Would the Pseudocoordination Centre Method Be Appropriate To Describe the Geometries of Lanthanide Complexes?

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The correct prediction of the ground-state geometries of lanthanide complexes is an important step in the development of efficient light conversion molecular devices (LCMD). Considering this, we evaluate here the capability of semiempirical approaches and ab initio effective core potential (ECP) methodology in reproducing the coordination polyhedron geometries of lanthanide complexes. Initially, we compare the facility of two semiempirical approaches: Pseudocoordination centre method (PCC) and Sparkle model. In the first step, we considered only high-quality crystallographic structures and included 633 complexes, and in the last step, we compare the capability of two semiempirical approaches with ab initio/ECP calculations. Because this last methodology was found to be computationally very demanding, we further used a subset containing 91 high-quality crystallographic structures. A total of 91 ab initio full geometry optimizations were performed. Our results suggest that only the semiempirical Sparkle model (hundreds of times faster) present accuracy similar to what can be obtained by present-day ab initio/ECP full geometry optimization calculations on such lanthanide complexes. In addition, it further indicates that the PCC approach has a poor prediction related to the coordination polyhedron geometries of lanthanide complexes.

INTRODUCTION

In the last three decades, the search for efficient light conversion molecular devices (LCMDs) based on lanthanide complexes has been a fascinating area of interest for many research groups. This interest comes from the fact that lanthanide complexes play a very important role in the design of new luminescent systems, such as electroluminescent devices,[1] liquid crystalline materials,[2] sensors,[3] powerful catalysts for various organic transformations,[4] and luminescent labels for specific biomolecule interactions.[5] Because of the wide range of application, a great diversity of organic ligands have been strategically developed and used in the synthesis of new lanthanide complexes. However, the experimental design of these systems is a hard task.[6] The main reasons are as follows: (i) the high cost of many reagents; (ii) the difficulty of characterization of many complexes; and (iii) the long time required in carrying out the synthesis and characterization of many structures.

An interesting alternative is the use of theoretical combinatory chemistry, TCC, in the design of efficient luminescent devices.[7,8] In the TCC procedure, the first step is the calculation of the ground-state geometry for all new structures proposed, which are used afterward to calculate the energies of the electronic excited states. The second step is the calculation of the intensity parameters Ω_λ ($\lambda = 2, 4,$ and 6), which requires the spherical coordinates of the coordination polyhedron, the excited states energies, and the R_L, the distance from the donor state located at the organic ligands and the lanthanide ion nucleus. The third step is the calculation of the energy transfer and back-transfer rates, which requires the previously calculated intensity parameters

Ω_λ. These quantities are also used to calculate the radiative (A_{rad}) and nonradiative (A_{nrad}) decay rates. The last step is the calculation of the efficiency (η) and quantum yield (q), which in turn requires the energy transfer and back-transfer rates, the A_{rad} and A_{nrad} values. All equations and methods involved in this procedure are widely discussed in the literature.[9−12]

It is clear from the procedure described above that the correct calculation of the ground state geometry of the complex is essential to correctly predict spectroscopic properties.[13−16] As the processing capacity of modern computers has greatly improved, quantum chemical methods are being increasingly used to perform this kind of calculation. Nowadays, there are two different quantum chemical approaches to calculate the ground-state geometries of lanthanide complexes: (i) ab initio methodologies, which use effective core potentials (ECPs) for lanthanide atoms[17,18] and demand relatively high computational efforts; and (ii) semiempirical models, which are less computationally demanding but lose accuracy as compared to the first ones. Among the semiempirical models, two are more frequently used in the study of lanthanides: (i) the Sparkle model[19] and the pseudocoordination centre method (PCC).[20,21]

The Sparkle model was developed in 1994[22] and was further improved.[23] Recently, we developed a new paradigm for lanthanide complex semiempirical calculations, called Sparkle/AM1,[19,24−32] Sparkle/PM3,[33−39] and Sparkle/PM6,[40] based on a more sophisticated parametrization scheme. All Sparkle models are now implemented in the MOPAC2009 package.[41]

Ottonelli and co-workers[20] proposed the replacement of the trivalent lanthanide ion (Ln^{3+}) by "equivalent" ions such as Al^{3+} or Ga^{3+} in the PCC method as an alternative to the Sparkle model. In their procedure, the structure of the

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complexes was afterward optimized using PM3 Hamiltonian. Although the PCC approach does not distinguish among the lanthanide ions, the authors stated that they can be replaced by the same "equivalent" ion. On the other hand, the Sparkle model indeed distinguishes the lanthanide ion because it is specifically parametrized for each lanthanide ion. The Sparkle model neglects the explicit treatment of all electrons in an analogous way as the core electrons are treated by other semiempirical methods. Besides, the validation procedures applied after parametrization of each trivalent lanthanide ion[19,24−39,44] evidenced that it was possible to develop a model to calculate the ground-state geometry of lanthanide complexes with high accuracy.

In a recent paper,[45] we evaluated the performance of ab initio/ECP as well as Sparkle methods in the structure prediction of relatively large lanthanide complexes. In this detailed study, we considered 52 different complexes of Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, and Tm^{3+}, and we found out that Sparkle/AM1 calculations are very accurate in geometry calculations, being quite competitive with ab initio/ECPs methods although hundreds of times faster.[19,34,44] Moreover, the results also show that the RHF/STO-3G/ECP appears to be the most efficient model for coordination polyhedron crystallographic geometry predictions. In contrast to what would be normally expected, we observed that either an increase in the basis set or inclusion of electron correlation, or both, consistently enlarged the deviations and aggravated the quality of the predicted coordination polyhedron geometries.

Here, we aimed to evaluate the accuracies of the quantum chemical methods in reproducing the coordination polyhedron of lanthanide complexes from calculations on the isolated single lanthanide complex ion. In the first stage, we compared the two semiempirical approaches (PCC method and Sparkle model). For this, we considered 633 different structures containing all lanthanide ions. In the second stage, we compared the two semiempirical approaches with the ab initio methodology. However, we then considered 91 complexes of all trivalent lanthanide ions except trivalent Pm ion.[32,34]

METHODOLOGY

We first studied only semiempirical approaches, considering 633 different lanthanide complexes containing all lanthanide ions except Pm^{3+}.[32,34] The experimental crystallographic structures used were all taken from the Cambridge Structural Database, CSD,[46−48] choosing only high-quality structures, that is, structures with R factors less than 5%. The RM1 Hamiltonian[49] was not considered in this work because currently it is only parametrized for 10 atoms. All semiempirical calculations were performed using the MO-PAC 2009 package.[41] For the Sparkle/AM1, Sparkle/PM3, and Sparkle/PM6 models, we use the keyword "Sparkle". In the PCC calculations, we only replaced the lanthanide ion in all 633 complexes by Al^{3+} and calculated each structure with the AM1, PM3, and PM6 Hamiltonian.

In the second stage, we compared the semiempirical approaches with the ab initio/ECP methodology. All ab initio calculations have been accomplished using the Gaussian 98 software,[50] and the crystallographic geometry was used as the starting point. For all lanthanides, we used the quasi-

relativistic effective core potential (ECP) of Dolg et al.[17,18] and the related [5s4p3d] - GTO valence basis set. This ECP includes $46 + 4f^n$ electrons in the core, allowing the outermost 11 electrons to be treated explicitly. We choose the STO-3G basis set because we have found out elsewhere[45] that RHF/STO-3G with Dolg et al. ECPs[17,18] appeared to be the most efficient model for coordination polyhedron crystallographic geometry predictions from isolated lanthanide complexes.

Because of the high computational costs involved in this stage, we performed a standard cluster analysis and classified these complexes according to their predominant type of ligands. After that, a subset was then chosen to constitute the test set as a "basis" of chemical environments, with the idea of being capable of spanning any type of ligand environment a trivalent lanthanide ion may be subjected to, with directly coordinated heteroatoms. The cluster analysis was run with Statistica software, using the Euclidean distances with complete linkage to cluster the complexes. The subset chosen for each lanthanide ion is presented in the Supporting Information.

In the two stages we used the unsigned mean error (eq 1) in the comparisons between crystallographic and calculated coordination polyhedron geometries. The UME's average was used to evaluate and compare the competence of each methodology.

$$UME_i = \frac{1}{n_i} \sum_{j=1}^{n_i} |R_{i,j}^{CSD} - R_{i,j}^{calc}| \tag{1}$$

where n is the number of ligand atoms directly coordinating the lanthanide ion. Two cases have been evaluated: (i) UME's involving the interatomic distances R_j between the lanthanide 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) $UME_{(Ln−L)}$'s involving only the interatomic distances R_j between the lanthanide ion and the atoms of the coordination polyhedron, which is important in the lanthanide spectroscopic properties calculations, and consequently in the design of efficient luminescent devices based on lanthanide complexes.

RESULTS AND DISCUSSION

The Semiempirical Approaches: Sparkle Model versus PCC Approach. Figure 1 shows UME for all interatomic distances between the lanthanide ion and the ligand atoms as well as interatomic distances between all ligand atoms of the coordination polyhedron. We can observe the UME of each semiempirical approach for each lanthanide ion. As can be seen from Figure 1, the Sparkle models are the more accurate in the prediction of the crystallographic coordination polyhedron of lanthanide complexes. Moreover, we can observe that the PCC approach presents high UME values in the prediction of the crystallographic coordination polyhedron of europium and terbium complexes (it appears more clearly for PM6 and AM1), which are the complexes more commonly used as luminescent molecular devices.

Figure 2 shows the average of all UME's observed for each semiempirical approach. This graph indicates more clearly that the Sparkle model is much more accurate than the PCC approach to predict the crystallographic coordination
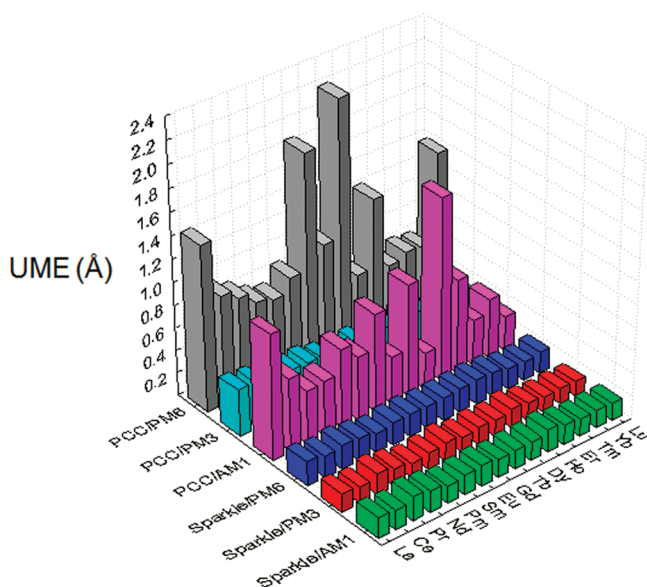
Polyhedron and Ln - L distances

Figure 1. Unsigned mean error (UME) of each semiempirical approach for each lanthanide ion considering all interatomic distances between the lanthanide ion and the ligand atoms, as well as interatomic distances between all ligand atoms of the coordination polyhedron.

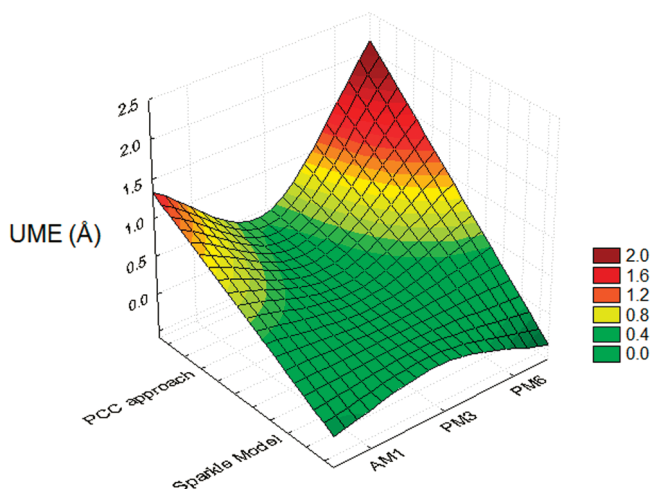## Polyhedron and Ln - L distances

Figure 2. Graphical visualization of unsigned mean errors, UME's, involving not only the interatomic distances between the lanthanide ion and the ligand atoms of the coordination polyhedron, but also the interatomic distances between all ligand atoms of the coordination polyhedron obtained from each semiempirical approach.

polyhedron of lanthanide complexes. As a rule, the Sparkle model is 4 times more accurate than the best PCC approach (PCC/PM3). As mentioned in the Introduction, the geometry of the coordination polyhedron, more precisely the Ln−L distances, is essential to correctly predict many spectroscopic properties of lanthanide complexes, so the data suggest the Sparkle model is more suitable to study lanthanide complexes, especially europium and terbium complexes.

The same tendency observed in Figure 1 is also observed in Figure 3, where we consider only Ln−L distances. The lowest $UME_{(Ln-L)}$ is observed when the Sparkle/AM1 model is used to predict the polyhedron of holmium complexes ($UME_{(Ho-L)} = 0.054$ Å), while the highest $UME_{(Ln-L)}$ is observed when the PCC/PM6 is used to predict the polyhe-
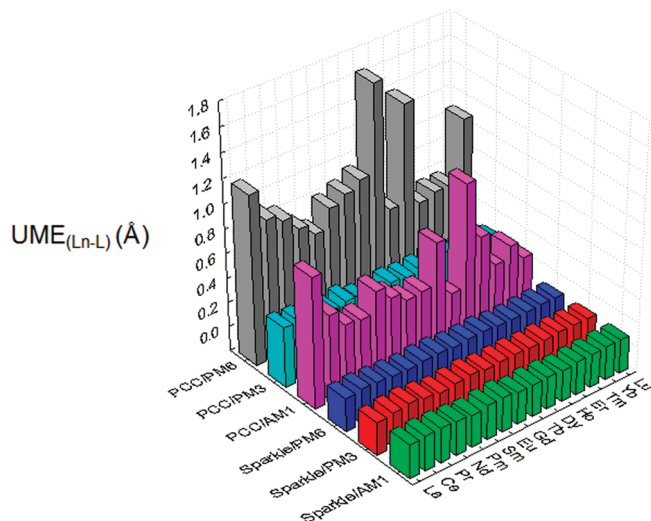
Ln - L distances

Figure 3. Unsigned mean error ($UME_{(Ln-L)}$) of each semiempirical approach for each lanthanide ion considering all interatomic distances between the lanthanide ion and the ligand atoms.
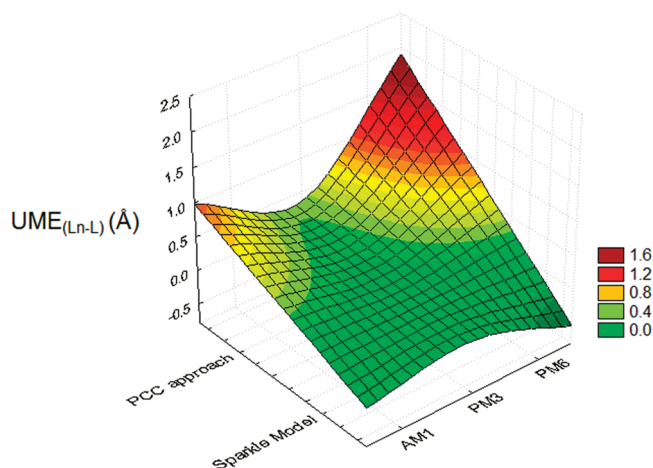
Ln - L distances

Figure 4. Graphical visualization of average unsigned mean errors, $UME_{(Ln-L)}$'s, involving only the interatomic distances between the lanthanide ion and the ligand atoms of the coordination polyhedron obtained from each semiempirical approach.

dron of europium complexes ($UME_{(Eu-L)} = 1.664$ Å). These values can be found in Table S2 (Supporting Information).

Figure 4 shows the average of all 15 $UME_{(Ln-L)}$'s observed for each semiempirical approach. Once again, we can note that the Sparkle model is much more accurate than the PCC approach. The worst Sparkle model (average $UME_{(Ln-L)}$'s $= 0.074$ Å) is 3.5 times more accurate than the best PCC approach (average $UME_{(Ln-L)}$'s $= 0.259$ Å). These values are also present in the Supporting Information (Table S2). The UME for specific distances such as Ln−Ln, Ln−O, and Ln−N can be found in Tables S3−S5 in the Supporting Information.

In some recent works,[33−39] we have shown that for all 15 lanthanide ions the interatomic distance deviations obtained from Sparkle models follow a gamma distribution within a 95% level of confidence, indicating that these errors appear to be random around a mean, freeing the model from systematic errors, at least within the validation set.

The question is: Do the interatomic distance deviations obtained from PCC approaches also follow a gamma distribution within a 95% level of confidence?

The quality of a gamma distribution fitting can be evaluated using the one-sample nonparametric Kolmogorov−Smirnov test[51] to verify statistically whether the distribution of the UME values is really a gamma distribution indexed by the estimated parameters. In this case, the null hypothesis is that the UME values do follow that gamma distribution. For the null hypothesis not to be rejected at the usual level of 5%, the p-value of the test must thus be larger than 0.05. Also, the higher is the p-value, whose maximum possible value is 1, the higher is the probability that the UME's are random, the more the Sparkle model captured the deterministic aspects of the problem, and the more justifiable is the use of the statistical tools employed here.

If the p-value is indeed larger than 0.05, then one can compute, from the gamma distribution fit, the probability of the UME, for an arbitrary lanthanide complex, to belong to an interval.

Once the Sparkle models have been evaluated in previous works,[33−39] we now examine results for PCC approaches. In Table 1, where we consider UME's of the interatomic distances R_j 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, we can observe that only the PCC/PM3 approach follows a gamma distribution within a 95% level of confidence for all 15 trivalent lanthanide ions. The PCC/AM1 approach shows eight p-values larger than 0.05, and PCC/PM6 shows only five.

In Table 2, where we consider UME$_{(Ln−L)}$'s involving only the interatomic distances R_j between the lanthanide central ion and the atoms of the coordination polyhedron, we can observe that all PCC approaches have at least one trivalent lanthanide ion, and one p-value smaller than 0.05.

In Tables 1 and 2, we can also observe the means and variances for UME and UME$_{(Ln−L)}$. The high values of

variances corroborate the fact that the PCC approaches are inappropriate for prediction of coordination polyhedron geometries of lanthanide complexes.

The Semiempirical versus Ab Initio Methodology. Recently, we studies the ability of various model chemistries, based on the ECP by Dolg et al.,[17,18] in reproducing the coordination polyhedron crystallographic geometries of lanthanide complexes from calculations on the isolated single lanthanide complex ion.[45] Using the $[Eu(H_2O)_9]^{3+}$ complex, this study demonstrated that the more accurate ab initio methodology is the RHF/STO-3G with Dolg et al.[17,18] ECPs. Thus, at that time, we considered 52 different complexes of Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, and Tm^{3+}, in the comparison between RHF/ECP/STO-3G methodology and the Sparkle model.

Now we will compare all semiempirical approaches (Sparkle models and PCC) with the ab initio RHF/ECP/STO-3G methodologies. For this, in this stage, we performed a total of 91 ab initio full geometry optimizations on 91 complexes of fourteen different lanthanide ions to confirm our findings.

Figure 5 presents the UME$_{(Ln−L)}$'s and UME's for all methodologies considered. Once again, the results corroborate that the PCC/PM6 is completely inadequate to predict the crystallographic coordination polyhedron of lanthanide complexes. The PCC/AM1 and PCC/PM3 approaches also present high UME's when compared to both Sparkle and ab initio methodology. We also note that the Sparkle models present accuracy similar to what can be obtained by present-day ab initio effective core potential full geometry optimization calculations on such lanthanide complexes.

Tables 3 and 4 display the UME's and UME$_{(Ln−L)}$'s, for each methodology, obtained considering the subsets chosen for each lanthanide trivalent ion. The mean values used to plot Figure 5 are also presented.

Table 1. Means and Variances of the Gamma Distribution Fits for the UME's Computed for the N Complexes for Each Trivalent Lanthanide Ion Using the PCC Approach[a]

		polyhedron and Ln−L distances (Å)								
		AM1			PM3			PM6		
ion	N^b	mean (Å)	variance (Å²)	p-value[c]	mean (Å)	variance (Å²)	p-value	mean (Å)	variance (Å²)	p-value
La^{3+}	73	1.101	24.286	**2.5×10^{-8}**	0.407	0.037	0.291	1.459	7.979	**2.6×10^{-4}**
Ce^{3+}	36	0.647	0.736	**0.046**	0.392	0.014	0.371	0.955	0.271	**0.022**
Pr^{3+}	47	0.470	0.051	0.705	0.375	0.010	0.740	0.867	0.102	0.263
Nd^{3+}	57	0.488	0.132	0.072	0.372	0.009	0.266	0.765	0.105	**0.048**
Pm^{3+}	15	0.695	1.308	0.160	0.367	0.017	0.960	0.726	0.239	**0.019**
Sm^{3+}	37	0.561	0.624	**0.008**	0.328	0.017	0.347	0.851	0.219	**0.041**
Eu^{3+}	88	0.865	11.813	**3.4×10^{-11}**	0.304	0.009	0.454	1.868	36.689	**2.9×10^{-9}**
Gd^{3+}	64	0.423	0.050	0.176	0.328	0.008	0.660	1.012	2.016	**1.2×10^{-4}**
Tb^{3+}	35	0.985	11.457	**0.001**	0.310	0.010	0.839	2.205	37.185	**1.7×10^{-5}**
Dy^{3+}	26	0.316	0.022	0.923	0.329	0.013	0.924	0.611	0.042	0.244
Ho^{3+}	28	1.609	41.183	**7.8×10^{-5}**	0.354	0.011	0.805	1.218	8.758	**0.001**
Er^{3+}	38	0.828	5.723	**2.5×10^{-4}**	0.335	0.006	0.941	0.565	0.033	0.240
Tm^{3+}	15	0.404	0.048	0.894	0.290	0.008	0.434	0.621	0.072	0.453
Yb^{3+}	44	0.527	1.511	0.056	0.289	0.013	0.114	0.600	0.134	0.131
Lu^{3+}	30	0.305	0.037	0.721	0.289	0.012	0.894	1.382	15.160	**0.004**

[a] The last column shows the p-values of the one-sample non-parametric Kolmogorov-Smirnov tests[51] carried out for each lanthanide ion, to verify statistically that its value is above 0.05, indicating that the distribution of the UME values can indeed be represented by a gamma distribution indexed by the estimated mean and variance. [b] N refers to the number of complexes used in the comparison. [c] The p-values below 0.05 are in bold. This indicates that the errors do not appear to be random around a mean, and so the model is not free of systematic errors.

Table 2. Means and Variances of the Gamma Distribution Fits for the $UME_{(Ln-L)}$'s Computed for the N Complexes for Each Trivalent Lanthanide Ion Using the PCC Approach[a]

		AM1			PM3			PM6		
ion	N[b]	mean (Å)	variance (Å²)	p-value[c]	mean (Å)	variance (Å²)	p-value	mean (Å)	variance (Å²)	p-value
La³⁺	73	0.868	10.980	**2.8×10^{-5}**	0.290	0.019	**0.042**	1.189	0.653	0.299
Ce³⁺	36	0.506	0.345	0.189	0.283	0.011	0.588	0.938	0.245	0.970
Pr³⁺	47	0.369	0.054	0.099	0.267	0.006	0.319	0.875	0.140	0.367
Nd³⁺	57	0.357	0.086	**0.022**	0.259	0.005	0.553	0.756	0.081	0.275
Pm³⁺	15	0.530	0.770	0.318	0.279	0.008	0.816	0.657	0.143	0.713
Sm³⁺	37	0.421	0.372	0.050	0.236	0.010	0.381	0.814	0.142	0.986
Eu³⁺	88	0.877	15.945	**3.0×10^{-10}**	0.227	0.007	0.459	1.664	28.022	**2.9×10^{-9}**
Gd³⁺	64	0.359	0.060	0.169	0.260	0.008	0.423	0.941	0.910	**0.026**
Tb³⁺	35	0.695	4.758	0.019	0.245	0.020	0.224	1.656	15.121	**5.2×10^{-5}**
Dy³⁺	26	0.223	0.030	0.161	0.270	0.014	0.457	0.591	0.055	0.704
Ho³⁺	28	1.063	15.804	**0.003**	0.284	0.014	0.562	1.397	15.393	**0.003**
Er³⁺	38	0.582	2.552	**0.004**	0.277	0.005	0.550	0.539	0.040	0.351
Tm³⁺	15	0.297	0.051	0.835	0.245	0.005	0.140	0.577	0.055	0.954
Yb³⁺	44	0.395	0.558	**0.047**	0.239	0.010	0.054	0.575	0.090	0.646
Lu³⁺	30	0.243	0.037	0.938	0.236	0.007	0.234	1.074	5.297	**0.011**

[a] The last column shows the p-values of the one-sample non-parametric Kolmogorov–Smirnov tests,[51] carried out for each lanthanide ion, to verify statistically that its value is above 0.05, indicating that the distribution of the $UME_{(Ln-L)}$ values can indeed be represented by a gamma distribution indexed by the estimated mean and variance. [b] N refers to the number of complexes used in the comparison. [c] The p-values below 0.05 are in bold. This indicates that the errors do not appear to be random around a mean, and so the model is not free of systematic errors.
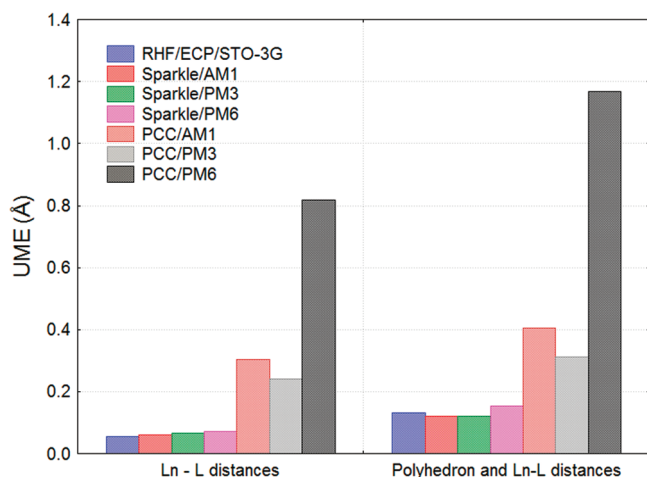
Figure 5. Average UME's and $UME_{(Ln-L)}$'s (in Å), obtained from semiempirical PCC and Sparkle models and ab initio/ECP.

Table 3. Unsigned Mean Errors, UME's, of the Interatomic Distances R_j 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 Obtained Considering the Subsets Chosen for Each Lanthanide Trivalent Ion

	polyhedron and Ln–L distances (Å)						
	Sparkle			PCC			RHF/STO-3G
	AM1	PM3	PM6	AM1	PM3	PM6	Dolg et al.[17] ECPs
La³⁺	0.135	0.112	0.194	0.386	0.328	1.744	0.128
Ce³⁺	0.119	0.105	0.147	0.543	0.444	1.357	0.171
Pr³⁺	0.110	0.124	0.147	0.467	0.293	0.919	0.072
Nd³⁺	0.125	0.121	0.148	0.693	0.330	1.148	0.149
Sm³⁺	0.083	0.102	0.152	0.521	0.318	0.680	0.114
Eu³⁺	0.122	0.154	0.142	0.270	0.217	0.828	0.119
Gd³⁺	0.100	0.096	0.111	0.288	0.288	0.855	0.116
Tb³⁺	0.110	0.117	0.126	0.548	0.221	4.576	0.164
Dy³⁺	0.136	0.136	0.202	0.271	0.315	0.696	0.166
Ho³⁺	0.175	0.161	0.176	0.288	0.292	0.700	0.131
Er³⁺	0.123	0.136	0.203	0.333	0.304	0.606	0.153
Tm³⁺	0.138	0.127	0.166	0.338	0.328	0.764	0.141
Yb³⁺	0.099	0.115	0.132	0.409	0.371	0.682	0.138
Lu³⁺	0.107	0.097	0.116	0.315	0.316	0.816	0.084
mean	0.120	0.122	0.154	0.405	0.312	1.169	0.132

Table 4. Unsigned Mean Errors, $UME_{(Ln-L)}$'s, Involving Only the Interatomic Distances R_j between the Lanthanide Central Ion, Ln, and the Atoms of the Coordination Polyhedron, L, Obtained Considering the Subsets Chosen for Each Lanthanide Trivalent Ion

	Ln–L distances (Å)						
	Sparkle			PCC			RHF/STO-3G
	AM1	PM3	PM6	AM1	PM3	PM6	Dolg et al.[17] ECPs
La³⁺	0.060	0.063	0.073	0.278	0.240	1.532	0.051
Ce³⁺	0.072	0.067	0.075	0.463	0.363	1.200	0.072
Pr³⁺	0.055	0.062	0.061	0.367	0.201	0.926	0.033
Nd³⁺	0.058	0.056	0.067	0.533	0.229	1.116	0.060
Sm³⁺	0.075	0.080	0.095	0.427	0.252	0.600	0.069
Eu³⁺	0.046	0.060	0.052	0.138	0.148	0.756	0.042
Gd³⁺	0.051	0.054	0.058	0.203	0.220	0.713	0.047
Tb³⁺	0.043	0.049	0.055	0.431	0.152	0.816	0.048
Dy³⁺	0.067	0.076	0.090	0.178	0.270	0.605	0.050
Ho³⁺	0.055	0.066	0.073	0.232	0.243	0.661	0.065
Er³⁺	0.060	0.060	0.076	0.221	0.227	0.531	0.046
Tm³⁺	0.071	0.079	0.085	0.223	0.269	0.686	0.060
Yb³⁺	0.076	0.071	0.079	0.286	0.274	0.580	0.075
Lu³⁺	0.055	0.067	0.067	0.261	0.279	0.715	0.042
mean	0.060	0.065	0.072	0.303	0.241	0.817	0.054

CONCLUSIONS

After this systematic and detailed study involving 633 different lanthanide complexes, we can conclude that the PCC approaches are inefficient to reproduce the crystallographic coordination polyhedron of lanthanide complexes. The high UME's observed, along with the statistic tests, suggest that the use of geometries calculated with the PCC approach is not recommended in the study of spectroscopic properties that strongly depend on the coordinates of the coordination polyhedron.

The results also confirmed that the Sparkle models (hundreds of times faster) present accuracy similar to what can be obtained by present-day ab initio/ECP full geometry optimization calculations on such lanthanide complexes. In this sense, the semiempirical Sparkle model in association with other theoretical methodologies can be used as a reliable tool in the study of spectroscopic properties[9] and/or in the design of new luminescent complexes.

Supporting Information Available: Additional tables comparing the semiempirical approaches with respect to various classes of coordinating bonds and tables containing $UME_{(Ln-L)}$'s and UME's for all 633 complexes of the validation set. A detailed tutorial about calculations using the Sparkle model in MOPAC 2009 package is available via the Internet at http://www.sparkle.pro.br. This material is available free of charge via the Internet at http://pubs.acs.org.

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