ORIGINAL PAPER

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Lanthanide complex coordination polyhedron geometry prediction accuracies of ab initio effective core potential calculations

Abstract The ability to efficiently and accurately predict solid-state geometries of lanthanide coordination compounds efficiently and accurately is central for the design of new ligands capable of forming stable and highly luminescent complexes. Accordingly, we present in this paper a report on the capability of various ab initio effective core potential calculations in reproducing the coordination polyhedron geometries of lanthanide complexes. Starting with all combinations of HF, B3LYP and MP2(Full) with STO-3G, 3-21G, 6-31G, 6-31G* and 6-31+G basis sets for $[Eu(H_2O)_9]^{3+}$ and closing with more manageable calculations for the larger complexes, we computed the fully predicted ab initio geometries for a total of 80 calculations on 52 complexes of Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III) and Tm(III), the largest containing 164 atoms. Our results indicate that RHF/STO-3G/ECP appears to be the most efficient model chemistry in terms of coordination polyhedron crystallographic geometry predictions from isolated lanthanide complex ion calculations. Moreover, both augmenting the basis set and/or including electron correlation generally enlarged the deviations and aggravated the quality of the predicted coordination polyhedron crystallographic geometry. Our results further indicate that Cosentino et al.'s suggestion of using RHF/3-21G/ECP geometries appears to be indeed a more robust, but not necessarily, more accurate recommendation to be adopted for the general lanthanide complex case.

Keywords Lanthanide · Rare-earth · Ab initio · ECP

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Introduction

Lehn's proposal in 1990 that lanthanide complexes could be regarded as light-conversion molecular devices [1] was followed by the discovery of numerous new compounds with many applications, such as luminescent and electroluminescent materials [2].

The "a priori" theoretical design of new and efficient light conversion molecular devices would require the calculation of the theoretical emission quantum yields, q, for which we would need the total radiative decay rate of the emitting level. This, in turn, depends on the Stark levels, which can be calculated by the diagonalization of the ligand field matrix, whose elements depend directly on the ligand field parameters, B_q^k. Finally, these B_q^k parameters depend both on the symmetry of the coordination polyhedron, as well as on the third, fifth and seventh inverse powers of the distances between the directly coordinating atoms and the central lanthanide ion [3, 4]. As such, any inaccuracies in these distances have far larger consequences than inaccuracies in the angles.

Accordingly, the ability to efficiently and accurately model the geometries of all these supramolecular systems efficiently and accurately is, therefore, central for the design of new ligands capable of forming stable and highly luminescent complexes, where the aim is to achieve strong ligand-to-metal energy transfer rates and intense metal-centred emission [5, 6].

Accurate ab initio all-electron electronic structure calculations for supramolecular lanthanide coordination compounds require the inclusion of relativistic effects [7] and are currently computationally prohibitive. Indeed, quantum chemical calculations on lanthanide complexes are presently restricted to two approaches that have been devised to circumvent this problem: effective core potentials (ECPs) [7, 8] and the Sparkle/AM1 model [9] recently introduced by our research group. Indeed, Sparkle/AM1 is a significant improvement over its previous versions [10, 11] and has been parameterized to

reproduce crystallographic structures of Eu(III), Gd(III) and Tb(III) complexes. The sparkle model assumes that the 4f orbitals do not contribute notably to the chemical bond due to their very small overlap with the orbitals of the ligand atoms, thus rendering the lanthanide–ligand chemical bond essentially electrostatic.

On the other hand, an ECP is a sum of potential functions that replaces core electrons and core orbitals that are considered to play a minor role in determining chemical phenomena. As such, mostly valence electrons are treated. Various lanthanide ECPs are available in the literature and recent studies have shown that ECPs with density functional calculations reproduce the crystallographic geometries of lanthanide and actinide compounds acceptably [12–18]. For this work, we chose the quasi-relativistic ECP of Dolg et al. [19] and its related [5s4p3d]—GTO valence basis set, which is available in Gaussian 98 [20] and has been used in recent papers on calculations on large lanthanide coordination compounds [21–23].

Materials design requires the prediction of solid-state geometries of complexes. Two sources of error exist when, as often, one tries to obtain crystallographic geometries from ab initio ECP calculations on isolated complexes: (i) crystal packing effects, which, for example, tend to reduce metal–ligand distances [24, 25] and (ii) the fact that ECPs are adjusted and calibrated approximations. In the literature, to the best of our knowledge, there are no studies that assess the crystallographic coordination polyhedron prediction accuracy of isolated complex ECP calculations for larger lanthanide coordination compounds extensively.

Methods

In this paper we present a report on the capability of various model chemistries, based on the ECP by Dolg et al. [19], in reproducing the coordination polyhedron crystallographic geometries of lanthanide complexes from calculations on the isolated single lanthanide complex ion. Due to the high computational costs involved, we first studied the isolated cation of nona-aqua-europium(III) tris (trifluoromethanesulfonate). To confirm the trends discovered, we further computed six larger representative complexes of Eu(III). Subsequently, we made an attempt to substantiate the generality of our findings by computing representative complexes of Sm(III), Gd(III), Tb(III), Dy(III), Ho(III), Eb(III) and Tm(III) for a total of 37 more structures. Finally, to establish the robustness of our findings, we further computed eight more dilanthanide ion complexes, where the two lanthanide ions face each other. In summary, a total of 80 ab initio full geometry optimizations on 52 complexes of eight different lanthanide ions were performed to confirm our findings.

Crystallographic data

The experimental crystallographic structure of nona-aqua-europium(III) tris (trifluoromethanesulfonate), was obtained from the 'Cambridge Structural Database 2004' (CSD) [26–28], where it is identified by code BU-VXAR11, [29] (28 atoms, Fig. 1). The CSD-deposited structure has an R-factor of 3.1% and the following cell parameters: $a = b = 13.722$ Å, $c = 7.504$ Å, $\alpha = 120.00°$ and $\beta = \gamma = 90.00°$. The complex cation (Fig. 1) is therefore $[Eu(H_2O)_9]^{3+}$, a europium ion coordinated to nine water molecules with a net charge of $+3$ e, balanced by three trifluoromethanesulfonate anions. Likewise, we obtained from CSD, crystallographic structures of the other 51 larger lanthanide complex ions, employed in this study, from the full complexes structures, all with R-factors less than 5%. The largest complex calculated in this study was WIRTUM, a gadolinium complex with 164 atoms.

Quantum chemistry software

All calculations were performed using the crystallographic geometry as the starting point.

The ab initio calculations used the Gaussian 98 package [20]. For the europium(III) ion, we used the quasi-relativistic ECP of Dolg et al. [19] and the related [5s4p3d]—GTO valence basis set. This ECP includes $46 + 4f^n$ electrons in the core, leaving the outermost 11 electrons to be treated explicitly. In consequence, we used MWB52 in the basis sets definition, which is Dolg's ECP Gaussian code for europium $3+$. We performed combinations varying the model chemistry (i.e. the method as well as the basis set) in a hierarchical manner; on one side, Hartree Fock, B3LYP and MP2(Full) methods and, STO-3G, 3-21G, 6-31G, 6-31G* and 6-31+G basis sets on the other, for a total of 15 calculations on an Athlon MP 1.53 GHz and 1 GB of RAM, totaling more than 352 h of CPU time for the nona-aqua-europium(III) tris (trifluoromethanesulfonate) alone. We further computed 51 more structures of other ligand and/or lanthanide ions with the less involved of the model chemistries with ECP keywords ranging from MWB51 for Sm(III) to MWB58 for Tm(III).

Geometry accuracy measures

Comparisons between crystallographic and ab initio/ECP coordination polyhedron geometries of $[Eu(H_2O)_9]^{3+}$ used the unsigned mean error (UME), calculated as the sum of all absolute values of differences between crystallographic R_j^{CSD} and calculated R_j^{calc}, interatomic distances, as in Eq. (1).

$$UME = \frac{1}{n} \sum_{j=1}^{n} \left| R_j^{CSD} - R_j^{calc} \right| \qquad (1)$$

Fig. 1 Schematic three-dimensional representation of the crystallographic structure of the cation nona-aqua-europium(III) obtained from 'Cambridge Structural Database 2004' [26–28]

Two cases were examined: (i) UMEs involving the interatomic distances R_j between the europium central ion and the atoms of the coordination polyhedron, as well as the interatomic distances R_j between all atoms of the coordination polyhedron, and (ii) $UME_{(Eu-L)}$s involving only the interatomic distances R_j between the europium central ion and the atoms of the coordination polyhedron, important in luminescent complex design.

Results and discussions

A small europium complex

Table 1 shows relative computational times for the various ab initio/ECP calculations of the $[Eu(H_2O)_9]^{3+}$ complex, using several model chemistries, varying both the method and the basis set, on an Athlon MP 1.53 GHz and 1 GB of RAM, all with respect to RHF/STO-3G. As expected, differences in timings are very large.

Figure 2 shows UMEs for all interatomic distances between the europium central ion and the oxygen atoms of the coordination polyhedron in graphical form, as well as interatomic distances between all oxygen atoms of the coordination polyhedron, for ab initio/ECP calculations of the $[Eu(H_2O)_9]^{3+}$ complex using several

Table 1 Computational times (relative to RHF/STO-3G) for complete geometry optimizations of the $[Eu(H_2O)_9]^{3+}$ complex ion, for various model chemistries, on an Athlon MP 1.53 GHz and 1 GB of RAM

Model chemistry	CPU time (relative to RHF/STO-3G)		
	RHF	B3LYP	MP2(Full)
STO-3G	1	16	7
3-21G	5	19	32
6-31G	8	30	46
6-31G*	15	36	194
6-31G$^+$	29	69	606

model chemistries, varying both the method and the basis sets. This measure of UME for polyhedron distances is therefore sensitive to the accuracy of the predicted angles of the coordination polyhedron.

As can be seen from Fig. 2, neither augmenting the basis set nor increasing the level of the method from HF, to B3LYP and MP2(full) necessarily improves the accuracy of the predicted crystallographic coordination polyhedron from calculations on a single isolated europium complex ion. Most of the time, it aggravates it. For example, by moving hierarchically from RHF/STO-3G/ECP up to RHF/6-31+G/ECP, the corresponding UMEs increase monotonically from 0.064 to 0.149 Å. Cosentino et al. [30] also carried out an extensive study on the $[Gd(H2O)_9]^{3+}$ ion, using various basis sets and different levels of calculation. They concluded by recommending RHF/3-21G/ECP calculations as being able to provide quite reliable geometries and conformational energies. However, in the present paper we will be concerned only with coordination polyhedron geometries, important for luminescent complex design. Although the best UME we obtained (Fig. 2) was from a B3LYP/3-21G/ECP, a similar one, slightly larger, is also obtained from an RHF/STO-3G/ECP calculation, which, according to Table 1, is nevertheless 19 times faster.

As mentioned in the introduction, the ligand-field parameters B_q^k, are important for the design of luminescent complexes and depend both on the symmetry of the coordination polyhedron, as well as on the third, fifth and seventh inverse powers of the distances between the directly coordinating atoms and the central lanthanide ion. Errors in these distances are, therefore, far more important than either errors in the angles or errors in the whole coordination polyhedron, and thus deserve to be examined separately.

Figure 3 shows $UME_{(Eu-L)}$s for only the interatomic distances R_j between the europium central ion and the oxygen atoms of the coordination polyhedron. The results show similar trends as before. However, RHF/STO-3G/ECP now seems to be the most accurate of all model chemistries for the prediction of crystallographic lanthanide ligand atom distances from isolated ion complex calculations.

Indeed, Fig. 3 indicates more clearly that accuracy in the crystallographic distances between the europium and the coordinating ligand atoms only seems to get worse when one either increases the basis set or includes electron correlation, or both.

Larger europium complexes

Since the europium–water complex is relatively small, we decided to test if this behaviour would also be found for ECP calculations on larger europium complexes of the type more commonly used as luminescent molecular devices. As such, we decided to use the six monoeuropium complexes already chosen by Freire et al. [9]

Fig. 4, to be representative of the following types of ligands: β-diketone (YOJDIK), nitrate (BAFZEO), monodentate (KELNOE), bidentate (QAKWUU), tridentate (NOHLOL), and polydentate (HAZGAQ), where the codes in parenthesis are their specific CSD [26–28] codes.

Because of computational constraints, we were only able to perform RHF/STO-3G/ECP, RHF/3-21G/ECP and RHF/6-31G*/ECP calculations for all these com-plexes. Figure 5 plots UMEs for the interatomic distances R_j between the europium central ion and the atoms of the coordination polyhedron, as well as the interatomic distances R_j between all atoms of the coordination polyhedron. Moving away from RHF/STO-3G/ECP only decreases the accuracy, as results for RHF/6-31G*/ECP were the least accurate for each and every one of the six monoeuropium complexes studied. For the larger complexes, RHF/STO-3G/ECP

Fig. 2 Graphical visualization of UMEs, involving not only the interatomic distances between the europium central ion and the oxygen atoms of the coordination polyhedron, but also the interatomic distances between all oxygen atoms of the coordination polyhedron of the cation nona-aqua-europium(III) for various model chemistries, all compared to the 'Cambridge Structural Database 2004' [26–28] crystallographic geometry
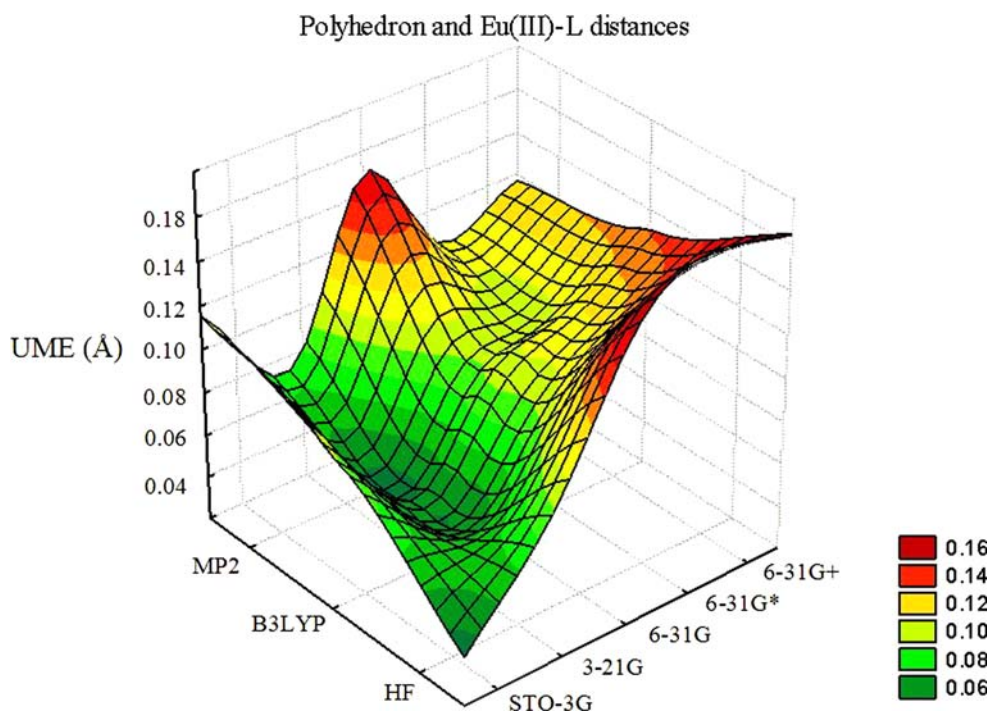
Fig. 3 Graphical visualization of UME$_{(Eu–L)}$s, involving only the interatomic distances between the europium central ion and the oxygen atoms of the coordination polyhedron of the cation nona-aqua-europium(III) for various model chemistries, all compared to the 'Cambridge Structural Database 2004' [26–28] crystallographic geometry
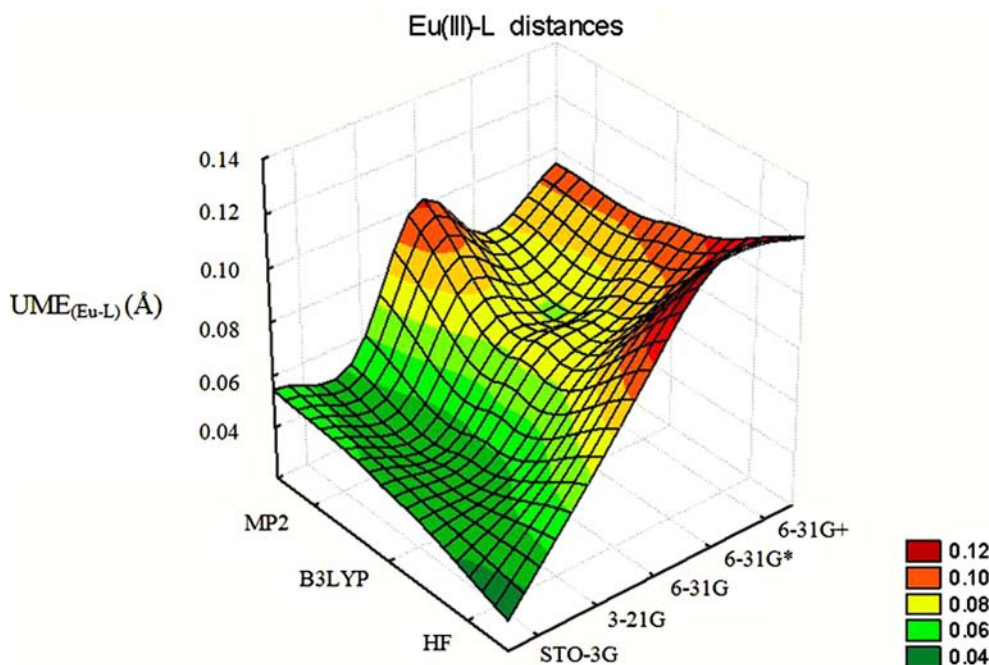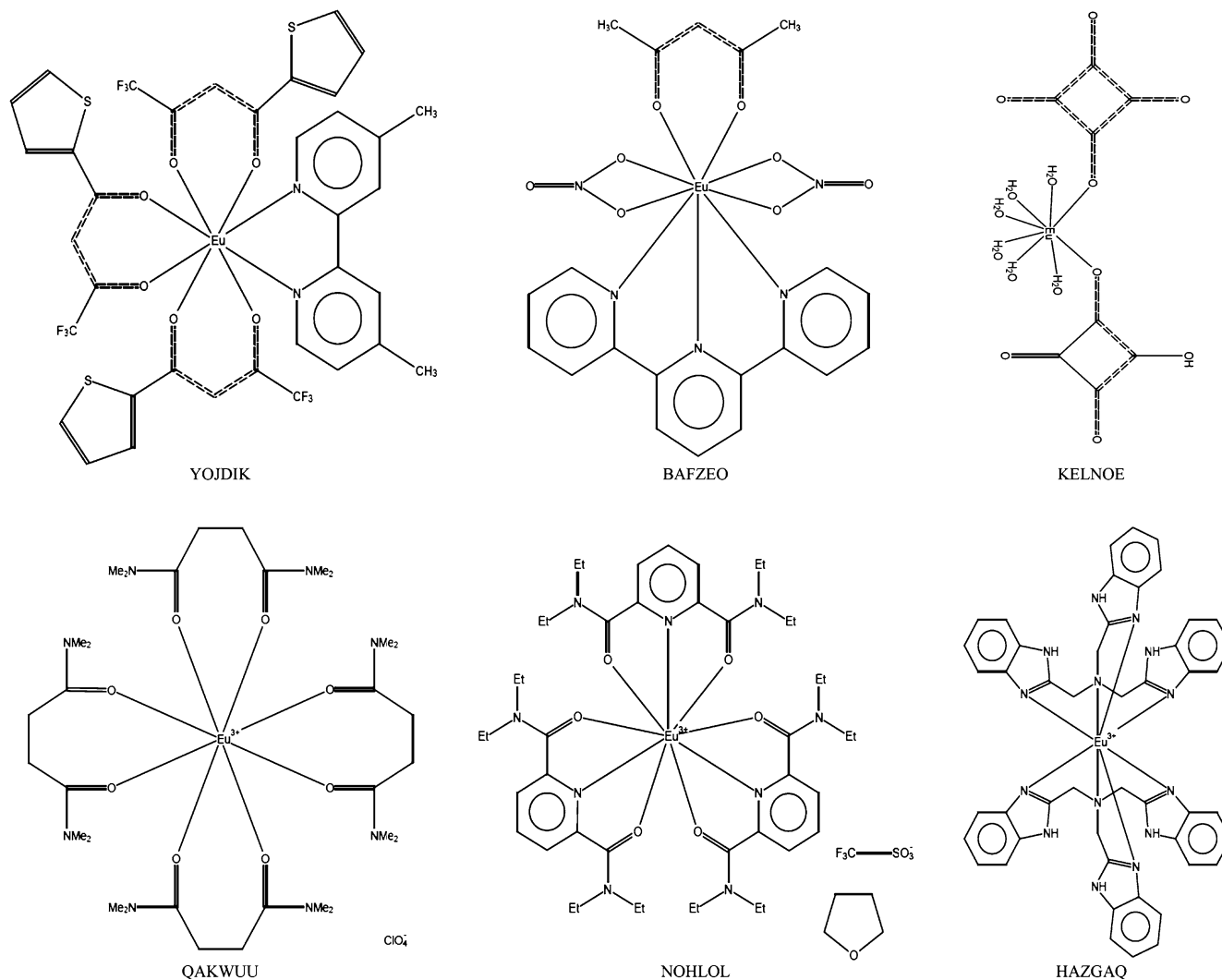
Fig. 4 Schematic two-dimensional representation of the structures of europium(III) complexes, used for comparison between Sparkle/AM1 and some ab initio model geometries with their crystallographic counterparts, where the complexes are identified by their respective Cambridge Structural Database 2004 [26–28] codes. The ab initio calculations have been performed using the Hartree–Fock method with STO-3G, 3-21G and 6-31G* basis sets for all atoms, except for the europium(III) ion, in which case we used the quasi-relativistic ECP of Dolg et al. [19]

calculations seem to be the most accurate for the purpose of prediction of the whole coordination polyhedron crystallographic geometry from isolated ion calculations.

Once again, let us examine the trend in the prediction accuracy of europium ligand–atom distances only important for the calculation of the ligand field parameters for luminescent complex design, as shown in Fig. 6 The trend that appeared in Fig. 2 for the cation nona-aqua-europium(III), once again crops up for the larger complexes, with RHF/STO-3G/ECP being the most accurate of the ab initio calculations in terms only of predictions of crystallographic distances between the europium ion and its directly coordinating ligand atoms.

Larger complexes of other lanthanide ions

Let us now verify whether or not RHF/STO-3G/ECP calculations on complexes of other lanthanide ions obey the general trends found so far for europium complexes. For that purpose, for each additional lanthanide ion, we chose sets of four to six complexes, representatives of the various types of ligand of importance to luminescent complex design—β-diketones, nitrates, monodentates, bidentates, tridentates and polydentates. We investigated Sm(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III) and Tm(III), for a total of 37 further complexes.

Figures 7, 9, 11, 13, 15, 17, 19, show schematic two-dimensional representations of the structures of the
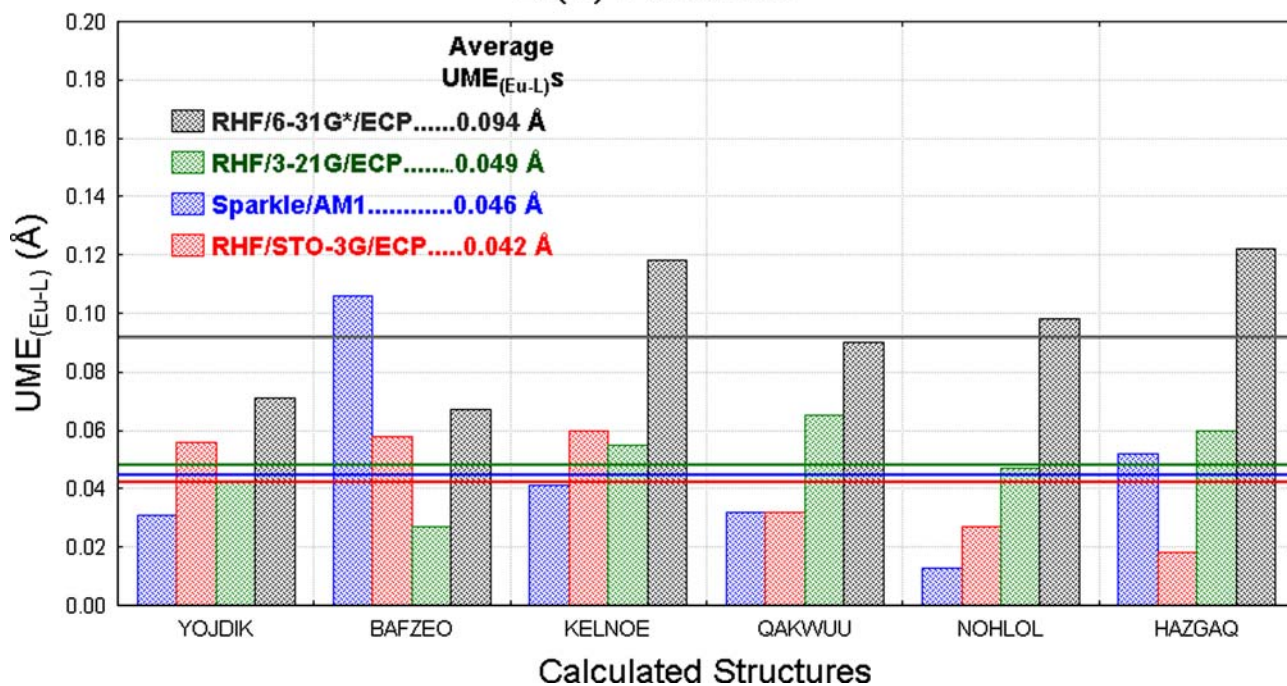
378

Polyhedron and Eu(III)-L distances
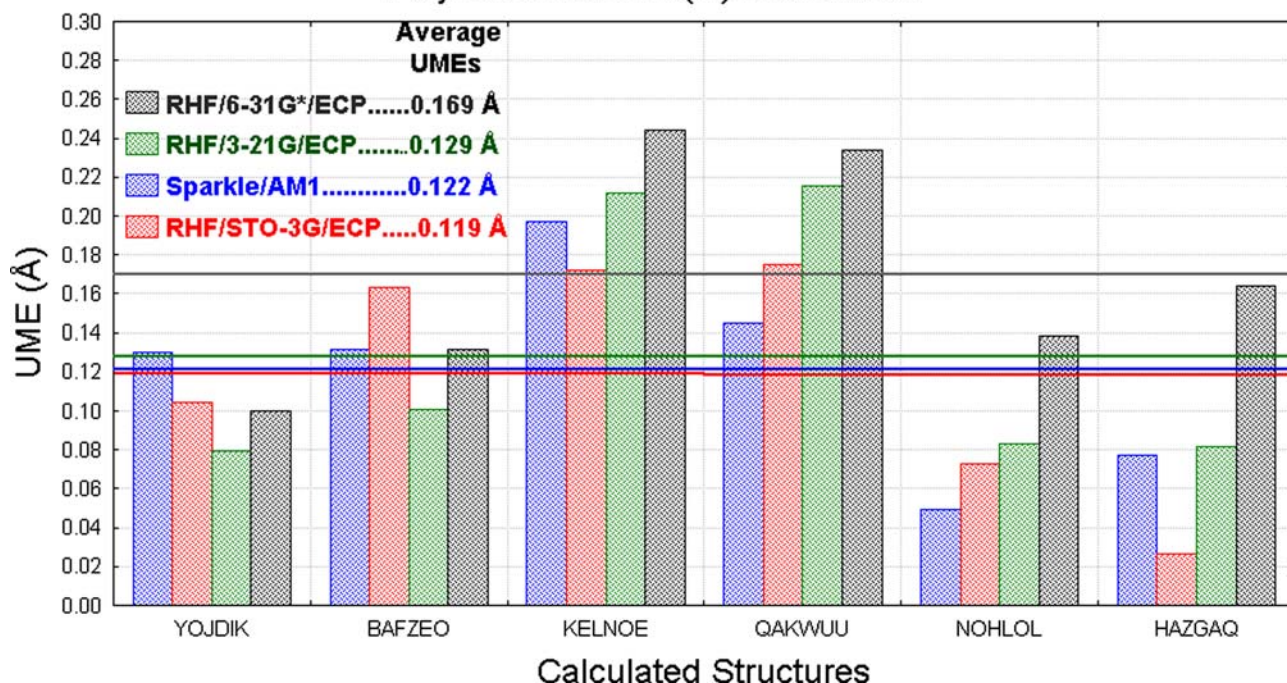
Fig. 5 Unsigned mean errors, UMEs (in Å), between the europium central ion and the atoms of the coordination polyhedron, as well as the interatomic distances R_j between all atoms of the coordination polyhedron obtained from Sparkle/AM1 and ab initio (RHF/STO-3G/ECP, RHF/3-21G/ECP, and RHF/6-31G*/ECP) 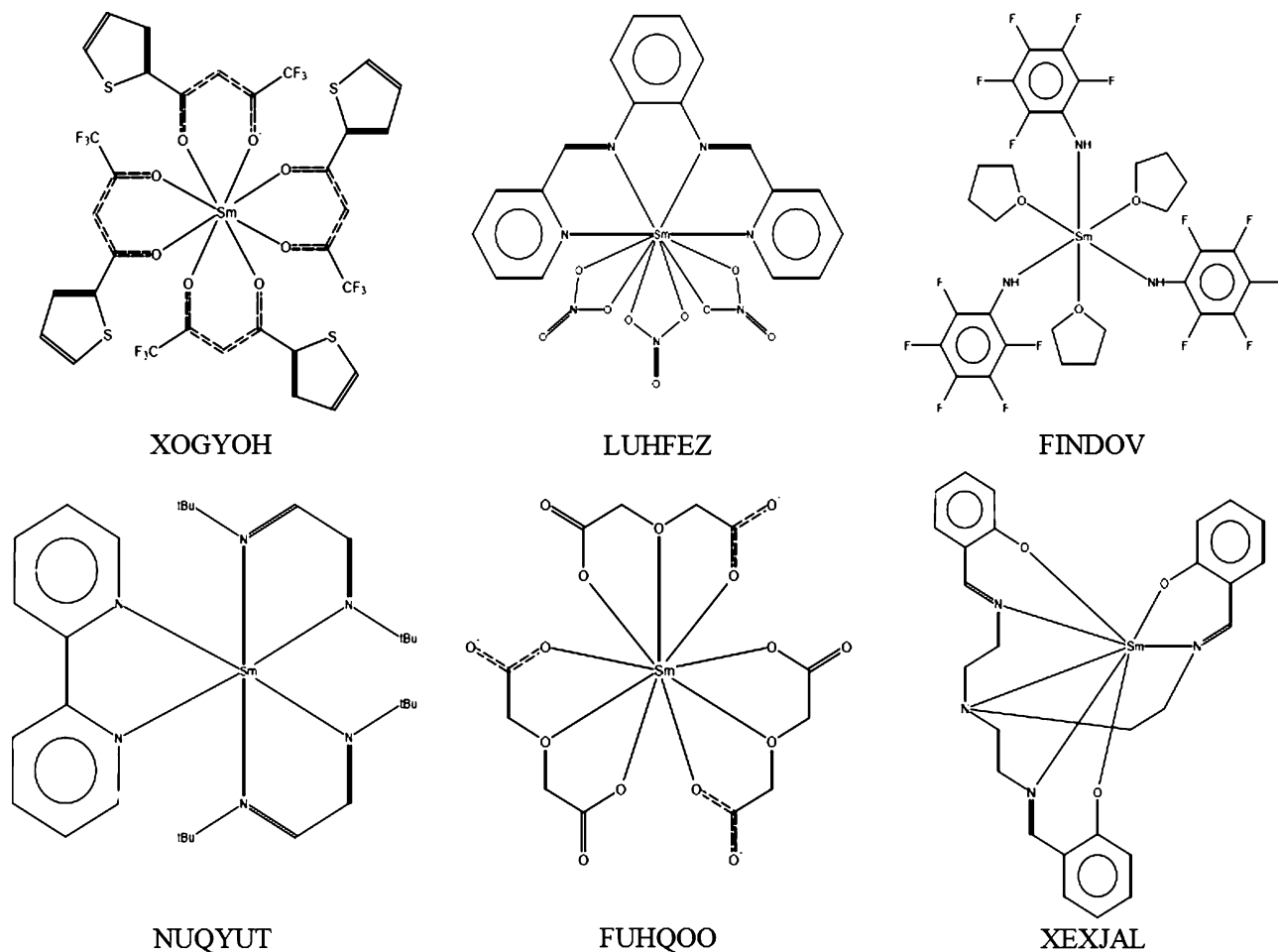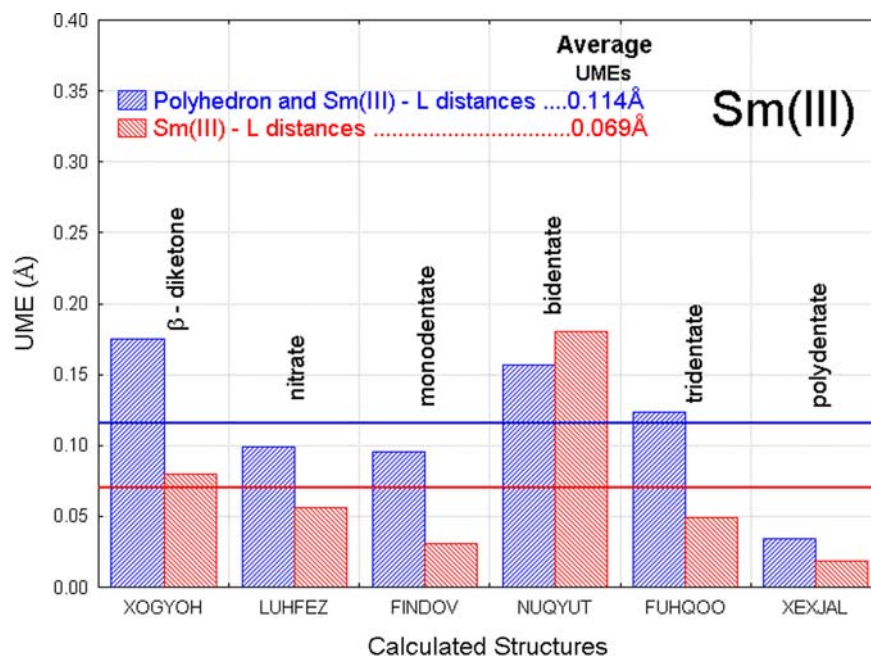calculations of the ground-state geometries, for each of the six representative europium(III) complexes identified by their respective Cambridge Structural Database 2004 [26–28] codes. UMEs for each model chemistry, averaged over all six complexes, have been indicated by horizontal solid lines at the levels presented in the *top left* corner of the figure

Eu(III)-L distances

Fig. 6 Unsigned mean errors, UME$_{(Eu-L)}$s, involving only the interatomic distances R_j between the europium central ion and the atoms of the coordination polyhedron (in Å), obtained from Sparkle/AM1 and ab initio (RHF/STO-3G/ECP, RHF/3-21G/ECP, and RHF/6-31G*/ECP) calculations of the ground-state geometries, for each of the six representative europium(III) complexes, identified by their respective Cambridge Structural Database 2004 [26–28] codes. UMEs for each model chemistry, averaged over all six complexes, have been indicated by horizontal solid lines at the levels presented in the *top left* corner of the figure

XOGYOH   LUHFEZ   FINDOV
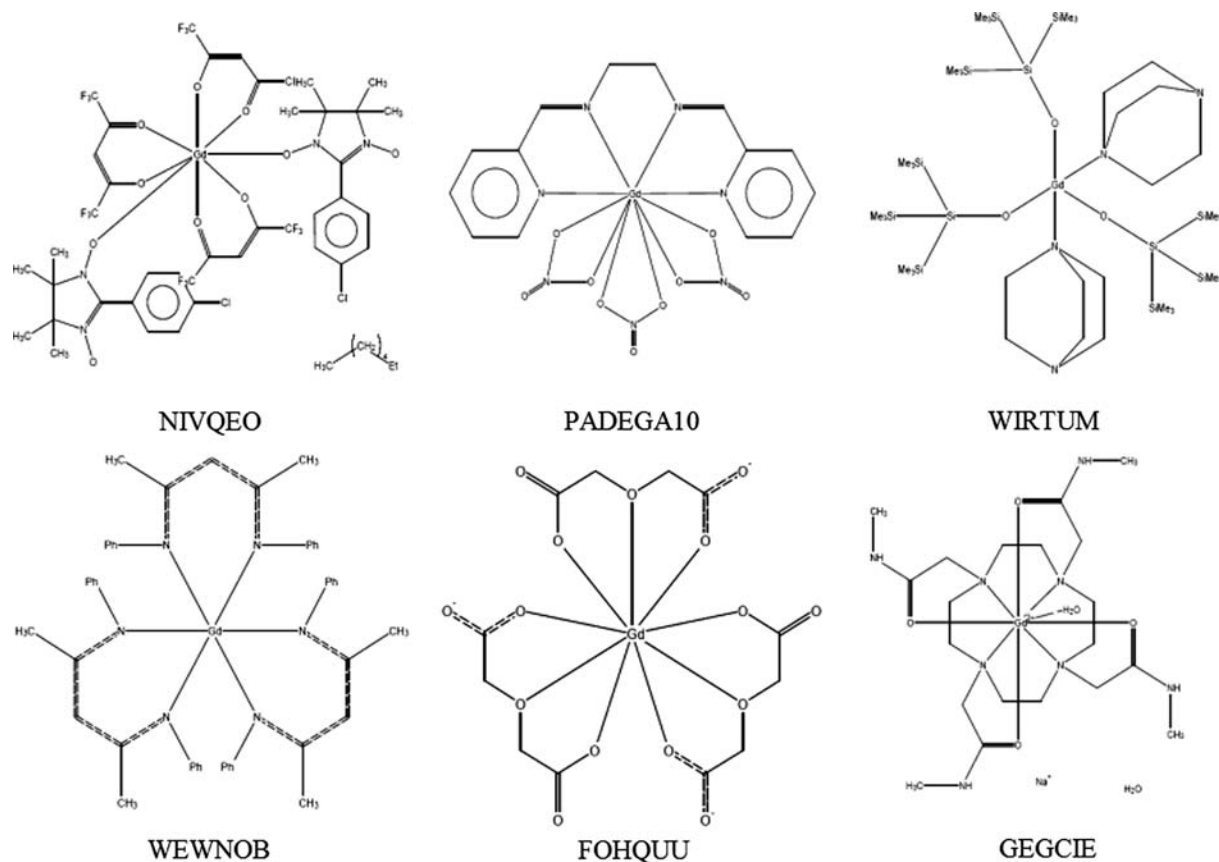
NUQYUT   FUHQOO   XEXJAL

Fig. 7 Schematic two-dimensional representation of the structures of samarium(III) complexes, used for comparison between ab initio model geometries and their crystallographic counterparts, identified by their respective Cambridge Structural Database 2004 [26–28] codes. The ab initio calculations have been performed using the Hartree–Fock method with STO-3G basis set for all atoms, except for the samarium(III) ion, in which case we used the quasi-relativistic ECP of Dolg et al. [19]

Fig. 8 Unsigned mean errors, UMEs (in Å), between the samarium central ion and the atoms of the coordination polyhedron, as well as all the interatomic distances R_j between all atoms of the coordination polyhedron (in *blue*), and the UMEs involving only the interatomic distances R_j between the samarium central ion and the atoms of the coordination polyhedron (in *red*), obtained from ab initio RHF/STO-3G/ECP calculations of the ground-state geometries, for each of the six representative samarium(III) complexes, identified by their respective Cambridge Structural Database 2004 [26–28] codes
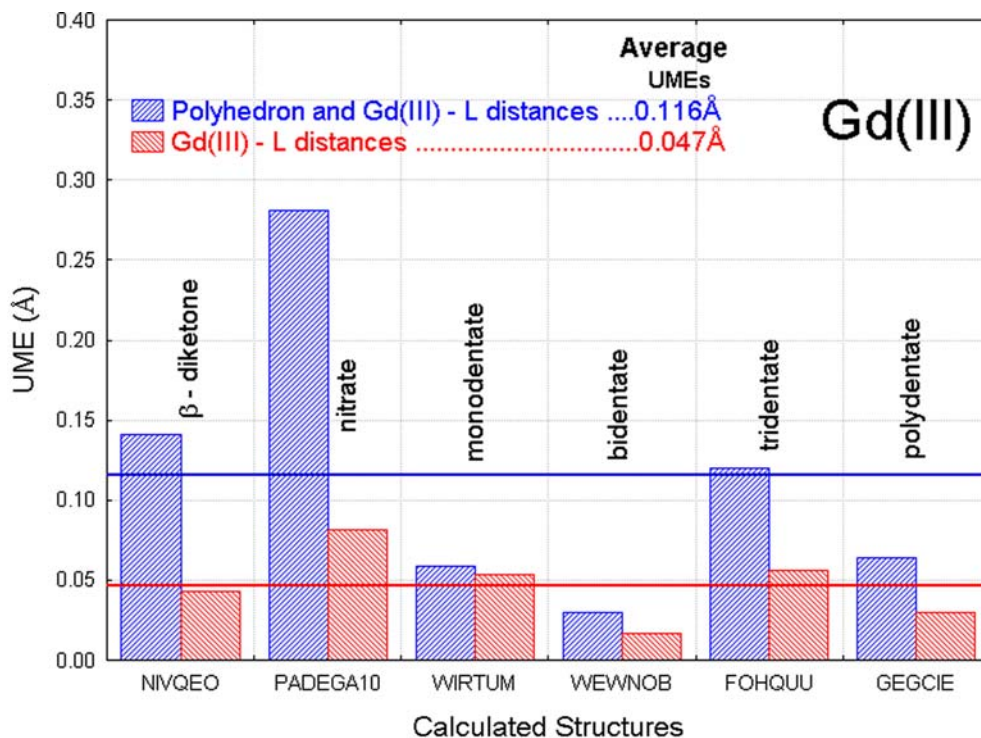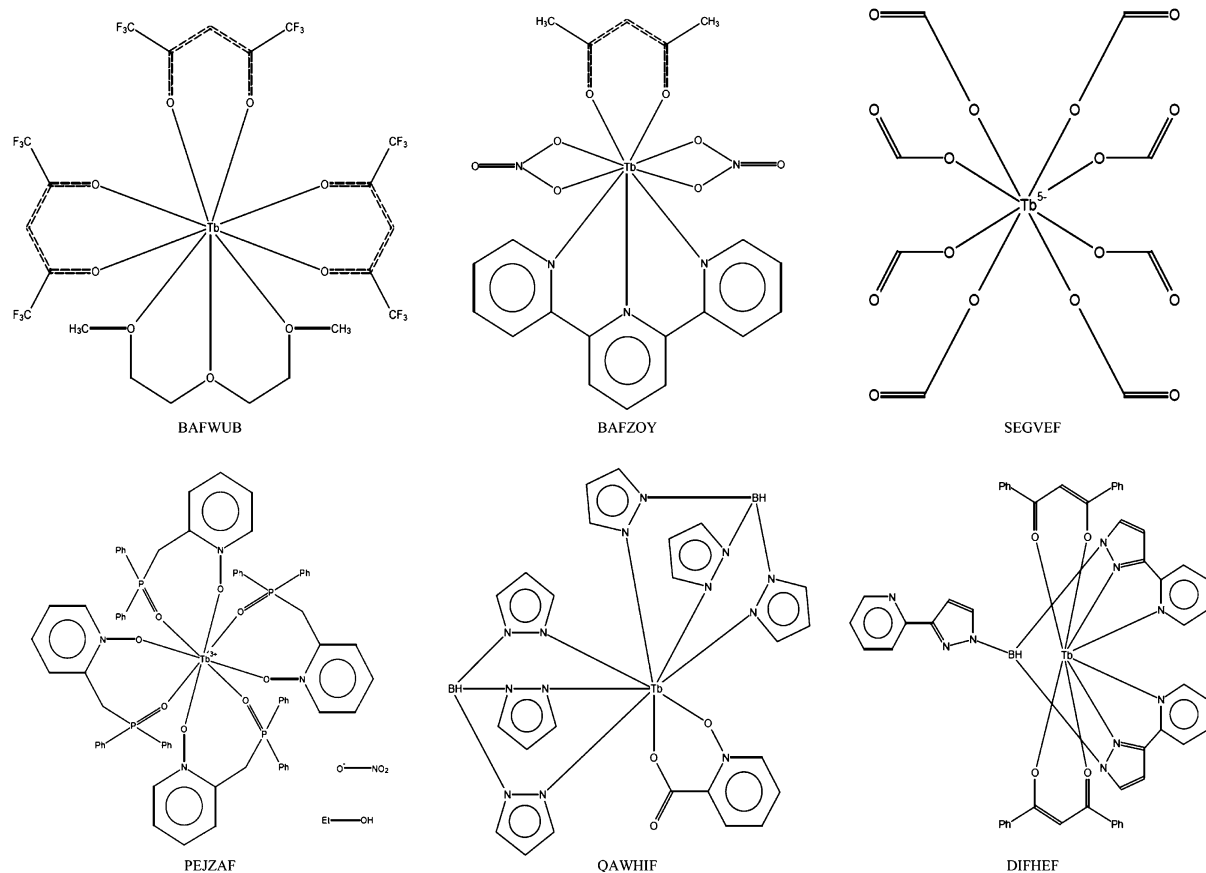
Fig. 9 Schematic two-dimensional representation of the structures of gadolinium(III) complexes, used for comparison between ab initio model geometries and their crystallographic counterparts, identified by their respective Cambridge Structural Database 2004 [26–28] codes. The ab initio calculations have been performed using the Hartree–Fock method with STO-3G basis set for all atoms, except for the gadolinium(III) ion, in which case we used the quasi-relativistic ECP of Dolg et al. [19]

Fig. 10 Unsigned mean errors, UMEs (in Å), between the gadolinium central ion and the atoms of the coordination polyhedron, as well as all the interatomic distances R_j between all atoms of the coordination polyhedron (in *blue*), and the UMEs involving only the interatomic distances R_j between the gadolinium central ion and the atoms of the coordination polyhedron (in *red*), obtained from ab initio RHF/STO-3G/ECP calculations of the ground-state geometries, for each of the six representative gadolinium(III) complexes, identified by their respective Cambridge Structural Database 2004 [26–28] codes
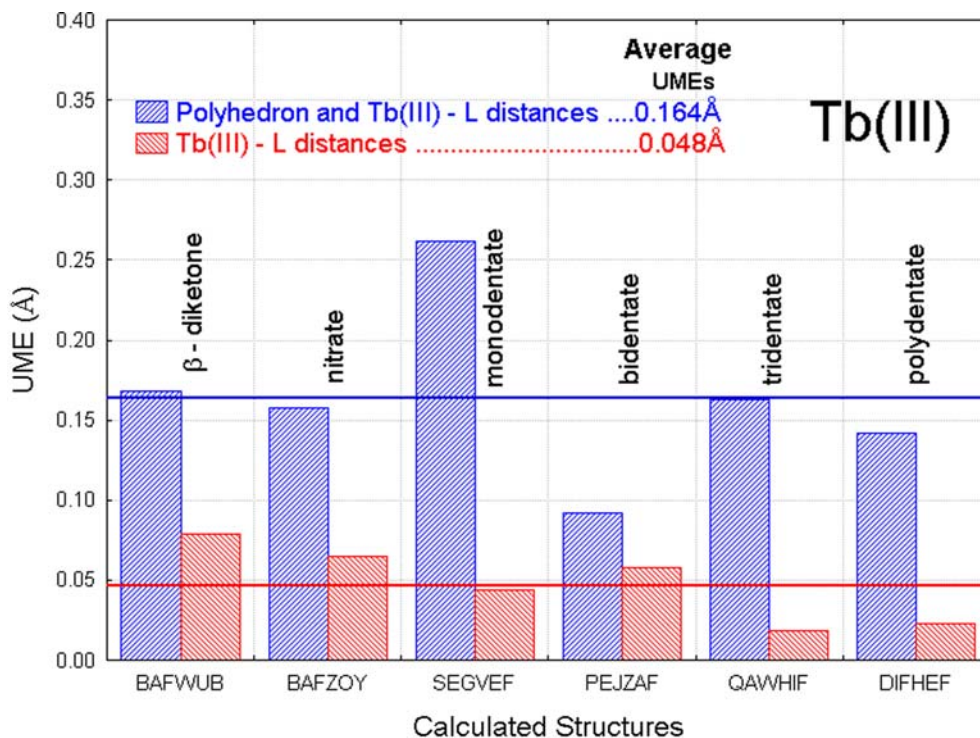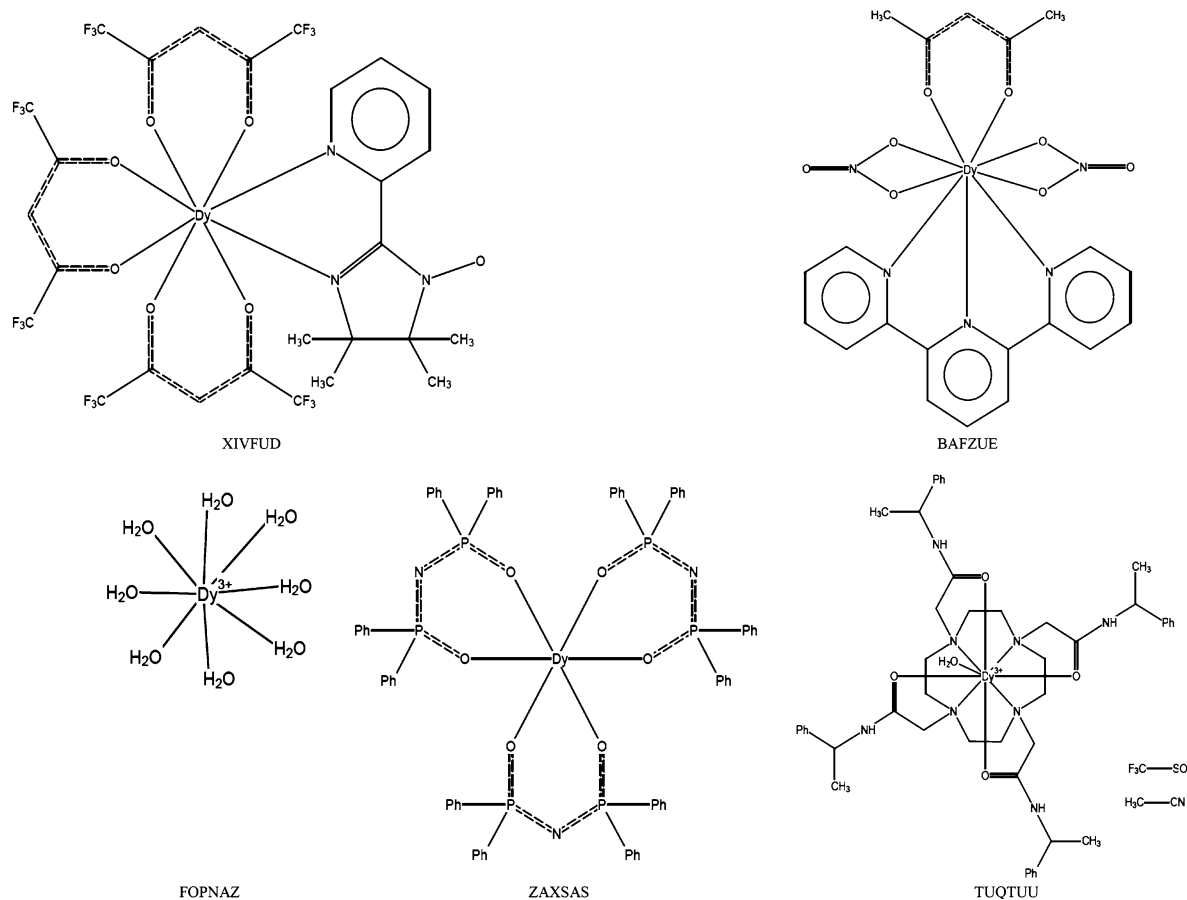
Fig. 11 Schematic two-dimensional representation of the structures of terbium(III) complexes, used for comparison between ab initio model geometries and their crystallographic counterparts, identified by their respective Cambridge Structural Database 2004 [26–28] codes. The ab initio calculations have been performed using the Hartree–Fock method with STO-3G basis set for all atoms, except for the terbium(III) ion, in which case we used the quasi-relativistic ECP of Dolg et al. [19]

Fig. 12 Unsigned mean errors, UMEs (in Å), between the terbium central ion and the atoms of the coordination polyhedron, as well as all the interatomic distances R_j between all atoms of the coordination polyhedron (in *blue*), and the UMEs involving only the interatomic distances R_j between the terbium central ion and the atoms of the coordination polyhedron (in *red*), obtained from ab initio RHF/STO-3G/ECP calculations of the ground-state geometries, for each of the six representative terbium(III) complexes, identified by their respective Cambridge Structural Database 2004 [26–28] codes
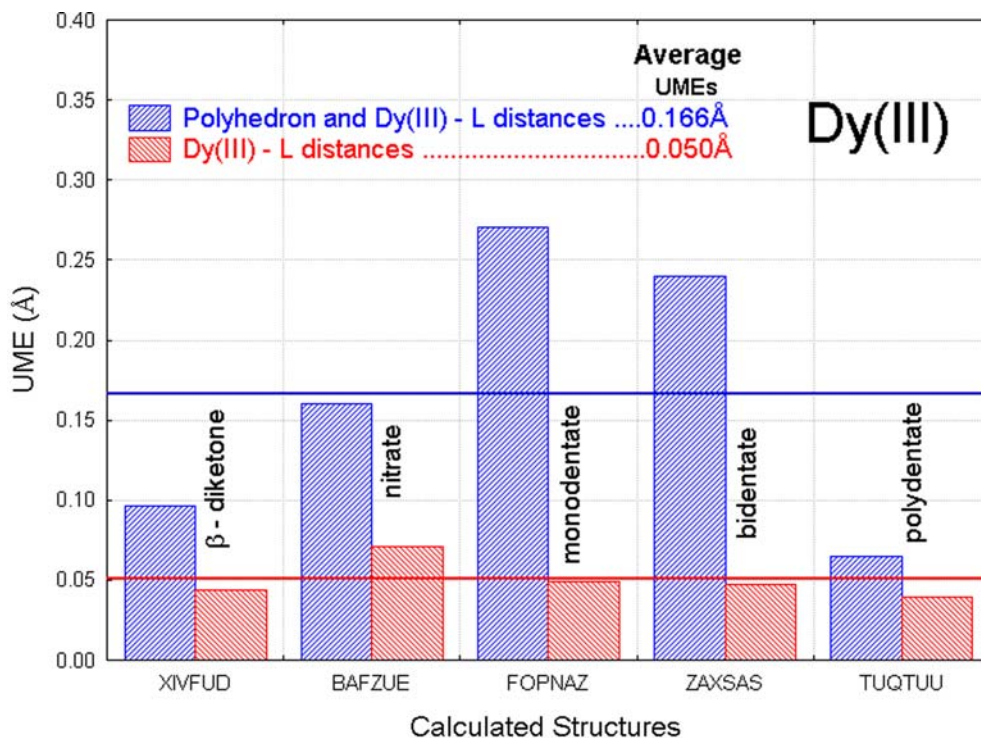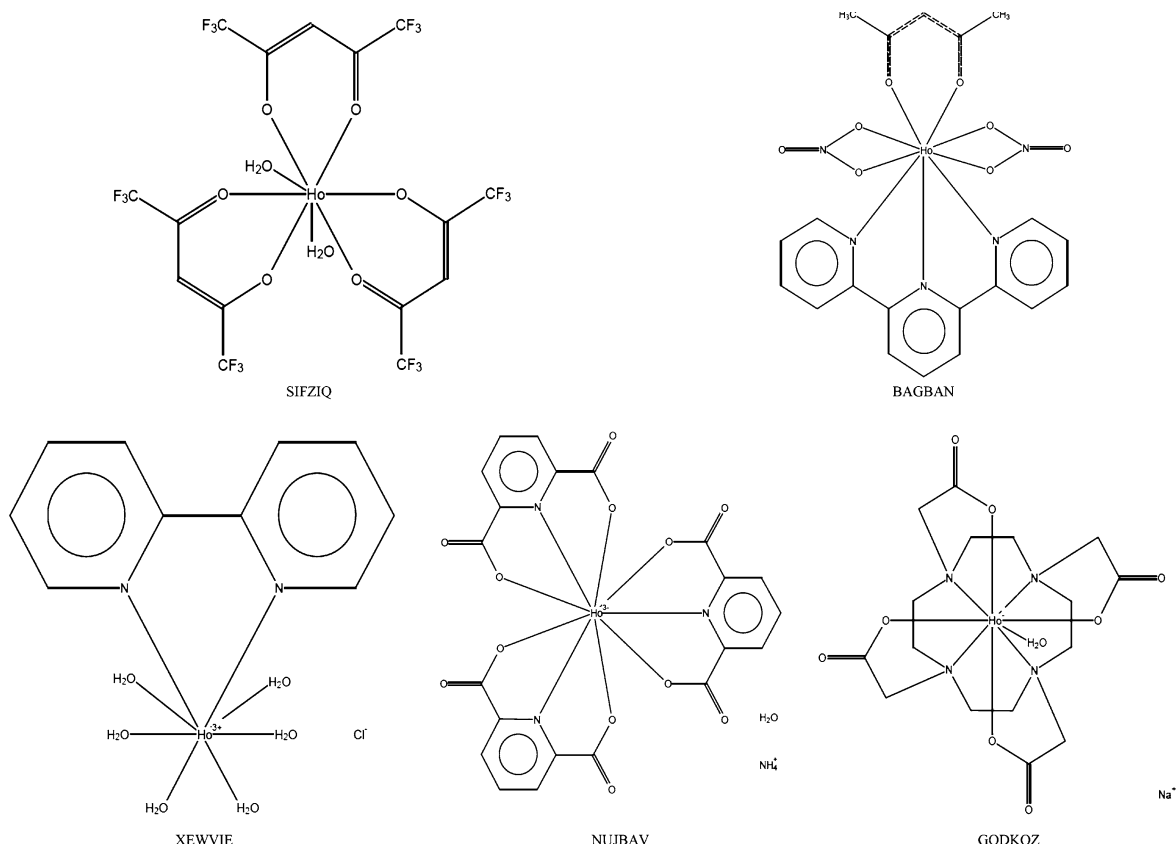
Fig. 13 Schematic two-dimensional representation of the structures of dysprosium(III) complexes, used for comparison between ab initio model geometries and their crystallographic counterparts, identified by their respective Cambridge Structural Database 2004 [26–28] codes. The ab initio calculations have been performed using the Hartree–Fock method with STO-3G basis set for all atoms, except for the dysprosium(III) ion, in which case we used the quasi-relativistic ECP of Dolg et al. [19]

Fig. 14 Unsigned mean errors, UMEs (in Å), between the dysprosium central ion and the atoms of the coordination polyhedron, as well as all the interatomic distances R_j between all atoms of the coordination polyhedron (in *blue*), and the UMEs involving only the interatomic distances R_j between the dysprosium central ion and the atoms of the coordination polyhedron (in *red*), obtained from ab initio RHF/STO-3G/ECP calculations of the ground-state geometries, for each of the five representative dysprosium(III) complexes, identified by their respective Cambridge Structural Database 2004 [26–28] codes
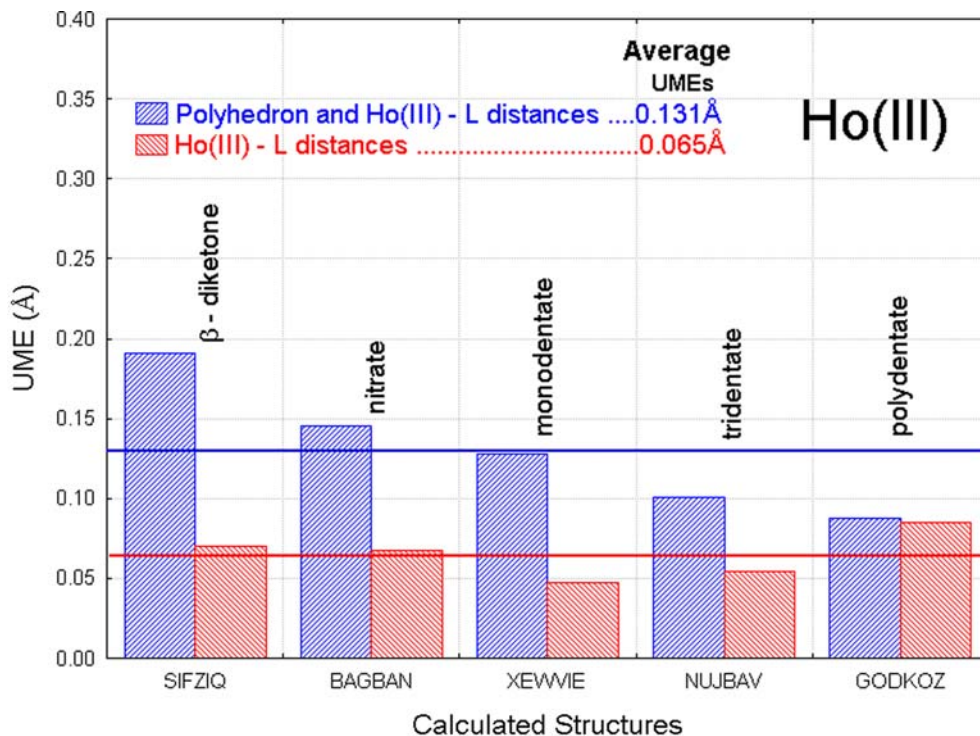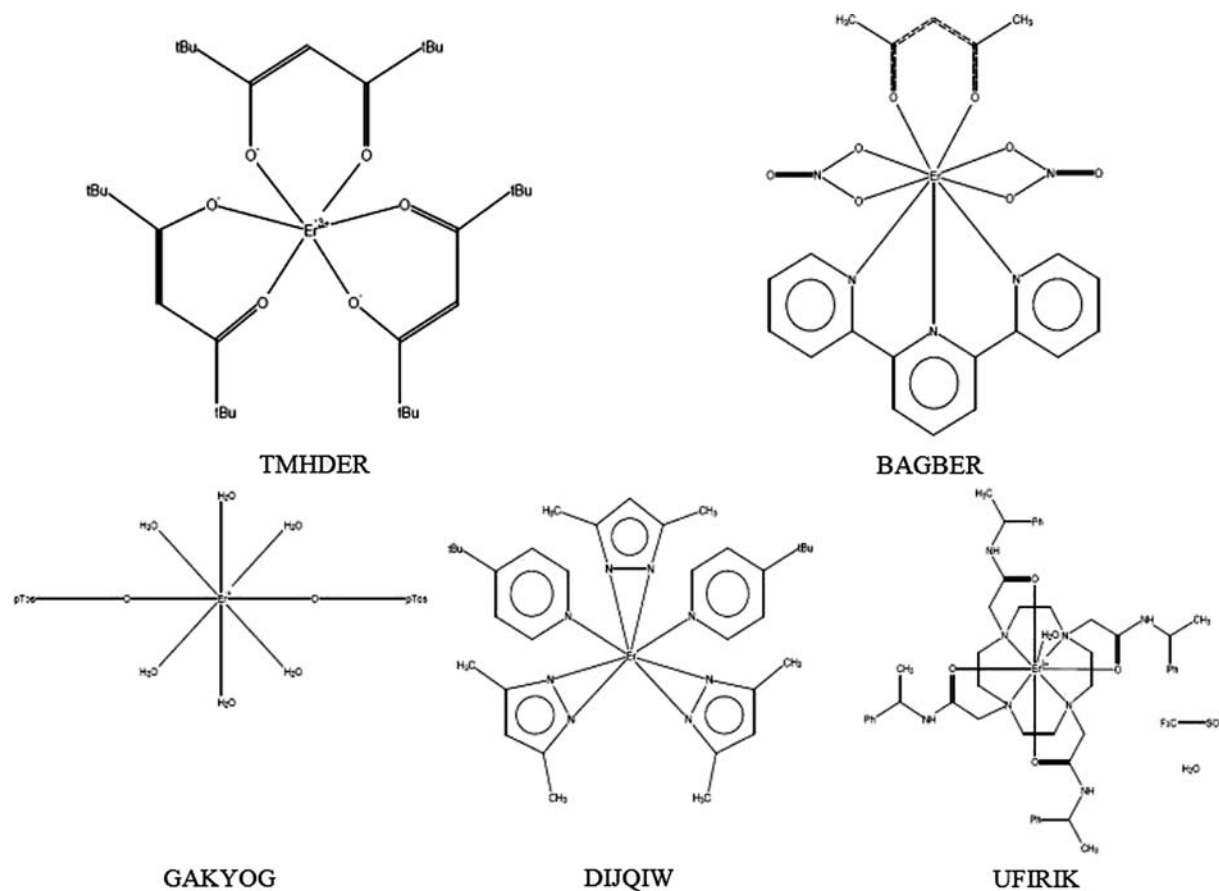
Fig. 15 Schematic two-dimensional representation of the structures of holmium(III) complexes, used for comparison between ab initio model geometries and their crystallographic counterparts, identified by their respective Cambridge Structural Database 2004 [26–28] codes. The ab initio calculations have been performed using the Hartree–Fock method with STO-3G basis set for all atoms, except for the holmium(III) ion, in which case we used the quasi-relativistic ECP of Dolg et al. [19]

Fig. 16 Unsigned mean errors, UMEs (in Å), between the holmium central ion and the atoms of the coordination polyhedron, as well as all the interatomic distances R_j between all atoms of the coordination polyhedron (in *blue*), and the UMEs involving only the interatomic distances R_j between the holmium central ion and the atoms of the coordination polyhedron (in *red*), obtained from ab initio RHF/STO-3G/ECP calculations of the ground-state geometries, for each of the five representative holmium(III) complexes, identified by their respective Cambridge Structural Database 2004 [26–28] codes
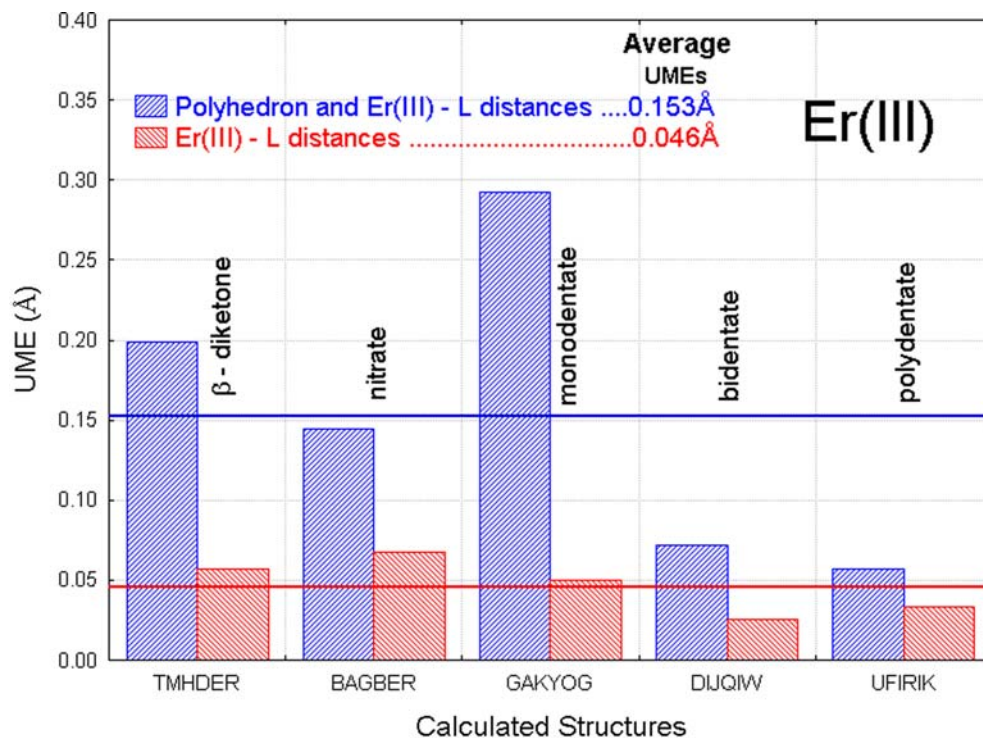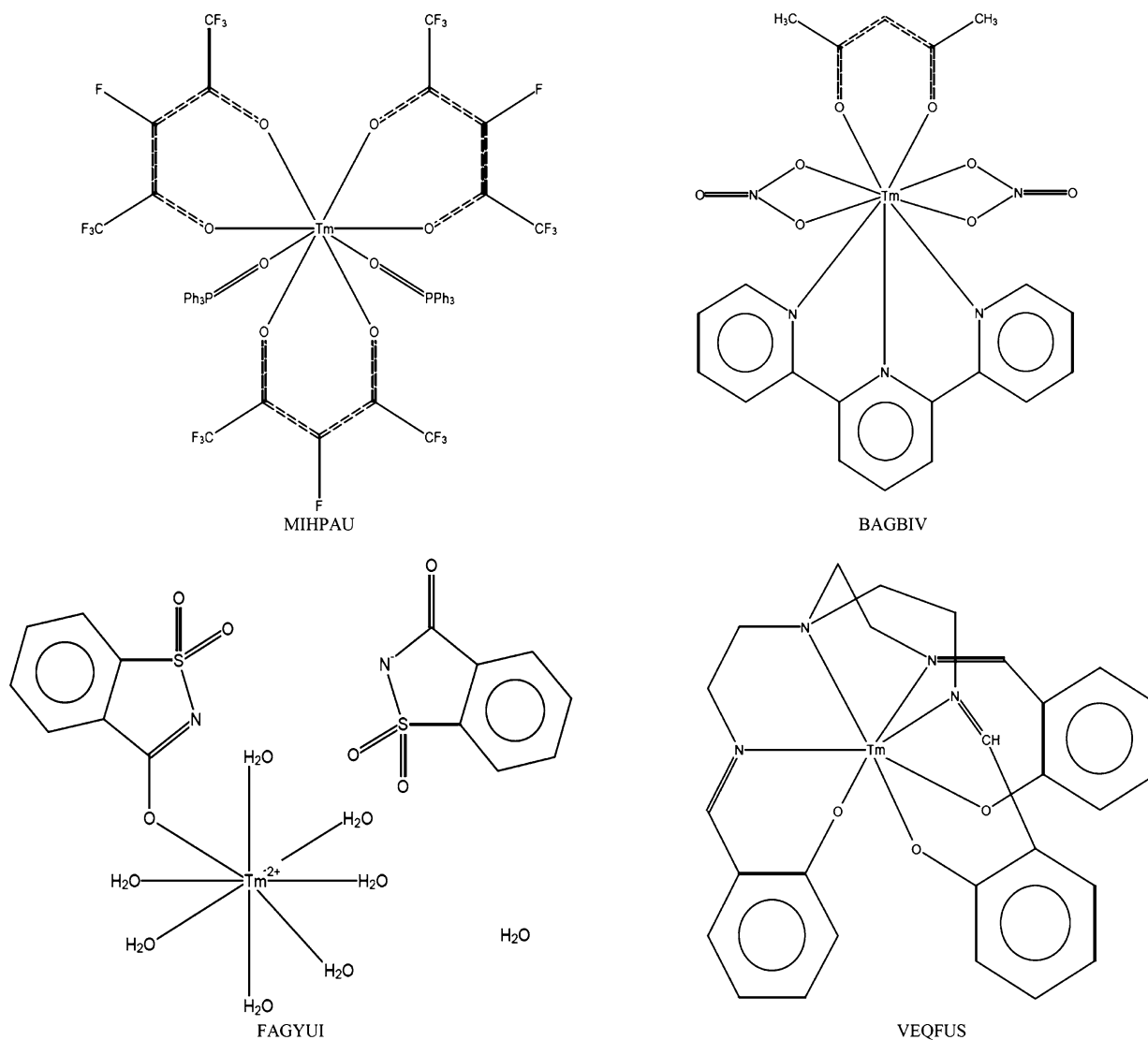
Fig. 17 Schematic two-dimensional representation of the structures of erbium(III) complexes, used for comparison between ab initio model geometries and their crystallographic counterparts, identified by their respective Cambridge Structural Database 2004 [26–28] codes. The ab initio calculations have been performed using the Hartree–Fock method with STO-3G basis set for all atoms, except for the erbium(III) ion, in which case we used the quasi-relativistic ECP of Dolg et al. [19]

Fig. 18 Unsigned mean errors, UMEs (in Å), between the erbium central ion and the atoms of the coordination polyhedron, as well as all the interatomic distances R_j between all atoms of the coordination polyhedron (in *blue*), and the UMEs involving only the interatomic distances R_j between the erbium central ion and the atoms of the coordination polyhedron (in *red*), obtained from ab initio RHF/STO-3G/ECP calculations of the ground-state geometries, for each of the five representative erbium(III) complexes, identified by their respective Cambridge Structural Database 2004 [26–28] codes
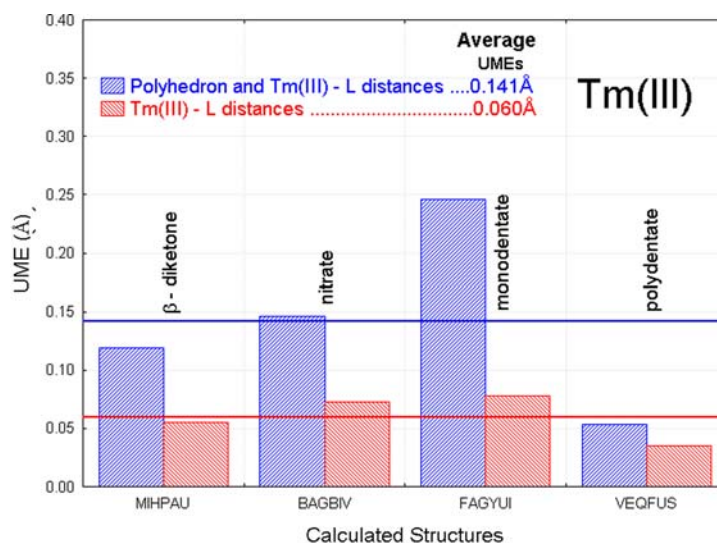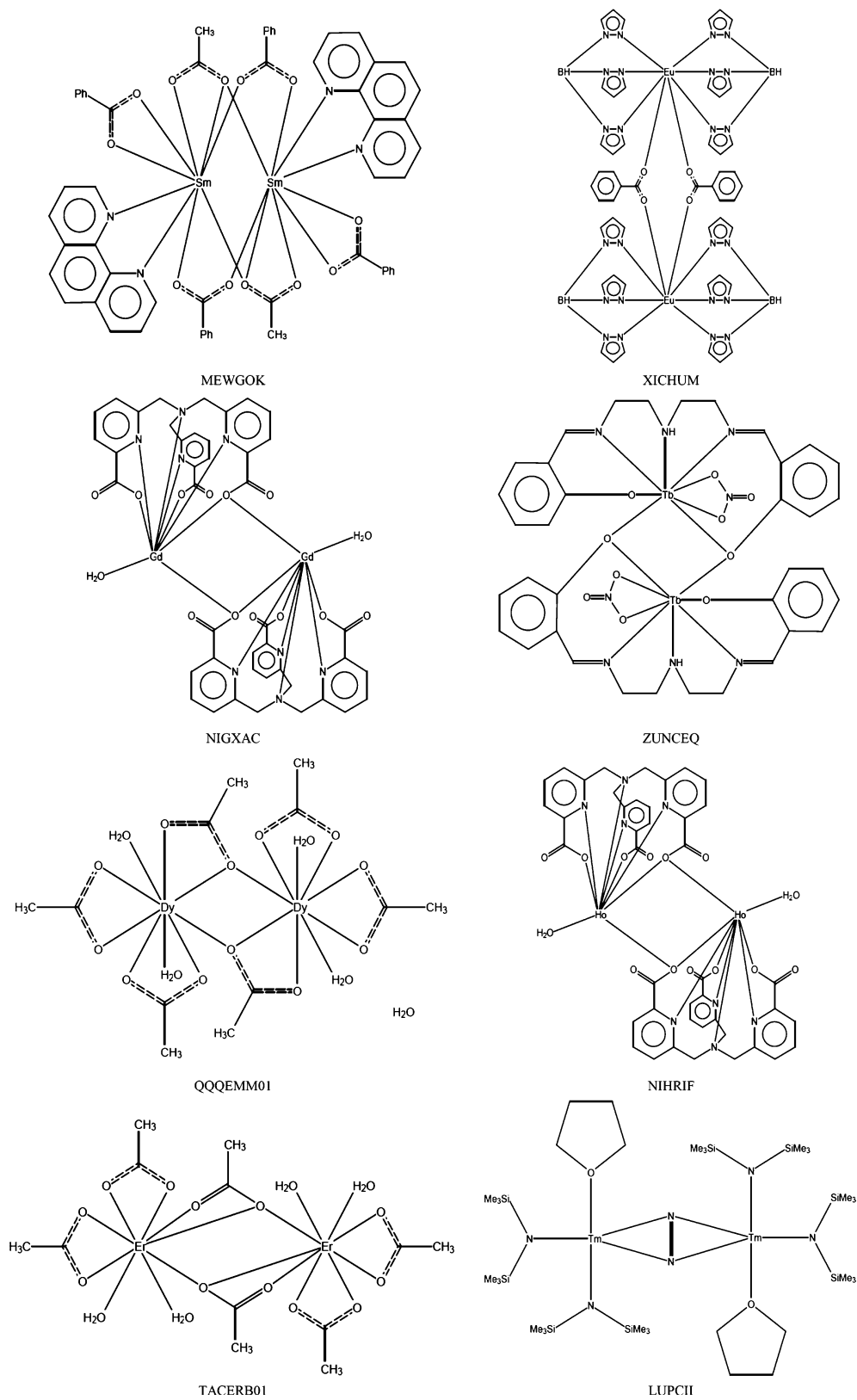
Fig. 19 Schematic two-dimensional representation of the structures of thulium(III) complexes, used for comparison between ab initio model geometries and their crystallographic counterparts, identified by their respective Cambridge Structural Database 2004 [26–28] codes. The ab initio calculations have been performed using the Hartree–Fock method with STO-3G basis set for all atoms, except for the thulium(III) ion, in which case we used the quasi-relativistic ECP of Dolg et al. [19]

Fig. 20 Unsigned mean errors, UMEs (in Å), between the thulium central ion and the atoms of the coordination polyhedron, as well as all the interatomic distances R_j between all atoms of the coordination polyhedron (in *blue*), and the UMEs involving only the interatomic distances R_j between the thulium central ion and the atoms of the coordination polyhedron (in *red*), obtained from ab initio RHF/STO-3G/ECP calculations of the ground-state geometries, for each of the four representative thulium(III) complexes, identified by their respective Cambridge Structural Database 2004 [26–28] codes

Fig. 21 Schematic two-dimensional representation of the structures of dilanthanide complexes, used for comparison between ab initio model geometries and their crystallographic counterparts, identified by their respective Cambridge Structural Database 2004 [26–28] codes. The ab initio calculations have been performed using the Hartree–Fock method with STO-3G basis set for all atoms, except for the lanthanide(III) ion, in which case we used the quasi-relativistic ECP of Dolg et al. [19]

lanthanide(III) complexes used for comparison between ab initio model geometries and their crystallographic counterparts, where the complexes are identified by their respective Cambridge Structural Database 2004 [26–28] codes. Figures 8, 10, 12, 14, 16, 18, 20, show the average UMEs for both the polyhedron and lanthanide–ligand distances, as well as the UMEs of the lanthanide–ligand distances only. With only one exception (the samarium complex NUQYUT in Fig. 8), all other 28 UMEs considering only the lanthanide–ligand distances are smaller than the UMEs that also consider the whole coordination polyhedron. Thus, RHF/STO-3G/ECP calculations do seem to predict lanthanide–ligand distances much more accurately than other distances of the coordination polyhedron. Indeed, for all eight lanthanide ions examined, the UMEs involving the lanthanide–ligand distances only, are all below 0.07 Å, rendering RHF/STO-3G/ECP useful for luminescent complex design—the value for Eu(III) being 0.04 Å (Fig. 3).

On the other hand, the UMEs involving all distances of the coordination polyhedron together with the metal–ligand distances, vary from 0.11 Å, Sm(III) to 0.17 Å, Dy(III)—the value for Eu(III) being 0.12 Å (Fig. 5). Thus, there are no noticeable differences between the behaviour of these UMEs for Eu(III) and those for the other seven lanthanide ions considered. So, we can safely state that our conclusion for europium is de facto general and occurs for all other lanthanide +3 ion complexes.
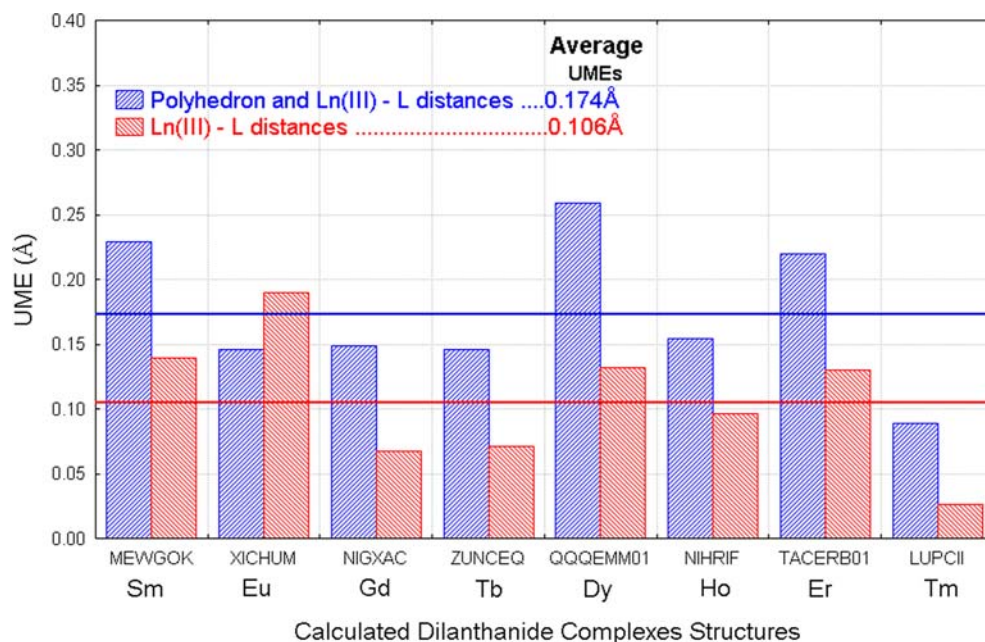
Larger dilanthanide complexes

We now turn to the calculation of dilanthanide complexes where the two lanthanide ions face each other. We chose one such dilanthanide complex for each of the ions studied: Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III) and Tm(III). RHF/STO-3G/ECP results for these complexes are shown in Fig. 21. Once more, the trend that the metal–ligand distances are more accurately predicted than the complete coordination polyhedron holds true for all dilanthanides, except for the sole case of the dieuropium complex XICHUM (Fig. 22). The reason for this inversion is that the RHF/STO-3G/ECP geometry for XICHUM has an exceedingly short Eu(III)–Eu(III) distance of 4.180 Å, as compared to the crystallographic value of 5.388 Å.

We decided to investigate whether improving the ab initio model chemistry would correct this problem and, indeed, the XICHUM Eu(III)–Eu(III) distance values from RHF/3-21G/ECP and RHF/6-31G*/ECP calculations are 5.538 Å and 5.549 Å, respectively. That this appears to be a rare situation of RHF/STO-3G/ECP failure, peculiar to XICHUM, does indeed seem to be the case. In order to confirm this uniqueness, we decided to investigate all other lanthanide–lanthanide RHF/STO-3G/ECP distances and found, as shown in Table 2, that they are all relatively acceptable. Nevertheless, Table 2 also indicates that RHF/STO-3G/ECP calculations generally tend to underestimate lanthanide–lanthanide distances in complexes where the metal ions face each other. Moreover, from Table 2, we again detect the pattern in XICHUM that, by augmenting the basis set from RHF/3-21G/ECP to RHF/6-31G*/ECP, both the metal–ligand and coordination polyhedron UMEs are increased.

In light of this RHF/STO-3G/ECP XICHUM failure, Cosentino et al.'s suggestion of using RHF/3-21G/ECP geometries seems to be a much safer and robust recommendation to be adopted for the general case, despite the fact that RHF/3-21G/ECP calculations take a much longer CPU time (Table 1) than RHF/STO-3G/

Fig. 22 Unsigned mean errors, UMEs (in Å), between the lanthanide central ion and the atoms of the coordination polyhedron, as well as all the interatomic distances R_j between all atoms of the coordination polyhedron (in *blue*), and the UMEs involving only the interatomic distances R_j between the thulium central ion and the atoms of the coordination polyhedron (in *red*), obtained from ab initio RHF/STO-3G/ECP calculations of the ground-state geometries, for each representative dilanthanide(III) complexes, identified by their respective Cambridge Structural Database 2004 [26–28] codes

Table 2 Comparison between crystallographic and calculated distances between the two lanthanide ions, facing each other, in the dilanthanide ion complexes considered, for each of the investigated ions

Lanthanide ion	Dilanthanide complex	Model chemistry	Ln(III)–Ln(III) distance (Å)		Signed deviation (Å)
			Calculated	Crystallographic	
Eu(III)	XICHUM[a]	RHF/6-31G*/ECP	5.549	5.388	0.161
		RHF/3-21G/ECP	5.538	5.388	0.150
		RHF/STO-3G/ECP	4.180	5.388	−1.209
Sm(III)	MEWGOK[a]	RHF/STO-3G/ECP	3.359	4.020	−0.661
Gd(III)	NIGXAC[a]	RHF/STO-3G/ECP	4.076	4.125	−0.049
Tb(III)	ZUNCEQ[a]	RHF/STO-3G/ECP	3.710	3.794	−0.084
Dy(III)	QQQEMM01[a]	RHF/STO-3G/ECP	3.665	4.169	−0.504
Ho(III)	NIHRIF[a]	RHF/STO-3G/ECP	3.985	4.098	−0.113
Er(III)	TACERB01[a]	RHF/STO-3G/ECP	3.607	4.141	−0.533
Tm(III)	LUPCII[a]	RHF/STO-3G/ECP	4.407	4.387	0.020

[a]Complexes are identified by their respective Cambridge Structural Database 2004 [26–28] codes

ECP, whose geometries are otherwise slightly more accurate.

Conclusions

Luminescent devices are normally solid-state devices. Therefore, prediction of coordination polyhedron crystallographic geometries of lanthanide complexes is both a prerequisite for luminescent complexes design and an open area of research. However, our results indicate that the usual expectation that either an increase in the basis set, or in the level of calculation, or both, should result in an increase in accuracy, does not seem to hold when what is sought is prediction of coordination polyhedron crystallographic geometries from isolated lanthanide ion complexes from ab initio calculations using the ECPs of Dolg et al. [19] at least not for the lanthanide ion complexes studied. Despite the possibility that these findings may not hold true, if other ECPs are used, our results suggest that RHF/STO-3G with Dolg et al. [19] ECPs appears to be the most efficient model chemistry in terms of coordination polyhedron crystallographic geometry predictions from isolated lanthanide complex ion calculations. Our results further indicate that Cosentino et al.'s suggestion of using RHF/3-21G/ECP geometries may be perhaps a more robust, although not necessarily more accurate, recommendation to be adopted for the general case.

Nevertheless, a question is naturally posed: why is RHF/STO-3G with Dolg et al. ECPs [19] coordination polyhedron crystallographic geometry predictions from isolated lanthanide ion complexes calculations generally so accurate? Presently we do not know, but fortunately this is so, because RHF/STO-3G/ECP is relatively fast ab initio calculations. Indeed, basic research must be carried out with the aim of identifying the root causes of why both augmenting the basis set and/or including electron correlation enlarged the deviations and aggravated the quality of the predicted ab initio/ECP lanthanide ion complex coordination polyhedron crystallographic geometries.

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