

COORDINATION COMPOUNDS OF LANTHANIDES WITH HYDRAZONES OF 3-METHYL-1-PHENYL- 4-FORMYLPYRAZOLE-5-ONE AND 1,3,5-BENZENETRICARBOXYLIC ACID

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We describe the results of the X-ray diffraction study of a dysprosium(III) complex with trihydrazone of 3-methyl-1-phenyl-4-formylpyrazole-5-one and 1,3,5-benzenetricarboxylic acid, as well as a heteroligand gadolinium(III) complex with tri- and dihydrazone of 3-methyl-1-phenyl-4-formylpyrazole-5-one and 1,3,5-benzenetricarboxylic acid (H_3L and H_3L^1 respectively). It is determined that the homoligand complex of dysprosium has a M_4L_4 composition and a pseudotetrahedral structure in which metal ions occupy vertices of a trigonal pyramid and trinucleating ligands are located on its sides. The heteroligand gadolinium complex $Gd_3(L)(HL^1)_3$ has a trigonal structure. Metal ions at the triangle vertices are linked by a trinucleating ligand located above the triangle plane, and three binucleating ligands link the central atoms in pairs. The geometry of dysprosium and gadolinium coordination polyhedra correspond to a three-capped trigonal prism.

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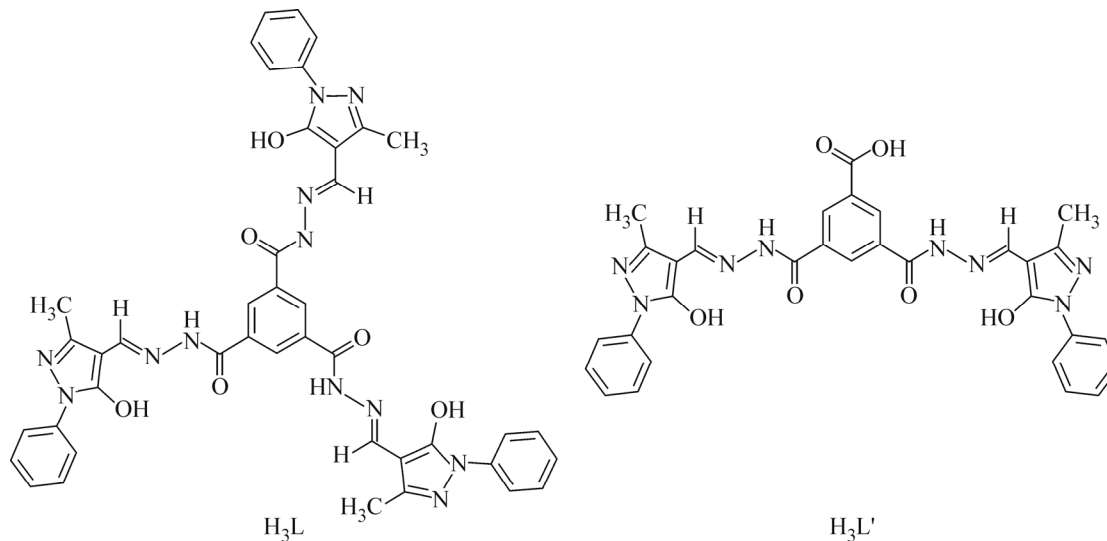
INTRODUCTION

One of the interesting objects for the study in modern coordination chemistry are metal-ligand systems based on spacer-armed polytopic organic ligands. Due to their ability to self-assembling these systems can be considered as model objects to study self-assembly processes in more complicated structures, first of all, biomolecules [1]. The use of ditopic ligands with a flexible spacer, such as hydrazones of saturated dicarboxylic acids (H_2L), is known to lead to the formation of binuclear molecular helicates of the Ln_2L_3 composition [2-4]. The use of acylhydrazones of 1,3,5-benzenetricarboxylic acid (H_3L) as ligands results in the formation of symmetric tetranuclear complexes of the M_4L_4 composition [5] or pseudooctahedral complex $[Ln_6(H_3L)_4(NO_3)_{12}]^{6+}$ cations [6, 7]. Due to their framework structure, the complexes form nanocells and nanochannels. Their sizes can be regulated by ligand modification and proper selection of a metal-complex

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former, thus achieving the selectivity within host-guest relations. The presence of ligands of high-polar amide groups in the structure able to form a system of hydrogen bonds with polar molecules plays an important role. In this case, UV absorption and luminescence spectra are extremely sensitive to any changes in the electron density distribution accompanying this binding. Due to these peculiar features, framework metal clusters can be used as good optical chemosensors [6] and also as efficient heterogenous catalysts for organic reactions [7], therefore, they can be used in analytical practice and organic synthesis.

The present article describes the results of the structure study of dysprosium(III) coordination compounds with trihydrazone of 1,3,5-benzenetricarboxylic acid, as well as the heteroligand gadolinium(III) complex with trihydrazone and dihydrazone of 1,3,5-benzenetricarboxylic acid (H_3L and H_3L^1 respectively). 3-Methyl-1-phenyl-4-formylpyrazole-5-one was used as a carbonyl component of acylhydrazones.



EXPERIMENTAL

The dysprosium complex of the composition $Dy_4L_4 \cdot 9C_3H_7NO \cdot 18H_2O$ (**1**) was obtained according to the following procedure. 3-Methyl-1-phenyl-4-formylpyrazole-5-one (0.77 g, 3.81 mmol) was added to a suspension of 0.32 g (1.27 mmol) of trihydrazone of 1,3,5-benzenetricarboxylic acid in 15 ml of DMF heated to 65–70 °C and the mixture was magnetically stirred for 30 min. Then a solution of 1.27 mmol of dysprosium chloride in 15 ml of ethanol, 0.8 ml of pyridine were added and the mixture was stirred until the dissolution of the precipitate. The reaction mixture was cooled to room temperature and left for several days. The precipitated crystals were filtered off, washed with ethanol, and dried in air. Yellow crystals (0.40 g) were obtained; the yield was 40% of the theoretically possible amount. Found, %: C 48.11, H 4.55, N 16.67. For $C_{191}H_{231}N_{57}O_{51}Dy_4$ calculated, %: C 47.88, H 4.86, N 16.66. IR spectrum (ν_{max} , cm^{-1}): 3396, 3204, 3060, 2956, 2925, 2858, 1724, 1620, 1584, 1525, 1499, 1456, 1438, 1352, 1274, 1199, 1179, 1101, 1044, 1028, 1002, 961, 900, 815, 758, 699, 625, 571, 512, 426.

Single crystals of the gadolinium complex (0.32 g) were obtained similarly using a mixture of trihydrazone of trimesic acid and dihydrazone of 5-methoxycarbonyl-1,3-benzenedicarboxylic acid (1:2 molar ratio). Yellow crystals of the composition $Gd_3(L)(HL^1)_3 \cdot 6C_3H_7NO \cdot 5.5H_2O$ (**2**) were isolated. Found, %: C 50.84, H 4.74, N 15.27. Calculated for $C_{159}H_{158}N_{42}O_{35.5}Gd_3$, %: C 51.66, H 4.31, N 15.91. IR spectrum (ν_{max} , cm^{-1}): 3391, 3226, 3064, 2930, 2861, 1724, 1620, 1587, 1523, 1501, 1463, 1440, 1388, 1350, 1277, 1203, 1180, 1101, 1044, 1028, 1004, 964, 902, 812, 760, 696, 665, 628, 571, 509, 495, 429.

Elemental carbon, hydrogen, and nitrogen analysis was carried out on an automated Euro EA3000 analyzer. IR spectra of the samples pressed with KBr were studied on an IR FSM 2202 spectrometer with the Fourier transform function in the range 4000-400 cm^{-1} .

The single crystal X-ray diffraction study of complex **1** was carried out on an Agilent Technologies SuperNova Dual diffractometer equipped with a CCD flat panel detector at 100 K using monochromatic $\text{CuK}\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$) by the standard procedure [8]. The unit cell parameters were refined by the least-square method. The absorption correction was applied empirically using spherical harmonics implemented in the SCALE ABSPACK scaling algorithm in the CrystalPro software. The structure was solved by direct methods and refined in the full-matrix anisotropic approximation for all non-hydrogen atoms using the SHELX software [9] of the OLEX2 package.

The single crystal X-ray diffraction study of complex **2** was carried out at 150 K on a Bruker Smart APEX II diffractometer equipped with a CCD detector and a monochromatic radiation source ($\text{MoK}\alpha$, $\lambda = 0.71073 \text{ \AA}$, graphite monochromator) by the standard procedure. The structure was solved by direct methods and refined in the full-matrix anisotropic approximation for all non-hydrogen atoms, with taking into account the disordering of a benzenecarboxylic acid moiety over two positions with occupancies of 0.472(6) and 0.528(6). DFIX and FLAT restraints were applied for the structure refinement of C_6 cyclic moieties; DFIX restraints were applied for the carboxylate group. The structure refinement was carried out using the RIGU and ISOR functions due to high values of the atomic displacement parameters of some N and C atoms. The calculations were carried out using the SHELXL2014 software package [9]. In both cases, hydrogen atoms were generated geometrically and refined by the rigid body model. Due to the disordering of a significant part of solvate water molecules, the X-ray diffraction data were corrected using the Squeeze procedure of the PLATON program [10].

The CIF-files containing the complete information on the structures studied have been deposited with the Cambridge Crystallographic Data Centre (CCDC Nos. 1825024 and 1832979), where they can be easily obtained by request via the following web-site: www.ccdc.cam.ac.uk/data_request/cif. The main crystallographic data and parameters of the structure refinement of complexes are summarized in Table 1.

TABLE 1. Crystallographic Data and Parameters of the Crystal Structure Refinement of Complexes **1** and **2**

Parameter	1	2
Crystal system	Cubic	Hexagonal
Space group	$I\bar{4}3d$	$R\bar{3}$
a , \AA	45.2327(5)	30.8057(9)
b , \AA		30.8057(9)
c , \AA		39.117(2)
Cell volume, \AA^3	92546(3)	32148(3)
Z	16	6
ρ_{calc} , g/cm^3	1.170	1.123
μ , mm^{-1}	7.328	0.984
$F(000)$	32832	11076
Crystal size, mm	0.22×0.22×0.22	0.08×0.06×0.04
θ , deg.	1.56-33.84	1.32-26.73
Completeness to $2\theta_{\text{max}}$	0.98	0.99
Total / independent reflections	23930 / 6156	63658 / 6528
Reflections / restraints/ number of parameters refined	9681 / 0 / 670	15099 / 273 / 763
$GOOF$	1.006	0.923
R_1	0.0706	0.0671
R_w	0.1771	0.1330
$\rho_{\text{max}}/\rho_{\text{min}}$, e/\AA^3	0.77 / -0.71	2.779 / -0.932

RESULTS AND DISCUSSION

According to the obtained data, the $\text{Dy}_4\text{L}_4 \cdot 9\text{C}_3\text{H}_7\text{NO} \cdot 18\text{H}_2\text{O}$ dysprosium complex has a molecular structure (Fig. 1). Solvent molecules are not coordinated and fill the crystal lattice voids. The oxygen atoms of three dimethylformamide molecules are linked by a hydrogen bond with NH groups of trihydrazone located above the base of the trigonal pyramid (the H bond parameters are as follows: $\text{N}(4) \dots \text{O}(1\text{S})$ is 2.768(9) Å, $\text{O} \dots \text{H}$ is 1.95 Å, the N–H–O angle is 160.2°).

The complex cluster is a slightly compressed trigonal pyramid; the $\text{Dy}(1) \dots \text{Dy}(1)$ and $\text{Dy}(1) \dots \text{Dy}(2)$ distances are 9.99(1) Å and 9.92(1) Å respectively. The pseudotetrahedron sides are occupied by triply deprotonated trinucleating ligands. In the acyltrihydrazone structure, enol groups of pyrazole moieties are deprotonated, and hydrazone moieties are coordinated in the molecular amide form. The coordination number of dysprosium cations is nine; the coordination polyhedron geometry can be described as a three-capped trigonal prism consisting of the DyN_3 triangle and the DyO_6 trigonal prism.

The bond lengths of $\text{Dy}(1)$ with enol oxygen atoms of the ligands are not equal; they are 2.28(1) Å, 2.31(1) Å, and 2.35(1) Å respectively. The bonds of $\text{Dy}(1)$ with the amide oxygen atoms are also non-equivalent. When the ligand lies at the base of the pyramid, the bond length is 2.44(1) Å. When the ligands occupy the side faces, they form shorter bonds (2.41(1) Å). The $\text{Dy}(1)$ –N bonds are also non-equivalent; their lengths are within the range 2.59(1)–2.67(1) Å. In the structure of the coordination polyhedron of the $\text{Dy}(2)$ atom, all the $\text{Dy}(2)$ –N bonds have equal lengths of 2.60(1) Å; the $\text{Dy}(2)$ – O_{en} bond lengths are 2.37(1) Å, and the $\text{Dy}(2)$ – O_{amide} bond lengths are 2.42(1) Å. All the bond lengths of the

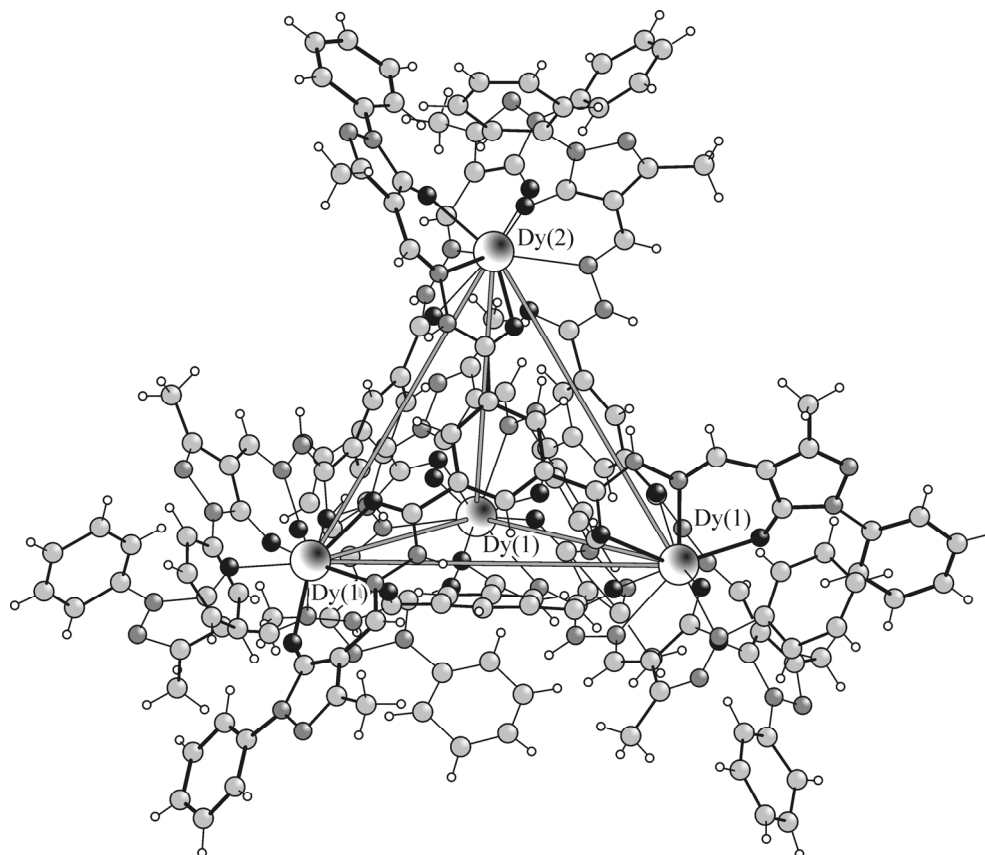


Fig. 1. Molecular structure of Dy_4L_4 complex (**1**). Bond lengths within the coordination polyhedra (Å): $\text{Dy}(1)$ – $\text{O}(1)$ 2.41(1), $\text{Dy}(1)$ – $\text{O}2$ 2.35(1), $\text{Dy}(1)$ – $\text{O}(3)$ 2.28(1), $\text{Dy}(1)$ – $\text{O}(4)$ 2.44(1), $\text{Dy}(1)$ – $\text{O}(7)$ 2.41(1), $\text{Dy}(1)$ – $\text{O}(8)$ 2.31(1), $\text{Dy}(1)$ – $\text{N}(3)$ 2.67(1), $\text{Dy}(1)$ – $\text{N}(5)$ 2.59(1), $\text{Dy}(1)$ – $\text{N}(10)$ 2.60(1), $\text{Dy}(2)$ – $\text{O}(5)$ 2.42(1), $\text{Dy}(2)$ – $\text{O}(5)$ 2.42(1), $\text{Dy}(2)$ – $\text{O}(6)$ 2.37(1), $\text{Dy}(2)$ – $\text{N}(14)$ 2.61(1). The structure of one of the trinucleating ligands is bold.

coordination polyhedron are within the ranges typical of lanthanide complexes with acylhydrazones of 3-methyl-1-phenyl-4-formylpyrazole-5-one [2-4]. The bond lengths and bond angles in the structure of the organic ligand molecules have typical values [11]. The planes of the five-membered chelate rings are turned by about 30° relative to the plane of the central benzene ring of the ligand. The five- and six-membered chelate rings are noticeably bent.

The $\text{Gd}_3(\text{L})(\text{HL}^1)_3 \cdot 6\text{C}_3\text{H}_7\text{NO} \cdot 5.5\text{H}_2\text{O}$ complex (Fig. 2) also has a molecular structure. The cluster is built of three equivalent gadolinium atoms forming an equilateral triangle with the sides of 9.84(1) Å, which are slightly less in comparison with the Dy(1)...Dy(1) distances in complex 1. The gadolinium ions are linked by the triply deprotonated trihydrazone molecule lying at the base of the cluster. The dianions of dihydrazone of 1,3,5-benzenetricarboxylic acid located at the sides of the triangle link metal cations in pairs. The coordination method of ligands of both types, as well as C.N and geometry of the coordination polyhedra are the same as in the case of the tetranuclear dysprosium complex. The carboxyl groups of the dihydrazone molecules are not coordinated and protonated.

The bond lengths formed by the gadolinium ions with the donor nitrogen atoms of tri- and dihydrazone are nearly the same: the Gd–N (L) distances are 2.67(1) Å, but for the diacylhydrazone nitrogen atoms they are 2.62-2.63(1) Å. The Gd–O_{amide} and Gd–O_{en} bond lengths are very similar for the ligands of both types (Gd–O_{amide} is 2.42-2.44(1) Å, Gd–O_{en} is 2.32-2.33(1) Å). The bond lengths and bond angles in the molecules of both diacylhydrazone and triacylhydrazone are typical of organic compounds [11].

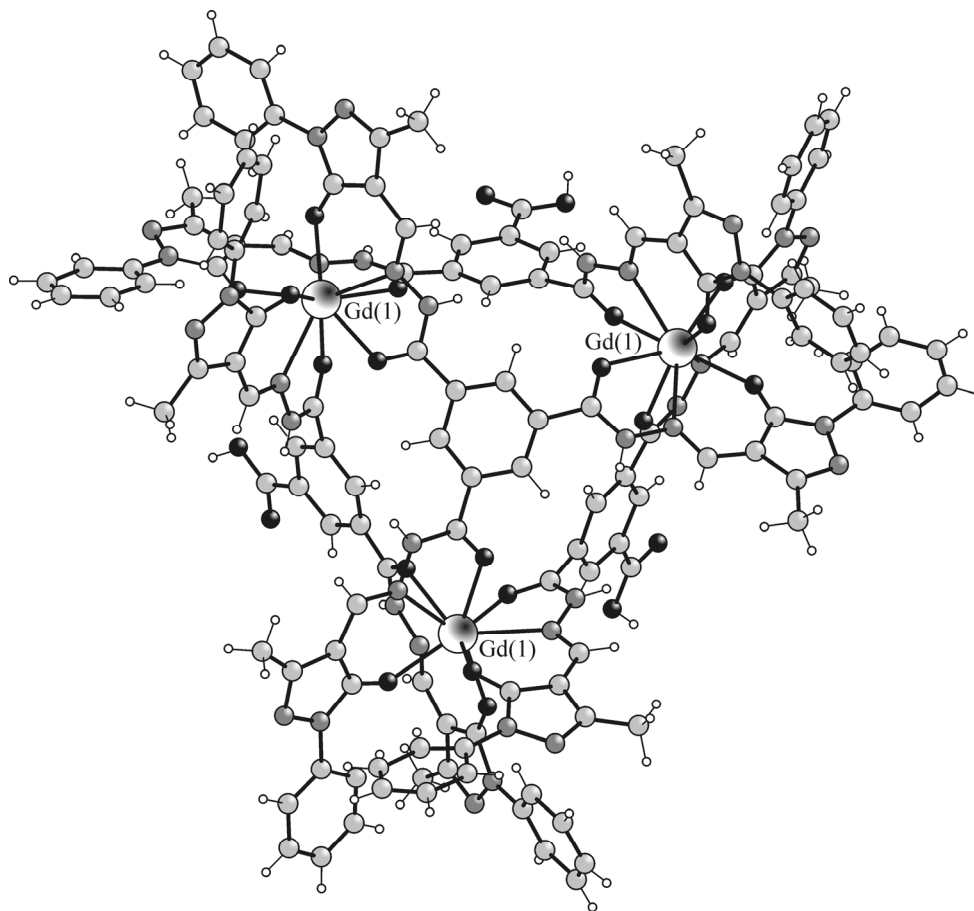


Fig. 2. Molecular structure of $\text{Gd}_3(\text{L})(\text{HL}^1)_3$ complex (2). Bond lengths within the coordination polyhedron (Å): Gd(1)–O(1) 2.32(1), Gd(1)–O(2) 2.42(1), Gd(1)–O(3) 2.33(1), Gd(1)–O(4) 2.44(1), Gd(1)–O(5) 2.32(1), Gd(1)–O(6) 2.44(1), Gd(1)–N(3) 2.67(1), Gd(1)–N(7) 2.63(1), Gd(1)–N(11) 2.63(1).

The mean square planes formed by the five-membered chelate rings of triacylhydrazone are turned relative to the plane of the central benzene ring by 30.6°, which nearly coincides with the value for complex **1**. Phenyl substituents and pyrazole rings in the structure of the tritopic ligand are nearly coplanar, but in the dihydrazone molecule they deviate from each other by about 20°.

The oxygen atoms of the solvate DMFA molecules are hydrogen bonded with NH groups of the hydrazone moieties (the H bond parameters are as follows: N(4)...O(1S) is 2.764(9) Å, O...H is 1.92 Å, the N–H–O angle is 159.1°; N(12)...O(2S) is 2.767(10) Å, O...H is 1.91 Å, the N–H–O angle is 164.0°). A part of the NH groups and the N atoms of the pyrazole ring form H bonds with water molecules (the H bond parameters are as follows: N(6)...O(1W) is 3.02(2) Å, N(8)...O(2W) is 2.813(11) Å, O...H is 1.95 Å, the N–H–O angle is 167.1°).

CONCLUSIONS

The self-organization of lanthanide coordination compounds with acylhydrazones of trimesic acid and 3-methyl-1-phenyl-4-formylpyrazole-5-one proceeds in accordance with the maximum site occupancy principle, meaning that polytopic ligands tend to maximally use their donor atoms (three atoms for one acylhydrazone moiety), and lanthanide cations reach coordination number 9 [12]. As a result, the dysprosium(III) complex with trihydrazone of 1,3,5-benzenetricarboxylic acid and 3-methyl-1-phenyl-4-formylpyrazole-5-one has a high-symmetry pseudotetrahedral structure. The heteroligand gadolinium(III) complex with di- and trihydrazone of 1,3,5-benzenetricarboxylic acid has a triangular structure in which the tritopic ligand is located above the triangle plane, and the ditopic ligands link lanthanide cations in pairs. The presence of free carboxyl groups makes it possible to suppose that this compound is able to coordinate additional metal ions and can be used as a building block for the synthesis of heteropolynuclear complexes. Both clusters have a highly-porous framework structure therefore they can participate in host–guest relations.

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CONFLICT OF INTERESTS

The authors declare that they have no conflict of interests.

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