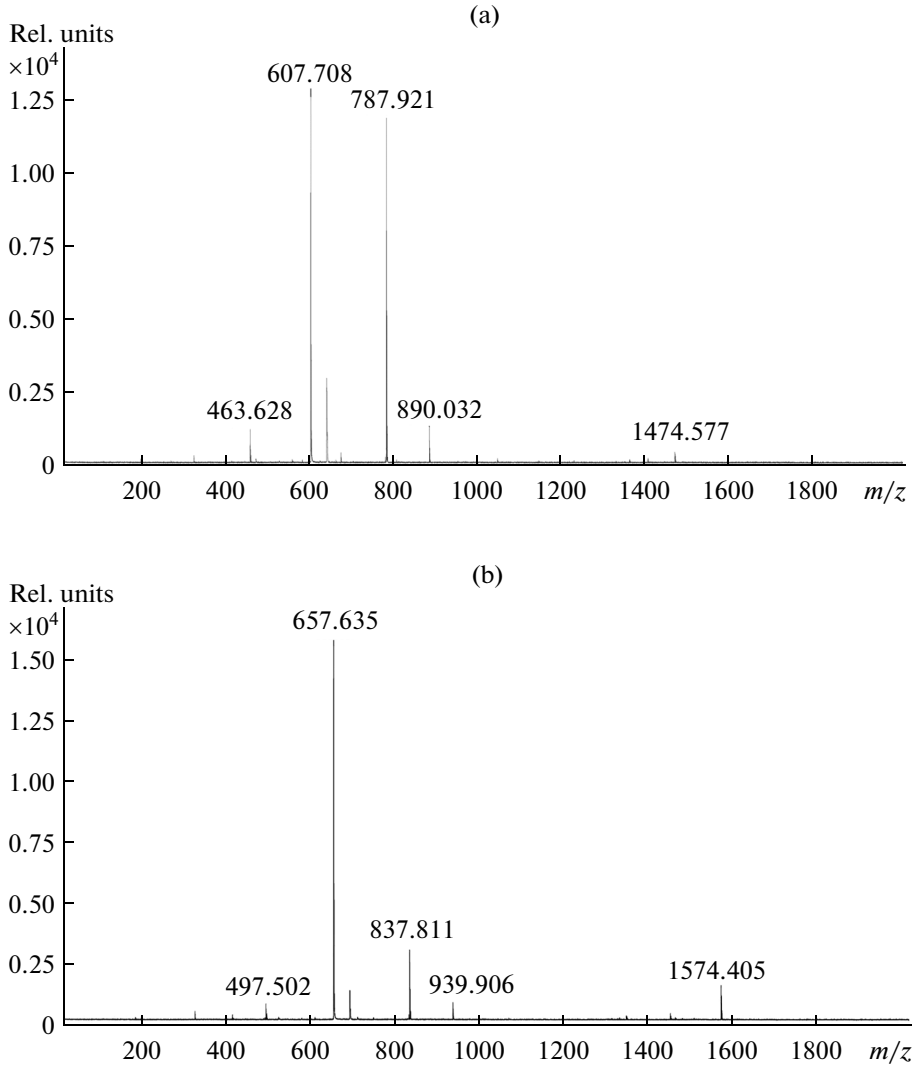


Fig. 4. LDI mass spectra of complexes (a) **I** and (b) **II**.

$[La(Phen)_3 + H]^+$, that with m/z = 837.8 can be ascribed to $[La(L)_2(Phen)]^+$ and, finally, the strongest signal with m/z = 657.6 corresponds to the $[La(L)_2]^+$ fragment.

Similar fragmentation is observed in the mass spectrum of complex **II**: the signal of the molecular ion (m/z = 1047) is absent, the signal with the maximum m/z = 1474.5 corresponds to cluster $[Y_2(L)_5]^+$, and two most intense signals with m/z = 787.9 and 607.7 correspond to the fragments $[Y(L)_2(Phen)]^+$ and $[YL_2]^+$.

Thus, the LDI method is fairly drastic, makes it possible to obtain molecular ions of compounds **I** and **II**, and also induces the complete fragmentation of the studied compounds.

The assignments of all signals are estimate, and a more precise assignment requires additional studies by secondary ion mass spectrometry (SIMS experiments).

Electrospray is a mild and flexible ionization method. Therefore, we also studied the possibility of using this method for obtaining the mass spectra of compounds **I** and **II**. Since their molecules include many nitrogen atoms, we could hope the possibility of performing mild ionization. Samples were injected into the ion source in a solvent flow containing a small amount of formic acid favoring the better formation of charged particles. The experimental results are presented in Fig. 5.

Signals of molecular ions for both compounds (signals with m/z = 1097 for compound **I** and with m/z = 1047 for compound **II**) were observed under these conditions. However, their intensity is low and does not exceed 5–6% of the full ionic current. In both cases, the formation of the major fragments can be described by the following scheme:

$$[M]^+ \rightarrow [Ln(L)_2(Phen)_2]^+ \rightarrow [Ln(L)_2(Phen)]^+.$$

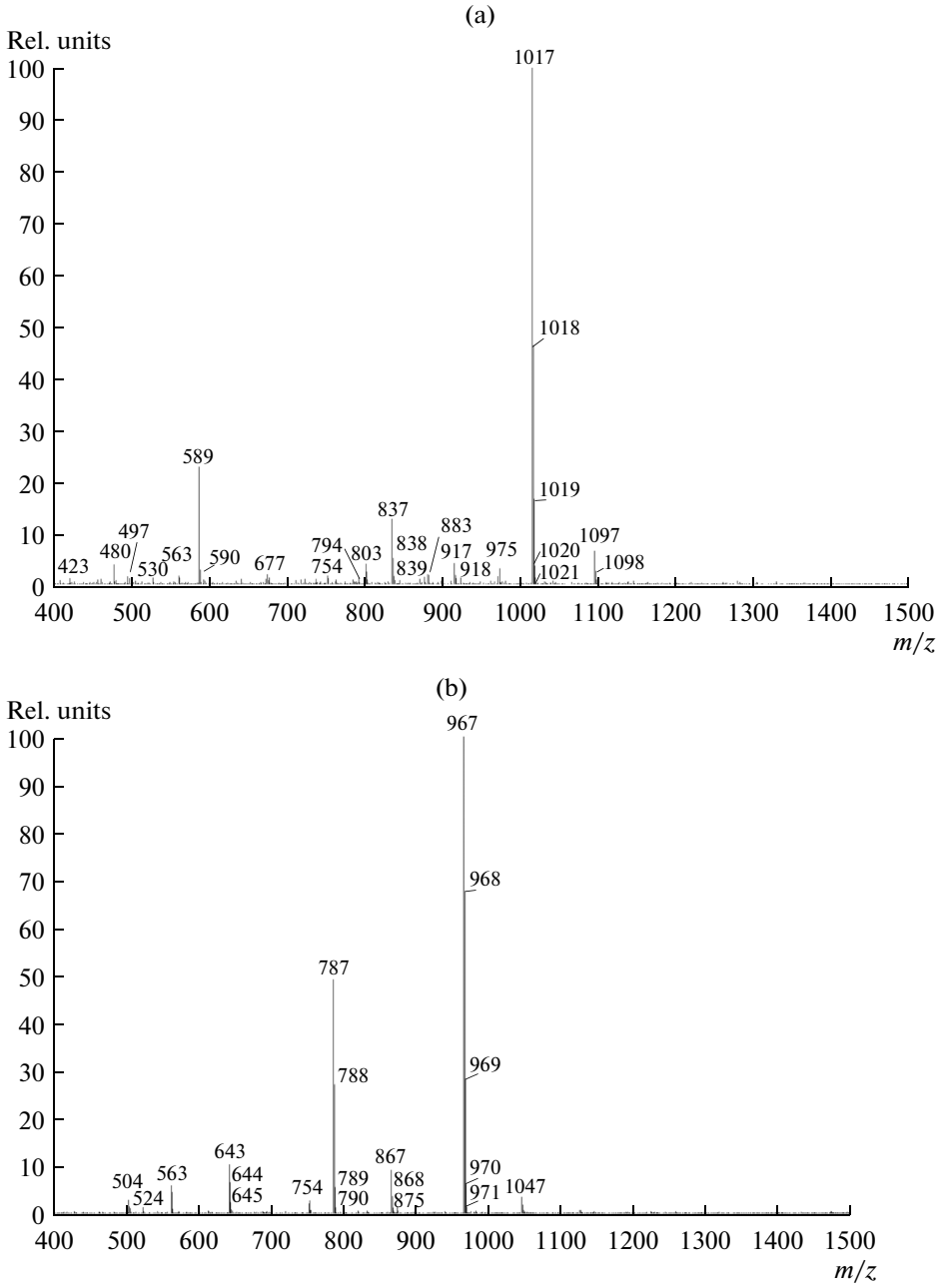


Fig. 5. ESI mass spectra of complexes (a) **I** and (b) **II**.

The intensity of both signals ($m/z = 967$ and 787) are comparable for the yttrium(III) complex and differ strongly for the lanthanum(III) derivative. In the latter case, the value of the signal corresponding to cluster $[La(L)_2(Phen)]^+$ ($m/z = 837$) is only 17% of the major signal from $[La(L)_2(Phen)_2]^+$ ($m/z = 1017$). The additional signals differed by 1–4 amu correspond, most likely, to the protonated species. No formation of heavy clusters is observed under the ESI conditions.

Generalizing the obtained results, one can assert that the ESI method is more appropriate, as a whole, for the establishment of the composition of the rare-earth metal complexes with pyrazole-containing diketonate ligands than the LDI method. Nevertheless, using both methods, one has to take into account the significant fragmentation of the complexes and processes of ligand exchange.

Probably, the driving force of this exchange is steric overloading of molecules of the complexes, which is additionally confirmed by the X-ray diffraction analysis data. The pyrazolylpropanedione-1,3 derivatives are very bulky ligands and, hence, their exchange for

smaller phenanthroline molecules can decrease, on the whole, the energy of the system, which is observed by an analysis of fragmentation.

ACKNOWLEDGMENTS

The authors are grateful to Dr. Yu.V. Nelyubina (Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow) for the X-ray diffraction analysis of compound **V**.

This work was supported in part by the Russian Foundation for Basic Research, project no. 12-03-00839-a.

REFERENCES

1. Binnemans, K., *Handbook of the Physics and Chemistry of Rare-Earths*, Gschneidner, K.A., Bunzli, J.G., and Pecharsky, V.K., Eds., Amsterdam: Elsevier, 2005, vol. 35, p. 107.
2. Jones, A.C. and Hitchman, M.L., *Chemical Vapor Deposition: Precursors, Processes, and Applications*, RCS Publishing, 2009, p. 380.
3. Ahmed, Z. and Iftikhar, K., *Inorg. Chim. Acta*, 2010, vol. 363, p. 2606.
4. Taidakov, I.V. and Krasnosel'skii, S.S., *Khim. Geterotsikl. Soedin.*, 2011, no. 6, p. 843.
5. Sheldrick, G.M., *SHELXTL PLUS (version 5.10). Structure Determination Software Suite,* Madison: Bruker AXS Inc., 1998.
6. Urbatsch, A., Gee, W.J., Deacon, G.B., and Batten, S.R., *Tetrahedron Lett.*, 2013, vol. 54, p. 2661.
7. Busev, A.I., Tiptsova, V.G., and Ivanov, V.M., *Rukovodstvo po analiticheskoi khimii redkikh elementov* (Guidelines on the Analytical Chemistry of Rare Elements), Moscow: Khimiya, 1978.
8. Minacheva, L.K., Rogachev, A.Y., Kuz'mina, N.P., et al., *Russ. J. Inorg. Chem.*, 2003, vol. 48, p. 1978.
9. Bi, Y., Guo, Y.-N., Zhao, L., et al., *Chem.-Eur. J.*, 2011, vol. 17, p. 12476.
10. Rogachev, A.Y., Sergienko, V.S., Kuz'mina, N.P., et al., *Russ. J. Inorg. Chem.*, 2004, vol. 49, p. 1549.
11. Fedotov, M.A., *Yadernyi magnitnyi rezonans v neorganicheskoi i koordinatsionnoi khimii* (Nuclear Magnetic Resonance in Inorganic and Coordination Chemistry), Moscow: Fizmatlit, 2009.
12. Rehder, D., *Early Transition Metals. Lanthanides and Actinides. Multinuclear NMR*, New York: Plenum, 1987, p. 479.
13. Bovens, E., Hoefnagel, M.A., Boers, E., et al., *Inorg. Chem.*, 1996, vol. 35, p. 7679.
14. Stilinović, V. and Kaitner, B., *J. Coord. Chem.*, 2009, vol. 62, p. 2698.

Translated by E. Yablonskaya