INVESTIGATION OF COORDINATION COMPOUNDS
OF GADOLINIUM (III) WITH β-DIKETONES

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Abstract. New coordination compounds of gadolinium with β-diketones containing unsaturated and aliphatic or aromatic substituents in the α-positions of the chelate ring have been synthesized. The performed quantum-chemical calculations of ligand molecules indicate the best acceptor properties of ligands with aromatic substituents. An analysis of the IR spectra and quantum chemical calculations of the metal complexes indicates the bidentate-chelate coordination of the ligand molecules and their arrangement in different planes, regardless of the nature and geometric structure of the substituent in the β-diketone molecule. The energies of the triplet levels of the ligands are calculated. The morphology and dispersion of the synthesized metal complexes have been studied.

Keywords: lanthanides, coordination compounds, luminescent properties, metal-polymer, gadolinium, β-diketones.

1. Introduction

For a long period of time, the interest of researchers in various lanthanide compounds does not disappear. This is due to a wide range of practical applications of oxide and coordination compounds, composite, hybrid and polymeric materials based on lanthanides.[1-4] They find application in various fields of science and technology: as emission and magnetic materials in molecular spintronics as single-molecule magnets for storing ultra-high-density information and quantum computing (quantum information processing)[5-10] for highly anisotopic systems based on Tb and Dy,[11] as low-temperature mo-

lecular magnetic coolers, which are evaluated by the magneto-caloric effect (MCE) [12], in magnetic resonance imaging (MRI) - contrast agents that, when introduced into the body, are localized in the internal organs, increasing the contrast between normal and affected tissue.[12-16]

First of all, these are complex compounds of gadolinium and dysprosium, which is due to their paramagnetic properties. The main feature of the method, in addition to its sensitivity, is the absence of harmful effects on the organism.[17-19]

In addition, gadolinium complexes are also of interest from a theoretical point of view. The high energy of the ground state of the gadolinium ion makes it possible, by recording the phosphorescence spectra, to calculate the energies of the triplet and singlet levels of ligands. This makes it possible to purposefully synthesize new luminescent compounds, taking into account the energy gap between the level of the triplet ligand and the resonant level of the lanthanide ion. The interests are the possibilities of synthesizing heterometallic complexes of dysprosium, europium, ytterbium, yttrium with gadolinium and doping the complexes of these metals with gadolinium complexes. This will make it possible to create new materials with interesting photophysical properties. The presence of a heavy paramagnetic ion increases the efficiency of the intercombination conversion due to the mixing of singlet and triplet levels (paramagnetic effect).

The synthesis of new ligands and lanthanide complexes based on them, the study of their structural characteristics and photophysical properties will make it possible to create a new generation of luminescent lanthanide-containing materials with desired properties. Therefore, the synthesis of new coordination compounds of gadolinium, the study of their structural features and spectral-luminescent properties are the main task of this study.

2. Experimental

Unsymmetrical β-diketones were chosen as ligand systems: (2,5-dimethylheptene-1-3,5,-dione (dmhpd), (2,6-dimethyloctene-1-3,5,-dione (dmokd), (2-methyl-5-

phenylpentene-1-3,5,-dione (mphpd) (2-methyl-5-biphenyl penten-1-3,5,-dione (mbphpd), containing unsaturated (methacrylic) and aliphatic or aromatic substituent in the α-position (Fig. 1).
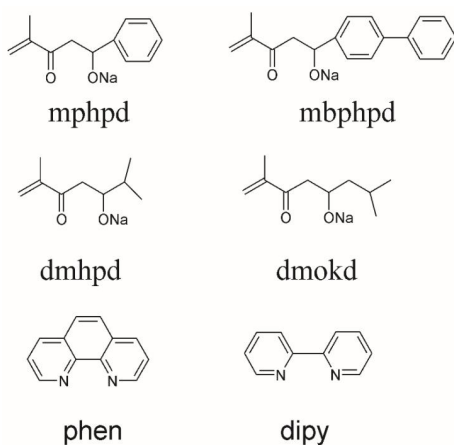
Scheme 1. Molecules of ligands used in the work

Ligands were synthesized by Claisen condensation according to the scheme previously described by the authors.[20,21]

The synthesis of complexes was performed by the interaction of aqueous solutions of metal salts gadolinium nitrate (III) $Gd(NO_3)_3 \cdot 5H_2O$ (c.p) with an aqueous solution of sodium salt of the corresponding ligand at a molar ratio of reagents 1: 3 (pH 8-9) at room temperature.

$$Gd(NO_3)_3 + xNaL \rightarrow GdL_3 + 3NaNO_3$$
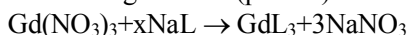
where Ln = Gd(III), L= dmhpd, dmokd, mphpd, mbphpd.

The resulting precipitates of the complexes were separated from the mother liquor by centrifugation, washed with water, and dried in a vacuum desiccator over anhydrous $CaCl_2$. All synthesized complexes have yellowish colour.

Polymer metal complexes of Gd (III) are obtained by the thermally initiated radical polymerization.

The polymerization was carried out in 10 wt.% dimethylformamide (DMF) solution of monomers with 2,2'-azobisisobutyronitrile (AIBN) as free radical initiator (1 wt.% with respect of monomers mass) at 353 K for more than 10 hours in the thermostat. The polymerization mixture was poured into methanol. The solid precipitate was filtered, dissolved in DMF, and reprecipitated into methanol and then dried at 293 K overnight.

Quantum-chemical calculations of molecules of ligands and metal complexes of Gd(III) were carried out: enthalpy of formation, total energy of the molecule and bond lengths, parameters of electronic population of ligands. The geometry of β-diketone molecules and gadolinium complexes was calculated using the MOPAC2016 program. The PM7 method was chosen for the calcula-

tion. The use of this method in combination with the SPARKLE model, in which the lanthanide atom is represented as a point charge,[22] allows obtaining reliable data on the geometry of lanthanide complexes with both aliphatic and aromatic ligands.

3. Results and Discussion

The values of enthalpies of formation of ligands are well correlated and depend on the nature of the substituents. The negative value of the heat of formation of ligand molecules indicates the exothermic process of their formation. The enthalpy value increases from -394.777 kJ/mol for dmokd ligand to -119.148 kJ/mol corresponding to mbphpd. Such a significant difference in the heats of formation is due to the different nature of the substituents in the ligand molecules. A larger dipole for molecules with aliphatic substituents dmokd and dmhpd (3.0289 and 2.985 Db) compared to aromatic ones - 2.179 and 2.336 Db for mphpd and mbphpd indicates asymmetric charge distribution. The biphenyl and phenolic substituents have a stabilizing effect on the molecule, as evidenced by the shorter bond length between the carbon atom of the β-diketone structure and the first atom of the radical. As expected, the negative charge in all ligands is concentrated on oxygen atoms. The results of the calculation of the energies of the highest filled molecular orbital (EHOMO) and the lowest vacant molecular orbital (ELUMO) indicate the electron-accepting properties of the ligands. They are better manifested in ligands with aromatic substituents (mphpd and mbphpd).

The lengths of the Ln-O bonds correlate quite well with those described in the literature, according to the results of X-ray diffraction analysis.[23] For the synthesized gadolinium complexes, the average length of the lanthanide–oxygen bond is approximately the same, ranging from 2.317 Å to 2.2353 for $Gd(dmokd)_3$ and $Gd(mphpd)_3$, respectively.

As a result of quantum chemical calculations, geometrically optimized molecules of gadolinium β-diketonate complexes were obtained (Fig. 2). The results showed that, regardless of the nature and geometric structure of the substituent in the β-diketone molecule, the complexes are characterized by a non-planar structure, the ligands are coordinated in a bidentate-chelate manner and are located in different planes. Complexes with aliphatic substituents are characterized by a more "rigid" structure.

IR spectra were recorded on a Specord M80 spectrometer in the range of 400-4000 cm^{-1} in KBr pellet.

As can be seen from Table 3, the shape and position of the bands in the IR spectra of monomeric, metal-polymer, and heteroligand compounds confirm the bidentate-chelate coordination of the ligands,[20, 22, 24] which is due

to the shape and position of the spectral lines in the region of 1400–1600 cm^{-1}. The oscillations in this part of the spectrum are assigned to $\nu_{as}(CC)$, $\nu_s(CC)$ and $\nu_{as}(CO)$, $\nu_s(CO)$. For heteroligand complexes, the presence of additional splitting is due to the band of the stretching vibration of the C-N bond, located in the region of 1590-1600 cm^{-1}.
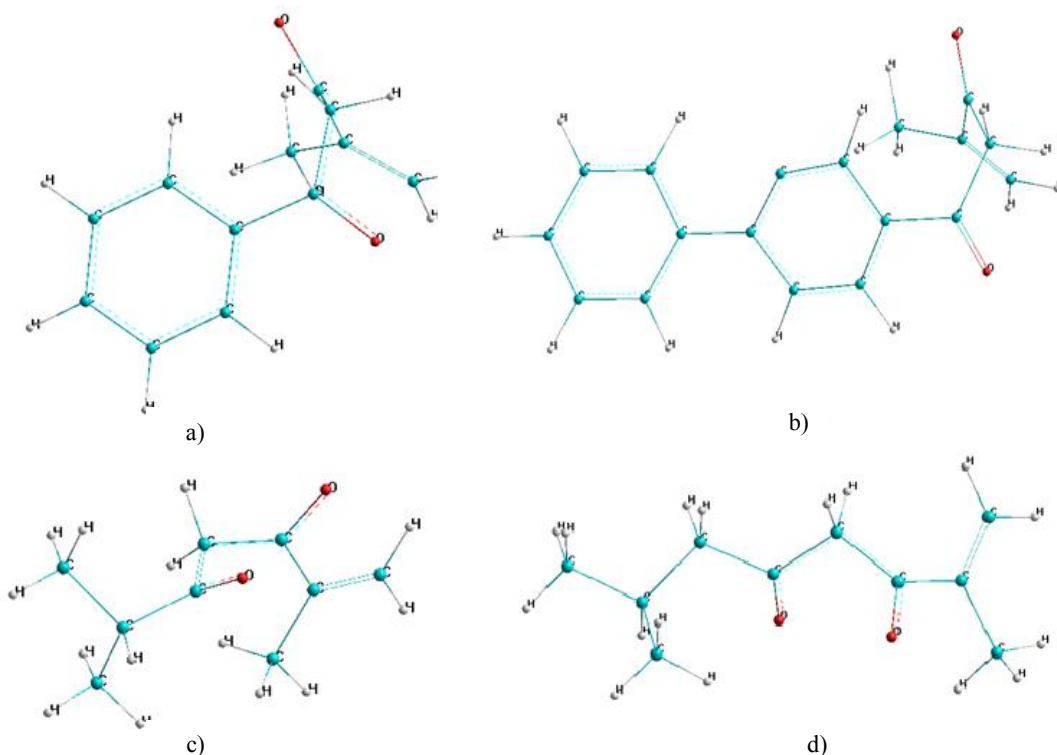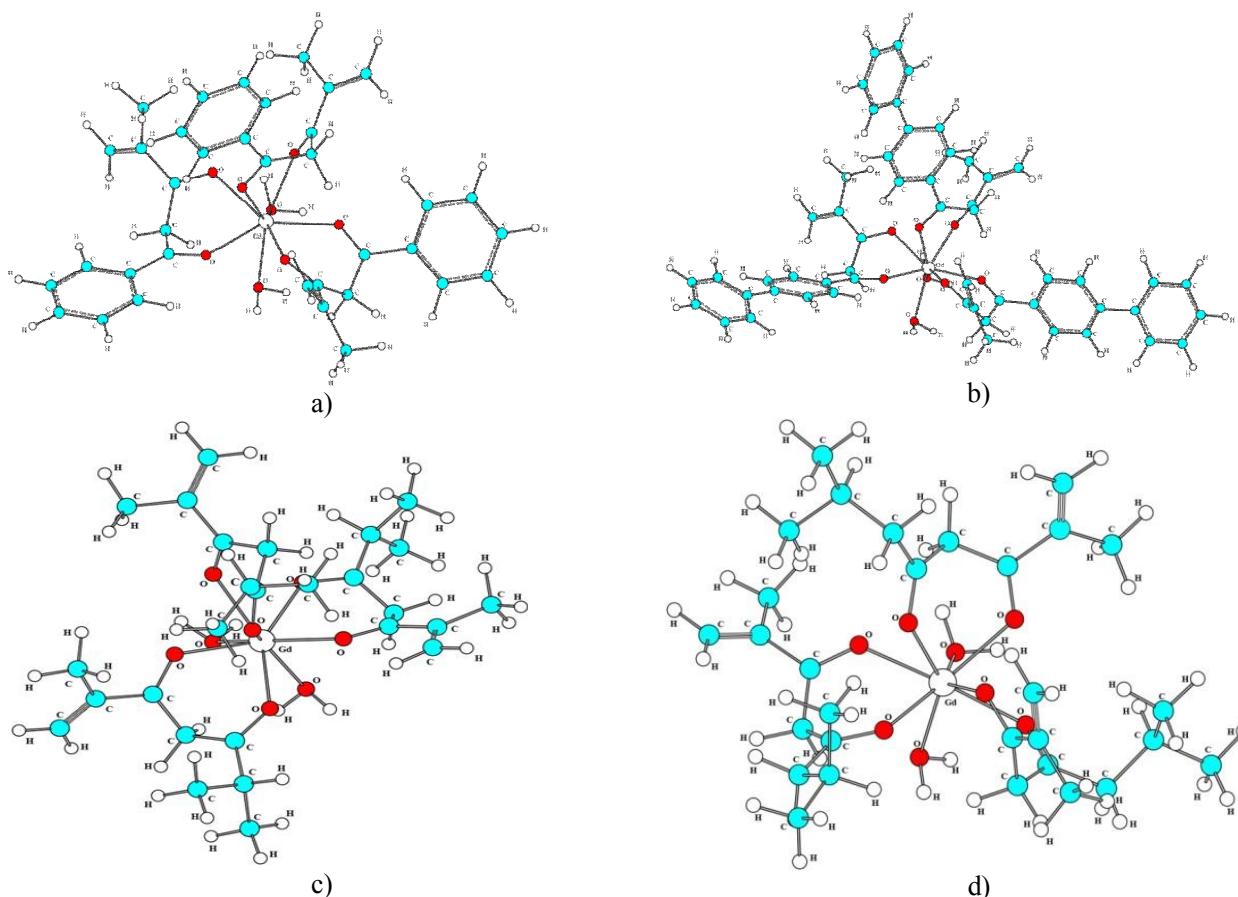

Fig.1. Geometrically optimized structural formulas of β-diketones (a – dmhpd, b – dmokd, c – mphpd, d – mbphpd)

Table 1. Characteristics of the structure and electronic population of β-diketone molecules

Calculation parameter	mphpd	mbphpd	dmhpd	dmokd
Total energy (eV)	-2225.898	-3001.148	-1885.182	-2035.239
Heat of formation (kJ/mol)	-187.341	-119.148	-364.273	-394.777
Dipole moment (debay)	2.179	2.526	2.985	3.0289
E_{homo}(eV)	-10.227	-9.561	-10.077	-10.186
E_{lumo}(eV)	-0.697	-1.061	0.101	0.408
Energy gap	9.53	8.5	9.976	9.778
Ionization potential (eV)	10.227	9.473	10.1858	10.186
Bond length (Å)				
C_{RCO} - R	1.48175	1.4824	1.50447	1.52279
C_{RCO} - O	1.20643	1.20565	1.20489	1.20395
$C_{RCO} - C_{CH2}$	1.50965	1.50799	1.51293	1.50654
$C_{CH2} - C_{CO}$	1.51066	1.5115	1.51581	1.51623
C_{CO} - O	1.20514	1.2051	1.20372	1.20522
$C_{CO} - C_{C-CH2}$	1.48905	1.4891	1.48876	1.48876
Atomic unit of charge:				
Q C_{RCO}/Q_{CR}	0.4832/-0.1651	0.4953/ -0.1693	0.5132 /-0.4014	0.4848/-0.1723
QC_{RCO} / QO	0.4832/-0.4296	0.4953/-0.4460	0.5132 /-0.4635	0.4848/ -0.4492
QC_{CH2} / QC_{CO}	-0.4988/ 0.4734	-0.501/0.4814	-0.5101 /0.4877	-0.5001 /0.4842
Q C_{CO} /QO	0.4734/-0.4309	0.4814/-0.4311	0.4877/-0.4319	0.4842/-0.4267
$QC_{CO} - QC_{C-CH2}$	0.4734/ -0.0605	0.4814/ -0.0406	0.4877/-0.0309	0.4842/-0.0727

Table 2. Parameters of gadolinium and dysprosium complexes

Estimated parameter	Gd(mphpd)₃	Gd(mbphpd)₃	Gd(dmokd)₃	Gd(dmhpd)₃
Total energy (eV)	-6675.884	-8230.603	-6746.124	-5653.835
Heat of formation (kJ / mol)	-105.962	-106.474	-742.875	-660.906
The dipole moment	0.696	0.576	0.695	0.479
E_{homo}(eB)	-9.249	-8.932	-9.343	-9.355
E_{lumo}(eB)	-0.548	-0.868	0.022	0.033
Energy gap	8.701	8.064	9.365	9.388
Ionization potential (eV)	9.249	8.931	9.343	9.354
Electron affinity (eV)	0.548	0.868	-0.022	-0.033
Hardness (eV)	4.3505	4.032	4.6825	4.694
Softness (eV)	0.23	0.248	0.213	0.213
Bond length l_{av} O-Ln (Å)	2.2355	2.2454	2.317	2.319

Fig. 2. Geometrically optimized structures of complexes Gd(mphpd)₃ –a, Gd(mbphpd)₃ – b, Gd(dmhpd)₃ – c, Gd(dmokd)₃ – d

In the region of 400-600 cm⁻¹, there are stretching vibrations of the M-O bond and bending vibrations of the chelate ring. In this region of the spectrum, a significant number of low-intensity bands is observed, which is due to the uneven distribution of the electron density in the chelate fragment and the different nature of the substituents. In heteroligand complexes, the Gd-O band is shifted to the low-frequency region compared to monoligand complexes. For complexes with nitrogen-containing donor molecules, the stretching vibration of the bond ν(Ln-N)=465-475 cm⁻¹. The shift in the position of the bands of metal polymers, as compared with monomers, to the low-frequency region indicates a weakening of the metal-ligand bond, which is due to an increase in the covalence of the M-O bond in the latter.

The broad band in the region of 3300–3400 cm⁻¹ corresponds to the stretching vibrations of ν(OH) of water molecules. High solubility in organic solvents, in particu-

lar DMSO, DMF, chloroform, excludes the formation of hydroxo complexes.

The diffuse reflectance spectra of the synthesized gadolinium compounds contain high-intensity bands in the region of 230-400 cm^{-1}, which can be attributed to $\pi \rightarrow \pi^*$ electronic transitions from the ground (S_0) to the excited state (S^1) of ligand molecules and charge transfer bands from the metal to ligand, but it is rather difficult to separate these bands. The charge transfer band lies in the long wavelength region of the spectrum above 280 nm. As can be seen from the figures, the shape and position of the bands depend on the nature of the substituents in the β-diketonate fragment and the nature of the complex itself. The main transitions of the gadolinium ion are observed in the UV region. In the case of the studied compounds, it is impossible to identify these bands, since charge transfer bands are present in this region. Therefore, it is impossible to identify

them for these compounds, since they are overlapped by an intense band of charge transfer from the metal to the ligand and $\pi \rightarrow \pi$ transitions of the ligand. In this case, the shape and position of the bands in this region significantly depends on the geometric structure of the ligands, the presence of additional ligands in the composition, and is different for polymeric and monomeric compounds. The replacement of the biphenyl substituent with an alkyl substituent causes a significant shift and expansion of the maximum, which is due to different energy characteristics of the studied ligand systems, which is consistent with quantum chemical calculations. The broadening of the bands is also observed upon passing from a monomer to a metal polymer, which is due to additional exchange interactions in polymer structures. The shift and position of the maxima in the SDR makes it possible to predict differences in the properties of these complexes.

Table 3. Characteristic frequencies in the IR spectra of Gd (III) complexes with β-diketones (cm^{-1})

| Complex	$\nu(Gd-O)$ $+\delta_{chel.ring}$	$\nu_{as}(CO)$	$\nu_{as}(CC)$	$\nu_s(CO)$	$\nu_s(CC)+$ $\nu_s(CPh)$	$\nu(H_2O)$
Gd(dmhpd)$_3$	415,420,433, 473, 518	1440	1540, 1557	1595	1645, 1652	3350
[Gd(dmhpd)$_3$]$_n$	412, 425, 490, 515	1445	1550	1590	1658	3380
Gd(dmokd)$_3$	455, 462, 478, 490, 514	1405	1540, 1560	1612	1675	3430
[Gd(dmokd)$_3$]$_n$	455, 470, 485,500, 520	1400	1550	1605	1670	3430
Gd(mphpd)$_3$	415,420,433, 473, 518	1440	1540, 1557	1595	1645, 1652	3350
[Gd(mphpd)$_3$]$_n$	412, 425, 490, 515	1445	1550	1590	1658	3380
Gd(mbphhd)$_3$	455, 462, 478, 490, 514	1405	1540, 1560	1612	1675	3430
[Gd(mbphhd)$_3$]$_n$	455, 470, 485,500, 520	1400	1550	1605	1670	3430

a)

b)
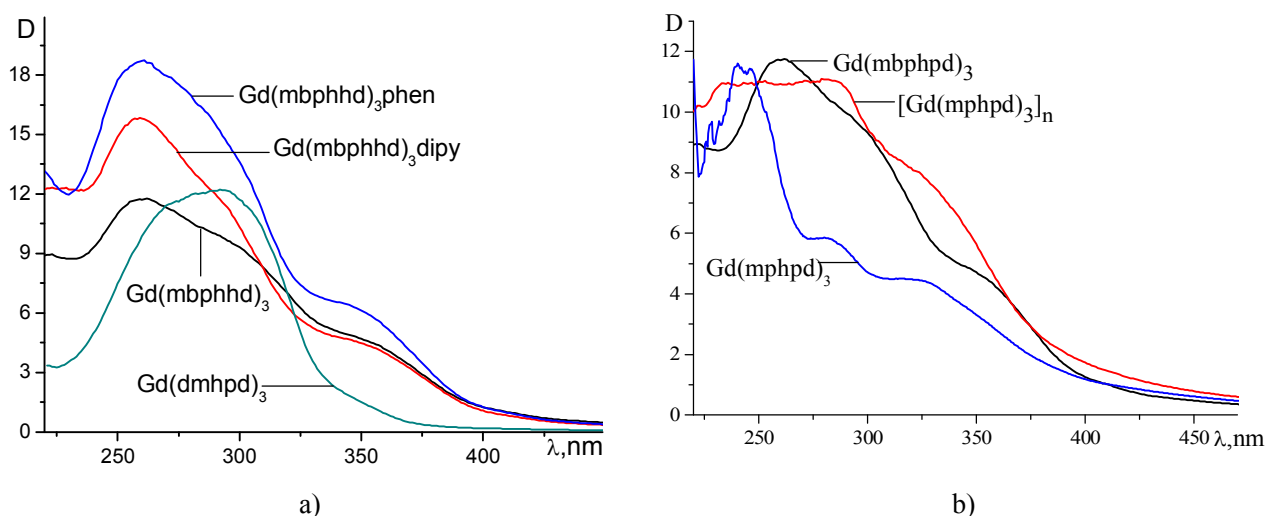
Fig. 3. Diffuse reflectance spectra of mono- and heteroligand complexes of gadolinium

Based on quantum chemical calculations, preliminary studies of similar complexes of europium, neodymium, samarium and the isomorphism of gadolinium complexes to them,[22][24] the results of chemical and thermal

analysis, IR and electron spectroscopy, we can state that monomer and polymer complexes are characterized by no cubic symmetry of the field of ligands, c.n.=8, coordination polyhedron is a square antiprism. The similarity of

the spectral characteristics of monomeric, heteroligand and metallopolymeric complexes allows us to assume the following structure of the compounds:
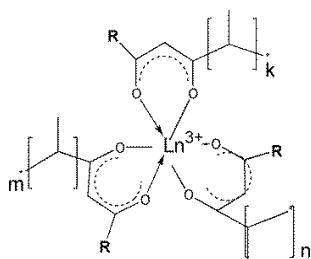
Ln = Gd^{3+} R=, -C$_6$H$_5$; C$_{12}$H$_9$; -CH(CH$_3$)$_2$; -CH$_2$CH(CH$_3$)$_2$

To determine the energy of singlet and triplet levels of ligands, it is more correct to record the fluorescence and phosphorescence spectra of gadolinium-containing complexes (Figs. 4, 5). The excitation and luminescence spectra of solid complexes were recorded on a spectrofluorimeter Fluorolog FL 3-22, Horiba Jobin Yvon (Xe-lamp 450 W) with a light filter OS 11, with their subsequent adjustment taking into account the radiation distribution of the xenon lamp and the sensitivity of the photomultiplier tube. The InGaAs (DSS-IGA020L, Electro-Optical Systems, Inc, USA) photoresistance was used as a radiation receiver for the IR region when cooled to liquid nitrogen temperature.

The energy of the ligands can be determined by recording the fluorescence (Fig. 4) and phosphorescence spectra of gadolinium complexes, which is due to the high position of the resonance level of Gd^{3+} (32000 cm^{-1}) compared to the triplet level of the ligand, which prevents the transfer of energy from the organic part of the complex to the lanthanide ion.

The position of the maxima in the phosphorescence spectra of monomer and metal-polymer complexes of gadolinium (Fig. 5) indicates slight differences in the energies of the triplet level of the monomer and metal-polymer. Thus, polymerization leads to an increase in the energy of the triplet and singlet levels of ligands for aromatic systems and a decrease for aliphatic ones. This is due to the delocalization of the electron density in the ligand molecules (Table 4).
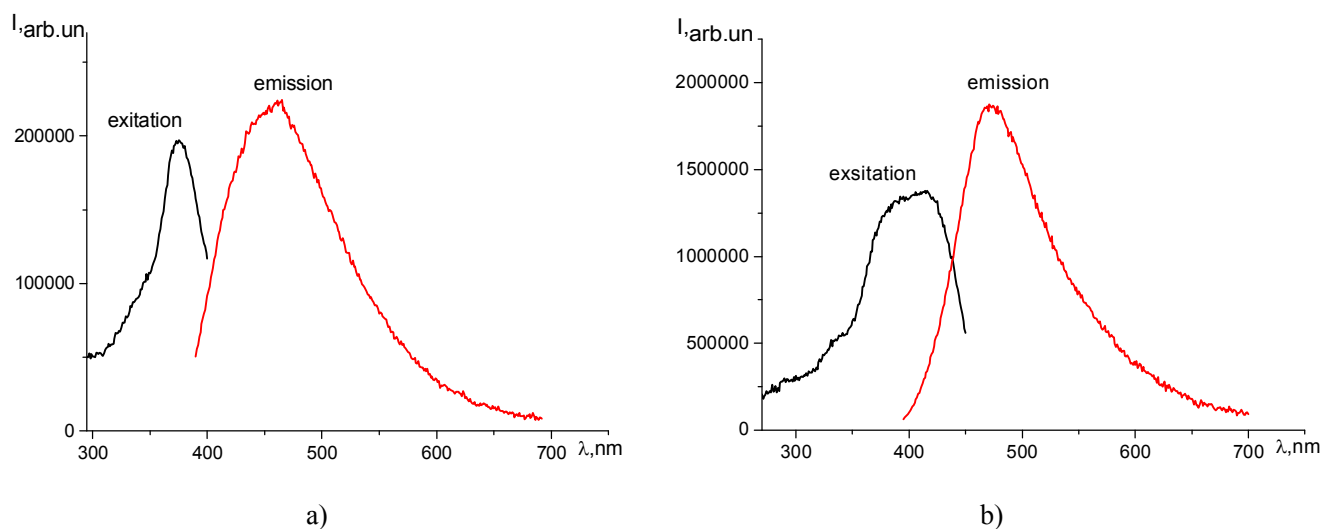

a)

b)

Fig. 4. Excitation and emission spectra of monomeric (a) and metallopolymeric (b) complexes of gadolinium (III) based on 2,6-dimethyloctene-1-3,5,-dione

Table 4. Calculated energies of the triplet levels of the studied ligand systems

Ligands	E$^{T}_{monomer}$, cm^{-1}	E$^{S}_{monomer}$, cm^{-1}	E$^{T}_{polymer}$, cm^{-1}	E$^{S}_{polymer}$, cm^{-1}
Dmhpd	21200	21550	18800(17700)	21000
Dmokd	19340	21645	18940	21230
Mphpd	19500*	22120	20800*	23200
Mbphpd	19960*	21800	21300*	23430

*[22]

In addition, it should be expected that such changes will cause different emission properties of monomeric and polymeric systems. For example, it was previously established that for the coordination compounds of europium and samarium with ligand systems containing aromatic substituents, the maximum emission intensity is characteristic of metal polymers. This is due to the optimal energy difference between the triplet level of the ligand and the resonant level of the lanthanide. Taking into account the given values of the energies of the triplet levels of ligands with aliphatic substituents, it can be assumed that polymerization will cause a decrease in the relative emission intensity of metal complexes.

Studies of the luminescent properties of gadolinium coordination compounds make it possible not only to determine the energy characteristics of ligand systems, but also to predict the emission efficiency of a number of metal complexes and metal polymers. Thus, additional donor ligands and polymerization make it possible to purposefully change the emission characteristics of the synthesized compounds.

As shown earlier,[22, 24] the fineness of the synthesized materials has a significant effect on the emission properties; however, there is no general pattern for the entire series of lanthanides; it depends on many factors. These include the electronic structure of the lanthanide ion, the energy of the triplet level of the ligand, and the excitation and emission wavelengths. As can be seen from the micrographs and distribution diagrams in Fig. 6,7 all studied compounds are nano dispersed systems. The particles are characterized by a spherical shape, and the existing deformation is due to partial agglomeration under the influence of electromagnetic radiation. The different nature of the substituents in the ligand molecules also has a decisive influence on the morphology and dispersity. Comparing micrographs and distribution diagrams of monomeric and polymeric samples, we observe certain agglomeration processes (Figs. 6, 7).
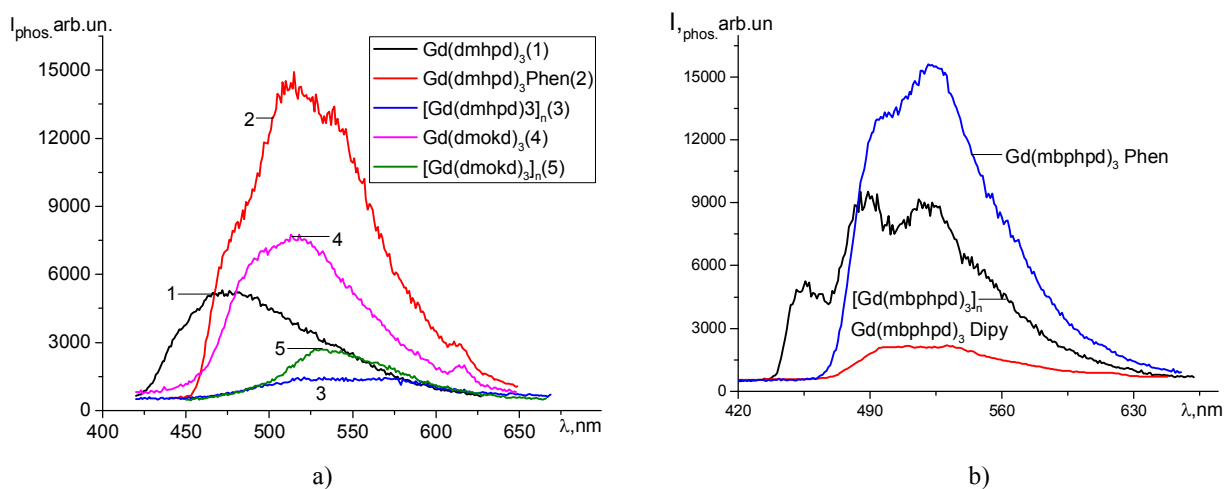

a)   b)

Fig. 5. Phosphorescence spectra of gadolinium complexes
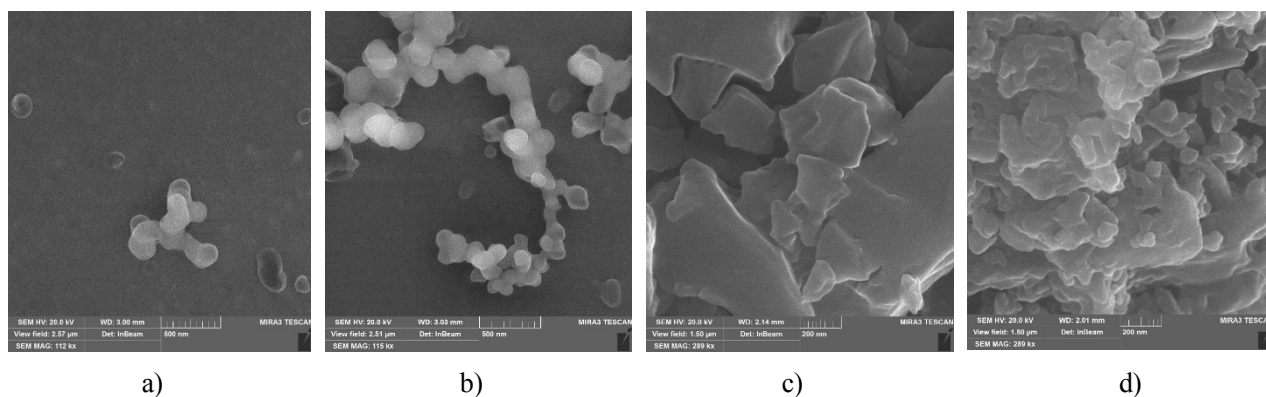with aliphatic (a) and aromatic (b) substituents, T=77K λ_{ex}=380nm

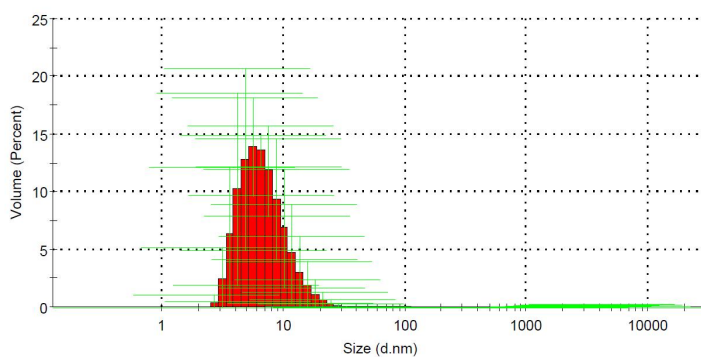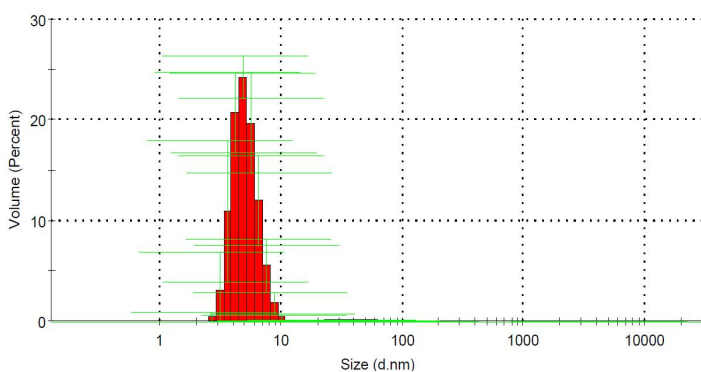

a)   b)   c)   d)

Fig. 6. SEM microphotographs a – Gd(dmokd)$_3$, b – [Gd(dmokd)$_3$]$_n$, c – Gd(mphpd)$_3$, d – Gd(mbphpd)$_3$, scale mark solution –
500 nm (a, b), powder – 200 nm (c, d)

a)

b)

Fig. 7. DLS analysis a – Gd(dmokd)$_3$, b – [Gd(dmokd)$_3$]$_n$

Comparative analysis of micrographs of powders of complexes with different ligands showed that monomeric, metalpolymer, and heteroligand complexes based on dmokd and dmhpd are characterized by the formation of spherical particles. The deformation of the latter is due to both agglomeration and solvation effects. The nature of the substituent in the α-position of the β-diketone has a significant effect not only on the dispersity, but also on the surface morphology. The compounds based on mphpd and mbphpd are characterized by the formation of layered, but ordered structures. On the one hand, this has a positive effect, since a clear organization is noticeable, and on the other hand, such structures reduce the freedom of independent translational movement of molecules. Therefore, the emission efficiency depends not only on the nature of the ligand, but also on the electronic structure of the c.i. lanthanide, in particular, on the energy of its resonant level.

4. Conclusions

Studies of mono and heteroligand complexes of gadolinium and metal polymers based on them have been

carried out. The introduction of substituents of different nature (aliphatic or aromatic) into the α-position of the β-diketone has a significant effect on the energy characteristics of both the ligands themselves and the metal complexes based on them. It has been established that, depending on the nature of the substituent in the β-diketonate fragment, not only the polymerization rate, but also its efficiency is different. This manifests itself in the difference between the energies of triplet and singlet levels of monomeric and polymeric systems. Obviously, depending on the nature of the substituent in the ligands, there is a different redistribution of partial charges on the double bond, which is revealed during polymerization, and, accordingly, different activity of the monomer in the polymerization reaction. The activity of a monomer in radical polymerization will be the greater, the more stable the radical corresponding to it will be. For aliphatic substituents, compared to aromatic substituents, a less stable radical is formed, and this affects the kinetic parameters of the radical polymerization process and the characteristics of the resulting polymer. For aromatic substituents, the increase in the energy of the triplet level of polymeric ligands (mphpd, mbphpd) compared to monomeric ones,

their morphology and dispersion indicates the possibility of effective energy transfer for complexes emitting in the visible spectral range (Eu, Sm, Tb, Pr). The emission intensity increases with the transition from monomer to metal-polymer complexes. This is due to the optimal energy gap between the triplet level of the ligand and the resonance level of the lanthanide ion. In addition, the formation of polymer structures contributes to the reduction of entropy and the leveling of concentration quenching processes, which in turn has a positive effect on the luminescence of metal complexes. At the same time, a decrease in the energy of the triplet levels of polymeric *dmhpd* and *dmokd* compared to monomeric ones will cause a decrease in the relative intensity of luminescence due to a slight difference in the energies of the triplet and resonance levels, as well as a lower polymerization efficiency, which is due to the rapid chain breakage and, probably, the formation of several oligomeric forms of metal complexes. Low symmetry of oligomers will cause a decrease in emission properties. At the same time, in the emission spectra, the splitting of bands characteristic of the presence of several emitting centers can be observed. Therefore, when synthesizing emissive materials for ligands containing aliphatic substituents in the α-position, it is optimal not to use metallopolymers, but monomeric mixed oligoligand complexes. Thus, when choosing ligand systems for the creation of new emission materials, a number of factors must be taken into account: the nature of the substituent, dispersion and morphology, energy characteristics. The conducted studies showed that despite the lack of general regularities of the effect of synthesized ligand systems on emission, they are effective precursors of luminescent materials based on lanthanide complexes.

Data Availability

The authors declare that the data supporting the findings of this study are available within the article.

Conflict of Interest

The authors declare that there is no conflict of interest regarding the publication of this article.

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ДОСЛІДЖЕННЯ КООРДИНАЦІЙНИХ СПОЛУК ГАДОЛІНІЮ (III) З β-ДИКЕТОНАМИ

Анотація. *Синтезовано нові координаційні сполуки гадолінію з* β-*дикетонами, що містять ненасичені та аліфатичні або ароматичні замісники в* α-*положеннях хелатного циклу. Проведені квантово-хімічні розрахунки молекул лігандів свідчать про кращі акцепторні властивості лігандів з ароматичними замісниками. Аналіз ІЧ-спектрів та квантово-хімічних розрахунків металокомплексів свідчить про бідентатно-хелатну координацію молекул ліганду та їх розташування в різних площинах незалежно від природи та геометричної структури замісника в молекулі* β-*дикетону. Розраховано енергії триплетних рівнів лігандів. Вивчено морфологію та дисперсність синтезованих комплексів металів.*

Ключові слова: *лантаноїди, координаційні сполуки, люмінесцентні властивості, металополімер, гадоліній,* β-*дикетони.*