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Article

Sparkle/PM3 for the Modeling of Europium(III), Gadolinium(III), and Terbium(III) Complexes

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O modelo Sparkle/PM3 é parametrizado para complexos de európio (III), gadolínio (III) e térbio (III). A validação do modelo foi realizada utilizando noventa e seis complexos de Eu(III), setenta complexos de Gd(III) e quarenta e dois complexos de Tb(III); todos a partir de estruturas cristalográficas de alta qualidade, com fator R < 5%. Os erros médios absolutos, obtidos com o modelo Sparkle/PM3, considerando todas as distâncias interatômicas do tipo lantanídeo-átomo ligante, foram 0,080 Å para Eu(III), 0,063 Å para Gd(III) e 0,070 Å para Tb(III). Estes valores médios são similares aos obtidos com o modelo Sparkle/AM1 (0,082 Å, 0,061 Å, e 0,068 Å, respectivamente). Além disso, a exatidão em reproduzir o poliedro de coordenação de complexos de Eu(III), Gd(III) e Tb(III) é similar à obtida utilizando métodos *ab initio* com potenciais efetivos de caroço. Finalmente, com o objetivo de avaliar se as geometrias preditas com o modelo Sparkle/PM3 são confiáveis, escolhemos um dos complexos de Eu(III), BAFZEO, para o qual geramos centenas de diferentes geometrias iniciais, onde variamos de forma aleatória as distâncias e ângulos entre os ligantes e o íon Eu(III). Em seguida, todas essas geometrias iniciais foram otimizadas usando o modelo Sparkle/PM3. Como resultado, observamos uma tendência significativa onde a geometria que apresentou o menor erro médio absoluto apresentou também a energia total mais baixa, o que reforça a validade do modelo Sparkle.

The Sparkle/PM3 model is extended to europium(III), gadolinium(III), and terbium(III) complexes. The validation procedure was carried out using only high quality crystallographic structures, for a total of ninety-six Eu(III) complexes, seventy Gd(III) complexes, and forty-two Tb(III) complexes. The Sparkle/PM3 unsigned mean error, for all interatomic distances between the trivalent lanthanide ion and the ligand atoms of the first sphere of coordination, is: 0.080 Å for Eu(III); 0.063 Å for Gd(III); and 0.070 Å for Tb(III). These figures are similar to the Sparkle/AM1 ones of 0.082 Å, 0.061 Å, and 0.068 Å respectively, indicating they are all comparable parameterizations. Moreover, their accuracy is similar to what can be obtained by present-day *ab initio* effective core potential full geometry optimization calculations on such lanthanide complexes. Finally, we report a preliminary attempt to show that Sparkle/PM3 geometry predictions are reliable. For one of the Eu(III) complexes, BAFZEO, we created hundreds of different input geometries by randomly varying the distances and angles of the ligands to the central Eu(III) ion, which were all subsequently fully optimized. A significant trend was unveiled, indicating that more accurate local minima geometries cluster at lower total energies, thus reinforcing the validity of sparkle model calculations.

Keywords: Sparkle model, AM1, PM3, lanthanide complexes, rare earth coordination compounds

Introduction

Lanthanide complexes of the trivalent ions of europium, gadolinium, and terbium display a wide range of applications, with newer ones appearing in increasing numbers.[1-11] More specifically, europium and terbium complexes exhibit luminescence and are thus mostly used as luminescent or phosphorescent sensors or probes. On the other hand, complexes of gadolinium are mainly used as magnetic resonance imaging contrast agents.

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The theoretical 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-centered emission, requires a description of ligand field effects. Accordingly, characterization of the interaction between the ligands and the central ion can be done through the ligand field parameters, which can be calculated provided that the coordination polyhedron geometry of the complex is known. Within the simple overlap model,[12,13] the values of ligand field parameters depend mainly on the interatomic distances between the ligand atoms and the central lanthanide ion. This dependence goes with the third, the fifth, and even with the seventh power of the lanthanide-ligand interatomic distances, thus amplifying any inaccuracies.

On the other hand, gadolinium complexes which serve as magnetic resonance imaging contrast agents normally contain one coordinated inner-sphere water molecule. Because this water molecule is in fast exchange with bulk solvent, the gadolinium ion is able to catalytically change the relaxation rate of solvent protons, a phenomenon called relaxivity. A larger relaxivity means either that imaging can be carried out in low concentration target regions, or that the contrast agent may be administered at a lower dose. For the inner-sphere water molecule, the relaxation occurs predominantly *via* the dipolar mechanism, which has a $1/r^6$ dependence where r is the distance of the gadolinium ion to the water proton.[14]

Hence, the geometry of a lanthanide complex is its single most relevant feature for complex design. Even more important is an accurate knowledge of the distances between the lanthanide ion and its directly coordinated ligand atoms. This knowledge is essential for a correct assessment of the influence of the chemical environment on the $4f^n$ lanthanide ion configuration and of its effect on the spectroscopic and magnetic properties of the complex.

However, modeling lanthanide complexes is a challenging task because lanthanide ions do not display stereochemical preferences, possess a handful of high coordination numbers, and display small energy variations among their various coordination polyhedron geometries.

In a recent paper we introduced Sparkle/AM1,[15] a new paradigm for semiempirical quantum chemical calculations on lanthanide complexes. In this model, when a lanthanide complex is calculated, the lanthanide is represented by a sparkle, whereas the ligands are modeled by AM1.[16] Besides the geometry, this allows the calculation of many other properties of the complexes, such as vibrational spectra, thermodynamic quantities, isotopic substitution effects and force constants, ionization potential, electron densities, dipole moments, etc.[17]

The Sparkle/AM1[18-24] was mainly designed to predict the ground state geometries of lanthanide complexes at a level of accuracy useful for complex design. Recent research on lanthanide complexes has in fact indicated that Sparkle/AM1 coordination polyhedron geometries are comparable to, if not better than geometries obtained from the best contemporary *ab-initio* full geometry optimization calculations with effective core potentials.[25,26] Besides, Sparkle/AM1 calculations are hundreds of times faster,[15] and have been recently employed for the study of quantum yields of luminescence.[27-34]

However, although AM1 generally produces satisfactory results and its trustworthiness has been extensively time-tested, other semiempirical models may prove more advantageous for some particular applications.

PM3[35,36] is also a very popular semiempirical molecular orbital model, which predominantly gives enthalpies of formation with lower average errors than AM1. Indeed, PM3 has a wide following and is available in a variety of quantum chemical softwares, both commercial and non-commercial.[17,37-45] Recently, for example, PM3 has been used by Lu *et al.*[46] to calculate molecular orbital properties of the ligands of lanthanide (III) double decker complexes, which were helpful to the understanding of the electrochemical properties of the complexes. Possibly, researchers in general will be able to gain more insights, as PM3 parameters for the lanthanides become available, because PM3 calculations will then become possible, not only for the ligands, but for the whole complexes as well.

In order to amplify the range of applications of our sparkle model, we advance, in the present article, Sparkle/PM3 parameters for the calculation of Eu(III), Gd(III), and Tb(III) complexes to complement the Sparkle/AM1 parameters that have already been published for these ions.[15] We also present some evidence that geometries obtained *via* Sparkle/PM3 calculations are indeed trustworthy.

Results and Discussion

The Sparkle model assumes that the angular effects of the f orbitals are negligible, and do not take them into account. The sparkle model replaces the lanthanide(III) ion by a Coulombic charge of $+3e$ superimposed to a repulsive exponential potential of the form $\exp(-\alpha r)$, which accounts for the size of the ion; provides three electrons to the orbitals of the ligands; adds two Gaussian functions to the core-core repulsion energy term; and includes the lanthanide atomic mass. Thus, the sparkle model assumes that the lanthanide trications behave like simple ions, without any angular steric properties.

The parameterization procedure used to obtain the Sparkle/PM3 parameters for Eu(III), Gd(III), and Tb(III) was essentially the same as the one of our previous work.[15] Accordingly, we only used high quality crystallographic structures (R-factor < 5%) of complexes taken from the Cambridge Structural Database 2003 (CSD),[47-49] having found a total of 96 structures of complexes of Eu(III), 70 of Gd(III), and 42 of Tb(III). As training sets we used the same three subsets of 15 complexes each, already chosen for the parameterization of Sparkle/AM1 for the same ions.[15]

The Sparkle/PM3 parameters found for the three lanthanide ions are shown in Table 1.

Table 1. Parameters for the Sparkle/PM3 model for the Eu(III), Gd(III) and Tb(III) ions

	Sparkle/PM3		
	Eu(III)	Gd(III)	Tb(III)
GSS	55.5863246694	54.8086404668	56.2564137683
ALP	2.1398139884	3.6813938335	2.8245126194
a_1	0.6101627168	0.7706615984	1.3428294115
b_1	7.1373146362	7.5453068267	7.5782265384
c_1	1.7807085112	1.7636673188	1.7181508908
a_2	0.3415714636	0.0936188340	0.2651000290
b_2	9.1732778046	8.2224517067	6.4476118233
c_2	3.0121099267	2.9879390071	2.9952711306
*EHEAT / (kcal mol^{-1})	1006.6	991.37	999.0
AMS / amu	151.9650	157.2500	158.92534

* The heat of formation of the Eu(III), Gd(III) and Tb(III) ions in Sparkle/PM3 and Sparkle/AM1 models were obtained by adding to the heat of atomization of each respective lanthanide, their first three ionization potentials.

As geometry accuracy measures, we used the average unsigned mean error for each complex *i*, UME_i, defined as:

$$UME_i = \frac{1}{n_i}\sum_{j=1}^{n_i}\left|R_{i,j}^{CSD} - R_{i,j}^{calc}\right| \qquad (1)$$

where n_i is the number of ligand atoms directly coordinating the lanthanide ion. Two cases have been examined: (*i*) $UME_{(Ln-L)}$s involving the interatomic distances R_j between the lanthanide central ion, Ln, and the atoms of the coordination polyhedron, L, important to complex design; and (*ii*) UMEs of all the edges of the pyramids, that is, 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. Tables S1, S2, and S3 of the supplementary material present the $UME_{(Ln-L)}$s and UMEs for both Sparkle/PM3 and Sparkle/AM1 for Eu(III), Gd(III), and Tb(III), respectively.

Table 2 presents the unsigned mean errors for both Sparkle/PM3 and Sparkle/AM1 for various types of distances in the Eu(III), Gd(III) and Tb(III) complexes considered. Results indicate that, for the three lanthanide ions considered, the two models are essentially equivalent. Distances between the lanthanide ion and its directly coordinated ligand atoms are predicted with higher accuracy than either the distances between two lanthanide ions in dilanthanide compounds, or the distances between atoms of the faces of the coordination polyhedron. This is fortunate, because radial lanthanide ion-ligand atom distances are far more important for both luminescent complex design[32,33,50] and magnetic resonance imaging contrast agent design.[14]

Assuming that the sparkle model is a good representation of the lanthanide ion, as well as of its interactions with the ligands, the distribution of these UMEs should be random around a mean, whose value can be used as a measure of accuracy of the model. Since the UMEs are positive, defined in the domain $(0,\infty)$, they should follow the gamma distribution which has the probability density function g(x; k, θ), where $x > 0$ stands for the UMEs, $k > 0$ is the

Table 2. Sparkle/PM3 and Sparkle/AM1 unsigned mean errors for all distances involving the central lanthanide ion, Ln, and the ligand atoms of the coordination polyhedron, L, for ninety-six Eu(III) complexes; seventy Gd(III) complexes and forty-two Tb(III) complexes considered

Model	Unsigned mean errors for specific types of distances / Å					
	Ln-Ln	Ln-O	Ln-N	L-L'	Ln-L and Ln-Ln	Ln-L, Ln-Ln and L-L'
Europium (III)						
Sparkle/PM3	0.212	0.098	0.056	0.183	0.080	0.161
Sparkle/AM1	0.162	0.085	0.088	0.217	0.082	0.183
Gadolinium (III)						
Sparkle/PM3	0.213	0.057	0.085	0.154	0.063	0.132
Sparkle/AM1	0.183	0.060	0.074	0.021	0.061	0.166
Terbium(III)						
Sparkle/PM3	0.208	0.071	0.059	0.175	0.070	0.155
Sparkle/AM1	0.225	0.075	0.044	0.212	0.068	0.172

shape parameter, and $\theta > 0$ is the scale parameter of the gamma distribution. The expected value of the gamma distribution is simply $k\theta$. The shape and scale parameters were estimated with the method of maximum likelihood in order to obtain the gamma distribution fit of the UME data.

The quality of the gamma distribution fit can be assessed *via* the one-sample non-parametric Kolmogorov-Smirnov[51] test. For the hypothesis that the UME values follow a gamma distribution not to be rejected at the usual level of 5%, the p-value of the test statistic must thus be larger than 0.05. And the higher the p-value, whose maximum possible value is 1, the higher the probability that the UMEs deviations of the mean are random, and the more justifiable is the use of the statistical tools employed here, and, by extension, of the sparkle model itself.

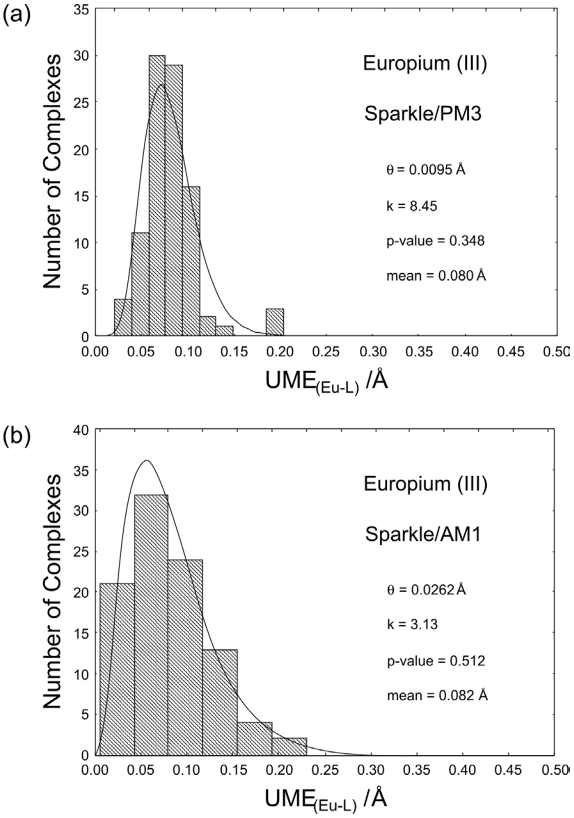

Figure 1. Probability densities of the Gamma distribution fits of the $UME_{(Ln-L)}$s for the Eu(III) Sparkle/PM3 and Sparkle/AM1 models, superimposed to histograms of the same data for all 96 Eu(III) complexes considered; where k is the shape parameter and θ is the scale parameter of the gamma distribution; the p-value is a measure of the significance of the gamma distribution fit; and mean is the expected value of the fitted gamma distribution, which is set to be equal to the arithmetic mean value of the 96 $UME_{(Ln-L)}$s.

Figure 1 presents a gamma distribution fit of the $UME_{(Eu-L)}$s for europium(III) for both Sparkle/PM3 and the already published Sparkle/AM1.[15] Superimposed to the fit, a histogram of the data with the number of bars chosen to best adjust the histogram to the curve obtained from the gamma distribution fit is also presented so that the reader can check the regions where the actual UMEs really occurred. The p-value of the gamma distribution fits for Sparkle/PM3 and Sparkle/AM1 are 0.348 and 0.512, respectively, both above the 0.05 value, thus attaching statistical significance to the fit and, by extension, to both sparkle models as well. Figures 2 and 3 present similar results for the sparkle models of gadolinium(III) and terbium(III), with similar results and conclusions.

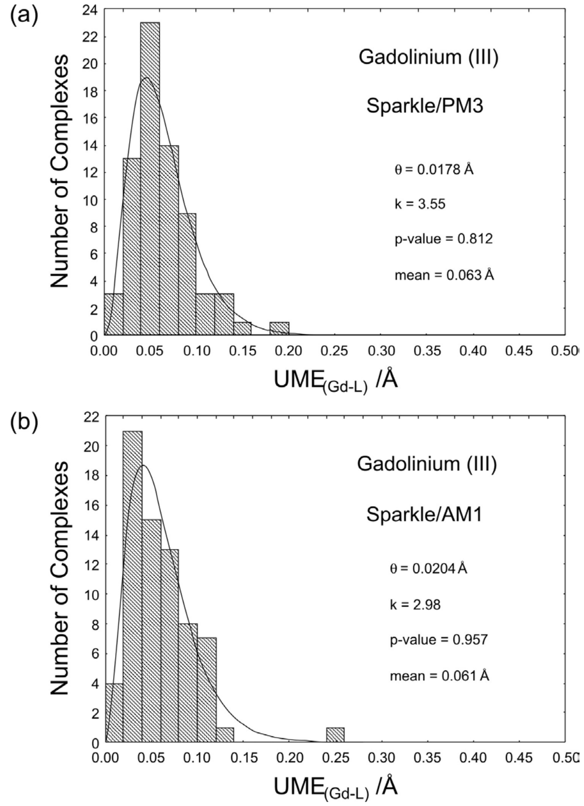

Figure 2. Probability densities of the Gamma distribution fits of the $UME_{(Ln-L)}$s for the Gd(III) Sparkle/PM3 and Sparkle/AM1 models, superimposed to histograms of the same data for all 70 Gd(III) complexes considered; where k is the shape parameter and θ is the scale parameter of the gamma distribution; the p-value is a measure of the significance of the gamma distribution fit; and mean is the expected value of the fitted gamma distribution, which is set to be equal to the arithmetic mean value of the 70 $UME_{(Ln-L)}$s.

When a complex, whose experimental geometry is unknown, is subject to a Sparkle/PM3 calculation, an input geometry must be provided by the user. Since lanthanide complexes are flexible, the conformational energy hypersurface of such complex may contain a number of local minima, and by definition, one global minimum. Thus, the input geometry may either converge to one of the local minima, or ideally, to the global minimum. For the sparkle model to be useful, the minima with lower energies

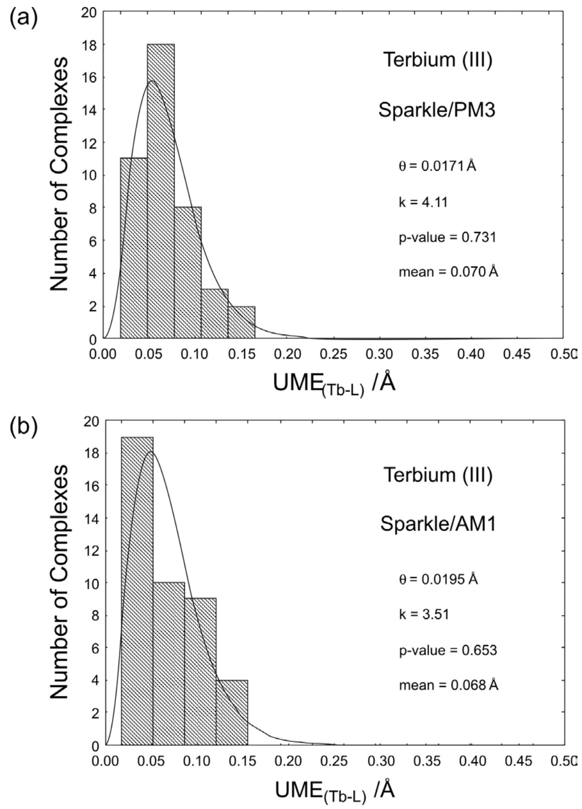

Figure 3. Probability densities of the Gamma distribution fits of the $UME_{(Ln-L)}$s for the Tb(III) Sparkle/PM3 and Sparkle/AM1 models, superimposed to histograms of the same data for all 42 Tb(III) complexes considered; where k is the shape parameter and θ is the scale parameter of the gamma distribution; the p-value is a measure of the significance of the gamma distribution fit; and mean is the expected value of the fitted gamma distribution, which is set to be equal to the arithmetic mean value of the 42 $UME_{(Ln-L)}$s.

must also be the ones closer to the experimental geometry. Likewise, as the energies of the local minima increase, we expect their $UME_{(Ln-L)}$s to also increase.

In order to verify this hypothesis, a particular europium(III) complex, of CSD code BAFZEO, was selected as a case study. BAFZEO was chosen because: (*i*) it is flexible; (*ii*) it is coordinated to four ligands of three different types: two nitrates, one β-diketone and one terpyridine; and (*iii*) a full Sparkle/PM3 optimization of its geometry is relatively fast.

We then generated 200 different input geometries for this complex. Each of the geometries resulted from the application of a procedure to each and every one of its ligands in an independent manner. In this procedure, the ligands are considered to be rigid and independent of each other and of the central europium ion. Starting with the experimental geometry, for each ligand we proceeded as follows: (*i*) we defined a randomly oriented Cartesian coordinate system whose origin is located at the center of mass of the ligand; (*ii*) we then randomly chose one of the three axis of this Cartesian coordinate system; (*iii*) we rotated the ligand around this chosen axis by a random angle in the interval [+30°, −30°]; (*iv*) subsequently, one of the atoms of the ligand, we called atom R, was randomly chosen to define the axis connecting it to the europium ion; (*v*) a random translation, in the direction of this axis, was finally applied to the whole ligand, the magnitude of this translation in the interval [−15%,+15%] of the interatomic distance between the europium ion and atom R of the ligand.

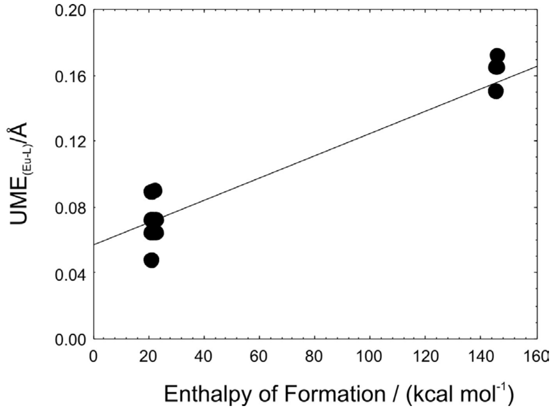

Figure 4. Clusters of output geometries obtained from Sparkle/PM3 full geometry optimizations of random input geometries for the europium complex of CSD code BAFZEO, showing that the group of clusters with the highest enthalpies of formation was also the group of clusters with the highest $UME_{(Eu-L)}$s. The number of optimized geometries comprising each group of clusters is also shown. The trendline is present just to guide the eye.

For each of the 200 different input geometries, we performed a full Sparkle/PM3 geometry optimization. For some of the input geometries, the starting distances of the originally coordinating atoms were so far away from the europium atom that the corresponding Sparkle/PM3 geometry optimizations converged to uncoordinated complexes. A total of 64 of the outputs were then discarded for this reason. The remaining 136 output geometries with properly coordinated ligands grouped themselves into two main clusters of local minima, as can be seen in Figure 4: one around an enthalpy of formation of 143 kcal mol^{-1}, with 10 outputs, and the other around 22 kcal mol^{-1}, with 126 outputs. As expected, the cluster with the highest enthalpies of formation was also the cluster with the highest $UME_{(Eu-L)}$s and this is precisely the trend we were expecting. Nevertheless, we then decided to examine in greater detail the cluster around 22 kcal mol^{-1}. Figure 5 shows that this cluster is actually comprised of seven different smaller clusters of local minima, all very similar and with very low $UME_{(Eu-L)}$s around 0.07 Å, a level of accuracy already useful for complex design. The number of outputs in each of the smaller clusters is also indicated in Figure 5. The cluster with the lowest enthalpy of formation, at 21.2 kcal mol^{-1}, happened to be also the cluster with the lowest $UME_{(Eu-L)}$s at 0.048 Å. As shown in Figure 5, seven different inputs converged to this minimum, which likely is also the global minimum.

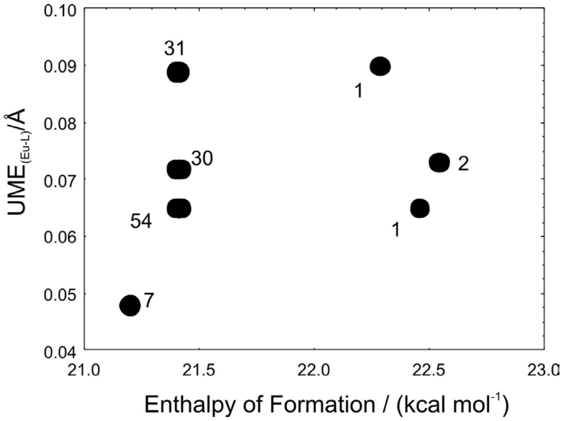

Figure 5. Enlargement of the group of clusters of Figure 4 located around 22 kcal mol^{-1}, showing the seven sub-clusters obtained, as well as the number of elements in each. The leftmost sub-cluster with the lowest enthalpy of formation, with 7 elements, happened to be also the cluster with the lowest $UME_{(Eu-L)}$s. The elements are output geometries obtained from Sparkle/PM3 full geometry optimizations of random input geometries for the europium complex of CSD code BAFZEO.

These results indicate that a significant trend was unveiled by this study: that more accurate geometry local minima tend to cluster at lower total energies. This trend confirms the validity of Sparkle/PM3 as a trustworthy geometry prediction tool.

Recently, an exhaustive study by our research group has been accomplished on coordination polyhedron geometry prediction accuracies of *ab initio* effective core potential (*ab initio*/ECP) calculations.[26] The study consisted of complete full geometry optimization calculations on dozens of complexes of various lanthanide ions, the largest containing 164 atoms, varying both basis sets (STO-3G, 3-21G, 6-31G, 6-31G*, and 6-31+G) and method (HF, B3LYP, and MP2 full). The amazing conclusion was 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. Contrary to what would normally be expected, 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.

For each of the Eu(III), Gd(III), and Tb(III) ions, the study reported *ab-initio*/ECP full geometry optimizations on six complexes.[26]

The RHF/STO-3G/ECP average UME and $UME_{(Ln-L)}$ for the six Eu(III) complexes calculated were 0.119 Å and 0.042 Å, similar to the respective Sparkle/PM3 numbers of 0.154 Å and 0.060 Å; and to the Sparkle/AM1 numbers of 0.122 Å and 0.046 Å.

Likewise, the RHF/STO-3G/ECP average UME and $UME_{(Ln-L)}$ for the six Gd(III) complexes calculated were 0.116 Å and 0.047 Å, also similar to the respective Sparkle/PM3 numbers of 0.096 Å and 0.054 Å; and to the Sparkle/AM1 numbers of 0.100 Å and 0.051 Å.

Finally, for the six Tb(III) complexes, the average UME and $UME_{(Ln-L)}$ for the RHF/STO-3G/ECP geometries were reported as 0.164 Å and 0.048 Å; again, comparable to the respective Sparkle/PM3 numbers of 0.117 Å and 0.049 Å; and to the Sparkle/AM1 numbers of 0.110 Å and 0.043 Å.

Conclusions

The most accurate *ab initio* full geometry optimization calculations that can be nowadays carried out on europium, gadolinium and terbium complexes, of a size large enough to be of relevance to present-day research, exhibit the same accuracy of either Sparkle/PM3 or Sparkle/AM1 models. Our results do indicate that the Sparkle model is an accurate and statistically valid tool for the prediction of coordination polyhedra of lanthanide complexes.

Given the fact that sparkle calculations are hundreds of times faster, potential energy surface scan searches for a global minimum become feasible. And from the results presented in this article, these searches appear to be indeed meaningful. Sparkle calculations can also be used in molecular dynamics when calculations on the same system must be carried out repeatedly.

More importantly, the ability to perform a screening on many different putative structures of lanthanide complexes in a combinatorial manner, made possible by both Sparkle/PM3 and Sparkle/AM1, may prove to be of importance for luminescence or magnetic resonance imaging research.

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Supplementary Information

Instructions on how to run lanthanide complexes Sparkle calculations with MOPAC 2007 (from http://

openmopac.net) and also on how to visualize the structures of the complexes using RASMOL (from http://www.umass.edu/microbio/rasmol/); sample MOPAC 2007 input (.mop) and output (.arc) files for the complex Eu[TREN-1,2-HOIQO(H_2O)$_2$. Tables of UME$_{(Ln-L)}$s and UMEs for both Sparkle/PM3 and Sparkle/AM1 for Eu(III), Gd(III), and Tb(III), respectively. Figures with gamma distribution fits of the UME data for both Sparkle/PM3 and Sparkle/AM1 models for Eu(III), Gd(III) and Tb(III). This material is available free of charge at http://jbcs.sbq.org.br, as PDF file.

References

1. Lenaerts, P.; Görller-Walrand, C.; Binnemans, K.; *J. Lumin.* **2006**, *117*, 163.
2. Kautenburger, R.; Nowotka, K.; Beck, H. P.; *Anal. Bioanal. Chem.* **2006**, *384*, 1416.
3. Tsuchiya, D.; Kunishima, N.; Kamiya, N.; Jingami, H.; Morikawa, K.; *Proc. Natl. Acad. Sci.* **2002**, *99*, 2660.
4. Buunzli, J.-C. G.; Piquet, C.; *Chem. Rev.* **2002**, *102*, 1897.
5. Tsukube, H.; Shinoda, S.; *Chem. Rev.* **2002**, *102*, 2389.
6. Parker, D.; Dickins, R. S.; Puschmann, H.; Crossland, C.; Howard, S. A. K.; *Chem. Rev.* **2002**, *102*, 1977.
7. Lei, K.; Liu, W.; Huang, X.; Wang, D.; *Chem. Pharm. Bull.* **2006**, *54*, 1150.
8. Viguier, R. F. H.; Hulme, A. N.; *J. Am. Chem. Soc.* **2006**, *128*, 11370.
9. Skripinets, Yu. V.; Egorova, A. V.; Ukrainets, I. V.; Antonovich, V. P.; *J. Anal. Chem.* **2006**, *61*, 44.
10. Tan, M.; Song, B.; Wang, G. N.; Yuan, J.; *Free Radical Biol. Med.* **2006**, *40*, 1644.
11. Liu, Y.; Zhang, N.; Chen, Y.; Chen, G.-S.; *Bioorg. Med. Chem.* **2006**, *14*, 6615.
12. Malta, O. L.; *Chem. Phys. Lett.* **1982**, *87*, 27.
13. Malta, O. L.; *Chem. Phys. Lett.* **1982**, *88*, 353.
14. Caravan, P.; Astashkin, A. V.; Raitsimring, A. M.; *Inorg. Chem.* **2003**, *42*, 3972.
15. Freire, R. O.; Rocha, G. B.; Simas, A. M.; *Inorg. Chem.* **2005**, *44*, 3299.
16. Dewar, M. J. S.; Zoebish, E. G.; Healy, E. F.; Stewart, J. J. P.; *J. Am. Chem. Soc.* **1985**, *107*, 3902.
17. Stewart, J. J. P.; *MOPAC93.00 Manual*; Fujitsu Limited: Tokyo, 1993.
18. Costa Jr., N. B.; Freire, R. O.; Rocha, G. B.; Simas, A. M.; *Polyhedron* **2005**, *24*, 3046.
19. Freire, R. O.; Rocha, G. B.; Simas, A. M.; *Chem. Phys. Lett.* **2005**, *411*, 61
20. Costa Jr., N. B.; Freire, R. O.; Rocha, G. B.; Simas, A. M.; *Inorg. Chem. Commun.* **2005**, *8*, 831.
21. Freire, R. O.; Costa Jr., N. B.; Rocha, G. B.; Simas, A. M.; *J. Chem. Theory Comput.* **2006**, *2*, 64.
22. Freire, R. O.; Monte, E. V.; Rocha, G. B.; Simas, A. M.; *J. Organomet. Chem.* **2006**, *691*, 2584.
23. Freire, R. O.; Costa Jr., N. B.; Rocha, G. B.; Simas, A. M.; *J. Phys. Chem. A* **2006**, *110*, 5897.
24. Bastos, C. C.; Freire, R. O.; Rocha, G. B.; Simas, A. M.; *J. Photochem. Photobiol., A* **2006**, *117*, 225.
25. Freire, R. O.; Rocha, G. B.; Albuquerque, R. Q.; Simas, A. M.; *J. Lumin.* **2005**, *111*, 81.
26. Freire, R. O.; Rocha, G. B.; Simas, A. M.; *J. Mol. Model.* **2006**, *12*, 373.
27. Nobre, S. S.; Lima, P. P.; Mafra, L.; Sa Ferreira, R. A.; Freire, R. O.; Fu, L.; Pischel, U.; de Zea Bermudez, V.; Malta, O. L.; Carlos, L. D.; *J. Phys. Chem. C* **2007***, 111,* 3275.
28. de Mesquita, M. E.; Junior, S. A.; Oliveira, F. C.; Freire, R. O.; Júnior, N. B. C.; de Sá, G. F.; *Inorg. Chem. Commun.* **2002**, *5*, 292.
29. de Mesquita, M. E.; Junior, S. A.; Júnior, N. B. C.; Freire, R. O.; Silva, F. R. G.; de Sá, G. F.; *J. Solid State Chem.* **2003**, *171*, 183.
30. Faustino, W. M.; Malta, O. L.; Teotonio, E. E. S.; Brito, H. F.; Simas, A. M.; de Sa, G. F.; *J. Phys. Chem. A* **2006**, *110*, 2510.
31. de Mesquita, M. E.; Gonçalves e Silva, F. R.; Albuquerque, R. Q.; Freire, R. O.; da Conceição, E. C.; da Silva, J. E. C.; Júnior, N. B. C.; de Sá, G. F.; *J. Alloys Comp.* **2004**, *366*, 124.
32. Freire, R. O.; Gonçalves e Silva, F. R.; Rodrigues, M. O.; de Mesquita, M. E.; Junior, N. B. C. ; *J. Mol. Model.* **2005**, *12*, 16.
33. Freire, R. O.; Albuquerque, R. Q.; Alves Jr., S.; Rocha, G. B.; de Mesquita, M. E.; *Chem. Phys. Lett.* **2005**, *405*, 123.
34. Pavithran, R.; Reddy, M. L. P.; Junior, S. A.; Freire, R. O.; Rocha, G. B.; Lima, P. P.; *Eur. J. Inorg. Chem.* **2005**, *20*, 4129.
35. Stewart, J. J. P.; *J. Comp. Chem.* **1989**, *10*, 209.
36. Stewart, J. J. P.; *J. Comp. Chem.* **1989**, *10*, 221.
37. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A. Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A.; *Gaussian 98*; revision A.7; *Gaussian*; Inc.: Pittsburgh; PA; 1998.
38. *HyperChem(TM) Professional 7.51*; Hypercube, Inc., 1115 NW 4th Street, Gainesville, Fl 32601, USA.
39. *Spartan '04*; Wavefunction, Inc., 18401 Von Karman Avenue, Suite 370 Irvine, CA 92612, USA.

40. Case, D. A.; Darden, T. A.; Cheatham III, T. E.; Simmerling, C. L.; Wang, J.; Duke, R. E.; Luo, R.; Merz, K. M.; Wang, B.; Pearlman, D. A.; Crowley, M.; Brozell, S.; Tsui, V.; Gohlke, H.; Mongan, J.; Hornak, V.; Cui, G.; Beroza, P.; Schafmeister, C.; Caldwell, J. W.; Ross, W. S.; Kollman, P. A.; *AMBER* version 8; University of California San Francisco, 2004.
41. Field, M. J.; Albe, M.; Bret, C.; Proust-De Martin, F.; Thomas, A.; *J. Comput. Chem.* **2000**, *21*, 1088.
42. *VAMP, version 8*; Accelrys Corporate Headquarters: San Diego, USA, 2001.
43. Rowley, C.; Hassinen, T.; *Ghemical for GNOME*, version 1.00, University of Iowa: Iowa City, USA, 2002.
44. Jorgensen, W. L. In *The Encyclopedia of Computational Chemistry*; Schleyer, P. v. R., ed., John Wiley & Sons Ltd.: Athens, USA, 1998, vol. 5, p. 3281.
45. *AMPAC, version 8*; Semichem Inc.: Shawnee, USA, 2004.
46. Lu, G.; Bai, M.; Li, R.; Zhang, X.; Ma, C.; Lo, P.-C.; Ng, D.K.P.; Jiang, J.; *Eur. J. Inorg. Chem.* **2006**, *18*, 3703.
47. Allen, F. H.; *Acta Crystallogr., Sect. B: Struct. Sci.* **2002**, *58*, 380.
48. Bruno, I. J.; Cole, J. C.; Edgington, P. R.; Kessler, M.; Macrae, C. F.; McCabe, P.; Pearson, J.; Taylor, R.; *Acta Crystallogr., Sect. B: Struct. Sci.* **2002**, *58*, 389.
49. Allen, F. H.; Motherwell, W. D. S.; *Acta Crystallogr., Sect. B: Struct. Sci.* **2002**, *58*, 407.
50. de Sá, G. F.; Malta, O. L.; Donega, C. D.; Simas, A. M.; Longo, R. L.; Santa-Cruz, P. A.; da Silva, E. F.; *Coord. Chem. Rev.* **2000**, *196*, 165.
51. Conover, W. J. In *Practical Nonparametric Statistics*; 3rd ed., Wiley II, B.; John Wiley & Sons: New York, USA, 1999, p. 428.

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