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Synthesis, crystal structures and theoretical study of mixed ligand complexes of lanthanides acetylacetonates with *o*-phenanthroline and 2,2'-dipyridyl: The unexpected inverted electrostatic trend in stability

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Abstract

Synthesis of mixed ligand complexes $[\text{Lu}(\text{acac})_3\text{phen}]$ **1** and $[\text{Lu}(\text{acac})_3\text{dipy}]$ **2** was carried out. Complexes **1** and **2** have mononuclear structures with six oxygen atoms and two nitrogen atoms in the coordination sphere of the central Lu^{3+} ion. Theoretical calculations of structures and properties of mixed ligand complexes $[\text{Ln}(\text{acac})_3\text{Q}]$ (where $\text{Ln} = \text{La, Gd, Lu}$; $\text{Q} = \text{phen, dipy}$) were performed at the DFT/B3PW91 level. The natural bond orbital analysis (NBO) was used to characterize the electronic structures of complexes. The features of crystal structures of complexes $[\text{Ln}(\text{acac})_3\text{Q}]$ in lanthanide row were explained taking into account the bond nature. The influence of both nature of central lanthanide ion and neutral additional ligand on structures and properties of complexes under investigation is discussed. The $\text{Ln}(\text{acac})_3\text{—Q}$ bond energy was found to be decreased from La-based complexes to Lu-based compounds. Thus, the unexpected inverted electrostatic trend, i.e. a decrease in stability along the lanthanide series, has been found out.

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Keywords: Mixed ligand complexes; Lanthanides; Electronic structure; Bond energy; Density functional calculations

1. Introduction

The interest shown in coordination chemistry of lanthanide β -diketonates, $[\text{Ln}(\text{dik})_3]$, is based on their use as NMR shift reagents [1], luminescent and electroluminescent materials [2,3] and as volatile precursors in the chemical vapor deposition of thin films of electro and magnetoceramic materials [4,5]. One of the most important properties of lanthanide β -diketonates is their coordinative unsaturation and, as a consequence, the possibility to coordinate an additional neutral donor ligands (Q) under formation of mixed ligand complexes $[\text{Ln}(\text{dik})_3(\text{Q})_n]$. The transformation of $[\text{Ln}(\text{dik})_3]$ into $[\text{Ln}(\text{dik})_3(\text{Q})_n]$ offers a wide variety of possibilities to modify lanthanide β -diketonate functional properties [6–9]. In the last four decades an extensive literature, devoted to synthesis, structure and properties of mixed ligand lanthanide β -diketonates, has been evolved.

The analysis of these data shows that in general the composition and structure of such mixed ligand complexes strongly depend on the nature of the central metal ion, electronic features of the β -diketonate ligand, and additional neutral ligand Q.

In particular, this can be demonstrated by the well-known mixed ligand complexes of $[\text{Ln}(\text{dik})_3]$ with *N*-donor bidentate ligands 1,10-phenanthroline (phen) and 2,2'-dipyridyl (dipy). The experimental data [10–12] have shown that in the case of fully fluorinated β -diketone-hexafluoroacetylacetone (Hhfa), the composition of complexes changes in the lanthanide row. The hexafluoroacetylacetonates of earlier lanthanides (La–Nd) coordinate two molecules of phen or dipy, forming complexes $[\text{Ln}(\text{hfa})_3\text{Q}_2]$, whereas, in the case of heavier lanthanides only one molecule of Q is coordinated. Contrastingly, in the case of non-fluorinated and non-bulky β -diketone-acetylacetone (Hacac) all lanthanides form the mixed ligand complexes of invariable composition— $[\text{Ln}(\text{acac})_3(\text{Q})]$ ($\text{Q} = \text{phen, dipy}$) [13]. According to [14–19], the central lanthanide ion in $[\text{Ln}(\text{acac})_3(\text{Q})]$ is eight coordinated and forms four chelate rings—three with β -diketonate ligands and one—with phen or dipy. However,

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some features of structures and stability of these complexes need an extended clarification. This is particularly true for stability of $[\text{Ln}(\text{dik})_3(\text{Q})]$ ($\text{Q}=\text{phen}$, dipy) complexes in respect to decomposition into $\text{Ln}(\text{acac})_3$ and Q and for some details of their crystal packing. Indeed, till now it is not evident how the nature and stability of $\text{Ln}(\text{acac})_3\text{--Q}$ bonds change in the lanthanide row and what the reason of difference in the packing ways of $[\text{Ln}(\text{acac})_3(\text{Q})]$ molecules in crystal structures is [19].

Theoretical approach can be efficient for clarification of these problems. In this paper, we report synthesis, crystal structure investigations of $[\text{Lu}(\text{acac})_3\text{phen}]$ (**1**) and $[\text{Lu}(\text{acac})_3\text{dipy}]$ (**2**) and density functional calculations (DFT/B3PW91) of **1–2** and $[\text{Ln}(\text{acac})_3\text{Q}]$ ($\text{Ln}=\text{La}$, $\text{Q}=\text{phen}$ (**3**), dipy (**4**); $\text{Ln}=\text{Gd}$, $\text{Q}=\text{phen}$ (**5**), dipy (**6**)). Such choice of objects for theoretical modeling allows to reveal the dependence of stability and structure on lanthanide (La vs Gd , Lu) and neutral ligand (phen or dipy) nature.

2. Results and discussion

2.1. Description of the crystal structures

The mixed ligand complexes $[\text{Lu}(\text{acac})_3\text{phen}]$ **1** and $[\text{Lu}(\text{acac})_3\text{dipy}]$ **2** have similar molecular structure (Figs. 1a and 2a), consisting of isolated mononuclear molecules, with the coordination number of the central metal atom being eight. The eight donor atoms (six oxygen atoms from β -diketonate ligands and two nitrogen atoms from phen or dipy) are situated in a coordination sphere of the central lutetium atom, forming a distorted square antiprism as the coordination polyhedron (Figs. 1b and 2b). The dihedral angles between the upper and lower distorted square faces are equal to 2.0° and 1.3° for **1** and **2**, respectively. In crystal structure of **2**, there are two symmetrically independent molecules (type I and type II), which differ slightly in values of bond lengths and valence angles (Table 1).

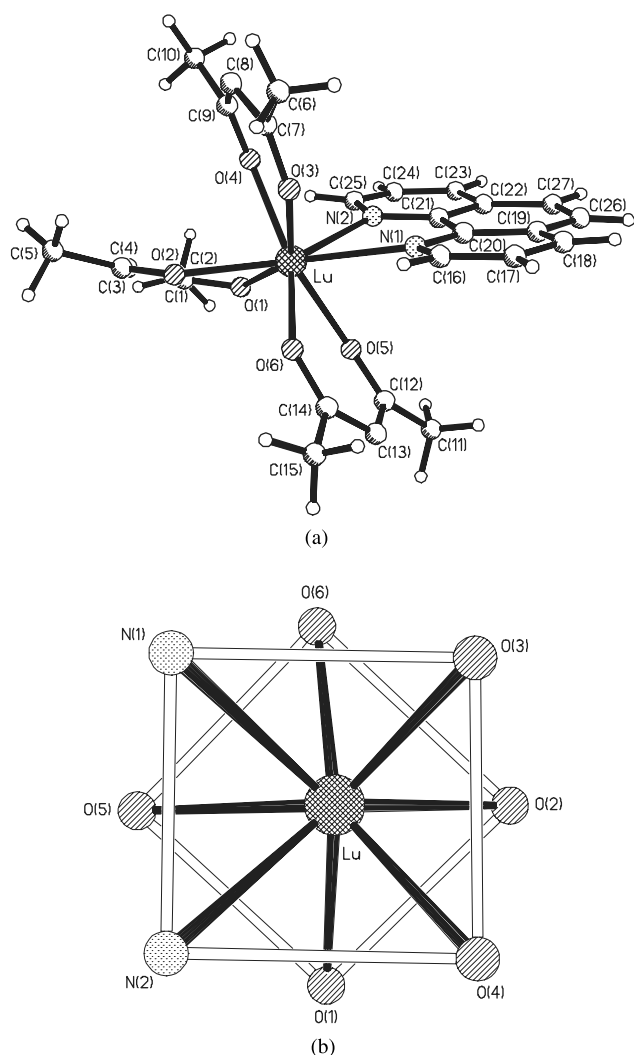


Fig. 1. The molecular structure (a) and coordination polyhedron (b) of $[\text{Lu}(\text{acac})_3\text{phen}]$ **1**.

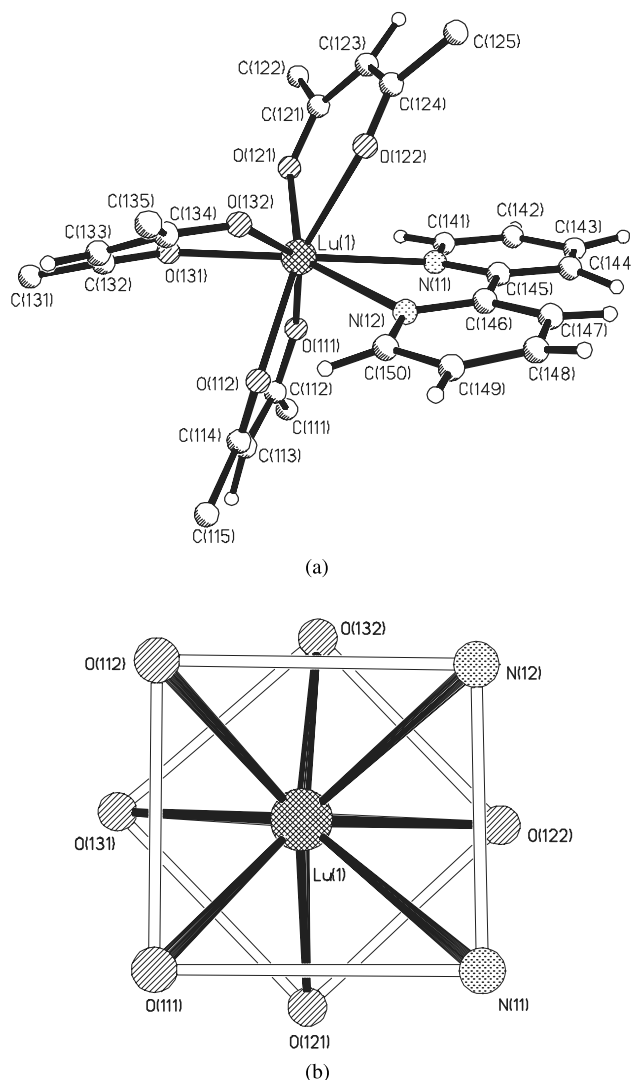


Fig. 2. The molecular structure (a) and coordination polyhedron (b) of $[\text{Lu}(\text{acac})_3\text{dipy}]$ **2**.

Table 1
Selected experimental bond lengths and valence angles values for **1**, **2** and **3**

Parameter	[La(acac) ₃ phen] ^{a,b}		[Lu(acac) ₃ phen] ^a	[Lu(acac) ₃ dipy] ^a	
	Type I	Type II		Type I	Type II
Ln–O(1)	2.460(8) Å	2.474(13) Å	2.297(25) Å	2.273(9) Å	2.272(8) Å
Ln–O(2)	2.433(16) Å	2.463(12) Å	2.261(34) Å	2.260(7) Å	2.269(7) Å
Ln–O(1a)	2.469(24) Å	2.499(26) Å	2.255(33) Å	2.260(6) Å	2.267(6) Å
Ln–O(2a)	2.418(6) Å	2.428(8) Å	2.277(1) Å	2.284(9) Å	2.279(9) Å
Ln–O(1b)	2.468(14) Å	2.527(21) Å	2.307(7) Å	2.260(8) Å	2.288(8) Å
Ln–O(2b)	2.454(21) Å	2.451(10) Å	2.267(1) Å	2.266(7) Å	2.289(9) Å
Ln–N(1)	2.800(2) Å	2.665(8) Å	2.521(6) Å	2.535(9) Å	2.517(8) Å
Ln–N(2)	2.764(12) Å	2.733(19) Å	2.499(19) Å	2.497(9) Å	2.508(8) Å
N(1)–Ln–N(2)	58.50(3)°	59.69(3)°	65.03(1)°	64.06(3)°	63.35(20)°
O(1)–Ln–O(2)	70.06(4)°	69.32(4)°	74.06(1)°	74.72(3)°	75.72(3)°
O(1a)–Ln–O(2a)	69.37(5)°	69.16(5)°	74.66(1)°	73.97(3)°	74.42(3)°
O(1b)–Ln–O(2b)	68.84(6)°	69.83(6)°	73.84(1)°	74.30(3)°	74.06(3)°

^a For experimental structure data of [La(acac)₃phen] **3**, [Lu(acac)₃phen] **1** and [Lu(acac)₃dipy] **2** the atoms labelling has been changed in respect with Figs. 1. and 2. and structure files to introduce uniform labelling system. The following labelling has been accepted (in square parentheses—labelling in accordance with structure files): [Lu(acac)₃Phen] **1**: O(1) [O(2)], O(2) [O(1)], O(1a) [O(3)], O(2a) [O(4)], O(1b) [O(5)], O(2b) [O(6)], N(1) [N(1)], N(2) [N(2)]; [Lu(acac)₃dipy] **2**: O(1) [O(131), O(231)], O(2) [O(132), O(232)], O(1a) [O(122), O(222)], O(2a) [O(121), O(221)], O(1b) [O(112), O(212)], O(2b) [O(111), O(211)], N(1) [N(11), N(21)], N(2) [N(12), N(22)]; [La(acac)₃Phen] **3**: O(1) [O(4), O(9)], O(2) [O(3), O(10)], O(1a) [O(6), O(12)], O(2a) [O(5), O(11)], O(1b) [O(2), O(8)], O(2b) [O(1), O(7)], N(1) [N(1), N(4)], N(2) [N(2), N(3)].

^b From available literature data [14].

In **1**, the Lu–O bond vary in the range of 2.255–2.307 Å (Table 1), while the Lu–N bond being equal to 2.521 and 2.499 Å. The acetylacetonate fragments are planar with the maximum deviation from average plane Δ_{\max} being equal to 0.031 Å, which indicates that the conjugation occurs. This fact agrees with the experimental [20] and theoretical modeling data for lanthanide *tris*- β -diketonates [21]. The phen fragment also retains planar structure at the coordination by lutetium ion (Δ_{\max} =0.052 Å). As expected, the molecular structure of **1** is very similar to those of related mixed ligand complexes [Ln(acac)₃phen]: [La(acac)₃phen] **3** [14], [Ce(acac)₃phen] **7** [15], [Pr(acac)₃Phen] **8** [16], [Sm(acac)₃phen] **9** [17] and [Eu(acac)₃phen] **10** [18]. In mixed ligand complexes of such type, the Ln–O bond lengths decrease from La to Lu, the average value of Ln–O distances for **3** is equal to 2.46 Å, for **7**—equal to 2.46 Å, for **8**—equal to 2.41 Å, for **9**—equal to 2.37 Å, for **10**—equal to 2.38 Å, for **1**—equal to 2.28 Å. Similar changes of Ln–N bond lengths occurred (the average value of Ln–N distances for **3** is equal to 2.74 Å, for **7**—equal to 2.74 Å, for **8**—equal to 2.67 Å, for **9**—equal to 2.62 Å, for **10**—equal to 2.64 Å, for **1**—equal to 2.51 Å). These are directly connected with the ionic radius of the La(III) which is significantly larger than the ionic radius of the Lu(III) (1.06 vs. 0.88 Å, respectively). The small radius gives rise to the decrease of the bond lengths in Lu-compounds. The decrease of the Ln–O and Ln–N distances leads to change of the bond angles \angle Ln–O–C and \angle Ln–N–C in these complexes.

In **2**, the Lu–O bond lengths vary in the range of 2.260–2.284 Å for the I type of molecules and 2.267–2.289 Å for the II type of molecules (Table 1). At the same time, the Lu–N bond lengths are equal to 2.535 and 2.497 Å for the I type and 2.517 and 2.508 Å for the II type of molecules of **2**. All ligands as acac-anionic fragment (Δ_{\max} =0.026 Å for I type and Δ_{\max} =0.018 Å for II type) and neutral dipy-fragment (Δ_{\max} =

0.06 Å for I type and Δ_{\max} =0.048 Å for II type) have a plain structure analogous to those in the molecular structure of **1**. Only one example of the crystal structure of the lanthanide acetylacetonate based mixed ligand complexes with dipy as an additional ligand is available in literature—[Yb(acac)₃dipy], **11** [19]. The molecular structures of **2** and **11** are very similar. The structure of **11** also contains two independent molecules. The average value of the Yb–O bond lengths in **11** is equal to 2.27 Å, while the average value of the Yb–N bond lengths is equal to 2.52 Å, which are very close to the corresponding parameters for **2**. Comparison of crystal packings of **2** and **11** also shows a close analogy between these structures.

The analysis of packing mode of crystal structures of **1** and **2** gave the supporting evidence for the structural similarity (Figs. 3 and 4). This fact indicates that the use of phen as an

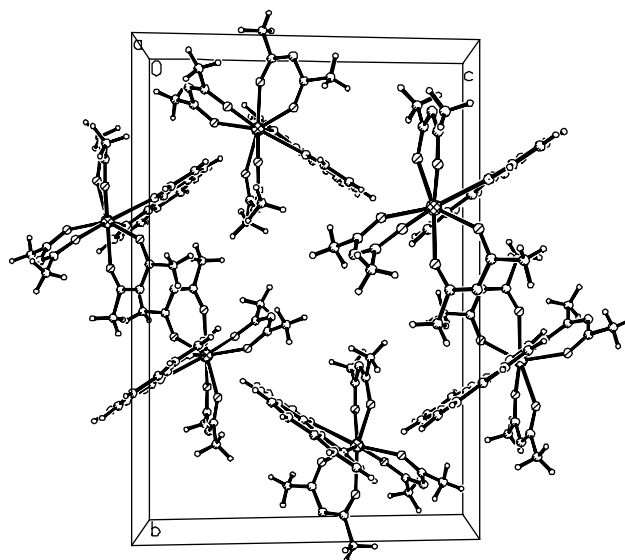


Fig. 3. The crystal packing of [Lu(acac)₃phen] **1** (along *a* axes).

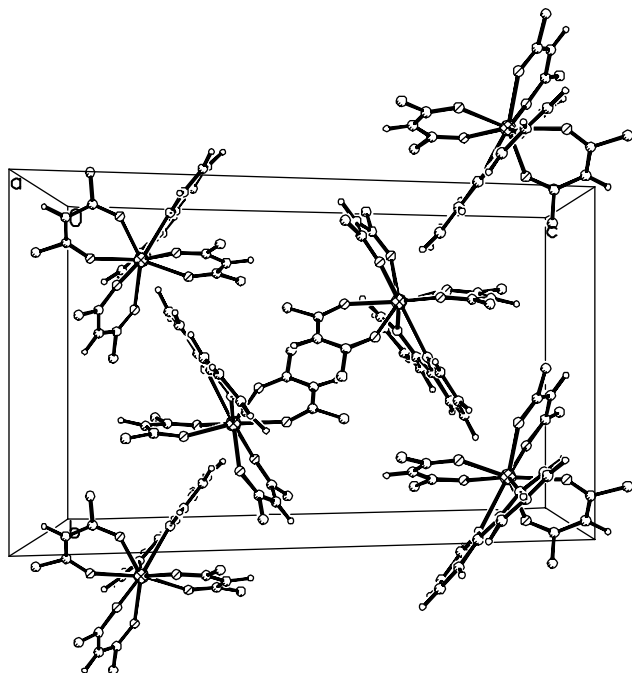


Fig. 4. The crystal packing of $[\text{Lu}(\text{acac})_3\text{dipy}]$ **2** (along a axes).

additional neutral ligand instead of dipy does not lead to significant changes in crystal structure of the lanthanide mixed ligand complexes.

However, it should be noted that in spite of similar molecular structures for **1**, **3**, **7**, **8**, **9** and **10**, the crystal packing of these mixed ligand complexes is dramatically different. So, in the crystal structures of **3** and **7**, the mutual orientation of phen-fragment of mixed ligand molecules occurs (Fig. 5). Probably, it can be explained by the weak interactions between aromatic systems of phen fragments. At the same time, in the crystal structures of **1**, **7**, **8**, **9** and **10** there is no such a mutual orientation and the phen-fragment lies in the cavity between two acac-rings of neighboring mixed ligand molecules (Figs. 3 and 4).

Such reorganization of the crystal packing in going from La- to Lu-based mixed ligand compounds is evidently connected with the changes in the nature of the intramolecular interactions in complexes under investigation. The covalent contribution to the Ln-ligand bond nature increases at transition from La- to Lu-based compounds [13]. It leads to

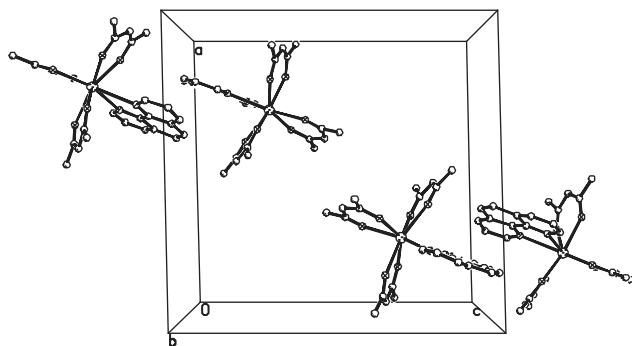


Fig. 5. The crystal packing of $[\text{La}(\text{acac})_3\text{phen}]$ **3** (along a axes) [14].

the increase of the metal–ligand bond strength and, as a consequence, to the increase of the thermodynamic stability of lanthanide complexes. At the same time, the change of the bond nature leads also to other consequences. For instance, the ionic bond is not directed in space that leads to the possibility of the ‘fine tuning’ of the ligand positions in crystal structure of such complexes under crystal packing force influence, while the metal–ligand bond with a significant covalent character has a strong direction in space that results in inflexibility ligand positions in coordination sphere of central ion. In the crystal structure of the La-based complex **3**, where the metal–ligand bonds have the most ionic character, the reorganization of complex molecules packing mode is occurred so that the mutual orientation of phen-fragment becomes possible. The same packing mode was found for Ce compound [15]. Whereas for analogous compounds of other rare-earth elements starting from Pr-based ones, such orientation is not observed.

To investigate the influence of the nature of the central ion and the neutral additional ligands on the structure and properties of the mixed ligand complexes $[\text{Ln}(\text{acac})_3\text{Q}]$, the theoretical modeling (DFT/B3PW91) of $[\text{Ln}(\text{acac})_3\text{Q}]$ **1–6** has been carried out in this work.

2.2. Theoretical modeling of the mixed ligand complexes

Equilibrium geometry configurations of the lanthanide mixed ligand complexes are presented in Fig. 6. Selected computed bond lengths and valence angles are summarized in Table 2. One can see that the calculated geometry parameters for mixed ligand complexes $[\text{Ln}(\text{acac})_3\text{Q}]$ are in good agreement with available experimental data obtained by single crystal X-ray crystallography (Table 1). The experimental Ln–O bond lengths are somewhat shorter than the corresponding calculated values, which can be attributed to the crystal packing force, not taken into account in theoretical models, and to effects of uncompleteness of the basis sets and the inherent approximation of the method. The same tendency holds for bond angles of all complexes (Table 2). The chelating rings of the acetylacetonate ligands as well as the chelating ring of the phen or dipy fragment possess a nearly planar geometry that confirms the presence of conjugation in the acac-fragment, the conjugation proposed in Section 2.1. The metal–oxygen and metal–nitrogen bond lengths for La-based compounds are distinctly longer than those for Gd- and Lu-derivatives (see Table 2) in a good accord with X-ray experimental data due to the lanthanide contraction.

The Ln–N bond lengths in phen- and dipy-derivatives are almost equal to each other that indicating that the behaviour of these neutral additional ligands at the coordination by metal ion in the complexes is very similar. It is also confirmed by Ln–O bond lengths in complexes considered (Table 2).

The geometry calculations show the unequivalence of acac-fragment in mixed ligand complexes with an additional ligand, although the $\text{Ln}(\text{dik})_3$ have three equivalent β -diketonate ligands according to [21–24]. So, the acac-ligands which are situated in *cis*-position related to Q, have a very similar geometry configurations, while the acac-ligand in

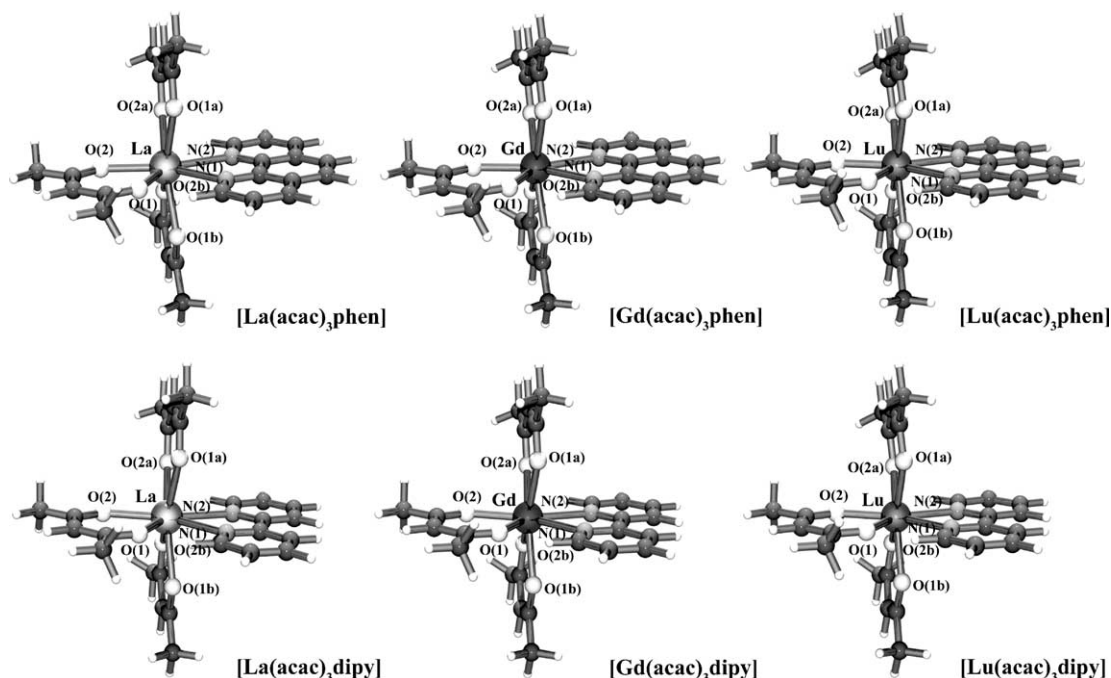


Fig. 6. Equilibrium geometry configurations (DFT/B3PW91) of the 1–6.

trans-position has geometry parameters differed from those for *cis*-ones. It is directly connected with the interactions of homoligand complexes with an additional ligand—phen or dipy. Nevertheless, the crystal packing forces makes less evident the differences between *cis*- and *trans*-acetylacetonate ligands in the experimental X-ray study of such complexes.

In order to understand the features of electronic structure of the lanthanide mixed ligand complexes, we have carried out the natural orbital analysis (NBO), based on equilibrium geometry configurations. The NBO atomic charges are presented in Table 3. The NBO-analysis has been performed for La and Lu compounds 1–4—for most representative examples.

It should be noticed that the central lanthanide atom in 1–4 has a significant positive charge. Especially, it is concerned with the La-based compounds 3 and 4. This indicates that the bonding between additional ligand and lanthanide ion is primarily electrostatic interaction between the lone pairs of the nitrogen atoms of the phen or dipy and highly charged central

metal ion, so-called ion–dipole interaction. The less positive charge of lutetium atom results in a decrease of oxygen and nitrogen atoms charges in comparison to lanthanum ones. The ion–dipole nature of $\text{Ln}(\text{acac})_3\text{--Q}$ interactions can indicate weaker interaction of $\text{Lu}(\text{acac})_3$ with phen or dipy than those of the La-based compounds.

The increasing role of the covalent component in the intramolecular interactions of the Lu-derivatives can be easily confirmed by the natural atomic orbital population resulted from NBO-analysis of electron density. The results of population analysis are presented in Table 4. These data show that the d-orbitals of lutetium atom are significantly populated. Moreover, it results from the interaction of the Lu-ion with acetylacetonate ligands, but not from Lu-phen or dipy interactions according to the comparison of natural atomic population of lutetium in $[\text{Lu}(\text{acac})_3\text{Q}]$ and in $\text{Lu}(\text{acac})_3$ [25] (Table 4). At the same time, the natural atomic population of the d-orbitals attributed to lanthanum ion in $[\text{La}(\text{acac})_3\text{Q}]$ and

Table 2
Calculated equilibrium geometry parameters for mixed ligand complexes 1–6

Parameter	$[\text{Lu}(\text{acac})_3\text{phen}]$	$[\text{Lu}(\text{acac})_3\text{dipy}]$	$[\text{La}(\text{acac})_3\text{phen}]$	$[\text{La}(\text{acac})_3\text{dipy}]$	$[\text{Gd}(\text{acac})_3\text{phen}]$	$[\text{Gd}(\text{acac})_3\text{dipy}]$
Ln–O(1)	2.33 Å	2.32 Å	2.51 Å	2.51 Å	2.40 Å	2.39 Å
Ln–O(2)	2.26 Å	2.26 Å	2.46 Å	2.45 Å	2.34 Å	2.34 Å
Ln–O(1a)	2.30 Å	2.30 Å	2.49 Å	2.49 Å	2.38 Å	2.38 Å
Ln–O(2a)	2.31 Å	2.31 Å	2.49 Å	2.49 Å	2.39 Å	2.38 Å
Ln–O(1b)	2.30 Å	2.30 Å	2.49 Å	2.49 Å	2.38 Å	2.38 Å
Ln–O(2b)	2.31 Å	2.31 Å	2.49 Å	2.49 Å	2.39 Å	2.38 Å
Ln–N(1)	2.57 Å	2.57 Å	2.76 Å	2.75 Å	2.65 Å	2.64 Å
Ln–N(2)	2.56 Å	2.56 Å	2.77 Å	2.76 Å	2.65 Å	2.65 Å
N(1)–Ln–N(2)	63.6°	62.7°	68.5°	58.4°	61.8°	60.9°
O(1)–Ln–O(2)	72.0°	72.0°	67.8°	68.4°	70.9°	70.8°
O(1a)–Ln–O(2a)	72.0°	72.0°	67.8°	67.9°	70.2°	70.3°
O(1b)–Ln–O(2b)	72.6°	72.4°	59.4°	67.9°	70.2°	70.3°

Table 3
The NBO-charge distributions for **1**, **2**, **3** and **4**

Atom	[Lu(acac) ₃ -phen]	[Lu(acac) ₃ -dipy]	[La(acac) ₃ -dipy]	[La(acac) ₃ -phen]
Ln	+1.979	+1.977	+2.638	+2.637
O(1)	−0.720	−0.722	−0.802	−0.800
O(2)	−0.726	−0.724	−0.813	−0.815
O(1a)	−0.730	−0.729	−0.804	−0.804
O(2a)	−0.718	−0.720	−0.803	−0.803
O(1b)	−0.730	−0.729	−0.804	−0.804
O(2b)	−0.718	−0.720	−0.803	−0.803
N(1)	−0.469	−0.477	−0.520	−0.514
N(2)	−0.488	−0.495	−0.528	−0.520

in La(acac)₃ [25] (Table 4) is very small that indicates more ionic character of La—acac bonding than the same for Lu-based complexes. The greater population of d-orbitals of Lu atom leads to the decrease of the metal charge in going from La to Lu compounds. Also, it should be noticed that the occupancies of d-orbitals of La or Lu ions do not significantly change at the neutral ligand coordination. It also confirms the ion–dipole nature of Ln(acac)₃–Q interactions.

The use of phen as an additional neutral ligand instead of dipy does not lead to significant changes in atomic charge distribution in mixed ligand complexes under investigation. However, introduction of neutral additional ligand into lanthanide coordination sphere results in unequivalence of charge distribution in the acac-fragments. Thus, the acetylacetonate fragment taking place in *trans*-position related to phen or dipy has different charges on the oxygen atoms compared to the corresponding values of ligands in *cis*-position. The difference between *trans*- and *cis*-acac ligands can be explained by their different positions in the coordination sphere of the central metal ion and by influence of the neutral ligand. The unequivalence of oxygen atoms in *trans*-acac ligand can also be resulted from the weak interaction between O(1) atoms from this ligand and neighboring hydrogen atom from the neutral additional ligand (phen or dipy). These distances are short enough to realise such a weak interaction (*d*(O(1)–H)=2.12 Å for **1**, *d*(O(1)–H)=2.08 Å for **2**, *d*(O(1)–H)=2.18 Å for **3**, *d*(O(1)–H)=2.15 Å for **4**). It can lead to the decrease of negative charge on this oxygen atom and to the different atomic charge on the other oxygen atom of *trans*-acac ligand. This situation is observed for the both lanthanum based and lutetium based compounds. Similar short *d*(O(1)–H)

Table 4
The NBO atomic orbital population of central metal ion for **1**, **2**, **3** and **4**

Compound	Population ^a
[Lu(acac) ₃ phen] 1	[core]6s ^{0.26} 5d ^{0.69} 6p ^{0.02} 6d ^{0.05}
[Lu(acac) ₃ dipy] 2	[core]6s ^{0.26} 5d ^{0.69} 6p ^{0.02} 6d ^{0.05}
[La(acac) ₃ phen] 3	[core]6s ^{0.18} 5d ^{0.16} 6p ^{0.01} 6d ^{0.01}
[La(acac) ₃ dipy] 4	[core]6s ^{0.18} 5d ^{0.16} 6p ^{0.01} 6d ^{0.01}
La(acac) ₃ ^b	[core]6s ^{0.12} 5d ^{0.20} 6p ^{0.02} 6d ^{0.01}
Lu(acac) ₃ ^b	[core]6s ^{0.22} 5d ^{0.68} 6p ^{0.01} 6d ^{0.03}

^a [core] is 1s²2s²2p⁶3s²3p⁶3d¹⁰4s²4p⁶4d¹⁰4f¹⁴ for Lu-based compounds; [core] is 1s²2s²2p⁶3s²3p⁶3d¹⁰4s²4p⁶4d¹⁰ for La-based compounds.

^b From Ref. [25].

Table 5
The Ln(acac)₃–Q bond energies for **1–6**

Central ion	La	Gd	Lu
[Ln(acac) ₃ phen]	20.79	17.62	13.11
[Ln(acac) ₃ dipy]	20.52	17.52	13.14

distances are observed in Gd mixed ligand complexes (2.15 Å and 2.11 Å for **5** and **6**, respectively).

To estimate the thermodynamic stability of mixed ligand complexes under investigation, the Ln(acac)₃–Q bonding energies have been calculated by using the following formula:

$$E(\text{bonding}) = E([\text{Ln}(\text{acac})_3\text{Q}]) - E(\text{Ln}(\text{acac})_3) - E(\text{Q})$$

The bonding energy for all mixed ligand complexes are summarized in Table 5. These values characterize the total energy of bonding between lanthanide acetylacetonate and additional neutral ligand including two Ln–N bond energies as well as all possible additional interactions such as weak oxygen–hydrogen and other intramolecular donor–acceptor interactions. The data presented in Table 5 show that the Ln(acac)₃–Q bond energies are decreased in passing from [La(acac)₃Q] (**3** and **4**) through [Gd(acac)₃Q] (**5** and **6**) to [Lu(acac)₃Q] (**1** and **2**). This can be explained by the ion–dipole nature of the Ln(acac)₃–Q interaction. Thus, the less covalent character of La–acac interactions leads to the greater positive charge of La—ion compared to Lu—one that in turn results in a decrease of the Ln(acac)₃–Q bond energies in going from La- to Lu-based mixed ligand complexes. The compounds of gadolinium have middle position between lanthanum and lutetium ones. At the same time, the exchange of phen with the dipy does not cause the significant overpatching in the Ln(acac)₃–Q bonding energies. These values can be used to estimate the thermodynamic stability of compounds of such type, which turns out to be fairly low. The findings are consistent with a tendency of mixed ligand molecules to dissociate to parent species in the gas phase [8,11,26]. Low bonding energies are in agreement with the experimentally determined energies of the gas-phase dissociation of complexes studied in mass-spectrometry experiments [11,26].

3. Conclusion

In accordance with the theoretical modeling of [Ln(acac)₃Q], the Ln(acac)₃–Q interaction has a primarily electrostatic nature which can be interpreted as an ion–dipole interaction. This confirms by NBO atomic charge distributions in [Ln(acac)₃Q] and natural atomic orbital populations of central lanthanide ions. The increase of the covalent contribution in Ln–acac bond in Lu-derivatives compared to La-derivatives leads to the decrease of central ion charge from La to Lu. In view of the electrostatic nature of the Ln(acac)₃–Q interaction results in the decrease of Ln(acac)₃–Q bonding energies in Lu-based complexes in comparison with La-based compounds. So, the unexpected inverted electrostatic trend, i.e. a decrease in stability of mixed ligand complexes along with the lanthanide

series, has been found for $\text{Ln}(\text{acac})_3\text{-Q}$ interactions. Moreover, the charge compensation occurring when small $\text{Ln}(\text{III})$ ion binds to the negatively charged acac-ligands, and which is responsible for the decrease of the global positive charge of the cation, represents an interesting issue for designing novel neutral Ln -complexes. Also, it should be especially noted that a decrease of $\text{Ln}(\text{acac})_3\text{-Q}$ bond energy mentioned above is caused by primarily electrostatic reasons but not a steric factor.

The more ionic character of Ln -acac bond in lanthanum complexes than those for lutetium ones reflects in the crystal structures of mixed ligand complexes $[\text{Ln}(\text{acac})_3\text{Q}]$. Thus, in spite of the similar molecular structures **1** and **3** the mutual orientation of phen-fragments can be realized only in the case of La-derivatives due to the enhanced flexibility of ligand position in lanthanum coordination sphere compared to Lu-based compounds.

The replacement of phen ligand by dipy does not lead to the noticeable changes neither in equilibrium geometry configuration of lanthanide mixed ligand complexes nor in electron density distribution according to the NBO-analysis. As a consequence, the $\text{Ln}(\text{acac})_3\text{-Q}$ bonding energies of phen-based and dipy-based compounds do not have any differences.

4. Experimental section

Analytically pure reagents $\text{Lu}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$, KOH, Hacac, phen $\cdot\text{H}_2\text{O}$ and dipy from Merck were used without further purification. Dry phen was obtained by dehydration of phen $\cdot\text{H}_2\text{O}$ at 140 °C (0.01 Torr). Original complex $\text{Lu}(\text{acac})_3 \cdot 2\text{H}_2\text{O}$ was prepared according to the standard procedure [27], was purified by recrystallization from EtOH and identified by elemental and IR spectroscopic analyses.

The C, H, N contents were determined by conventional elemental analysis. The lanthanide content was determined titrimetrically with titrant solutions of Na_2EDTA , pH5.5.

IR spectra were recorded on a Perkin–Elmer 1600 FTIR spectrometer as Nujol and hexachlorobutadiene mulls between KBr plates in the region 4000–400 cm^{-1} .

NMR spectra were recorded on a Bruker AC-600P spectrometer in CDCl_3/TMS .

Mass-spectra desorption chemical ionization (DCI-MS) were obtained on a SSQ-710 (Finigan MAT, USA) spectrometer. Isobutane was used as reactant gas. The sample was heated ‘in beam’ up to 800 °C. The rate of heating is equal to 3855 degree per minute.

The mixed ligand complex $[\text{Lu}(\text{acac})_3\text{Phen}]$ **1** was obtained by following technique. A solution of 0.18 mg (0.1 mmol) phen in 25 ml of EtOH was mixed with a hot solution of 0.508 mg (0.1 mmol) $\text{Lu}(\text{acac})_3 \cdot 2\text{H}_2\text{O}$ in 25 ml of EtOH. The mixture was refluxed under stirring for 2 h, resulting in a clear colourless solution. The volume of the solution was reduced to a half by slow evaporation of the solvent at room temperature, and yielded a microcrystalline precipitate. Yield ~86%. Found: C, 49.50; H, 4.80; N, 4.13; Lu, 26.5. $\text{C}_{27}\text{H}_{29}\text{O}_6\text{N}_2\text{Lu}$ requires C, 49.69; H, 4.45; N, 4.29; Lu, 26.84%. IR $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$: 1602 (C=O), 1516 (CC), 1462, 854, 756, 734 (phen). ^1H NMR (CDCl_3) δ/ppm : 9.44 (d, 2H), 8.28 (dd, 2H), 7.78 (s, 2H), 7.72

(dd, 2H), 5.14 (s, 3H), 1.75 (s, 18H). DCI-MS m/z : 653 (MH^+), 473 ($\text{MH}^+ - \text{phen}$), 553 ($\text{M}^+ - \text{acac}$).

The mixed ligand complex **2** was obtained by analogous procedure, by using dipy instead of phen. Yield ~90%. Found: C, 47.29; H, 4.17; N, 4.17; Lu, 27.7. $\text{C}_{25}\text{H}_{29}\text{O}_6\text{N}_2\text{Lu}$ requires C, 47.77; H, 4.62; N, 4.46; Lu, 27.87%. IR $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$: 1602 (C=O), 1516 (CC), 1462, 784, 760, 7400 1(dipy). ^1H NMR (CDCl_3) δ/ppm : 9.04 (d, 2H), 8.08 (d, 2H), 7.84 (dd, 2H), 7.37 (dd, 2H), 5.23 (s, 3H), 1.83 (s, 18H). DCI-MS m/z : 629 (MH^+), 473 ($\text{MH}^+ - \text{dipy}$), 529 ($\text{M}^+ - \text{acac}$).

4.1. Crystal structure determination

Suitable single crystals of $[\text{Lu}(\text{acac})_3\text{phen}]$ **1** and $[\text{Lu}(\text{acac})_3\text{dipy}]$ **2** were grown by recrystallization of the crude products from EtOH solution.

Data collection for $[\text{Lu}(\text{acac})_3\text{Phen}]$ **1** and $[\text{Lu}(\text{acac})_3\text{dipy}]$ **2** were carried out, respectively, on a STADI4 (Stoe) and CAD4 (Enraf–Nonius) four-circle diffractometers using graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Structure solutions and refinements for **1** were carried out by using SHELXS-97 [28] and SHELXL-97 [29] programs. Non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques based on F^2 . Hydrogen atoms were placed at the calculated positions and were included in the final refinements in a riding mode.

The structure **2** was solved by direct methods using SIR2002 program package [30]. Absorption correction by ψ -scanning method was applied to the set of experimental data. All non-hydrogen atoms except one were found from E-synthesis and the left atom—from difference Fourier synthesis, then refined by full matrix least squares in isotropic and anisotropic approximations successively. Positions hydrogen atoms were calculated from structure data and refined with restriction of bond length and bond angle with fixed isotropic atomic displacement parameters. It is present in Table 6. Difference Fourier synthesis revealed residual weak peaks close to existing atoms. The description and results of the single crystal experiment are given in Table 6. Selected bond lengths and angles for **1** and **2** are listed in Table 1.

CCDC-264393 and 267005 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) _44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

4.2. Calculation details

Full geometry optimization of the molecular structures was performed at the DFT level of theory using the hybrid functional B3PW91, which show a good results for the lanthanide complexes [31]. The relativistic effective large core potential (RECP), optimized by the Stuttgart–Bonn group [32], was applied, since 4f-electrons did not participate in the metal–ligand bonding [33]. The corresponding basis sets consistent with these RECP's augmented by the f-type

Table 6

Crystallographic and structure refinement for [Lu(acac)₃phen] **1** and [Lu(acac)₃dipy] **2**

	[Lu(acac) ₃ phen]	[Lu(acac) ₃ dipy]
Empirical formula	LuC ₂₇ H ₂₉ N ₂ O ₆	LuC ₂₅ H ₂₉ N ₂ O ₆
Formula weight	652.49	628
Temperature (K)	110	293
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	9.465(2)	18.845(3)
<i>b</i> (Å)	20.932(4)	13.417(1)
<i>c</i> (Å)	14.548(3)	22.614(2)
β (°)	98.54(3)	109.676(9)
<i>V</i> (Å ³)	2850(1)	5384(1)
<i>Z</i>	4	8
<i>D</i> _{calc} (g/cm ³)	1.521	1.432
μ (Mo K α) (mm ^{−1})	3.503	3.691
Reflections collected	4258	14,010
Independent reflections	3972	6730
Goodness-of-fit on <i>F</i> ²	1.123	1.18
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.069	0.041
<i>wR</i> ₂ [all]	0.176	0.0597

polarization functions were used for lanthanide ion [34]. The standard basis set 6-31G [35] was applied for all ligand atoms. The geometry optimization of the molecular structures was carried out without imposing symmetry constraints on the system. For each compound under consideration, calculations of harmonic frequencies were performed. Real harmonic frequencies indicated that the optimized structures corresponded to the true minimum on the potential energy surface. The natural bond analysis (NBO) [36,37] has been used for a detailed description of the electronic structure of compounds under investigation.

All calculations were carried out using the PC GAMESS [38] version of the GAMESS (US) [39] program package for quantum chemical modelling.

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