ISSN 0036-0244, Russian Journal of Physical Chemistry A, 2021, Vol. 95, No. 9, pp. 1948–1954. © Pleiades Publishing, Ltd., 2021.
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Synthesis and Physicochemical Properties of Coordination Compound of Gadolinium(III) with 2,5-Dimetoxybenzoic Acid

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Received December 12, 2020; revised February 12, 2021; accepted February 12, 2021

Abstract—A new coordination compound of gadolinium(III) with 2,5-dimethoxybenzoic acid was obtained via electrochemical synthesis. The composition of the coordination compound was investigated by means of C–H analysis, X-ray spectral energy dispersive microanalysis, IR spectroscopy, and thermogravimetric analysis. The triplet level of 2,5-dimethoxybenzoic acid was determined from the luminescence spectra of the metal complex. The parameters of fine structure are determined using EPR spectra of the powder of the metal complex.

Keywords: gadolinium, complex compounds, triplet level, EPR spectroscopy

DOI: 10.1134/S0036024421090181

INTRODUCTION

It is known [1] that lanthanide ions, which have high coordination numbers (>7), form coordination compounds with complex compositions and structures that often have bi-, tri- and polynuclear structures with organic ligands. The special electronic structure of lanthanide ions associated with the screening of electrons of 4*f* orbitals and the prohibition of electronic transitions between states of different multiplicities (transitions with a change in the spin moment) explains the unique properties of lanthanide compounds. These include paramagnetism (up to seven unpaired electrons per lanthanide ion for gadolinium compounds), long lifetimes of excited states, and electronic transitions from the ultraviolet to the long-wavelength range. These properties offer the possibility of using lanthanide compounds in the manufacture of organic transistors, superconducting magnets, photovoltaic arrays, organic light-emitting diodes, thermoelectric elements, spintronic data storage devices, and laser radiation generators. They can also serve as components of contrast reagents for magnetic resonance imaging MRI, and as markers and probes for studying metabolic processes in living objects [2–6].

Complexes of Gd^{3+} with aromatic carboxylic acids are used to determine experimentally the triplet levels of ligands in order to establish their photophysical properties and predict the luminescence of complexes with other lanthanide ions. [7–10]. We can therefore synthesize complex compounds of lanthanides with specified luminescent characteristics [11].

Much attention is also given to studying the magnetic properties of mono- and polynuclear complex compounds Gd(III) [12, 13]. In addition, the dependences of the magnetic and dielectric permittivities of metal complexes Gd(III) on the frequency of applied electromagnetic radiation were studied in [14–16].

When using classical chemical means of synthesizing coordination compounds of lanthanides (based on ion exchange reactions), it is not always possible to obtain substances that fully satisfy their requirements, due to the possible hydrolysis, hydration, or contamination of the target substance with by-products of the reaction. As was shown in [17], these disadvantages are not observed in electrochemical synthesis, which allows single-stage processes that produce anhydrous compounds with no foreign ions, and variations of the composition of the target product and the direction of synthesis [17].

Electrochemical synthesis refers to direct means of synthesis in which a coordination sphere forms through the oxidation of ligands and metals in the zero oxidation state. Its main advantage is the possibility of synthesizing coordination compounds that cannot be obtained by other classical means, and conducting synthesis under mild conditions with relatively high yields of the target product [18].

The aim of this work was to study the structure and characteristics of a new complex compound: gadolinium(III) with 2,5-dimethoxybenzoic acid obtained by means of electrochemical synthesis.

EXPERIMENTAL

Gadolinium plates (purity, 99.9%) were used as Gd^{3+} source in the synthesis. Chemically pure 2,5-dimethoxybenzoic acid was used as the ligand in the synthesis of the coordination compound (2,5-MeOBenzH).

Direct electrochemical synthesis of coordination compound of gadolinium(III) was conducted using a soluble anode [18]. The scheme of the setup for the synthesis of coordination compounds included an electrochemical cell, a source of direct current, a coulometer, an ammeter, and a voltmeter. An electrochemical cell for the anodic synthesis of anhydrous complex compounds was described in [17].

Anhydrous acetonitrile of analytical grade was used as a non-aqueous solvent in electrochemical synthesis. The duration of complex synthesis (2.5 h) was determined from the initial concentration of the ligand (0.01 M) according to Faraday's law. The processes were conducted in an inert atmosphere inside a sealed system.

Soluble gadolinium(III) complex with 2,5-dimethoxybenzoic acid was preliminarily isolated via salting out with a mixture of toluene and chloroform. A white precipitate of the complex compound was filtered off on a Schott filter and dried to constant weight.

The content of gadolinium(III) in the resulting complex was determined via complexometric titration and energy dispersive microanalysis (EDA) using an INCA x-sight attachment on a JEOL JSM-7500F scanning electron microscope. The contents of carbon and hydrogen were determined via elemental microanalysis on a VARIO MICRO CUBE in a stream of oxygen at a furnace temperature of 1200°C.

Scanning electron microscopy on a JEOL JSM-7500F microscope was used to determine the microstructure of the product.

Thermal analysis was performed on a NETSCH STA 409 PC/PG synchronous thermal analyzer. Our analysis was done in air at 25 to 1000°C and a heating rate of 10 K/min.

The IR spectra of the complex and the ligand were recorded on a VERTEX 70 (Bruker) IR Fourier spectrometer in the range of 4000–400 cm^{-1} in solid form using an attenuated total internal reflection attachment with a diamond crystal. The optical system of the VERTEX 70 FT-IR spectrometer is evacuated, due to which the maximum sensitivity in the near, middle and far infrared ranges is achieved. The overlapping of weak signals by the absorption bands of water or carbon dioxide is also excluded.

Before recording the IR spectra, the measuring head was wiped with alcohol to remove any impurities. A small amount of powder of the test compound was then applied to the measuring head with a spatula, after which the IR spectra were recorded.

The luminescence spectrum of the complex was recorded on a Fluorat-02 Panorama spectrofluorimeter (Lumex) using a fiber optic attachment for measuring the spectra of solid samples with a delay of 20 μs and durations of 4000 μs. The spectrum was recorded at a temperature of 77 K, with the sample and optical fiber being placed in liquid nitrogen.

The EPR spectra of the powder of the complex compound were recorded on a JEOL JES FA-300 EPR spectrometer. The solid powder was placed in a quartz ampule. EPR spectra were recorded in the X-band with a modulation frequency of 100 kHz. Measurements were made in the temperature range of 103–293 K by pumping liquid nitrogen vapor through the resonator.

RESULTS AND DISCUSSION

Electrochemical Synthesis

To achieve maximum efficiency of synthesis, we had to determine the optimum parameters of the process: composition of the electrolyte system, applied voltage, temperature, and current strength, density, and efficiency.

The choice of the solvent (acetonitrile) was due to it meeting the requirements for electrochemical synthesis: availability, electrochemical stability, weak coordinating ability, solubility of the ligand and background electrolyte contained in it, and ease of drying.

To increase the electrical conductivity of the system during synthesis, lithium perchlorate was used as a background electrolyte. It is readily soluble in acetonitrile, and whose ions have a low coordinating ability with respect to lanthanide ions.

The optimum current during the synthesis of a complex compound of gadolinium(III) with 2,5-dimethoxybenzoic acid was 0.015–0.02 A. To achieve this, voltage of 6–8 V was applied to the electrochemical cell. The chosen range of current strength was due to synthesis being slow at lower values of it, and the possibility of side processes occurring if the solution were heated at higher values. Synthesis was therefore conducted at temperatures of no more than 30°C. The optimum anodic current density during the process was in the range 0.008–0.011 A/cm^2. Intense destruction of the anode begins at higher values of current density, reducing the efficiency of synthesis and contaminating the final product with metal-containing solid particles.

The ligand concentration was 0.01 M and was determined on the basis of its solubility, the calculated duration of synthesis, and the optimum current strength.

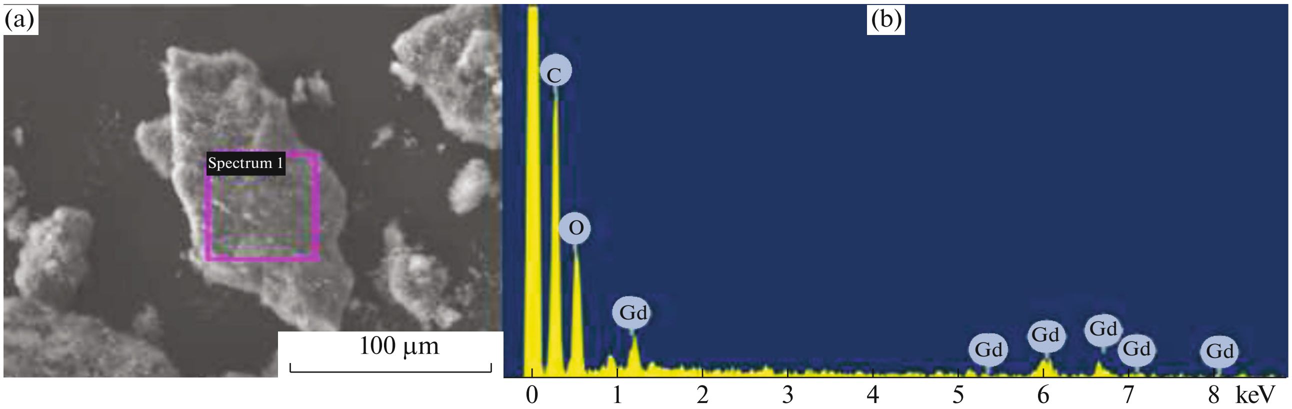

Fig. 1. (a) Photo of a particle of synthesized Gd(2,5-MeOBenz)$_3$ with a selected zone for energy dispersive analysis and (b) spectrum of energy dispersive analysis.

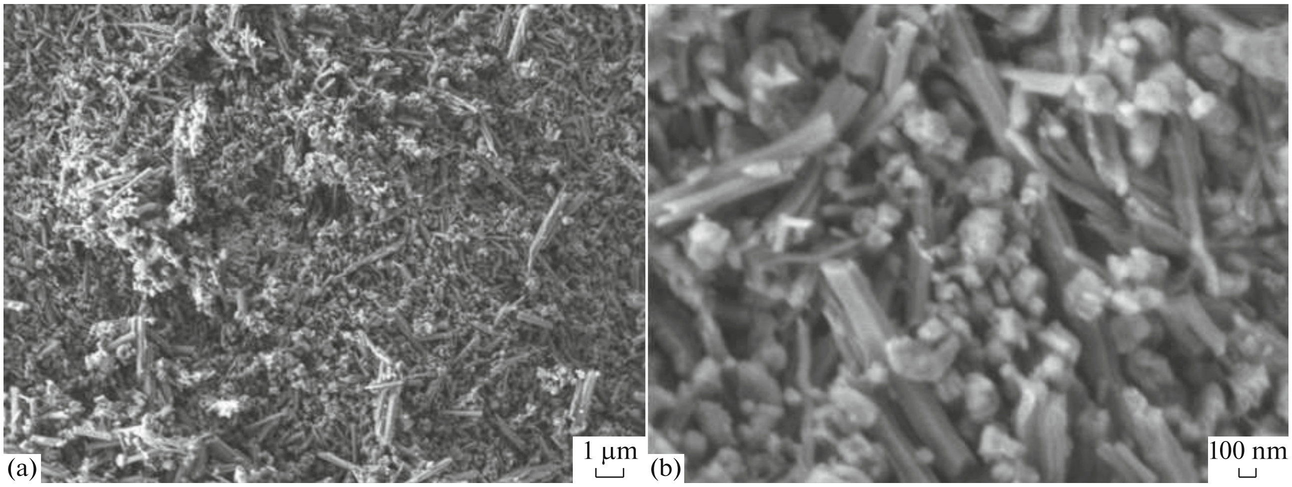

Fig. 2. Photo of synthesized Gd(2,5-MeOBenz)$_3$, obtained at (a) ×5000 and (b) ×30000 magnification.

The yield with respect to metal in the synthesis of the complex compound was 80%. The current efficiency was 75%, testifying to the efficiency of electrochemical anodic synthesis in preparing this substance under optimum conditions [17, 18].

Elemental Analysis

According to the results from elemental analysis of the synthesized Gd (2,5-MeOBenz)$_3$ ($C_{27}H_{27}O_{12}Gd$) powder, the contents of chemical elements were

- found, %: C 46.02, H 4.12 (for the compound $GdC_{27}H_{27}O_{12}$);
- calculated, %: C 46.28, H 4.11.

The content of gadolinium(III) in the resulting complex compound was determined via complexometric titration. According to the obtained data, the percentage (contained/calculated) of gadolinium(III) ions in compound Gd(2,5-MeOBenz)$_3$ was (22.39/22.43).

EDA and SEM Microscopy

In addition to the data from elemental analysis and complexometric titration, the presence of gadolinium, oxygen, and carbon atoms in the synthesized complex compound was confirmed by the energy dispersive microanalysis spectrum shown in Fig. 1b. Figure 1a shows a Gd(2,5-MeOBenz)$_3$ powder particle with the zone selected for energy dispersive analysis. The results from EDA also indicate there were no impurities of chlorine-containing compounds in the studied compound.

Figure 2 shows photographs of the microstructure of synthesized Gd (2,5-MeOBenz)$_3$. Analyzing Figs. 1a and 2, we may conclude the synthesized compound was agglomerates of nanosized, filamentary particles with clearly defined edges. The size of the agglomer-

Table 1. Attribution of characteristic absorption bands of functional groups in the IR spectrum of the ligand and its coordination compound with Gd^{3+}

Compound	Frequency reference, cm^{-1}			
	$\nu(C=O)_{carboxyl\ gr}$	$\nu_{as}(COO^-)$	$\nu_s(COO^-)$	$\Delta\nu(COO^-)$
2,5-MeOBenzH	1730	—	—	—
$Gd(2,5\text{-}MeOBenz)_3$	—	1530	1394	136

ates was 20–120 μm, and the crystalline particles were ≈150 nm in diameter and >1 μm long (Fig. 2b).

IR Spectroscopy

Comparison of the IR spectra of the obtained $Gd(2,5\text{-}MeOBenz)_3$ and initial 2,5-dimethoxybenzoic acid (Table 1, Fig. 3) shows that the acid in the complex was in ionized form, since absorption bands of asymmetric and symmetric vibrations of the deprotonated carboxyl group appear in the range of 1530 and 1400–1360 cm^{-1}, respectively. The absorption band in the 1730–1680 cm^{-1} region, which belongs to the stretching vibrations of the C = O bond of the unionized carboxyl group, disappears. The difference between the asymmetric and symmetric stretching vibrations of the ionized carboxyl group $\Delta\nu$ (COO^-) is less than 220 cm^{-1}, suggest [19] its bidentate coordination with the gadolinium(III) ion in the resulting compound. For the same reason, we may conclude the type of bond between the carboxylate oxygen atom of the ligand with the gadolinium(III) ion was predominantly ionic.

The spectrum of the $Gd(2,5\text{-}MeOBenz)_3$ complex lacks a broad absorption band of the stretching vibration of the O–H group of coordinated water molecules in the region of 3600–3300 cm^{-1}, indicating the formation of an anhydrous compound.

A symmetric shift of the absorption bands of ester asymmetric stretching vibrations $\nu_{as}(COC)_{ester}$ in the complex is observed for 2,5-dimethoxybenzoic acid, indicating atmospheric oxygen did not interact with gadolinium(III) ions. This also testifies to the formation of a symmetric outer sphere on the complex compound [20]. We may therefore assume that the coordi-

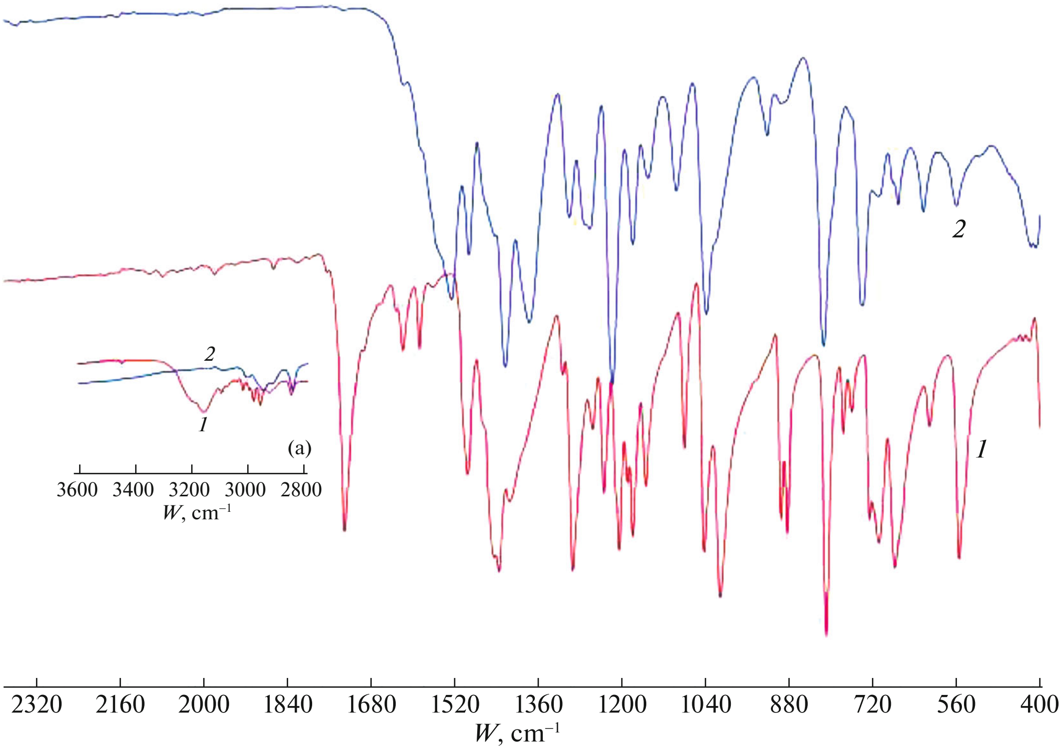

Fig. 3. IR spectra of (*1*) 2,5-MeOBenzH and (*2*) $Gd(2,5\text{-}MeOBenz)_3$. Inset: (a) fragment of the spectra in the range 2800–3600 cm^{-1}.

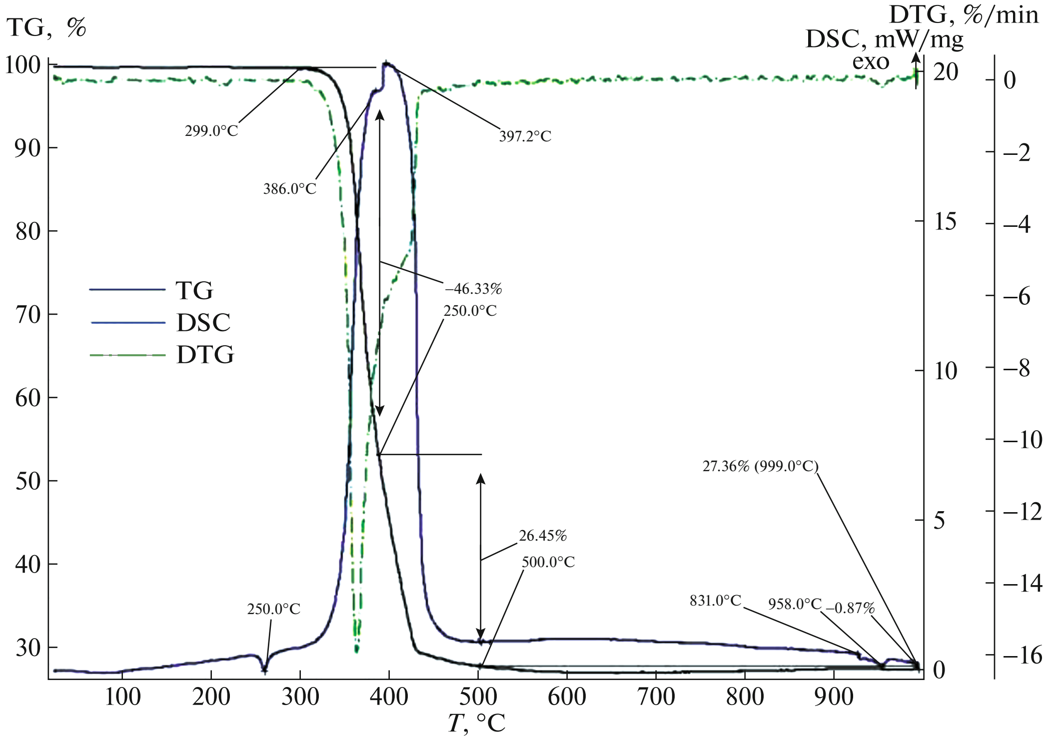

Fig. 4. Thermogram of complex compound Gd(2,5-MeOBenz)$_3$.

nation of the ligand with the Gd^{3+} ion in the obtained Gd(2,5-MeOBenz)$_3$ is similar to that of benzoic acid.

Thermogravimetric Study of Complexes

According to thermogravimetric analysis (Fig. 4), the synthesized Gd(2,5-MeOBenz)$_3$ was thermally stable up to 250–300°C. Data from thermal analysis confirm there were no water molecules in the resulting complex compound, since no effects corresponding to dehydration are observed up to 200°C. The residual weight corresponds to gadolinium oxide Gd_2O_3, confirming the composition of the complex. Exothermic effects accompanied by a sharp weight loss associated with the thermal oxidative destruction of the complex are observed in the temperature range of 300–600°C.

Data from elemental analysis, thermogravimetry, energy dispersive analysis, and IR spectroscopy show that the resulting complex was a separate anhydrous compound with the composition Gd(2,5-MeO-Benz)$_3$.

Luminescence of Coordination Compounds

Luminescence spectra were recorded for the obtained complex compound Gd^{3+} at liquid nitrogen temperature (77 K) (for maximum leveling of thermal quenching of phosphorescence) by means of Gaussian deconvolution according to the maxima of emission bands from which the triplet level of the used 2,5-dimethoxybenzoic acid was determined (Fig. 5). The triplet level of the ligand was determined by the position of the short-wavelength edge of the phosphorescence band corresponding to the 0–0 transition [21, 22]. The triplet levels of ligands were determined experimentally in order to establish their photophysical properties and predict the efficiency of luminescence of complexes with other lanthanide ions [7–10]. The calculated triplet level of 2,5-dimethoxybenzoic acid in Gd(2,5-MeOBenz)$_3$ was 19646 cm^{-1}.

It is known [23] that for intense luminescence to be observed in complex compounds of lanthanides emitting in the visible region, the triplet level of the ligand must be located 1500–4000 cm^{-1} above the resonance level of the Ln^{3+} ion. At higher values, energy transfer becomes ineffective, due to the low probability of such a transition of electrons. At lower values, the reverse transfer of part of the energy to the ligand molecule increases, due to the thermal vibration of molecules. Determining the triplet level of the considered ligand is therefore an important problem.

EPR Spectroscopy of Coordination Compounds

Figure 6a shows the EPR spectra of the powder of the synthesized complex compound Gd(2,5-MeO-Benz)$_3$ in the studied range of temperatures.

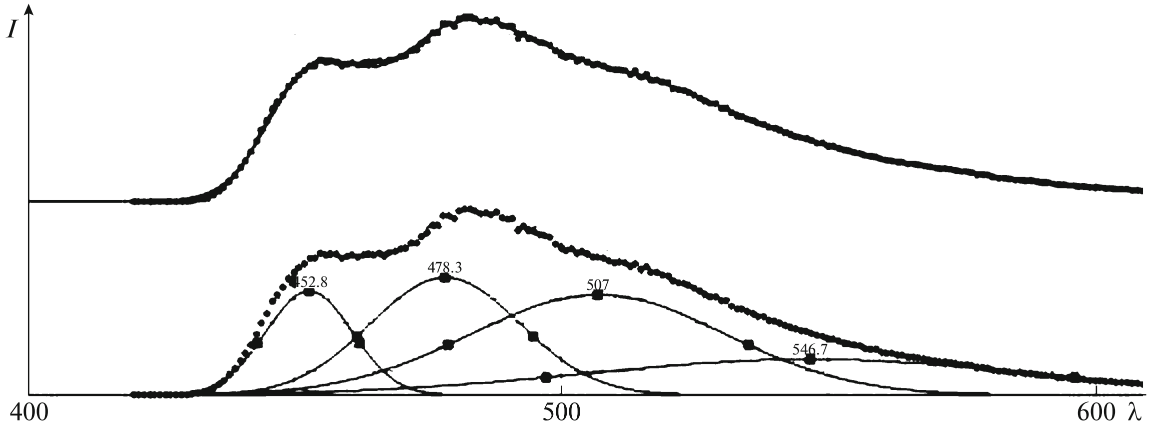

Fig. 5. Phosphorescence spectrum of Gd(2,5-MeOBenz)$_3$.

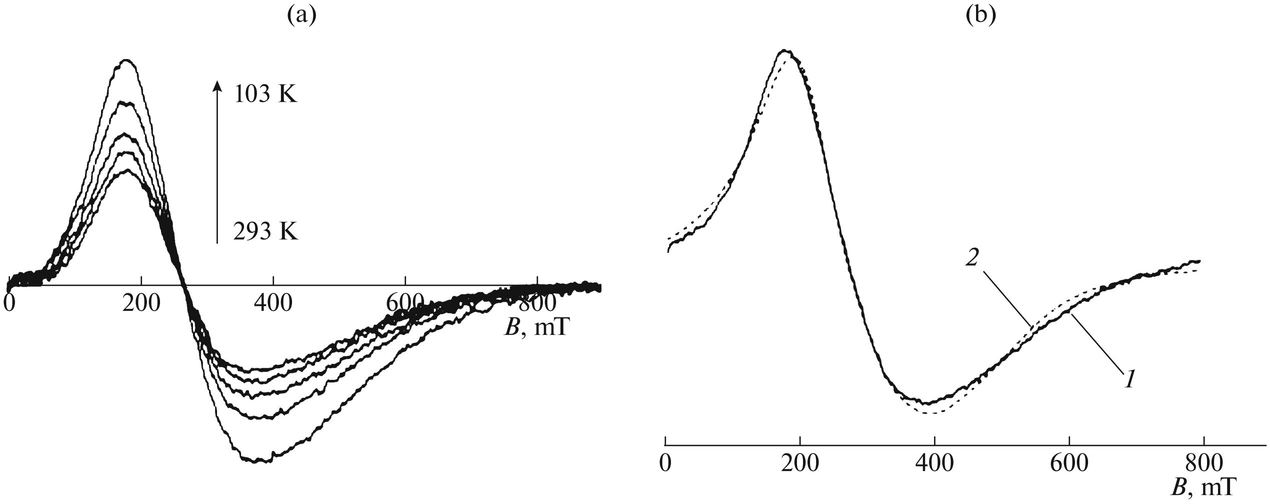

Fig. 6. (a) EPR spectra of the investigated Gd(2,5-MeOBenz)$_3$, obtained in the temperature range of 293–103 K; (b) comparison of (*1*) an experimental spectrum obtained at 103 K and (*2*) the theoretical EPR spectrum.

Figure 6a shows that the EPR signals of Gd(2,5-MeOBenz)$_3$ consisted of an asymmetric wide line with an unresolved structure. The intensity of the EPR spectrum grows as the temperature falls, but the widths of the absorption lines and the shape of the EPR spectrum do not change.

For our theoretical description of the EPR spectrum of the considered complex compound, we used a spin Hamiltonian in the form

$$\hat{H} = \mu_B \hat{S} g B_0 + \sum_{k=2,4,6} \sum_{q=-k}^{k} k,q B_k^q \hat{O}_k^q, \qquad (1)$$

where μ_B is a Bohr magneton, $\hat{S}$ is the total spin operator, g is the Lande spectroscopic splitting factor, B_0 is the magnitude of the static magnetic field, $\hat{O}_k^q$ denotes Stevens spin operators, and coefficients B_k^q are parameters of the fine structure determined from the experiment.

Figure 6b shows the (*1*) experimental and (*2*) theoretical EPR spectra for the investigated complex compound. The theoretical spectrum for the investigated complex compound Gd(2,5-MeOBenz)$_3$ was modeled using the MATLAB program based on the EasySpin module version 5.2.28 [24, 25]. The parameters were approximated according to least squares using the Nelder–Mead optimization algorithm when the least root mean square deviation (rmsd) value was reached. The lowest value (*rmsd* = 0.038) was obtained using the parameters ΔH_{pp} = 107.8 mT (line width from peak to peak), parameter B_2^0 = 453.7 MHz, B_4^0 = 8.4 MHz, and g-factor = 1.99. The Lorentz line shape was used. As can be seen from Fig. 6b, the theoretical spectrum describes the shape of the experimental EPR spectrum of the compound Gd(2,5-MeOBenz)$_3$ for the given set of parameters used to modulate the EPR spectrum.

Considering the data from scanning electron microscopy and our set of parameters of the fine structure of the EPR spectrum [26], we may assume the coordination polyhedron of the studied complex compound Gd(2,5-MeOBenz)$_3$ has high symmetry that is above trigonal.

CONCLUSIONS

A new anhydrous thermostable complex compound of gadolinium(III) with 2,5-dimethoxybenzoic acid was synthesized electrochemically. According to IR spectroscopy data, the bonds between the carboxylate atom of the ligand and the Gd^{3+} ion were predominantly ionic. The triplet level of 2,5-dimethoxybenzoic acid used as a ligand was determined from the phosphorescence spectra of Gd^{3+} complexes.

FUNDING

This work was performed on equipment belonging to the Scientific and Educational Center for Diagnostics of the Structure and Properties of Nanomaterials at the shared resource center of Kuban State University. It was supported by the RF Ministry of Science and Education, state task no. FZEN-2020-0022; and by the Russian Foundation for Basic Research and the Administration of Krasnodar krai as part of scientific project no. 19-43-233003 r_mol_a.

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Translated by M. Drozdova