



QUANTUM-CHEMICAL SEMI-EMPIRICAL CALCULATION FOR NEODYMIUM (Nd), SAMARIUM (Sm) AND GADOLINIUM (Gd) COMPLEXES ON THE GENERALIZED SPARKLE MODEL

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Annotation. Neodymium, samarium, and gadolinium complexes with terephthalic acid were synthesized for the first time, and it was found that, unlike complexes with phthalic acid, they are isostructural. A number of physical and chemical studies established their composition and chemical formula. Quantum-chemical semi-empirical calculation for neodymium, samarium and gadolinium complexes was carried out on the generalized Sparkle model, intended for lanthanide complexes on PM6, and the Sparkle/PM6 parameters for other trivalent lanthanides were also presented. The comparative analysis procedure took into account only qualitative crystallographic structures. The unsigned average errors (UME) of Sparkle/PM6, corresponding to all interatomic distances between neodymium, samarium, gadolinium ions and atoms directly coordinated with them, range from 0.066 to 0.086 Å, for Nd (III) – 0.086, Gd (III) – 0.066 and Sm (III) – 0.066, respectively. As a result of the application of Sparkle/PM6 to the synthesized lanthanide complexes, in particular, the values of the final heat of formation, the energy of repulsion of the nucleus-nucleus area and volume COSMO - (conductor-like screening model), the ionization potential, the energy of binding (homo) and antibonding (lumo) orbitals.

Keywords: *Complex compounds, computational chemistry of lanthanide complexes, quantum-chemical semi-empirical calculation, p-values of nonparametric Kolmogorov-Smirnov tests, the energy of binding (homo) and antibonding (lumo) orbitals.*

Introduction

In recent years, we have carried out a lot of work in the field of modeling chemical processes [1-8]. In the scientific literature there is a significant amount of information on the synthesis, study of the structure and properties of complexes of transition d-elements with dicarboxylic aromatic (phthalic) acids.

Interest in phthalates and terephthalates of various d-elements is determined by the possibility of their wide application. So, zinc terephthalate is used as an activator of rubber vulcanization, ruthenium terephthalate exhibits semiconductor properties. The layered structure of phthalates and terephthalates makes it possible to use them as molecular sieves and adsorbents [9, 10]. The coordination polymer of cadmium terephthalate $[Cd(C_6H_4N_2)(C_6H_4(COO)_2(H_2O))]_n$ was obtained by hydrothermal synthesis, its crystal structure was deciphered, and it was shown that it is a fluorescent emulsion [11]. The structure consists of CdN_2O_4 octahedral units that are interconnected terephthalate anions and due to hydrogen and π - π stacking interactions, a 3D supramolecular structure is formed from a 1D structure [12]. However, information on complex compounds of aromatic carboxylic acids with rare earth elements is not so extensive in the literature.

Rare earth elements (REE) form complexes with benzoic acid and its derivatives, which are used as effective materials for liquid lasers, blood anticoagulants, catalysts, etc. It is assumed that the crystallization of such complexes is related to the order of filling of f-orbitals in lanthanides and lanthanide contraction. The study of the structural features of these complexes makes it possible to reveal the principle of the formation of REE complexes with dicarboxylic-phthalic acids and to explain their general stereochemical features.

Computational chemistry of lanthanide complexes at a semi-empirical level began in 1994 with the introduction of the Sparkle model, which for the first time allowed rapid quantum-chemical optimization of the geometry of relatively large complexes. The Sparkle model filled an important gap in the modeling of lanthanide complexes [13–14], opening up the possibility of predicting the spectra of complexes in the UV-visible region and the parameters of the ligand field. Overall, the results show that all Sparkle models are only very accurate when all atoms directly coordinated to the lanthanides in the complex are either oxygen or nitrogen—generally the most common binding situation.

The purpose of this work is the synthesis of complexes of some rare earth elements (neodymium, samarium and gadolinium) with terephthalic acid, the study of their physicochemical characteristics and the creation of a virtual model of the complexes to save the cost of starting materials; calculation of their quantum parameters and identification of the adequacy of the proposed model.

Experimental part

Previously, complexes of rare-earth elements (neodymium, samarium, and gadolinium) with phthalic acid were synthesized. A number of physicochemical methods of analysis have shown that these complexes are nonisostructural, despite the fact that the metals belong to the same first subgroup in the lanthanide series [15-16].

However, the correspondence of some lines in the diffraction patterns of the complexes indicates the presence of common structural units and motifs in their crystal structure.

Coordination compounds of neodymium, samarium and gadolinium with terephthalic acid were synthesized for the first time. These complexes were obtained by an exchange reaction between sodium terephthalate and a soluble salt of the corresponding lanthanides. The main factor in complex formation is the coordination of these metals with carboxyl groups and its effect on the properties of the complex. Based on X-ray, derivatographic data and the results of elemental analysis of the reaction products, the chemical compositions of the resulting complexes were determined and their chemical formulas were compiled:



and found that they are isostructural.

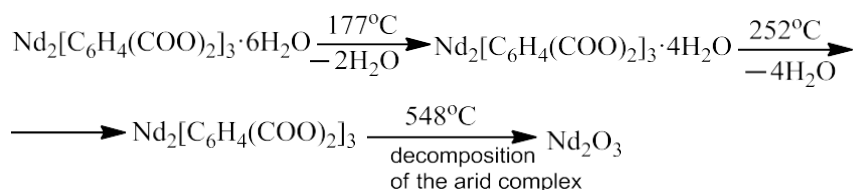
To determine the thermal stability of the synthesized complexes, the course of their thermal degradation was studied.

Neodymium terephthalate with six water molecules is stable up to 148°C, after which its decomposition begins, accompanied by a shallow but clear endothermic effect with a maximum at 177°C. This effect corresponds to the removal of two water molecules.

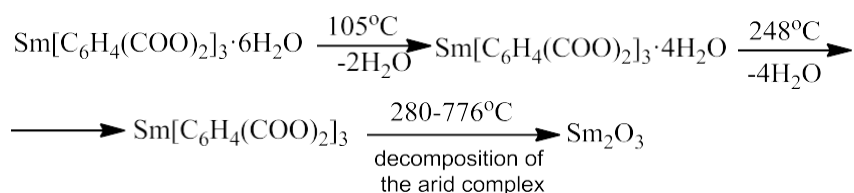
The weight loss is 4.52% (calculated 4.10%). Immediately after this, a broad endothermic effect appears on the DTA curve with a maximum at 252°C. In this case, the mass loss is 6.58% (calculated 8.2%), which corresponds to the removal of four water molecules. After removal of the water of crystallization, decomposition of the anhydrous complex begins.

In a narrow temperature range of 510–606°C, an intense burnout of the arid complex occurs with a pronounced exothermic effect (maximum 548.7°C). The mass loss is 48% (calculated 49%) and this corresponds to the complete burnout of the organic part of the molecule. The final thermolysis product of this complex is Nd₂O₃.

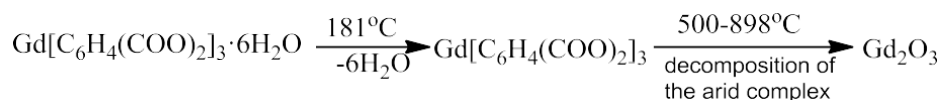
Scheme of thermal destruction of the complex:



The thermal decomposition of samarium and gadolinium complexes with terephthalic acid does not proceed according to a single scheme. On the derivatogram of the samarium complex, two endoeffects observed at 105°C and 248°C correspond to the removal of 4.9% and 7.9% of the weight, i.e. two and four water molecules in two stages.



In the case of the gadolinium complex, the same amount of water is removed immediately at 181°C, which is accompanied by a clear endothermic effect. This is obviously due to the special position of gadolinium in the lanthanide series, which differs in that in its ion all the existing n-sublevels without exception are half-filled. Such a half-filling of the n-sublevels leads to strengthening of the electronic bond in the atomic shell of gadolinium. The complex is stable up to 280°C, after which decomposition of the anhydrous complex begins. The organic part of the complex burns out in the temperature range 280–898°C (max 540°C). A very high temperature does not ensure complete burnout of the organic part, the process is blocked by the resulting end effect. In this case it is 48.77% (calculated 48.55%).



Computational chemistry of lanthanide complexes at a semi-empirical level began in 1994 with the introduction of the Sparkle model [17], which for the first time allowed rapid quantum-chemical optimization of the geometry of relatively large complexes. The Sparkle model filled an important gap in the modeling of lanthanide complexes [17–21], opening up the possibility of predicting the spectra of complexes in the UV-visible region and the parameters of the ligand field. Overall, the results show that all Sparkle models are only very accurate when all atoms directly coordinated to the lanthanides in the complex are either oxygen or nitrogen – usually this is the most common binding situation.

In 2004, the model was improved by introducing Gaussian functions into its nuclear repulsion to make it compatible with the semi-empirical AM1 model [17-19]. This significantly improved the Sparkle model, and later, in 2005, the Sparkle model was fully parameterized within AM1 for thulium, ytterbium, and lutetium. Because different semi-empirical models have different characteristics and applications, it soon became clear that Sparkle model parameterization would be useful for all of the most commonly used and widely available semi-empirical models.

X-ray phase analysis was performed on a Commander Sample ID instrument (Coupled Two Theta) with a copper cathode. IR absorption spectra were taken on a ThermoScientific Nicole 1810 spectrometer in the range 400–4000 cm⁻¹. Samples were prepared as suspensions in vaseline oil at room temperature. Derivatograms were recorded on a STA-449, F-3 derivatograph (Germany). Elemental analysis for C, H was performed on a CHNSO «E» analyzer from CarloERBA. The content of metals was calculated from the weight loss curve by the amount of oxides obtained after heating on a derivatograph to 900°C.

For the synthesis of complex compounds, SmCl₃•6H₂O, GdCl₃•6H₂O, NdCl₃•6H₂O, NaHCO₃ "chemically pure" and terephthalic acid "chemically pure" were used. Two portions of terephthalic acid, 0.498 g (0.003 mol) each, were weighed and each was dissolved in 50 ml of distilled water with the addition of 0.504 g (0.006 mol) of NaHCO₃ to each. 0.717 g (0.002 mol), 0.729 g (0.002 mol) and 0.743 g (0.002 mol) of water-soluble salts NdCl₃•6H₂O, SmCl₃•6H₂O and GdCl₃•6H₂O, respectively, were gradually added to the obtained hot solutions.

The filtered precipitates were first washed several times with distilled warm water and then with benzene and dried first in air and then in an oven at 50°C. Polycrystalline powders have a yellowish color.

Computational experiment

Quantum-chemical semi-empirical calculation was carried out for Neodymium, Samarium and Gadolinium complexes on the generalized Sparkle model, designed for lanthanide complexes on PM6. Also, the Sparkle/PM6 parameters are presented for other trivalent lanthanides. The results of these calculations are shown in Table 1.

Table 1. Average values and variants of the γ distribution calculated for Nd(III), Sm(III), Gd(III) complexes

Lanthanide ion	UME			
	N	Mean (Å)	Variance (Å ²)	p-value
Nd ³⁺	57	0.198	0.0086	0.865
Sm ³⁺	37	0.188	0.0066	0.262
Gd ³⁺	64	0.186	0.0066	0.460

Table 1 also summarizes the UME data for each trivalent lanthanide. In this case, the mean of all means is 0.191 Å and the mean of all deviations is 0.0073 Å².

PM6 is a neglect of the diatomic differential overlap method, modified by adopting a slightly improved version of diatomic parameters as well as inert gas interactions. On the other hand, the Sparkle model does not require two-atom parameters, and therefore, for PM6, the potential of a single-atom Sparkle kernel with only two Gaussian functions was used. Efforts have also been made to make available PM6 for the trivalent ions of these atoms to make the kit compatible with Sparkle/AM1 and Sparkle/PM3. The Sparkle / PM6 parameters were obtained using the same parameterization procedure that was carried out to obtain the Sparkle / AM1 and Sparkle / PM3 parameters.

Thus, we used only high quality crystallographic structures (R-factor<5%) obtained from the Cambridge Structural Database (CSD). Of these, we took as preliminary sets for each trivalent lanthanide - neodymium, samarium, and gadolinium, previously selected for Sparkle / AM1 parameterization, and carried out the optimization. The Sparkle/PM6 parameters found for all 3 trivalent lanthanides are shown in Table 2.

To continue testing and similar calculations, the unsigned mean error (UME) was used, for each complex *i*, defined as

$$UME_i = \frac{1}{n} \sum_{j=1}^n |d_{i,j}^{CSD} - d_{i,j}^{RM1}|,$$

where *n* is the number of atoms in the coordination polyhedron of the lanthanide ion. Two cases were considered: a) UMEs, where we considered only interatomic distances between the lanthanide ion, in particular neodymium, samarium, gadolinium, and atoms directly coordinated with them, and b) UMEs of all edges of all pyramid faces defined by the lanthanide ion at the apex, as well as all interatomic distances between all atoms of the coordination polyhedron. The results of these studies are presented in Table 2.

Table 2. Sparkle / PM6 model parameters for trivalent Nd(III), Sm(III), Gd(III)

	Nd ³⁺	Sm ³⁺	Gd ³⁺
α	4.1738480733	4.0858458124	2.1346333468
GSS	57.6974644976	56.8573294165	56.8944696903
a_1	1.1507966088	1.5645679440	0.2517865588
b_1	6.4949658378	6.4255324886	8.7505991931
c_1	1.5653255583	1.4885991013	1.7313405711
a_2	0.1889516026	0.1021969444	0.1221903028
b_2	10.9231117908	9.4102061689	7.4979582981
c_2	3.0169407149	3.1094973204	2.9344373061

Sparkle PM7 possesses eight parameters for each lanthanide trication: α , the core-core repulsion term, in Å⁻¹, GSS, the s-s atomic orbital one-center two-electron repulsion integral, in eV, and the six parameters for the two Gaussian functions:

$$(R) = \sum_{i=1}^2 \alpha e^{[b_i(R-c_i)^2]}$$

where a_i – height, dimensionless; b_i – inverse broadness, in Å⁻²; c_i – displacement, in Å; *R* – is the interatomic distance between the lanthanide and the other atom, in Å.

Results and discussion

Once again, it is important to assess whether Sparkle/PM6 provides a good and reliable representation of the lanthanide complexes, without bias, at least within the validation set of complexes. In order to confirm this, the UME of all distances of all complexes of the test set should be randomly distributed about the

average value, the value of which can be used as a measure of the accuracy of the model. Therefore, UME and $UME_{(Ln-L)}$ must follow the probability density function of the distribution γ , since UME are positive and defined in the region $(0, \infty)$. We then proceeded to fit the UME to the γ distribution function, from which the mean and variance could be determined. The fit quality of the γ distribution can be assessed using the non-parametric single-sample Kolmogorov-Smirnov test to statistically test whether the distribution of UME values can be represented by the γ distribution indexed by the calculated mean and variance. If the p-value of the test is greater than 0.05, the fit of the γ distribution is indeed justified within the 95% confidence interval, and the mean and variance can be used as measures of model accuracy. The results of the comparative calculation are shown in tables 1 and 3.

Table 3. Mean values and variants of γ -distribution fit for $UME_{(Ln-L)}$ s calculated for N complexes for Nd(III), Sm(III), Gd(III)

$UME_{(Ln-L)}$				
Lanthanide ion	N	Mean (\AA)	Variance (\AA^2)	p-value
Nd ³⁺	57	0.0744	0.0011	0.679
Sm ³⁺	37	0.0748	0.0010	0.956
Gd ³⁺	64	0.0663	0.0008	0.249

The last column shows the p-values of the non-parametric Kolmogorov-Smirnov tests for a single sample performed on Neodymium, Samarium, Gadolinium to statistically verify that its value is greater than 0.05, indicating that the distribution of UME values could indeed be represented by a γ distribution indexed by mean and variance estimates. N is the number of complexes used in the comparison.

Given the successful results of Sparkle/PM7 for lanthanide complexes, this software package was applied to the compounds we obtained. As a result of the computational experiment, in particular, the following data were obtained: final heat of formation = 4832997.07045 Kcal/mol = 20221259.74277 kJ/mol; total energy = 202869.43828 eV; electronic energy = -24007.99893; nucleus-nucleus repulsion = 226877.43721 eV; COSMO region – (conductor-like screening model) = 1255.12 \AA^2 ; COSMO volume = 911.76 \AA^3 ; the COSMO procedure creates a conductive polygonal surface around the molecule system at a van der Waals distance, ionization potential = 4.088084 eV, the amount of energy required to remove an electron from an isolated molecule; homo-lumo energies = -4.088 eV and -4.087 eV respectively, bonding molecules, they are also called bonding orbitals and antibonding orbitals: homo participates in bonding orbitals, and lumo participates in antibonding orbitals.

When compared, homo orbitals naturally have lower energy than lumo. Bonding orbitals (homo) are created by combining orbitals that are in phase. The result is the creation of bonds between atoms. If there are electrons in the orbitals, there is no electron density between the two hydrogen atoms. Therefore, it does not promote bond formation, but rather works to break it.

Also, as a result of the work of Sparkle / PM7, rectangular coordinates (Cartesian coordinates) of atoms of the complexes, net atomic charges and dipole contributions (net atomic charges and dipole contributions), the population of atomic orbital electrons (atomic orbital electron populations), etc. were obtained. The obtained calculated results are adequate to the experimental ones. data from various literary sources. This once again proves that Sparkle/PM7 can be applied to synthesized complexes of neodymium, samarium, and gadolinium.

Conclusions

1. Neodymium, samarium, and gadolinium complexes with terephthalic acid were synthesized for the first time, and it was found that, unlike complexes with phthalic acid, they are isostructural. A number of physical and chemical studies established their composition and chemical formula.
2. It has been established that the Sparkle / PM7 software package, one of the options in the set of semi-empirical models applicable to the quantum-chemical calculation of lanthanide complexes, can be used for the synthesized complexes of neodymium, samarium and gadolinium.
3. The obtained calculation results will provide researchers with a computer model of the predicted synthesis of lanthanide complexes, in particular neodymium, samarium, gadolinium complexes and their geometric characteristics.

4. As a result of the application of Sparkle/PM6 to the synthesized lanthanide complexes, in particular, the values of the final heat of formation, the energy of repulsion of the nucleus-nucleus area and volume of COSMO, the ionization potential, the energies of bonding and antibonding orbitals were obtained, which makes it possible to evaluate the quantum and physical characteristics of the synthesized lanthanide complexes.

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