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Ab Initio Study of Energy Transfer Pathways in Dinuclear Lanthanide Complex of Europium(III) and Terbium(III) Ions

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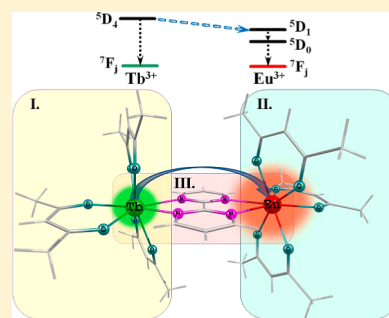
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S Supporting Information

ABSTRACT: An ab initio XMCQDPT2/CASSCF study of energy transfer processes in the dinuclear lanthanide complex $[(\text{Acac})_3\text{Eu}(\mu\text{-Bpym})\text{Tb}(\text{Acac})_3]$ (Acac is acetylacetonate, and Bpym is 2,2'-bipyrimidine) and a corresponding computational procedure are presented. Because ligands in lanthanide complexes weakly interact with each other, the large dinuclear complex bearing seven organic ligands is divided into fragments that reproduce the electrostatic effects of the ions on the electronic and geometrical structure of the ligands. The multireference XMCQDPT2/CASSCF approach is directly applied to these relatively small fragments with reasonable computational cost. The calculated energies of the singlet and triplet excited states agree well with the experiment. Based on the calculated energies, the energy level diagrams of the complex are constructed and intramolecular energy transfer channels are determined.



1. INTRODUCTION

Lanthanide complexes are known for their remarkable emission properties: significant lifetimes, large Stokes shifts, and narrow emission bands, which correspond to the characteristic $f-f$ transitions in the inner $4f$ shell of Ln^{3+} shielded from the influence of the environment by the outer $5s$ and $5p$ shells. The radiative transition in Ln^{3+} ions is parity-forbidden;¹ therefore, their own absorbance is very weak. The radiation efficiency of the Ln^{3+} complex is mainly governed by its strongly absorbing ligands: a ligand absorbs light in the ultraviolet region and transfers energy from its triplet excited level to the resonant level of the ion, which can emit light or decay nonradiatively. This phenomenon is called the “antenna effect”.²

The Ln^{3+} emission covers all the spectral range from UV to visible and near-infrared wavelengths (0.3–2.2 μm). Because of the narrow width of their emission lines, Ln^{3+} compounds are used in optical electronic devices, light-emitting devices,^{3,4} displays, optical fibers,⁵ lasers,⁶ solar cells, and other light sources.⁷ A deep insight into the nature and main features of energy transfer in lanthanide complexes is essential in order to predict materials with low energy loss and high radiation efficiency.

Liquid-crystalline adducts of lanthanides with β -diketones and Lewis bases exhibit high luminescence efficiency and high anisotropy of magnetic susceptibility.^{8–10} One of the most interesting properties of these thermally stable liquid-crystalline complexes is their ability to align in various directions and at any angle in external electric or magnetic fields. They also show

the nematic phase, which is stable at room temperature and has the lowest viscosity of all types of mesophases, and the easiest alignment in external electric or magnetic fields.

At present, considerable attention is paid to the study of dinuclear lanthanide complexes, which exhibit enhanced emission efficiency in comparison with mononuclear complexes with the same ion and similar ligands.^{11–14} Among them, there are complexes that contain only lanthanide ions and those containing a lanthanide ion and some transition element (Cu, Zn, Ru, Re, Ir, or Pt).^{15–20} The presence of a transition metal ion not only enhances lanthanide luminescence but also imparts some interesting magnetic properties to the complex. Dinuclear complexes with different ions are used to enhance the luminescence of a certain ion. For example, in terbium-containing complexes, Tb^{3+} receives excitation energy from the ligands and transfers it to the other ion. Gadolinium ions do not participate in the energy transfer process but they provide better energy transfer through the bridged atoms and groups to the nearby Ln^{3+} .¹³

Chemically stable β -diketones, which have high molar absorptivities, are the most widespread ligands used in the synthesis of lanthanide complexes.^{21,22} 2,2'-Bipyrimidine (Bpym) (see ref 23 and references therein) is used in lanthanide

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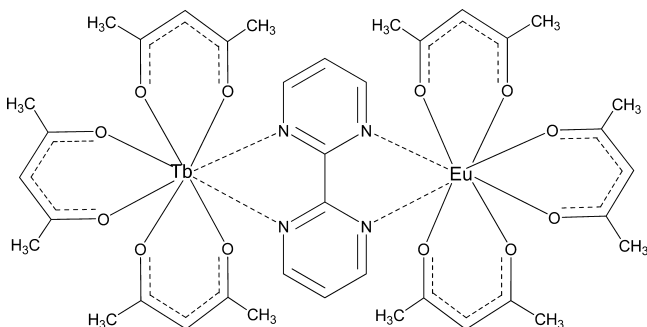
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chemistry due to its ability to act as a terminal or a bridging ligand for the lanthanides. This can lead to a wide variety of structures (monomeric, oligomeric, or polymeric) and to interesting magnetic properties and photophysics of the resulting compounds. In addition, Bpym can act as a sensitizer for visible-emitting Ln^{3+} ions.

In this work, we study a dinuclear complex of Eu^{3+} and Tb^{3+} with 2,2'-bipyrimidine and one of the simplest representatives of β -diketones, acetylacetonate (Acac) (Chart 1).

Chart 1. Chemical Structure of $[(\text{Acac})_3\text{Eu}(\mu\text{-Bpym})\text{-Tb}(\text{Acac})_3]$



It was found that the emission efficiency of lanthanide complexes correlates with the energy of the lowest triplet state of the ligands. Later, it was confirmed by further experiments and calculations.^{24,25} Commonly, the energy gap between the lowest triplet level of the ligand and the emitting level of Ln^{3+} remained the prime factor used in discussions and diagnostics of energy transfer processes in such compounds.^{26,27} However, photoexcitation of Ln^{3+} is a complex multistage process involving several mechanisms and rate constants.^{28,29}

Malta and co-workers developed a computational procedure to completely describe the light absorption by ligand environment in Ln^{3+} complexes and to calculate the energy transfer rates and theoretical quantum yields.^{28,30} They considered contributions from the dipole- 2^1 -pole, dipole-dipole, and exchange mechanisms to energy transfer from the excited ligand levels to the resonant levels of Ln^{3+} . However, this model is based on the use of semiempirical quantum-chemical data,^{31–34} which results in inaccurate values and dependence of the results on the parametrization.

Multireference ab initio methods were successfully used to describe triplet excited states in Ln^{3+} complexes and to estimate the efficiency of antenna ligands for Ln^{3+} complexes.³⁵ The proposed approach is more accurate and qualitatively correct than semiempirical and DFT methods.^{36–38} Multireference methods make it possible to treat singlet and triplet states with equal accuracy, which is crucial for further calculations of spin-orbit coupling matrix elements and corresponding rate constants.

There are only few theoretical studies of dinuclear lanthanide complexes. Their structure was simulated using the semiempirical³⁹ and density functional^{14,40} methods. The CASSCF method was used for the calculations of spin orbit, ligand field, and exchange effects.⁴¹ Density functional theory^{18–20,42,43} and wave function-based approaches (CASSCF, CASPT2, MS-CASPT2)⁴⁴ were successfully applied to study the structures and magnetic properties of dinuclear complexes with Ln^{3+} and transition metals (Fe, Cu, Co, Ni, Mn, V). However, theoretical results related to an investigation of the nature of their excited states are very limited.

In the present work, we use ab initio methods to study triplet excited states in a heterodinuclear complex $[(\text{Acac})_3\text{Eu}(\mu\text{-Bpym})\text{-Tb}(\text{Acac})_3]$. We present a computational technique that allows excited states in dinuclear lanthanide complexes to be studied ab initio, energy-transfer channels upon photoexcitation to be analyzed, and the role of the bridging ligand in the ion-to-ion energy transfer to be elucidated. The role of each component of the complex in this process is revealed, and the way of predicting photophysical properties of dinuclear lanthanide complexes, including liquid-crystalline ones, since there are no examples of liquid-crystalline lanthanide complexes with β -diketones and Lewis bases.

Energy Transfer Processes in Lanthanide Complexes.

Let us compare photoexcitation and light emission processes in mononuclear and dinuclear Ln^{3+} complexes. Upon photoexcitation of a mononuclear Ln^{3+} complex (for example, Eu^{3+} complex in Figure 1), a singlet excitation is localized on an

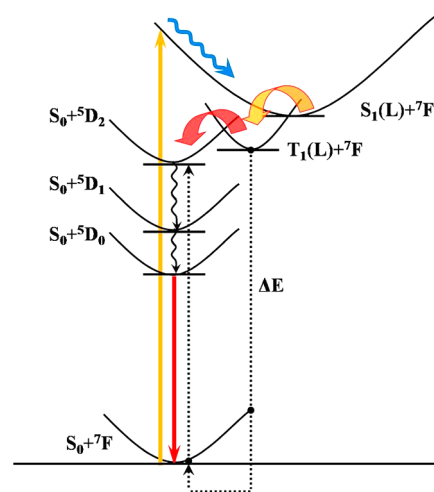


Figure 1. Energy transfer process in the mononuclear Eu^{3+} complex.

antenna ligand (orange arrow). The coincidence between the experimental absorption and excitation spectra of Ln^{3+} complexes with the corresponding spectra of the individual ligands indicates that the lowest excited states are localized on individual ligands rather than delocalized over them.^{45–47} Subsequent fast non-radiative relaxation due to internal conversion (blue wavy arrow) leads to the bottom of the potential well of the lowest singlet state. The molecule can stay for a while in this geometrical configuration and deactivate by fluorescence, internal conversion, or intersystem crossing to the nearest triplet state (orange block arrow). Then it can quickly relax nonradiatively to the local minimum of the lowest triplet state. Finally, at this particular geometrical configuration, energy transfer to Ln^{3+} occurs (red block arrow). Structure relaxation in the singlet or triplet state takes $\sim 10^{-10}$ – 10^{-14} s, which is comparable to the molecular vibration period and is several orders of magnitude faster than the energy transfer process (10^{-6} – 10^{-10} s).^{48,49} It is important to note that energy transfer occurs from the lowest triplet excited state of the ligand.^{24,25,45,47,50} Next, the excited ion nonradiatively relaxes to the lowest radiative level (black wavy arrows) and emits a photon (red arrow). Hence, there are two rate-determining stages in the energy transfer process: singlet-triplet conversion of the excited ligand and ligand-to-metal energy transfer. Therefore, the emission of Ln^{3+} is governed by the relative position of the triplet and singlet excited states of the ligands and the resonant levels of the ion.

Energy transfer in dinuclear lanthanide complexes occurs by the same “antenna” mechanism. The most interesting case is the dinuclear complex with different ions, for example, europium(III) and terbium(III) (Figure 2). Similarly to mononuclear complexes,

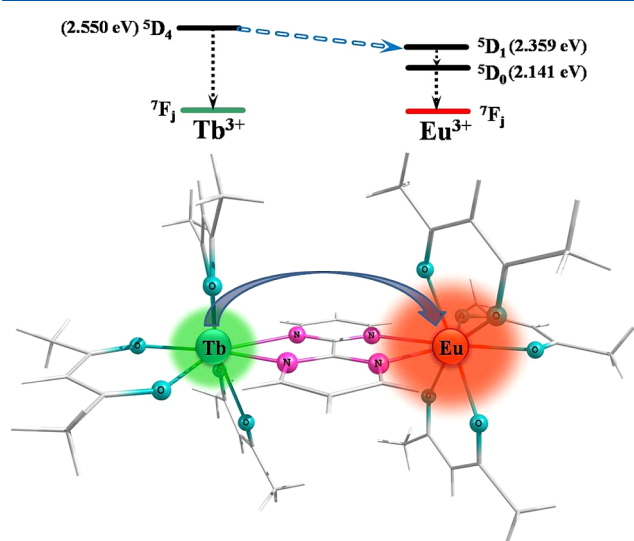


Figure 2. Energy transfer process in the dinuclear complex of Eu^{3+} and Tb^{3+} .

Tb^{3+} and Eu^{3+} receive energy from the ligands. However, up to a 70% increase in the emission efficiency in the dinuclear system in relation to the mononuclear complex with the same ion and ligands should originate from some other mechanisms.¹¹

In the case of a mononuclear complex, the ligands are usually selected for a particular ion. However, the ligands in a dinuclear complex can match only one of the ions because it is almost impossible to synthesize a complex with ligands matching each ion individually. For example, in the complex $[(\text{Acac})_3\text{Eu}(\mu\text{-Bpym})\text{Tb}(\text{Acac})_3]$ (Chart 1), the triplet level of Acac ligand (3.138 eV)^{51,52} is in resonance with the radiative $^5\text{D}_4$ level (2.550 eV) of Tb^{3+} . At the same time, Acac is not the optimal choice for Eu^{3+} with the nearest resonant level $^5\text{D}_3$ (3.024 eV).^{53,54} Energy transfer from the Acac triplet level to the $^5\text{D}_3$ level of Eu^{3+} is followed by nonradiative energy transfer between j multiplets of the $^5\text{D}_j$ state. It leads to an energy loss and reduces the radiation efficiency. In $[(\text{Acac})_3\text{Eu}(\mu\text{-Bpym})\text{Tb}(\text{Acac})_3]$, Eu^{3+} receives energy not only from the organic ligands of the complex, but also from Tb^{3+} , whose radiative levels lie above the levels of Eu^{3+} (energy transfer from $^5\text{D}_4$ multiplet of terbium to $^5\text{D}_1$ of europium) (Figure 2).

Thus, in a dinuclear complex with different rare earth ions, energy transfer from one ion to another leads to a lanthanide emission enhancement with a lower emission energy.^{11–13} This is supported by the experimental data. Emission bands that correspond to the donor ion have lower intensity than the bands of the acceptor ion. In addition, a remarkable decrease in the Tb^{3+} lifetime has been noticed, while the lifetime of Eu^{3+} slightly increased.^{55,56}

The role of the bridging ligand, Bpym, is not clear. The authors of ref 57 studied Tb^{3+} complexes with Bpym and Hfa (hexafluoroacetylacetonate). They state that Bpym $\pi\text{--}\pi^*$ transitions are too high in energy (5.21 eV for singlet and 4.46 eV for triplet, respectively) and, therefore, play a minor role in the excitation of Tb^{3+} complexes. However, Hfa has lower triplet energy than Acac. In the case of Acac complexes, Bpym

can probably compete with β -diketone for pumping Tb^{3+} . In addition, the triplet energy of Bpym can be adjusted by chemical substitution in the pyrimidine ring.

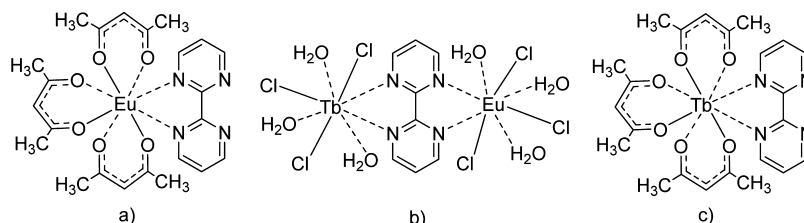
According to refs 4 and 58, when the energy level of the donor ion has a smaller lifetime and a higher energy at room temperature, energy transfer between rare earth ions occurs by the multipolar resonant interaction. The typical distance between two ions in the complexes with Bpym as a bridge is $\sim 7 \pm 0.2$ Å, which is sufficient for multipolar resonance energy transfer, but is too long for any other mechanism. It was also mentioned that better emission properties could be achieved in lanthanide systems with similar ionic radii (r_{ion}). In most systems, energy transfer occurs from terbium ($r_{\text{ion}} = 0.092$ nm) and lanthanum ($r_{\text{ion}} = 0.103$ nm) levels to the levels of europium ($r_{\text{ion}} = 0.095$ nm) or samarium ($r_{\text{ion}} = 0.096$ nm) ions.⁵⁹ Hence, Tb^{3+} acts as a “bridge” between the organic ligands of the complex and Eu^{3+} . Therefore, careful selection of the second ion in addition to the ligands can lead to the emission enhancement for the desired Ln^{3+} .

2. COMPUTATIONAL TECHNIQUE

The excited states of Ln^{3+} complexes are quasi-degenerate (the energy gap between them is about 0.1 eV); therefore, they should be treated with multireference methods. Similarly to our previous paper,³⁵ we used XMCQDPT2/CASSCF method.^{60–62} Unlike density functional-based methods, this method correctly predicts excitation localization. Since structural relaxation is faster than energy transfer (see above), the geometry of each excited state should be optimized.

The inner 4f shell of a Ln^{3+} ion is shielded from the environment by the 5s and 5p shells; it is localized near the nucleus and only slightly interacts with the ligands. This is supported by the fact that the observed 4f–4f emission bands are rather narrow and nearly coincide for different compounds of a given lanthanide.^{1,3} Therefore, the ligand-field effects on the 4f states are negligible, and there is no need to perform ab initio calculations for 4f levels of Ln^{3+} , as they can be easily obtained from the experimental data.⁵⁴ Hence, we used scalar quasirelativistic 4f-in-core pseudopotentials (ECP52MWB for Eu^{3+} ion, ECP53MWB for Gd^{3+} ion, and ECP54MWB for Tb^{3+} ion), which were specially developed to describe the Ln^{3+} ions with fixed f -shell occupations, with the associated valence basis sets.^{63,64} For other atoms we used the 6-31G(d,p) basis set, as the standard nonrelativistic approximation is sufficient for the light atoms. All the calculations were performed using the Firefly software⁶⁵ partially based on the GAMESS code.⁶⁶

However, the dinuclear complex $[(\text{Acac})_3\text{Eu}(\mu\text{-Bpym})\text{Tb}(\text{Acac})_3]$ includes seven organic ligands and the minimum active space for CASSCF calculations is (14,14): one HOMO and one LUMO from each β -diketone and 2,2'-bipyrimidine. This makes this task rather resource-intensive. We suppose that it is not necessary to consider the entire complex. Because all the excitations in such complexes are localized on individual ligands,^{36,45,47} the dinuclear complex can be divided into several parts (Chart 2): $\text{Eu}(\text{Acac})_3\text{Bpym}$, $\text{Tb}(\text{Acac})_3\text{Bpym}$, and the central part of the complex is represented by $[(\text{H}_2\text{O})_3\text{Cl}_3\text{Eu}(\mu\text{-Bpym})\text{Tb}(\text{H}_2\text{O})_3\text{Cl}_3]$, which simulates both of the lanthanide ions surrounding Bpym and their coordination spheres. The central bridging ligand Bpym, which connects two ions is of special interest. The coordination spheres of Ln^{3+} ions in this complex were filled with photochemically inactive chloride ions and water molecules in order to avoid artifacts. We calculated the triplet excited states of Acac and Bpym connected to

Chart 2. Model Complexes: Eu(Acac)₃Bpym (a), [(H₂O)₃Cl₃Eu(μ-Bpym)Tb(H₂O)₃Cl₃] (b), and Tb(Acac)₃Bpym (c)Table 1. Vertical Energies (eV) in Gd³⁺ Complexes in the Ground-State and Optimized-Triplet Geometries Compared to the Experimental Data

complex	active space	multiplicity	ΔE_{theor} eV	ΔE_{exp} eV
Gd(H ₂ O) ₃ Cl ₃ Bpym (S ₀)	(4;4)	3	3.863	—
		1	4.544	
Gd(H ₂ O) ₃ Cl ₃ Bpym* (T ₁)	(4;4)	3	2.810	2.988 ^{67–69}
		1	4.165	
Gd ₂ (H ₂ O) ₆ Cl ₆ (μ-Bpym) (S ₀)	(4;4)	3	4.091	—
		1	5.142	
Gd ₂ (H ₂ O) ₆ Cl ₆ (μ-Bpym*) (T ₁)	(4;4)	3	2.897	2.988 ^{67–69}
		1	4.063	
Gd(Acac) ₃ (H ₂ O) ₂ (S ₀)	(6;6)	3	3.894	—
		1	3.932	
		3	4.002	
		3	4.043	
Gd(Acac) ₂ Acac*(H ₂ O) ₂ (T ₁)	(6;6)	3	3.095	3.138, ^{51,52} 3.224, ⁷⁰ 3.174 ⁷¹
		1	3.410	
		3	4.122	
		3	4.193	

Eu³⁺ and Tb³⁺ and the triplet excited states of Bpym connected simultaneously to Eu³⁺ and Tb³⁺.

The geometries of the complexes in the ground and triplet excited states were optimized by the state-specific CASSCF. The vertical triplet and singlet excitation energies were calculated at the optimized geometries using the state-averaged CASSCF and corrected by XMCQDPT2. XMCQDPT2 calculations were performed separately for singlet and triplet excited states.

The active space for CASSCF calculations of Eu(Acac)₃Bpym and Tb(Acac)₃Bpym included one HOMO and one LUMO from each Acac and Bpym (CASSCF(8,8)). In SA-CASSCF calculations, we studied four singly excited singlet states plus S₀ or four singly excited triplet states. In XMCQDPT2 calculations, we used the effective Hamiltonian spanned by 34 lowest states (including the S₀ state) in the case of the singlets and 34 lowest states in the case of triplets.

The active space for CASSCF calculations of the dinuclear [(H₂O)₃Cl₃Eu(μ-Bpym)Tb(H₂O)₃Cl₃] included two HOMOs and two LUMOs from Bpym (CASSCF(4,4)). In SA-CASSCF calculations, we considered two singly excited singlet states plus S₀ and two singly excited triplet states. The effective Hamiltonian in XMCQDPT2 was spanned by 15 lowest states (including the S₀ state) in the case of singlets and 15 lowest states in the case of triplets.

To verify the accuracy of the calculated triplet energies, we also studied some model complexes from Table 1. The effective Hamiltonian in XMCQDPT2 was also spanned by 15 lowest states (plus the S₀ state) in the case of singlets and 15 lowest

Table 2. Experimental and Theoretical Transition Energies (eV) of 2,2'-Bipyrimidine⁶⁷

Bpym position	ΔE_{exp} (S ₀ →S ₁)	ΔE_{exp} (S ₁ →S ₀)	ΔE_{theor} (T ₁ →S ₀)	ΔE_{exp} (T ₁ →S ₀)
terminal	4.980	4.110	2.980	2.810
bridging	4.670–4.910 4.58 ⁷²	—	2.900	2.897

Table 3. Vertical Energies (eV) in Eu³⁺ and Tb³⁺ Complexes in the Ground-State and Optimized-Triplet Geometries with the Reference of the Excited State Localization

complex	active space	multiplicity	ΔE_{theor} eV	localization of excitation
Tb(Acac) ₃ Bpym (S ₀)	(8;8)	3	3.212	Acac
		1	3.299	Acac
		3	3.313	Acac
		3	3.341	Acac
		3	3.612	Bpym
Tb(Acac) ₂ Acac*Bpym (T ₁)	(8;8)	3	3.160	Acac
		1	3.301	Acac
		3	3.456	Acac
		3	3.468	Acac
		3	4.592	Bpym
Tb(Acac) ₃ Bpym* (T ₁)	(8;8)	3	2.794	Bpym
		1	2.914	Bpym
		3	3.346	Acac
		3	3.351	Acac
		3	3.353	Acac
Eu(Acac) ₃ Bpym (S ₀)	(8;8)	3	3.093	Acac
		1	3.267	Acac
		3	3.077	Acac
		3	3.151	Acac
		3	3.156	Bpym
Eu(Acac) ₂ Acac*Bpym (T ₁)	(8;8)	3	3.063	Acac
		1	3.270	Acac
		3	3.362	Acac
		3	3.374	Acac
		3	4.489	Bpym
Eu(Acac) ₃ Bpym* (T ₁)	(8;8)	3	2.727	Bpym
		1	2.892	Bpym
		3	3.124	Acac
		3	3.155	Acac
		3	3.327	Acac
[(H ₂ O) ₃ Cl ₃ Eu(μ-Bpym)Tb(H ₂ O) ₃ Cl ₃] (S ₀)	(4;4)	3	3.790	Bpym
		1	4.805	Bpym
[(H ₂ O) ₃ Cl ₃ Eu(μ-Bpym*)Tb(H ₂ O) ₃ Cl ₃] (T ₁)	(4;4)	3	2.902	Bpym
		1	4.327	Bpym

states in the case of triplets for Gd(H₂O)₃Cl₃Bpym and Gd₂(H₂O)₆Cl₆(μ-Bpym). For Gd(Acac)₃(H₂O)₂, the effective Hamiltonian was spanned by 34 and 34 states, respectively.

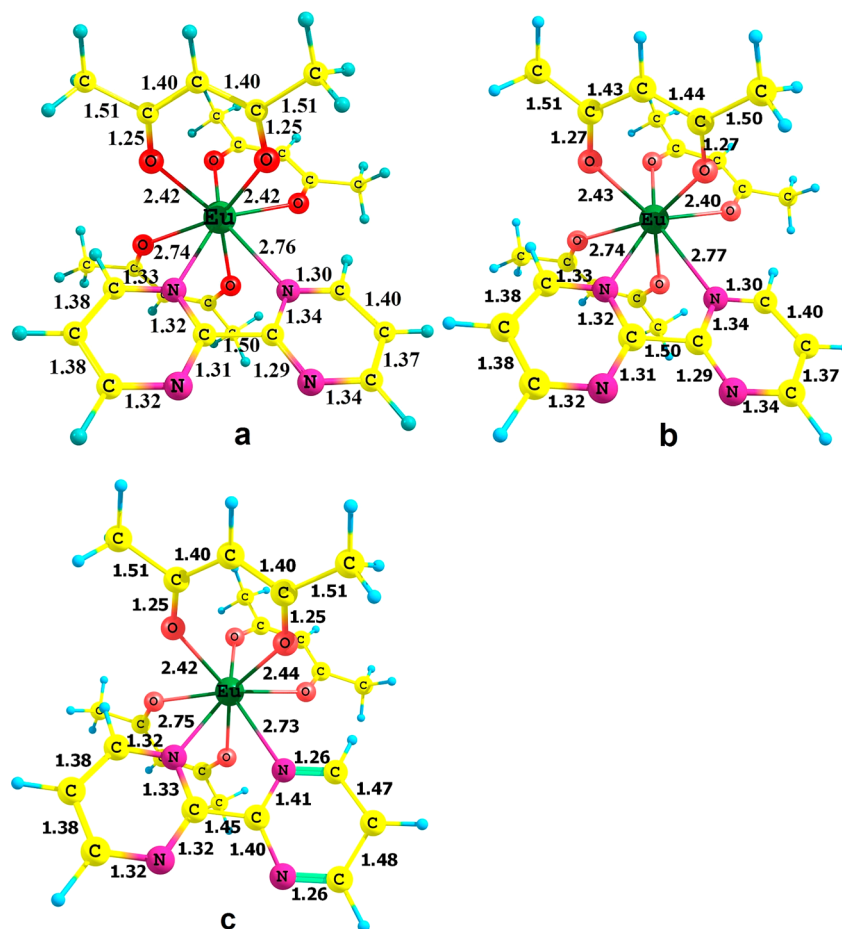


Figure 3. Optimized ground-state structure (a) and optimized triplet-state structures of $\text{Eu}(\text{Acac})_3\text{Bpym}$ with triplet localization on β -diketone $\text{Eu}(\text{Acac})_2\text{Acac}^*\text{Bpym}$ (b) and on 2,2'-bipyrimidine $\text{Eu}(\text{Acac})_3\text{Bpym}^*$ (c) (bond lengths in Angstroms).

3. RESULTS AND DISCUSSION

Model Gd^{3+} Complexes. To evaluate the accuracy of the used ab initio technique the lowest singlet and triplet excited levels of some Gd^{3+} complexes with corresponding ligands were calculated (Table 1). Experimental values of triplet levels of the ligands were taken from the literary data from phosphorescence spectra of Gd^{3+} complexes (Table 1 and Table 2).^{51,52,67–72}

The calculated values are in good agreement with experimental data; therefore, our next step was to simulate the excited states of the target Eu^{3+} and Tb^{3+} complexes (Table 3). The lowest triplet excited states with Bpym-localized excitation in $\text{Eu}(\text{Acac})_3\text{Bpym}^*$, $\text{Tb}(\text{Acac})_3\text{Bpym}^*$, $[(\text{H}_2\text{O})_3\text{Cl}_3\text{Eu}(\mu\text{-Bpym}^*)\text{-Tb}(\text{H}_2\text{O})_3\text{Cl}_3]$, and $\text{Gd}_2(\text{H}_2\text{O})_6\text{Cl}_6(\mu\text{-Bpym}^*)$ are rather similar. Similar values were also obtained for Acac-localized excited states. Thus, our calculations showed that the excited states localized on the same ligand virtually do not depend on the nature of Ln^{3+} and the presence of other ligands in the complex. This result agrees well with the experimental data,^{45–47} which means that the method of dividing the dinuclear complex into fragments is rather reasonable.

The lowest energy of the triplet excited state is achieved in the geometry of its triplet excitation. The calculated ligand-localized triplet excited states appears to be quasi-degenerate with an energy difference between them of ~ 0.1 eV.

Experimental excited states of 2,2'-bipyrimidine (Table 2) have lower energies when Bpym acts as a bridging ligand between two ions than when it occupies a terminal position.⁶⁷

The opposite situation is observed with the results of quantum chemical simulation. When Bpym occupies a terminal position like in $\text{Gd}(\text{H}_2\text{O})_3\text{Cl}_3\text{Bpym}$, the ligand experiences larger relaxation during the optimization of the excited state of the complex, which results in lower energies (Table 3).

Ground-State Geometries of Model Complexes.

Figures 3a and 4a show the optimized geometries of $\text{Eu}(\text{Acac})_3\text{Bpym}$ and $[(\text{H}_2\text{O})_3\text{Cl}_3\text{Eu}(\mu\text{-Bpym})\text{Tb}(\text{H}_2\text{O})_3\text{Cl}_3]$ complexes in their ground state. The agreement with the available experimental data⁵⁴ is good. In optimized ground-state geometries, the first three triplet excited states are localized on β -diketone and the last triplet state on Bpym.

Excited-State Geometries of Model Complexes.

Similarly to ref 35, the triplet states in this geometry are localized on individual ligands. The location of the excitation is specified by symbol “*”. Thus, $\text{Eu}(\text{Acac})_3\text{Bpym}^*$ (Figure 3c) refers to the optimized geometry of the triplet excited state when excitation localizes on 2,2'-bipyrimidine. The geometry optimization of these states leads to the corresponding minima (Figures 3b,c and 4b). Similar deformations of ligands upon excitation were observed in refs 27 and 35.

In the case of Bpym-localized excitations, the geometries of 2,2'-bipyrimidine changed similarly in $\text{Eu}(\text{Acac})_3\text{Bpym}^*$ (Figure 3c) and $[(\text{H}_2\text{O})_3\text{Cl}_3\text{Eu}(\mu\text{-Bpym}^*)\text{Tb}(\text{H}_2\text{O})_3\text{Cl}_3]$ (Figure 4b). However, the C–H bond in position 5 of pyridine ring in $\text{Eu}(\text{Acac})_3\text{Bpym}^*$ comes out of the plane by $\sim 15^\circ$. In $[(\text{H}_2\text{O})_3\text{Cl}_3\text{Eu}(\mu\text{-Bpym}^*)\text{Tb}(\text{H}_2\text{O})_3\text{Cl}_3]$, due to the coordination of Bpym with two ions (Eu^{3+} and Tb^{3+}), it remains planar

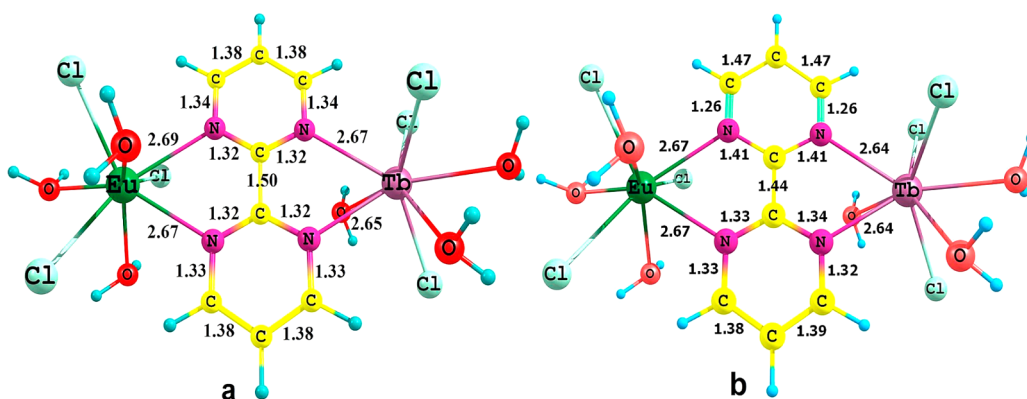
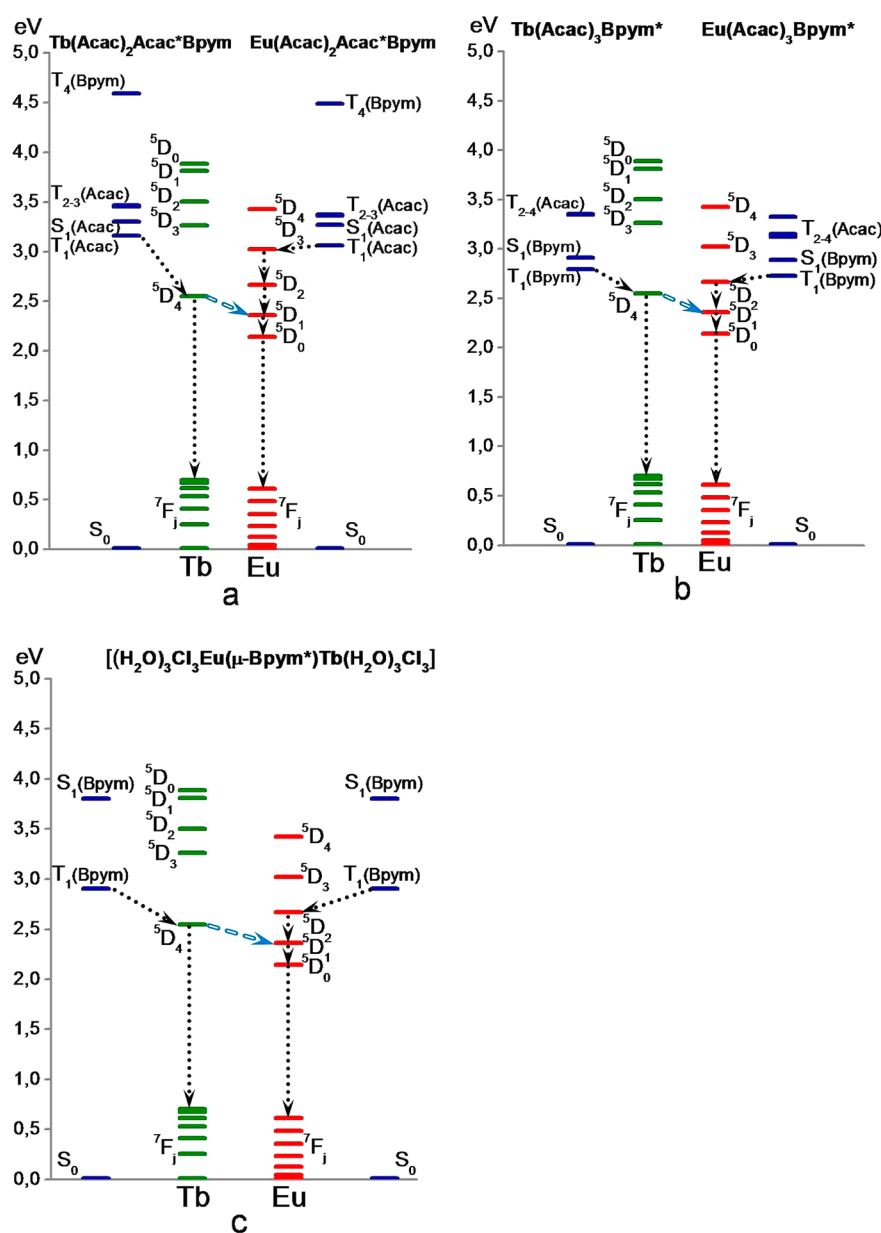


Figure 4. Optimized ground-state structure (a) and optimized triplet-state structures of $[(\text{H}_2\text{O})_3\text{Cl}_3\text{Eu}(\mu\text{-Bpym})\text{Tb}(\text{H}_2\text{O})_3\text{Cl}_3]$ with triplet localization on 2,2'-bipyrimidine $[(\text{H}_2\text{O})_3\text{Cl}_3\text{Eu}(\mu\text{-Bpym}^*)\text{Tb}(\text{H}_2\text{O})_3\text{Cl}_3]$ (b) (bond lengths in Angstroms).



on excitation. Probably, the rigid geometry of the dinuclear complex minimizes the contribution of nonradiative deactivation to the energy transfer process and, as consequence, increases the emission efficiency.

It is also necessary to consider the differences in molecular geometries of the ground and excited states. The significant distortion of the complex in its excited state geometry leads to a notable displacement of the energy minima of the ground and excited states and to crossing of the curves that belongs to those states. As a result, during the relaxation process, the molecule can move to the ground-state curve and nonradiatively drop down to its steady state. Thus, in mononuclear complexes $\text{Eu}(\text{Acac})_3\text{Bpym}$ and $\text{Tb}(\text{Acac})_3\text{Bpym}$, the localization of the excitation on 2,2'-bipyrimidine leads to a geometry distortion and to a decrease in emission efficiency in comparison with the dinuclear complex. Furthermore, the rigid structure of bonds between Eu^{3+} and Tb^{3+} increases the interaction time between ions and promotes the complete energy transfer between them.

According to the calculated singlet and triplet excited levels, the energy level diagrams were constructed for $\text{Eu}(\text{Acac})_2\text{Acac}^*\text{Bpym}$ and $\text{Tb}(\text{Acac})_2\text{Acac}^*\text{Bpym}$ excitations (Figure 5a), for $\text{Eu}(\text{Acac})_3\text{Bpym}^*$ and $\text{Tb}(\text{Acac})_3\text{Bpym}^*$ (Figure 5b), and $[(\text{H}_2\text{O})_3\text{Cl}_3\text{Eu}(\mu\text{-Bpym}^*)\text{Tb}(\text{H}_2\text{O})_3\text{Cl}_3]$ (Figure 5c). As mentioned above, there is no need to perform ab initio calculations for 4f–4f excited levels of Ln^{3+} , because they can be easily obtained from the experimental data.^{53,54}

Acac-localized triplet excitations are quite degenerate with the $^5\text{D}_3$ level of Eu^{3+} and the $^5\text{D}_4$ level of Tb^{3+} (black dotted arrow). At the same time, the Tb^{3+} ion also transfers additional energy to Eu^{3+} through the $^5\text{D}_4(\text{Tb}) \rightarrow ^5\text{D}_1(\text{Eu})$ channel (blue dashed arrow). If the excitation acts on Bpym, the triplet level transfers energy to the $^5\text{D}_2$ level of Eu^{3+} and $^5\text{D}_4$ level of Tb^{3+} .

4. CONCLUSIONS

The nature of excited states of the dinuclear $[(\text{Acac})_3\text{Eu}(\mu\text{-Bpym})\text{Tb}(\text{Acac})_3]$ complex has been studied for the first time by the ab initio XMCQDPT2/CASSCF approach. The calculations of the lowest singlet and triplet excited states showed that excitation can be localized on each ligand. The theoretical results agree well with experimental data. On the basis of the calculated triplet and singlet excited states, the energy level diagrams are constructed, and the main channels of intramolecular energy transfer are determined. It is found that, in spite of a significant difference in the luminescence spectra of the lanthanide ions, the ligand-localized excited states in their complexes only slightly depend on the nature of the Ln^{3+} ion and on the presence of other ligands. A computational procedure has been developed, according to which the entire complex is divided into relatively small functional fragments to which the multireference approach is applicable.

It is found that, in the case of pentane-2,4-dione-localized excitation, energy transfer occurs from the triplet level of the ligand to the $^5\text{D}_3$ level of Eu^{3+} and $^5\text{D}_4$ level of Tb^{3+} . From the 2,2'-bipyrimidine-localized triplet state, excitation energy transfers to the $^5\text{D}_2$ level of Eu^{3+} and the $^5\text{D}_4$ level of Tb^{3+} . The enhanced emission efficiency of the dinuclear complexes can be explained by the additional light pumping of the excited level ($^5\text{D}_1$) of the acceptor ion (Eu^{3+}) by energy transfer from the resonant level ($^5\text{D}_4$) of the donor ion (Tb^{3+}).

It follows from the obtained results that it is very promising to synthesize dinuclear liquid-crystalline lanthanide complexes in order to use them in organic electronics and as fluorescent sensors.

■ ASSOCIATED CONTENT

■ Supporting Information

The differences in internuclear distances in optimized ground- and triplet-state structures of $\text{Eu}(\text{Acac})_3\text{Bpym}$ and $[(\text{H}_2\text{O})_3\text{Cl}_3\text{Eu}(\mu\text{-Bpym})\text{Tb}(\text{H}_2\text{O})_3\text{Cl}_3]$ complexes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

- Bünzli, J.-C. G.; Eliseeva, S. V. Basics of Lanthanide Photophysics. In *Lanthanide Luminescence: Photophysical, Analytical, and Biological Aspects*; Hänninen, P., Härmä, H., Eds.; Springer Series on Fluorescence; Springer-Verlag: Berlin, 2011; Vol. 7, pp 1–45.
- Crosby, G. A.; Whan, R. E.; Alire, R. M. Intramolecular Energy Transfer in Rare Earth Chelates. Role of the Triplet State. *J. Chem. Phys.* **1961**, 3, 743–748.
- Bünzli, J.-C. G.; Comby, S.; Chauvin, A.-S.; Vandevyver, C. D. B. New Opportunities for Lanthanide Luminescence. *J. Rare Earths* **2007**, 25, 257–274.
- Comby, S.; Bünzli, J.-C. G. Lanthanide Near-Infrared Luminescence in Molecular Probes and Devices. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneidner, K. A., Bünzli, J.-C. G., Pecharsky, V. K., Eds.; Elsevier: Amsterdam, 2007; Vol. 37, pp 217–470.
- Bünzli, J.-C. G.; Eliseeva, S. V. Lanthanide NIR Luminescence for Telecommunications, Bioanalyses and Solar Energy Conversion. *J. Rare Earths* **2010**, 28, 824–842.
- Santa-Cruz, P.; Morin, D.; Dexpert-Ghys, J.; Sadoc, A.; Glas, F.; Auzel, F. New Lanthanide-Doped Fluoride-Based Vitreous Materials for Laser Applications. *J. Non-Cryst. Solids* **1995**, 190, 238–243.
- van der Ende, B. M.; Aarts, L.; Meijerink, A. Lanthanide Ions as Spectral Converters for Solar Cells. *Phys. Chem. Chem. Phys.* **2009**, 11, 11081–11095.
- Dzhabarov, V. I.; Knyazev, A. A.; Strelkov, M. V.; Molostova, E. Yu.; Schustov, V. A.; Haase, W.; Galyametdinov, Yu. G. Tris(β -Diketonates) Lanthanum Nematic Adducts. *Liq. Cryst.* **2010**, 37, 285–291.
- Galyametdinov, Yu. G.; Knyazev, A. A.; Dzhabarov, V. I.; Cardinaels, T.; Driesen, K.; Görller-Walrand, C.; Binnemans, K. Polarized Luminescence from Aligned Samples of Nematogenic Lanthanide Complexes. *Adv. Mater.* **2008**, 20, 252–257.
- Romanova, K. A.; Datskevich, N. P.; Taidakov, I. V.; Vitukhnovskii, A. G.; Galyametdinov, Yu. G. Luminescent Characteristics of Some Mesogenic Tris(β -Diketonate) Europium(III) Complexes with Lewis Bases. *Russ. J. Phys. Chem. A* **2013**, 87, 2108–2111.

- (11) de Lill, D. T.; de Bettencourt-Dias, A.; Cahill, C. L. Exploring Lanthanide Luminescence in Metal–Organic Frameworks: Synthesis, Structure, and Guest-Sensitized Luminescence of a Mixed Europium/Terbium-Adipate Framework and a Terbium-Adipate Framework. *Inorg. Chem.* **2007**, *46*, 3960–3965.
- (12) Xu, Y.-Y.; Hemmälä, I. A.; Lövgren, T. N.-E. Co-Fluorescence Effect in Time-Resolved Fluoroimmunoassays. A Review. *Analyst* **1992**, *117*, 1061–1069.
- (13) Liu, Y.-F.; Rong, D.-F.; Xia, H.-T.; Wang, D.-Q.; Chen, L. Synthesis, Crystal Structure, and Luminescence Properties of [TbGd(NAA)₆(phen)₂] and [Tb₂(NNA)₆(phen)₂]-2C₃H₇NO. *J. Coord. Chem.* **2009**, *62*, 1835–1845.
- (14) Shuvaev, S.; Utochnikova, V.; Marciniak, L.; Freidzon, A.; Sinev, I.; Van Deun, R.; Freire, R. O.; Zubavichus, Y.; Grünert, W.; Kuzmina, N. Lanthanide Complexes with Aromatic o-Phosphorylated Ligands: Synthesis, Structure Elucidation and Photophysical Properties. *Dalton Trans.* **2014**, *43*, 3121–3136.
- (15) Ramade, I.; Kahn, O.; Jeannin, Y.; Robert, F. Design and Magnetic Properties of a Magnetically Isolated Gd^{III}Cu^{II} Pair. Crystal Structures of [Gd(hfa)₃Cu(salen)], [Y(hfa)₃Cu(salen)], [Gd(hfa)₃Cu(salen)(Meim)], and [La(hfa)₃(H₂O)Cu(salen)] [hfa = Hexafluoroacetylacetonato, salen = N,N'-Ethylenebis(salicylideneaminato), Meim = 1-Methylimidazole]. *Inorg. Chem.* **1997**, *36*, 930–936.
- (16) Pasatoiu, T. D.; Madalan, A. M.; Kumke, M. U.; Tiseanu, C.; Andruh, M. Temperature Switch of LMCT Role: From Quenching to Sensitization of Europium Emission in a Zn^{II}–Eu^{III} Binuclear Complex. *Inorg. Chem.* **2010**, *49*, 2310–2315.
- (17) Chen, F. F.; Jiang, W. L.; Lou, B.; Bian, Z. Q.; Huang, C. H. Synthesis and photophysical properties of Ir^{III}–Ln^{III} (Ln = Nd, Yb, Er) bimetallic complexes containing bipyrimidines as bridging ligands. *Sci. China, Ser. B* **2009**, *52*, 1808–1813.
- (18) Singh, S. K.; Tibrewal, N. K.; Rajaraman, G. Density functional studies on dinuclear {Ni^{II}Gd^{III}} and trinuclear {Ni^{II}Gd^{III}Ni^{II}} complexes: Magnetic exchange and magneto-structural maps. *Dalton Trans.* **2011**, *40*, 10897–10906.
- (19) Singh, S. K.; Rajeshkumar, T.; Chandrasekhar, V.; Rajaraman, G. Theoretical studies on {3d-Gd} and {3d-Gd-3d} complexes: Effect of metal substitution on the effective exchange interaction. *Polyhedron* **2013**, *66*, 81–86.
- (20) Singh, S. K.; Rajaraman, G. Decisive interactions that determine ferro/antiferromagnetic coupling in {3d-4f} pairs: A case study on dinuclear {V(IV)–Gd(III)} complexes. *Dalton Trans.* **2013**, *42*, 3623–3630.
- (21) Binnemans, K. Rare-Earth Beta-Diketonates. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneidner, K. A., Bünzli, J.-C. G., Pecharsky, V. K., Eds.; Elsevier: Amsterdam, 2005; Vol. 35, pp 107–272.
- (22) Fernandes, J. A.; Ferreira, R. A. S.; Pillinger, M.; Carlos, L. D.; Jepsen, J.; Hazell, A.; Ribeiro-Claro, P.; Gonçalves, I. S. Investigation of Europium(III) and Gadolinium(III) Complexes with Naphthoyltri-fluoroacetone and Bidentate Heterocyclic Amines. *J. Lumin.* **2005**, *113*, 50–63.
- (23) Zucchi, G.; Le Goff, X. F. Magnetic Properties of Structurally Characterized Binuclear Lanthanide Complexes Bridged by 2,2'-Bipyrimidine. *Polyhedron* **2013**, *52*, 1262–1267.
- (24) Sato, S.; Wada, M. Relations between Intramolecular Energy Transfer Efficiencies and Triplet State Energies in Rare Earth β-Diketone Chelates. *J. Bull. Chem. Soc. Jpn.* **1970**, *43*, 1955–1962.
- (25) Latva, M.; Takalo, H.; Mukkala, V.-M.; Matachescu, C.; Rodríguez-Ubis, J. C.; Kankare, J. Correlation Between the Lowest Triplet State Energy Level of the Ligand and Lanthanide(III) Luminescence Quantum Yield. *J. Lumin.* **1997**, *75*, 149–169.
- (26) Archer, R. D.; Chen, H.; Thomson, L. C. Synthesis, Characterization, and Luminescence of Europium(III) Schiff Base Complexes. *Inorg. Chem.* **1998**, *37*, 2089–2095.
- (27) Gutierrez, F.; Tedeschi, C.; Maron, L.; Daudey, J.-P.; Poteau, R.; Azema, J.; Tisnès, P.; Picard, C. Quantum Chemistry-Based Interpretations on the Lowest Triplet State of Luminescent Lanthanides Complexes. Part 1. Relation between the Triplet State Energy of Hydroxamate Complexes and Their Luminescence Properties. *Dalton Trans.* **2004**, *39*, 1334–1347.
- (28) de Sá, G. F.; Malta, O. L.; de Mello Donegá, C.; Simas, A. M.; Longo, R. L.; Santa-Cruz, P. A.; da Silva, E. F. Spectroscopic Properties and Design of Highly Luminescent Lanthanide Coordination Complexes. *Coord. Chem. Rev.* **2000**, *196*, 165–195.
- (29) Gonçalves e Silva, F. R.; Malta, O. L.; Reinhard, C.; Güdel, H.-U.; Piguet, C.; Moser, J. E.; Bünzli, J.-C. G. Visible and Near-Infrared Luminescence of Lanthanide-Containing Dimetallic Triple-Stranded Helicates: Energy Transfer Mechanisms in the Sm^{III} and Yb^{III} Molecular Edifices. *J. Phys. Chem. A* **2002**, *106*, 1670–1677.
- (30) Malta, O. L. Ligand-Rare-Earth Ion Energy Transfer in Coordination Compounds. A Theoretical Approach. *J. Lumin.* **1997**, *71*, 229–236.
- (31) de Andrade, A. V. M.; da Costa, N. B.; Simas, A. M.; de Sá, G. F. Sparkle model for the quantum chemical AM1 calculation of europium complexes of coordination number nine. *J. Alloy. Compd.* **1995**, *225*, 55–59.
- (32) Rocha, G. B.; Freire, R. O.; da Costa, N. B.; de Sá, G. F.; Simas, A. M. Sparkle Model for AM1 Calculation of Lanthanide Complexes: Improved Parameters for Europium. *Inorg. Chem.* **2004**, *43*, 2346–2354.
- (33) Dutra, J. D. L.; Filho, M. A. M.; Rocha, G. B.; Freire, R. O.; Simas, A. M.; Stewart, J. J. P. Sparkle/PM7 Lanthanide Parameters for the Modeling of Complexes and Materials. *J. Chem. Theory Comput.* **2013**, *9*, 3333–3341.
- (34) Dutra, J. D. L.; Bispo, T. D.; Freire, R. O. LUMPAC Lanthanide Luminescence Software: Efficient and User Friendly. *J. Comput. Chem.* **2014**, *35*, 772–775.
- (35) Freidzon, A. Ya.; Scherbinin, A. V.; Bagaturyants, A. A.; Alifimov, M. V. Ab Initio Study of Phosphorescent Emitters Based on Rare-Earth Complexes with Organic Ligands for Organic Electro-luminescent Devices. *J. Phys. Chem. A* **2011**, *115*, 4565–4573.
- (36) Gutierrez, F.; Tedeschi, C.; Maron, L.; Daudey, J.-P.; Azema, J.; Tisnès, P.; Picard, C.; Poteau, R. Quantum Chemistry-Based Interpretations on the Lowest Triplet State of Luminescent Lanthanides Complexes. Part 2. Influence of the Electrostatic Interactions on the Triplet State Energy of Terbium Complexes. *J. Mol. Struct. (THEOCHEM)* **2005**, *756*, 151–162.
- (37) Guillaumont, D.; Bazin, H.; Benech, J. M.; Boyer, M.; Mathis, G. Luminescent Eu(III) and Gd(III) Trisbipyridine Cryptates: Experimental and Theoretical Study of the Substituent Effects. *Chem-PhysChem* **2007**, *8*, 480–488.
- (38) Puntus, L. N.; Lyssenko, K. A.; Pekareva, I. S.; Bünzli, J.-C. G. Intermolecular Interactions as Actors in Energy-Transfer Processes in Lanthanide Complexes with 2,2'-Bipyridine. *J. Phys. Chem. B* **2009**, *113*, 9265–9277.
- (39) Selektor, S. L.; Sheinina, L. S.; Shokurov, A. V.; Raitman, O. A.; Arslanov, V. V.; Lapkina, L. A.; Gorbunova, Yu. G.; Tsivadze, A. Yu. Physicochemical Properties of Solutions and Ultrathin Films of Triple-Decker Gadolinium Tetra-15-Crown-5-Phthalocyaninate. *Protection of Metals and Physical Chemistry of Surfaces* **2011**, *47*, 447–456.
- (40) Roy, L. E.; Hughbanks, T. Magnetic Coupling in Dinuclear Gd Complexes. *J. Am. Chem. Soc.* **2006**, *128*, 568–575.
- (41) Ferbinteanu, M.; Kajiwar, T.; Choi, K.-Y.; Nojiri, H.; Nakamoto, A.; Kojima, N.; Cimpoesu, F.; Fujimura, Y.; Takaishi, S.; Yamashita, M. A Binuclear Fe(III)/Dy(III) Single Molecule Magnet. Quantum Effects and Models. *J. Am. Chem. Soc.* **2006**, *128*, 9008–9009.
- (42) Cremades, E.; Gómez-Coca, S.; Aravena, D.; Alvarez, S.; Ruiz, E. Theoretical Study of Exchange Coupling in 3d–Gd Complexes: Large Magnetocaloric Effect Systems. *J. Am. Chem. Soc.* **2012**, *134*, 10532–10542.
- (43) Stoian, S. A.; Paraschiv, C.; Kiritsakas, N.; Lloret, F.; Münck, E.; Bominaar, E. L.; Andruh, M. Mössbauer, Electron Paramagnetic Resonance, and Magnetic Susceptibility Studies on Members of a New Family of Cyano-Bridged 3d–4f Complexes. Demonstration of Anisotropic Exchange in a Fe–Gd Complex. *Inorg. Chem.* **2010**, *49*, 3387–3401.

- (44) Paulović, J.; Cimpoesu, F.; Ferbinteanu, M.; Hirao, K. Mechanism of Ferromagnetic Coupling in Copper(II)–Gadolinium(III) Complexes. *J. Am. Chem. Soc.* **2004**, *126*, 3321–3331.
- (45) Tobita, S.; Arakawa, M.; Tanaka, I. The Paramagnetic Metal Effect on the Ligand Localized $S_1 \rightarrow T_1$ Intersystem Crossing in the Rare-Earth-Metal Complexes with Methyl Salicylate. *J. Phys. Chem.* **1985**, *89*, 5649–5654.
- (46) Crosby, G. A.; Whan, R. E.; Freeman, J. J. Spectroscopic Studies of Rare Earth Chelates. *J. Phys. Chem.* **1962**, *66*, 2493–2499.
- (47) Faustino, W. M.; Malta, O. L.; Teotonio, E. E. S.; Brito, H. F.; Simas, A. M.; de Sá, G. F. Photoluminescence of Europium(III) Dithiocarbamate Complexes: Electronic Structure, Charge Transfer and Energy Transfer. *J. Phys. Chem. A* **2006**, *110*, 2510–2516.
- (48) de Andrade, A. V. M.; Longo, R. L.; Simas, A. M.; de Sá, G. F. Theoretical Model for the Prediction of Electronic Spectra of Lanthanide Complexes. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 1835–1839.
- (49) Ermolaev, V. L.; Sveshnikova, E. B.; Bodunov, E. N. Inductive-Resonant Mechanism of Nonradiative Transitions in Ions and Molecules in Condensed Phase. *Physica-Uspeski* **1996**, *39*, 261–282.
- (50) Whan, R. E.; Crosby, G. A. Luminescence Studies of Rare Earth Complexes: Benzoylacetate and Dibenzoylmethide Chelates. *J. Mol. Spectrosc.* **1962**, *8*, 315–327.
- (51) Zheng, Y.; Lin, J.; Liang, Y.; Lin, Q.; Yu, Y.; Meng, Q.; Zhou, Y.; Wang, S.; Wang, H.; Zhang, H. A Comparative Study on the Electroluminescence Properties of Some Terbium β -Diketonate Complexes. *J. Mater. Chem.* **2001**, *11*, 2615–2619.
- (52) Zheng, Y.; Lin, J.; Liang, Y.; Yu, Y.; Zhou, Y.; Guo, C.; Wang, S.; Zhang, H. A Novel Way to Enhance Electroluminescence Performance Based on Soluble Binary and Ternary Europium 1,1,1-Trifluoroacetylacetate Complexes. *J. Alloys Compd.* **2002**, *336*, 114–118.
- (53) Carnall, W. T.; Fields, P. R.; Rajnak, K. Electronic Energy Levels in the Trivalent Lanthanide Aquo Ions. I. Pr^{3+} , Nd^{3+} , Pm^{3+} , Sm^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} and Tm^{3+} . *J. Chem. Phys.* **1968**, *49*, 4424–4442.
- (54) Kramida, A.; Ralchenko, Yu.; Reader, J.; NIST ASD Team (2014). NIST Atomic Spectra Database, version 5, National Institute of Standards and Technology, Gaithersburg, MD, 2014, <http://physics.nist.gov/asd> (accessed Sep 10, 2014).
- (55) Zhong, Q.; Huaishan, W.; Qian, G.; Wang, Z.; Zhang, J.; Qiu, J.; Wang, M. Novel Stoichiometrically Erbium-Ytterbium Cocrystalline Complex Exhibiting Enhanced Near-Infrared Luminescence. *Inorg. Chem.* **2006**, *45*, 4537–4543.
- (56) Zhang, X.; Zhang, J.; Liang, L.; Su, Q. Luminescence of $\text{SrGdGa}_3\text{O}_7\cdot\text{RE}^{3+}$ (RE = Eu, Tb) Phosphors and Energy Transfer from Gd^{3+} to RE^{3+} . *Mater. Res. Bull.* **2005**, *40*, 281–288.
- (57) Fratini, A.; Richards, G.; Larder, E.; Swavey, S. Neodymium, Gadolinium, and Terbium Complexes Containing Hexafluoroacetylacetate and 2,2′-Bipyrimidine: Structural and Spectroscopic Characterization. *Inorg. Chem.* **2008**, *47*, 1030–1036.
- (58) van Uitert, L. G.; Johnson, L. F. Energy Transfer Between Rare-Earth Ions. *J. Chem. Phys.* **1966**, *44*, 3514–3522.
- (59) Ci, Y.-X.; Lan, Z.-H. Enhanced Fluorimetric Determination of Europium(III) with Thenoyltrifluoroacetone and 4,7-Diphenyl-1,10-Phenanthroline by Gadolinium(III). *Anal. Lett.* **1988**, *21*, 1499–1513.
- (60) Roos, B. O. Multiconfigurational Quantum Chemistry for Ground and Excited States. In *Radiation Induced Molecular Phenomena in Nucleic Acids*; Shukla, M. K., Leszczynski, J., Eds.; Challenges and Advances in Computational Chemistry and Physics; Springer Netherlands: Dordrecht, 2008; Vol. 5, pp 125–156.
- (61) Nakano, H. Quasidegenerate Perturbation Theory With Multiconfigurational Self-Consistent-Field Reference Functions. *J. Chem. Phys.* **1993**, *99*, 7983–7992.
- (62) Granovsky, A. A. Extended Multi-Configuration Quasidegenerate Perturbation Theory: The New Approach to Multi-State Multi-Reference Perturbation Theory. *J. Chem. Phys.* **2011**, *134*, 214113.
- (63) Dolg, M.; Stoll, H.; Savin, A.; Preuss, H. Energy-Adjusted Pseudopotentials for Rare Earth Elements. *Theor. Chim. Acta* **1989**, *75*, 173–194.
- (64) Dolg, M.; Stoll, H.; Preuss, H. A Combination of Quasirelativistic Pseudopotential and Ligand Field Calculations for Lanthanoid Compounds. *Theor. Chim. Acta* **1993**, *85*, 441–450.
- (65) Granovsky, A. A. Firefly version 8.1.0, 2014, <http://classic.chem.msu.su/gran/firefly/index.html> (accessed Sep 10, 2014).
- (66) Schmidt, M. W.; Baldrige, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. General Atomic and Molecular Electronic Structure System. *J. Comput. Chem.* **1993**, *14*, 1347–1363.
- (67) Zucchi, G.; Maury, O.; Thuéry, P.; Ephritikhine, M. Structural Diversity in Neodymium Bipyrimidine Compounds with Near Infrared Luminescence: From Mono- and Binuclear Complexes to Metal-Organic Frameworks. *Inorg. Chem.* **2008**, *47*, 10398–10406.
- (68) Irfanullah, M.; Iftikhar, K. A Comparative Study of ^1H NMR and Sensitized Visible Light Emission of an Extended Series of Dinuclear Lanthanide Complexes. *J. Photochem. Photobiol., A* **2011**, *224*, 91–101.
- (69) Zucchi, G.; Maury, O.; Thuéry, P.; Gumy, F.; Bünzli, J.-C. G.; Ephritikhine, M. 2,2′-Bipyrimidine as Efficient Sensitizer of the Solid-State Luminescence of Lanthanide and Uranyl Ions from Visible to Near-Infrared. *Chem.—Eur. J.* **2009**, *15*, 9686–9696.
- (70) Pereira, A.; Gallardo, H.; Conte, G.; Quirino, W. G.; Legnani, C.; Cremona, M.; Bechtold, I. H. Investigation of the energy transfer mechanism in OLEDs based on a new terbium β -diketonate complex. *Org. Electron.* **2012**, *13*, 90–97.
- (71) Yu, J.-A.; Lessard, R. B.; Bowman, L. E.; Nocera, D. G. Direct observation of intramolecular energy transfer from a β -diketonate to terbium(III) ion encapsulated in a cryptand. *Chem. Phys. Lett.* **1991**, *187*, 263–268.
- (72) Zucchi, G.; Le Goff, X. F. Magneto-structural and photophysical investigations on a dinuclear Sm(III) complex featuring 2,2′-bipyrimidine. *Inorg. Chim. Acta* **2012**, *380*, 354–357.
- (73) Voevodin, V. I.; Zhumatiy, S. A.; Sobolev, S. I.; Antonov, A. S.; Bryzgalov, P. A.; Nikitenko, D. A.; Stefanov, K. S.; Voevodin, V. I. Practice of “Lomonosov” Supercomputer. *Open Systems J.* **2012**, *7*, 36–39 <http://www.osp.ru/os/2012/07/13017641/>, (in Russian).