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Chemical Transformations of Lanthanide Nitrate Complexes: Synthesis and X-Ray Diffraction Analysis

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Abstract—The complexes $[Dy(NO_3)_3(Bipy)_2]$, $(HBipy)[Gd(NO_3)_4(Bipy)]$, and $[Fe^{III}(Me_2Bipy)_3][La(NO_3)_5(H_2O)]NO_3$ and the precursor of the latter, $[Fe^{II}Pc_2(Me_2Bipy)](CHCl_3) \cdot 1.5H_2O$ (where Bipy is the 2,2'-bipyridyl, Me_2Bipy is the 4,4'-dimethyl-2,2'-bipyridyl, and Pc^- is the pyridine-2-carboxylate anion), were obtained and characterized by X-ray diffraction analysis. Depending on the conditions of the synthesis and the reagents, the number of coordinated nitrate groups in the lanthanide complex increases from three to five: $[Dy(NO_3)_3(Bipy)_2]$, $[Gd(NO_3)_4(Bipy)]^-$, and $[La(NO_3)_5(H_2O)]^{2-}$.

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It is known that lanthanide complexes differ in both the oxidation state of the central atom and the architecture of the coordination entity of the metal [1–6]. They are characterized by a high coordination number of the metal atom (from 7 to 12) and various (often strongly deformed) coordination polyhedra. The elements of this group have an affinity for oxygen and nitrogen atoms [7], which accounts for the presence of water, acetylacetone, carboxylic acids, and nitriletriacetate complexones in their inner coordination spheres [8]. There are a variety of lanthanide complexes with nitrate anions exhibiting different dentate numbers and ways of coordination. Most often, the nitrate anion acts as a bidentate ligand [9]; however, monodentate [10], tridentate [11], and polydentate coordination [12] also occurs.

To study the coordination of the nitrate group to lanthanides, we obtained lanthanide complexes from lanthanide nitrates and different ligands. The resulting complexes $[Fe^{II}Pc_2(Me_2Bipy)](CHCl_3) \cdot 1.5H_2O$ (**II**), $[Fe^{III}(Me_2Bipy)_3][La(NO_3)_5(H_2O)]NO_3$ (**III**), $(HBipy)[Gd(NO_3)_4Bipy]$ (**IV**), and $[Dy(NO_3)_3(Bipy)_2]$ (**V**), where Bipy is the 2,2'-bipyridyl, Me_2Bipy is the 4,4'-dimethyl-2,2'-bipyridyl, and Pc^- is the pyridine-2-carboxylate anion, were examined by X-ray diffraction analysis.

EXPERIMENTAL

The aqua complex of iron(II) with picolinic acid, $[Fe^{II}Pc_2(H_2O)_2] \cdot 2H_2O$ (**I**), was prepared as described in [13].

Synthesis of complex II. A solution of Me_2Bipy (0.170 g, 1 mmol) in methanol (15 ml) was added dropwise to a solution of complex **I** (0.416 g, 1 mmol) in methanol (15 ml). The resulting dark red solution was stirred with a small amount of Na_2SO_4 for 20 min and then filtered. After several days, a dark red crystalline precipitate formed. The precipitate was recrystallized from chloroform–acetone–hexane (1 : 1 : 1). Crystals of complex **II** were suitable for X-ray diffraction analysis. The yield was 75%.

For $C_{25}H_{24}Cl_3FeN_4O_{5.5}$			
anal. calcd, %:	C, 47.61;	H, 3.84;	N, 8.88.
Found, %:	C, 47.16;	H, 3.80;	N, 8.85.

Synthesis of complex III. Complex **II** (0.609 g, 1 mmol) was dissolved under constant stirring in acetone (15 ml). Then $La(NO_3)_3 \cdot 6H_2O$ (0.618 g, 1 mmol) in acetone (15 ml) was added. The resulting red solution was vigorously stirred at room temperature for 30 min. Red crystals of complex **III** formed in two days. The yield was 70%.

For $C_{36}H_{38}FeLaN_{12}O_{19}$			
anal. calcd, %:	C, 38.01;	H, 3.37;	N, 14.78.
Found, %:	C, 38.70;	H, 3.28;	N, 14.73.

Synthesis of complex IV. Benzoic acid (0.37 g, 3 mmol) and Bipy (0.31 g, 2 mmol) were added under constant stirring to a solution of $Gd(NO_3)_3 \cdot 6H_2O$ (0.44 g, 1 mmol) in ethanol (10 ml). The resulting solution was heated to 60°C and allowed to cool. Colorless

Table 1. Crystallographic parameters and a summary of data collection and refinement for complexes **II–V**

Parameter	Value			
	II	**III**	**IV**	**V**
FW	630.68	1137.54	718.67	660.9
Temperature, K	100	100	180	200
Crystal system	Triclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	*Pccn*	*C*2/*Ò*	$P2_1/n$
a, Å	12.1420(3)	12.4823(4)	14.609(5)	9.0705(18)
b, Å	14.6823(4)	16.6230(7)	10.096(5)	15.025(3)
c, Å	16.1915(4)	22.0630(9)	16.766(5)	16.697(3)
α, deg	87.453(2)	90	90	90
β, deg	81.224(1)	90	96.864(5)	90.08(3)
γ, deg	76.539(2)	90	90	90
V, Å^3	2774.22(12)	4577.9(3)	2455.1(16)	2275.5(8)
Z; ρ_{calcd}, g/cm^3	4, 1.510	4, 1.649	4, 1.944	4, 1.929
μ_{Mo}, mm^{-1}	0.877	1.326	2.784	3.352
θ scan range, deg	2.30–28.34	2.22–26.00	3.35–30.51	2.9–26.01
Number of measured reflections	72185	266228	25715	17598
Number of independent reflections ($I > 2\sigma(I)$)	13705 (R_{int} = 0.0645)	4505 (R_{int} = 0.0369)	3606 (R_{int} = 0.0268)	4151 (R_{int} = 0.0732)
Number of parameters refined	714	320	186	334
GOOF on F^2	1.017	1.087	1.091	1.043
R factor ($I > 2\sigma(I)$)	R_1 = 0.0524	R_1 = 0.0325	R_1 = 0.0232	R_1 = 0.0277
	wR_2 = 0.1275	wR_2 = 0.0807	wR_2 = 0.0548	wR_2 = 0.0739
$\Delta\rho_{max}$ and $\Delta\rho_{min}$, *e* Å^{-3}	1.848, –1.727	1.277, –1.213	0.979, –0.705	0.709, –1.203

crystals of complex **IV** that formed were suitable for X-ray diffraction analysis. The yield was 45%.

For $C_{20}H_{17}N_8GdO_{12}$
anal. calcd, %: C, 33.43; H, 2.38; N, 15.59.
Found, %: C, 33.62; H, 2.29; N, 15.53.

Synthesis of complex V. Dysprosium trinitrate hexahydrate (0.45 g, 1 mmol) was dissolved in a 1 : 3 mixture of methanol and acetonitrile. 2,2'-Bipyridyl (0.39 g, 2.5 mmol) was added under constant stirring. The resulting solution was left for crystallization. Colorless crystals formed in a day. The yield was 40%.

For $C_{20}H_{16}DyN_7O_9$
anal. calcd, %: C, 36.35; H, 2.44; N, 14.84.
Found, %: C, 36.20; H, 2.38; N 14.83.

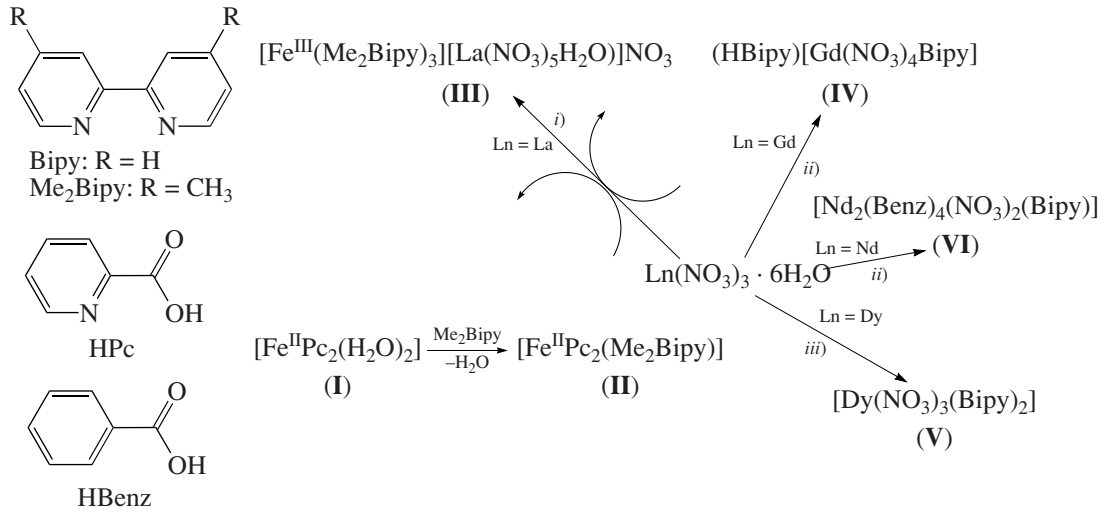
X-Ray diffraction analysis. Crystallographic parameters and a summary of data collection for complexes **II–V** are given in Table 1. Reflection intensities were measured on a Nonius Kappa CCD diffractometer (MoK_α radiation). Structures **II–IV** were solved by direct methods and refined in the anisotropic approximation for non-hydrogen atoms (SHELX-97 [14]). The O(3*w*) molecule is disordered in structure **II**. Part of

NO_3 molecules and the O(1*w*) molecule are disordered in structure **III**. In the above water molecules, the hydrogen atoms cannot be located. The rest of the H atoms were objectively located from the difference electron-density map and refined in the rigid-body model. Atomic coordinates and other parameters for complexes **II**–**V** have been deposited with the Cambridge Crystallographic Data Collection (nos. 690 366–690 369).

Selected bond lengths in structures **II**–**V** are given in Table 2.

RESULTS AND DISCUSSION

Complexes **II**–**V** were obtained as shown below:



(*i*) acetone; (*ii*) HBenz + Bipy; ethanol; (*iii*) Bipy; methanol–acetonitrile (1 : 3)

Table 2. Selected bond lengths in structures **II**–**V**

Bond	*d*, Å		
	II		
	Complex A	Complex B	
Fe(1)–O(1)	2.072(2)	2.063(2)	
Fe(1)–O(3)	2.050(2)	2.059(2)	
Fe(1)–N(1)	2.173(3)	2.159(3)	
Fe(1)–N(2)	2.171(3)	2.174(3)	
Fe(1)–N(3)	2.180(3)	2.190(3)	
Fe(1)–N(4)	2.210(3)	2.185(3)	
Bond	*d*, Å	Bond	*d*, Å
III		Gd(1)–O(12)	2.509(2)
Fe(1)–N(4)	1.967(2)	Gd(1)–O(21)	2.464(2)
Fe(1)–N(5)	1.968(2)	Gd(1)–O(22)	2.522(2)
Fe(1)–N(6)	1.959(2)	**V**	
La(1)–O(1)	2.651(2)	Dy(1)–N(1)	2.525(2)
La(1)–O(3)	2.590(2)	Dy(1)–N(2)	2.516(2)
La(1)–O(4)	2.596(2)	Dy(1)–N(3)	2.511(2)
La(1)–O(5)	2.630(2)	Dy(1)–N(4)	2.523(2)
La(1)–O(1*w*)	2.634(5)	Dy(1)–O(11)	2.463(2)
La(1)–O(1A)	2.666(4)	Dy(1)–O(12)	2.466(2)
La(1)–O(2A)	2.582(5)	Dy(1)–O(21)	2.467(2)
IV		Dy(1)–O(22)	2.555(2)
Gd(1)–N(1)	2.539(2)	Dy(1)–O(32)	2.471(2)
Gd(1)–O(11)	2.476(2)	Dy(1)–O(31)	2.554(2)

Complex **II** was obtained from complex **I** [13] through replacement of the coordinated water molecules by bidentate Me_2Bipy. The reaction was carried out in methanol in air. When recrystallized from chloroform, the crystals of complex **II** did not oxidize in air.

A reaction of complex **II** with lanthanum nitrate in acetone gives the ionic complex **III**. In the presence of a lanthanide ion in solution, the ligands around iron are redistributed and Fe(II) oxidizes into Fe(III). The oxidation is proved by X-ray diffraction analysis of the bond lengths in the coordination polyhedron of iron [15–17] and confirmed by the charge compensation condition for the complex containing two deprotonated molecules of picolinic acid.

Gadolinium complex **IV** (scheme) was obtained as described for neodymium complex **VI** in [18]. Addition of benzoic acid and 2,2'-bipyridyl (ligands with different electronic properties) to gadolinium nitrate gives a heteroleptic complex in which the Gd atom coordinates four bidentate nitrate anions and a Bipy molecule. Gadolinium complex **IV** is less soluble than a gadolinium analog of dimeric complex **VI** and precipitates immediately upon cooling. The aforesaid dimer and other minor reaction products are retained in solution.

A reaction of dysprosium nitrate with Bipy in methanol–acetonitrile gives the complex $[Dy(NO_3)_3(Bipy)_2]$ (**V**) (scheme).

In crystal structure **II**, the neutral complexes $[Fe^{II}Pc_2Me_2Bipy]$ occupy two independent positions A

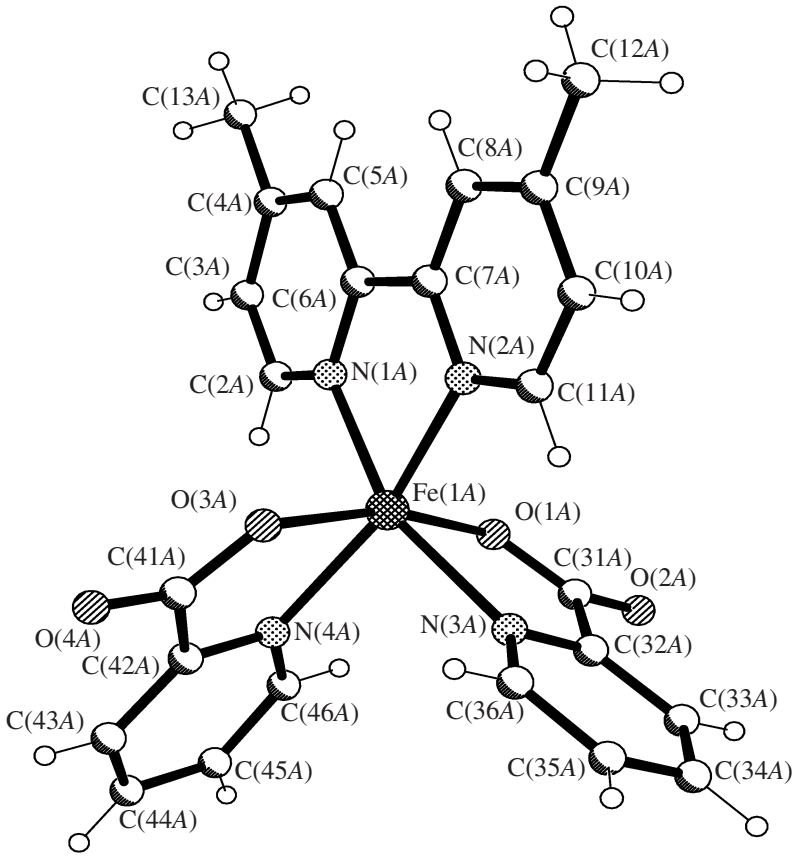


Fig. 1. Structure of $[Fe^{II}Pc_2(Me_2Bipy)]$ (A) in complex **II**.

and B in the unit cell (Fig. 1). The octahedral coordination of each Fe atom is made up of the N(1) and N(2) atoms of Me_2Bipy and the N(3), O(1), N(4), and O(3) atoms of two residues of picolinic acid. The latter are arranged in such a manner that the angle between their aromatic rings is 94.2° in molecule A and 84.7° in molecule B. The O atoms of the carboxyl groups are *trans* to each other. The geometrical parameters of the coordination polyhedra A and B are given in Table 2. In the ligands, the dihedral angles between the carboxyl groups and the molecular framework are 2.4° and 4.8° in A and 2.5° and 4.3° in B.

Independent complexes A and B are associated into dimers via π–π-interactions between the coordinated Me_2Bipy molecules. The distances between the centroids of the rings are 3.641 and 3.649 Å (Fig. 2).

The outer-sphere water and chloroform molecules unite the dimers into a three-dimensional framework through a system of O–H···O, C–H···O, and C–H···Cl hydrogen bonds. The hydrogen bonds O(2*w*)–H···O_{carb} and O(1*w*)–H···O_{carb} carb are used to form ribbons along axis *x* of the unit cell. The disordered water molecule O(3*w*) (O(3*w*A) and O(3*w*B)) links adjacent ribbons to form a layer parallel to the plane (*xz*) (Fig. 3).

Structure **III** is ionic. The Fe atom in the cation $[Fe^{III}(Me_2Bipy)_3]^{3+}$ has an octahedral coordination made up of six N atoms of three Me_2Bipy molecules (average Fe–N 1.965 Å). In the anion $[La(NO_3)_5H_2O]^{2-}$, the coordination number of lanthanum is 11 because of its coordination to ten O atoms of five bidentate NO_3^- anions and the O(1*w*) atom of the water molecule (La–O 2.581(6)–2.650(2) Å). The La and Fe atoms occupy special positions on axis 2 passing through the midpoint of the C(14)–C(14)* bond of one of two independent Me_2Bipy molecules. However, the coordination polyhedron of the La atom shows local breaking of the crystal symmetry because the water molecule and the NO_3^- group are disordered over two equiprobable positions. The outer-sphere NO_3^- anion is also disordered.

The cations and anions are linked by the C–H···O contacts (H···O ~2.4 Å; average C···O 2.27 Å) to form a layer with alternating series of cations and anions along axis *z*. A three-dimensional framework is built similarly, with a series of anions above a series of cations.

Structure **IV** is also ionic. The crystal consists of the cations $(HBipy)^+$ and the complex anions

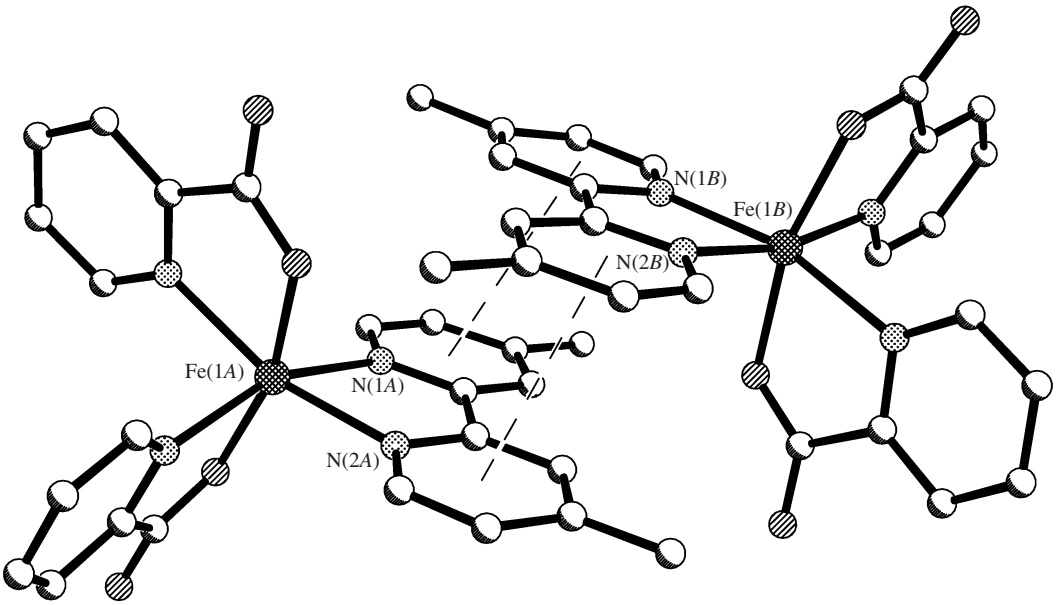


Fig. 2. π–π-Interactions between the independent complexes [$Fe^{II}Pc_2(Me_2Bipy)$] (A and B) in structure **II**.

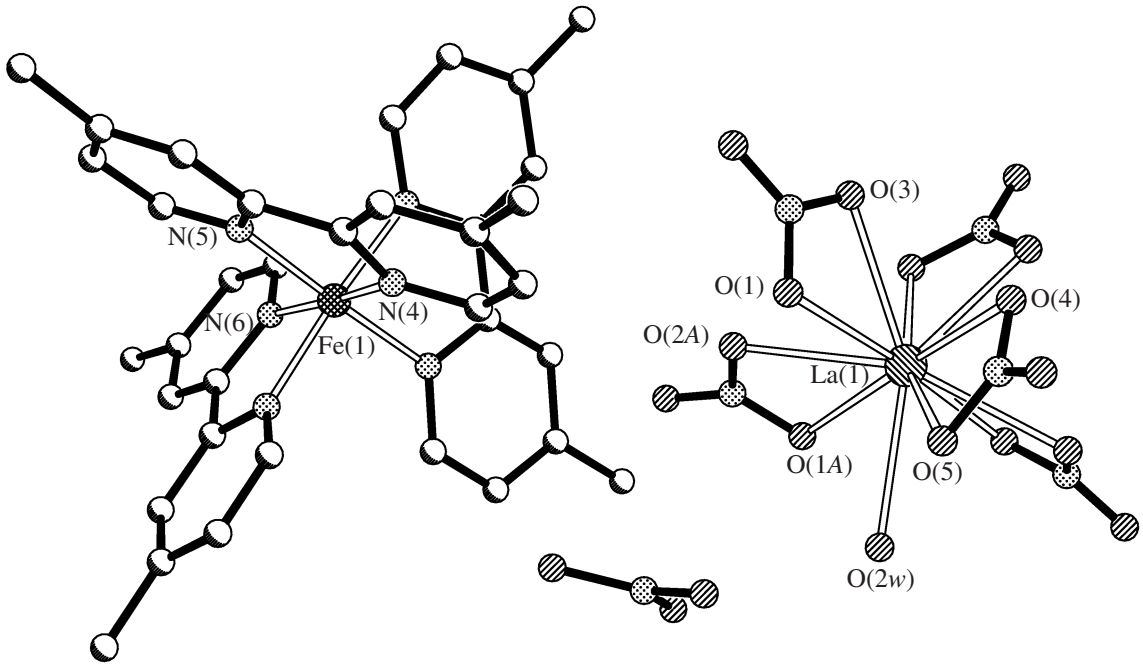


Fig. 3. Fragment of structure **III** with numbering of the independent atoms (disordered NO_3^- anions are indicated for only one of the possible positions).

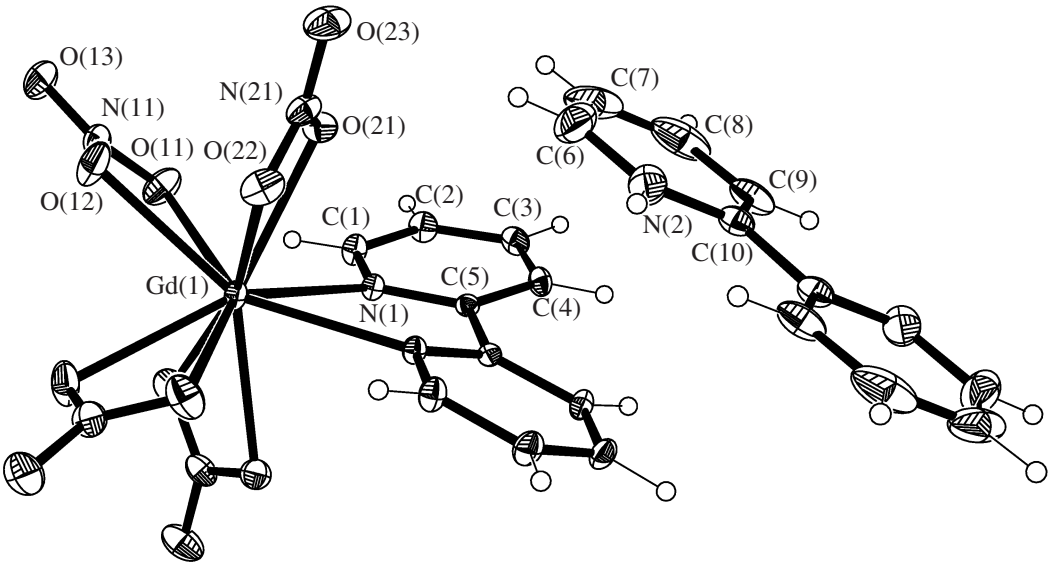


Fig. 4. Fragment of structure **IV** with numbering of the independent atoms.

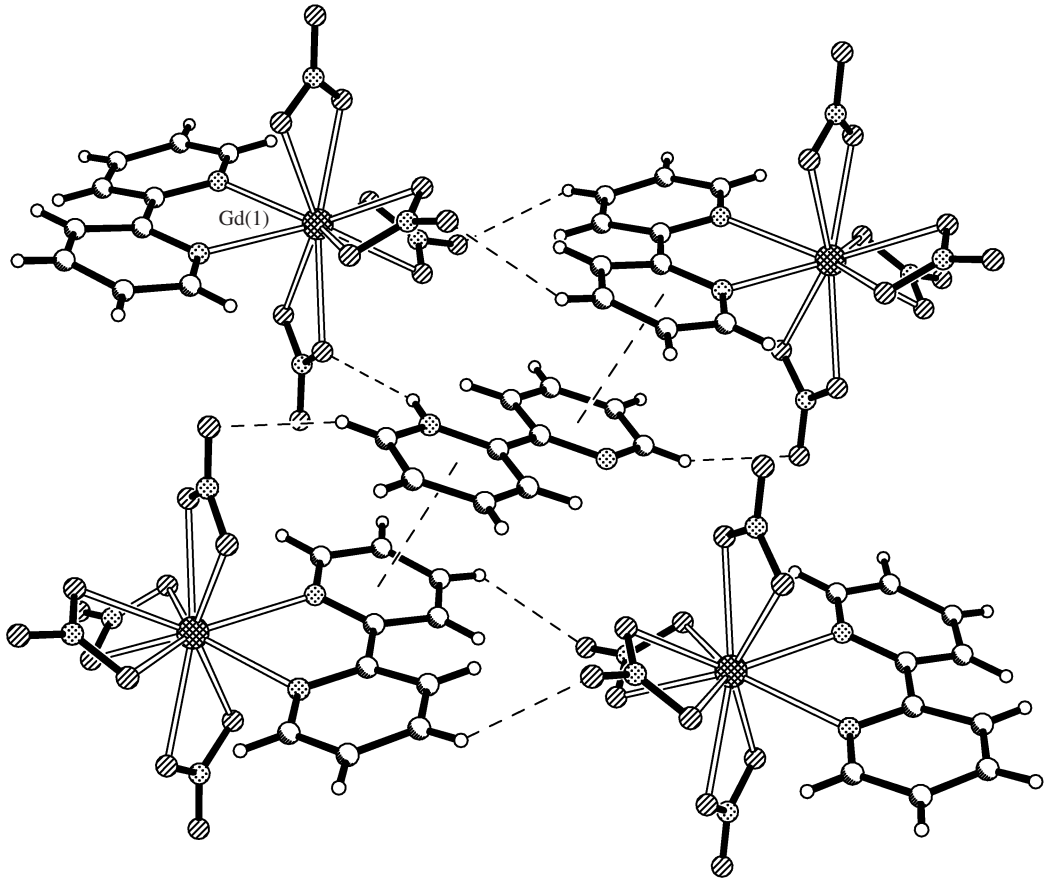


Fig. 5. π–π-Interactions and hydrogen bonds in crystal structure **IV**.

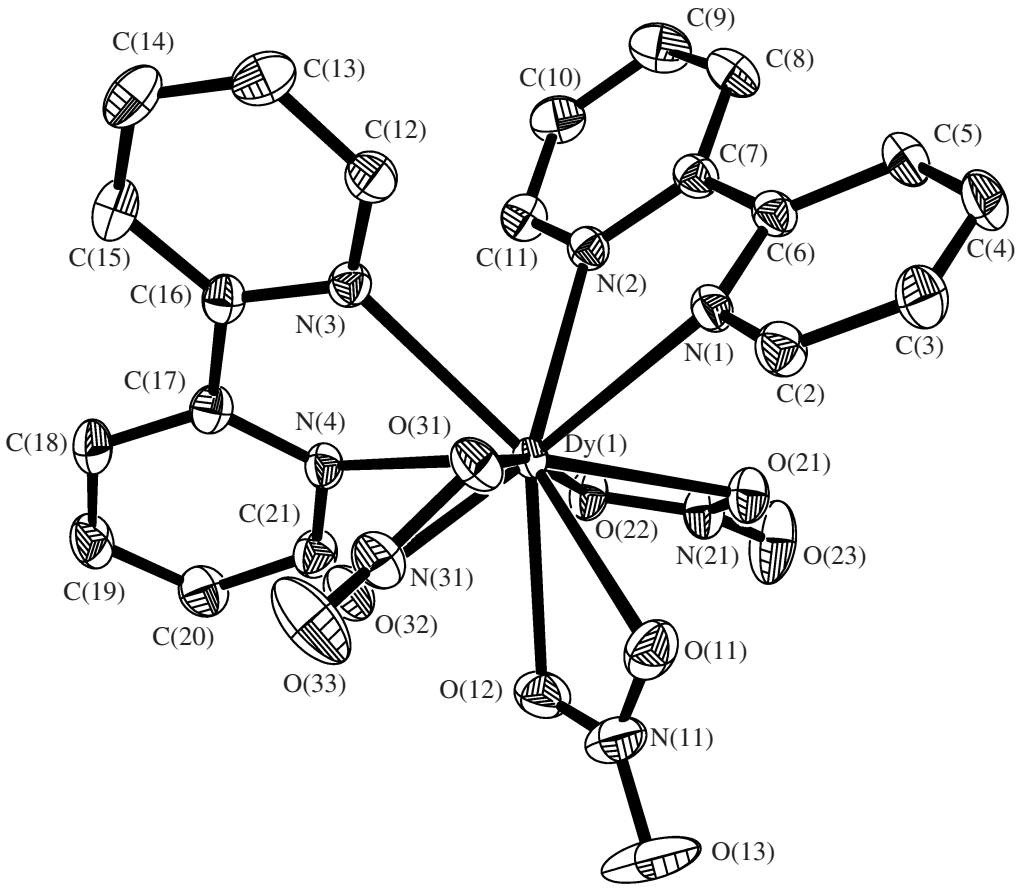


Fig. 6. Structure **V**.

$[Gd(NO_3)_4Bipy]^-$ (Fig. 4). The cation is centrosymmetric, with a center of symmetry on the midpoint of the C–C bond linking the pyridine moieties of Bipy. This leads to a randomly equiprobable distribution of the H atom over two positions at the N atoms. The cation $HBipy^+$ has a transoid configuration.

In the anion, the Gd atom (on axis 2) is coordinated by eight O atoms of four bidentate NO_3^- anions (average Gd–O 2.493 Å) and two N atoms of bipyridyl (Gd–N 2.539(2) Å). The coordinated neutral Bipy molecule in the cisoid configuration is substantially nonplanar. The angle between the planes of its pyridine rings is 19.8°.

The cations and anions are linked by π–π-interactions between the pyridine rings in such a way that each anion interacts with two cations (distance between the centroids is 3.647 Å) (Fig. 5). Axis 2_1 forms a zigzag chain along axis *z*. The weak hydrogen bond N–H···O (N···O 3.125, H···O 2.294 Å, angle NHO 148°), along with weak C–H···O contacts between the cations and between the cations and anions (H···O > 2.4 Å), gives rise to a three-dimensional framework.

Molecular structure **V** is built from the neutral mononuclear complexes $[Dy(NO_3)_3(Bipy)_2]$ (Fig. 6). The Dy atom (C.N. 10) is coordinated by six O atoms of three bidentate NO_3^- anions (average Dy–O 2.496 Å) and four N atoms of two bipyridyl molecules (average Dy–N 2.528 Å). The dihedral angles between the planes of the pyridine rings of two coordinated Bipy molecules are virtually equal (11.9° and 12.0°).

In the crystal, the neutral complexes $[Dy(NO_3)_3(Bipy)_2]$ are united through the contacts C–H···O (C(8)–H···O(32)(32) and C(15)–H···O(21)) into layers parallel to the plane *ac* (Fig. 7). The latter in turn are united through the hydrogen bonds C(3)–H···O(23) and C(20)–H···O(33) into a three-dimensional framework.

According to X-ray diffraction data, the resulting lanthanide complexes contain different numbers of nitrate groups and Bipy molecules in the inner coordination sphere, depending on the conditions of the synthesis and the reagents: $[Dy(NO_3)_3(Bipy)_2]$, $[Gd(NO_3)_4(Bipy)]^-$, and $[La(NO_3)_5(H_2O)]^{2-}$. The performed chemical transformations suggest the high

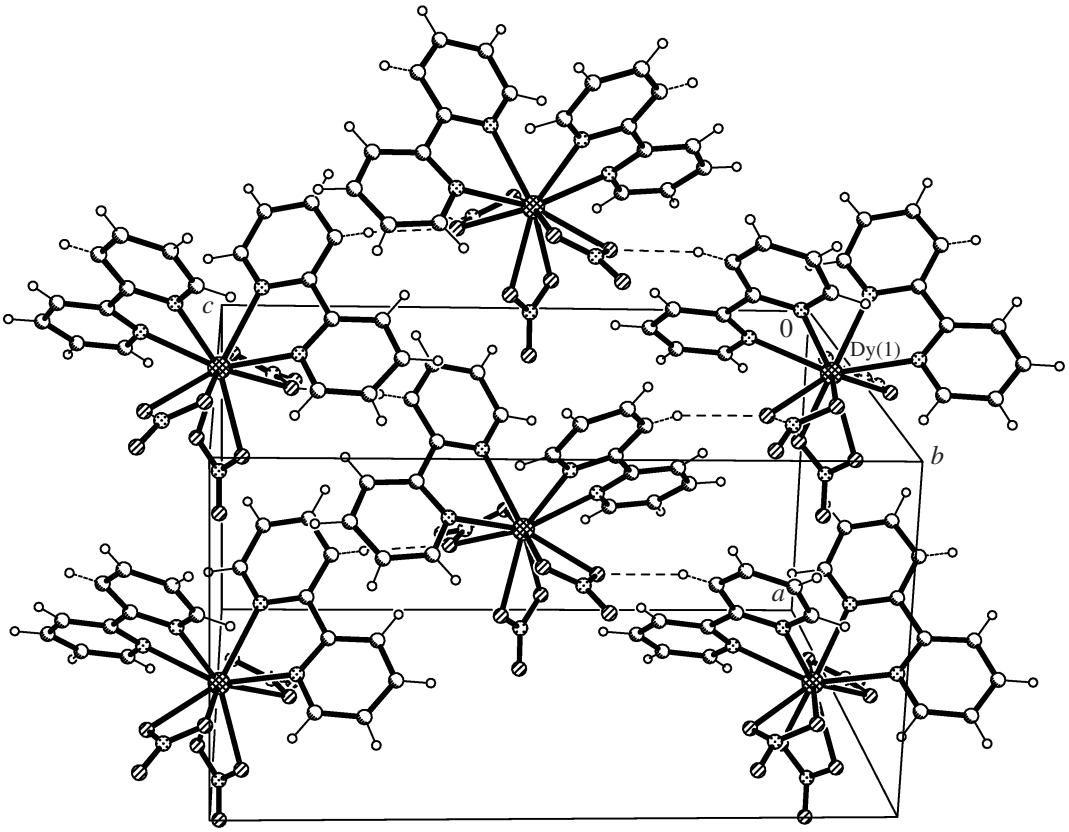


Fig. 7. Hydrogen-bonded (by C–H···O) layer parallel to the plane (*ac*) in crystal structure **V**.

lability of the lanthanide ions in solution, which allows ligand variation in the resulting complexes.

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