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Sparkle/PM3 Parameters for the Modeling of Neodymium(III), Promethium(III), and Samarium(III) Complexes

Ricardo O. Freire,[†] Nivan B. da Costa, Jr.,[‡] Gerd B. Rocha,[§] and Alfredo M. Simas*,[†]

Departamento de Química Fundamental, CCEN, UFPE, 50590-470 - Recife, PE, Brazil, Departamento de Química, CCET, UFS, 49100-000 - Aracaju, SE, Brazil, and Departamento de Química, CCEN, UFPB, 58.059-970 - João Pessoa, PB, Brazil

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Abstract: The Sparkle/PM3 model is extended to neodymium(III), promethium(III), and samarium(III) complexes. The unsigned mean error, for all Sparkle/PM3 interatomic distances between the trivalent lanthanide ion and the ligand atoms of the first sphere of coordination, is 0.074 Å for Nd(III); 0.057 Å for Pm(III); and 0.075 Å for Sm(III). These figures are similar to the Sparkle/AM1 ones of 0.076 Å, 0.059 Å, and 0.075 Å, respectively, indicating they are all comparable models. Moreover, their accuracy is similar to what can be obtained by present-day ab initio effective potential calculations on such lanthanide complexes. Hence, the choice of which model to utilize will depend on the assessment of the effect of either AM1 or PM3 on the quantum chemical description of the organic ligands. Finally, we present a preliminary attempt to verify the geometry prediction consistency of Sparkle/PM3. Since lanthanide complexes are usually flexible, we randomly generated 200 different input geometries for the samarium complex QIPQOV which were then fully optimized by Sparkle/PM3. A trend appeared in that, on average, the lower the total energy of the local minima found, the lower the unsigned mean errors, and the higher the accuracy of the model. These preliminary results do indicate that attempting to find, with Sparkle/PM3, a global minimum for the geometry of a given complex, with the understanding that it will tend to be closer to the experimental geometry, appears to be warranted. Therefore, the sparkle model is seemingly a trustworthy semiempirical quantum chemical model for the prediction of lanthanide complexes geometries.

Introduction

Recently, we introduced Sparkle/AM1,¹ a new paradigm for lanthanide complexes semiempirical calculations, at a level of accuracy useful for coordination compounds design. And, subsequently, we presented Sparkle/AM1 parameters for neodymium(III),² promethium(III), and samarium(III).³ Recent research on lanthanide complexes has indeed indicated that Sparkle/AM1 coordination polyhedron geometries are comparable to, if not better than, geometries obtained with

the best contemporary ab initio calculations with effective core potentials (ab initio/ECP) on complexes of a size large enough to be of value to practical use.^{1,3,4} Besides, sparkle model calculations are hundreds of times faster.

Sparkle/AM1 lanthanides function as new elements to the semiempirical molecular orbital model AM1.⁵ That is, when a lanthanide complex is calculated, the lanthanide ion is modeled as a sparkle, whereas the ligands are modeled by AM1.

Another very popular semiempirical model is PM3,^{6,7} which mainly gives enthalpies of formation with lower average errors than AM1. PM3 is presently available in a variety of quantum chemical softwares, both commercial and noncommercial.^{8–17} The usefulness of PM3 has been recently

* Corresponding author phone: +55 81 2126-8447; fax: +55 81 2126-8442; e-mail: simas@ufpe.br.

[†] Departamento de Química Fundamental, UFPE.

[‡] Departamento de Química, UFS.

[§] Departamento de Química, UFPB.

expanded due to the availability of parameters for many elements, such as for the transition metals,¹⁸ for sodium,¹⁹ and for all nonradioactive elements of the main group, excluding the noble gases.²⁰ Specific parameters for some types of chemical interactions are also available, such as the parameters for zinc for the calculation of metalloenzyme active sites,¹⁹ or the parameter set to describe iron-sulfur proteins.²¹

Novel lanthanide complexes of neodymium^{22–27} and samarium^{28–32} are always emerging, and new applications are frequently been reported.^{33–37} Promethium, on the other hand, does not have any stable isotopes. However, a few of the unstable isotopes, mainly ¹⁴⁷Pm and ¹⁴⁹Pm, find a variety of applications, mainly in medicine.^{38–40} Recently, PM3 semiempirical calculations were carried out on the ligands of lanthanide(III) double decker complexes, illuminating the role of ligand substituents on the electrochemical properties of such complexes.⁴¹ However, calculations were not performed on the complexes themselves, due to a lack of parameters for the lanthanide ions involved.

Therefore, in order to expand the bounds of applications of our sparkle model, we advance, in this paper, Sparkle/PM3 parameters for Nd(III), Pm(III), and Sm(III) ions. We further present a preliminary attempt to attest the geometry prediction coherence of Sparkle/PM3.

The Sparkle Model

Modeling lanthanide complexes is challenging because the ions lack stereochemical preference, possess a handful of high coordination numbers, and display small energy variations among their various coordination geometries.

The Sparkle model recognizes the contracted nature of the 4-f orbitals of the lanthanide trications, of electronic configuration [Xe]4fⁿ, coexisting with a poor overlap with the orbitals of the ligands, which assigns a predominantly ionic character to organolanthanide complexes.⁴² Accordingly, the angular effects of the f orbitals are shielded from external perturbations by the filled 5s² and 5p⁶ orbitals and are not taken into account. As such, the sparkle model regards the lanthanide trications as triple positively charged closed shell inert gas electron densities without any angular steric properties. The sparkle model thus replaces the trivalent rare earth 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.

Parametrization

The parametrization procedure used for obtaining the Sparkle/PM3 parameters for Nd(III), Pm(III), and Sm(III) was essentially the same as the one of our previous works.^{2,3} Accordingly, for neodymium and samarium, we only used high quality crystallographic structures (R-factor <5%) of complexes taken from the “Cambridge Structural Database 2004” (CSD),^{43–45} having found a total of 57 structures of complexes of Nd(III) and 42 of Sm(III). Thus, as training sets for Nd(III) and Sm(III), we used the same two subsets

of 15 complexes each, already chosen for the Sparkle/AM1 parametrization for the same ions, and presented in Figure 1 of the article on Nd(III)² and in Figure 2 of the Sm(III) article.³

Again, since there are no crystallographic structures of promethium coordination compounds available in CSD, we followed the same procedure as for Sparkle/AM1: (i) we picked for both training and validation the same set of 15 representative samarium complexes previously chosen;³ (ii) we then replaced samarium with promethium; and (iii) fully optimized the geometries with RHF/STO-3G/ECP using the quasirelativistic MWB ECP of ref 46. We defined a special code for the promethium parametrization set which we presented in Figure 9 of the Pm(III) article.³ XILGOO{Pm}, for example, would be the samarium complex of CSD code XILGOO with promethium instead of samarium. And we used RHF/STO-3G/ECP because, apparently, this is the most efficient model chemistry in terms of coordination polyhedron crystallographic geometry predictions from isolated lanthanide complex ion calculations, as repeatedly reported.^{1,3,4}

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 Nd(III), Pm(III), and Sm(III) Ions

	Sparkle/PM3		
	Nd(III)	Pm(III)	Sm(III)
GSS	57.4944898977	59.2924444913	54.8086404668
ALP	4.7057677595	3.1490918074	3.6813938335
<i>a</i> ₁	1.0715972265	1.6572814674	0.7706615984
<i>b</i> ₁	6.9565346287	9.2529413759	6.6020324700
<i>c</i> ₁	1.7812099249	1.7412637448	1.7636673188
<i>a</i> ₂	0.0886417116	0.1851223683	0.0936188340
<i>b</i> ₂	10.8664473398	7.4186533283	9.3136737687
<i>c</i> ₂	3.0992613820	3.0623727738	2.9879390071
EHEAT ^a (kcal·mol ^{−1})	962.8	976.9	974.4
AMS (amu)	144.2400	145.0000	150.3600

^a The heat of formation of the Nd(III), Pm(III), and Sm(III) ions in Sparkle/PM3 and Sparkle/AM1 models was obtained by adding to the heat of atomization of each respective lanthanide their first three ionization potentials.

Validation

Unlike ab initio model chemistries, semiempirical ones do not have strong theorems behind them. As such, their validation as useful tools must be established statistically.

Accordingly, as geometry accuracy measures, we used the average unsigned mean error for each complex *i*, UME_{*i*}, defined as

$$\text{UME}_i = \frac{1}{n_i} \sum_{j=1}^{n_i} |R_{ij}^{\text{CSD}} - R_{ij}^{\text{calc}}| \quad (1)$$

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 only the interatomic distances *R_j* between the lanthanide central ion, Ln, and the atoms of the coordination polyhedron, L, important to luminescent complex design and (ii) UMEs 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 1S–3S of the Supporting Information present the $UME_{(Ln-L)}$ s and UMEs and for both Sparkle/PM3 and Sparkle/AM1 for Nd(III), Pm(III), and Sm(III), respectively.

Assuming that the sparkle model is a well founded representation of the lanthanide ions as well as of their interactions with the ligands the distribution of these UMEs should be random around a mean, whose value can be used as a measure of the 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 $f(x; k, \theta)$

$$f(x; k, \theta) = x^{k-1} \frac{e^{-x/\theta}}{\theta^k \Gamma(k)} \quad (2)$$

where $x > 0$ stands for the UMEs, $k > 0$ is the shape parameter, $\theta > 0$ is the scale parameter of the gamma distribution, and $\Gamma(k)$ is the gamma function of k . The expected value of the gamma distribution is simply $k\theta$.

The gamma distribution fits of the UME data were obtained by estimates of the shape and scale parameters by the method of maximum likelihood.

The quality of a gamma distribution fit can be assessed via the one-sample nonparametric Kolmogorov-Smirnov test⁴⁷ in order 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. In order 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. And the higher the p -value, whose maximum possible value is 1, the higher the probability that the UMEs 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.

We now examine results for both the already published Sparkle/AM1 model for Nd(III), Pm(III), and Sm(III) as well as for the Sparkle/PM3 model being presented in this article for the same lanthanide ions.

Figure 1a presents a gamma distribution fit of the $UME_{(Ln-L)}$ data for the Sparkle/PM3 model for Nd(III). As indicated in the figure, the p -value is 0.667, thus indicating that the UMEs are indeed significantly randomly distributed around the mean and correctly follow a gamma distribution. Figure 1b shows the gamma distribution fit for the Nd(III) Sparkle/AM1 model, with a p -value of 0.704. We also superimposed to the gamma distribution fits, histograms of the actual data—the number of bars in each being chosen to best adjust the histogram to the curve obtained from the fit—in order to simply give a pictorial idea of where and how the actual UMEs occurred.

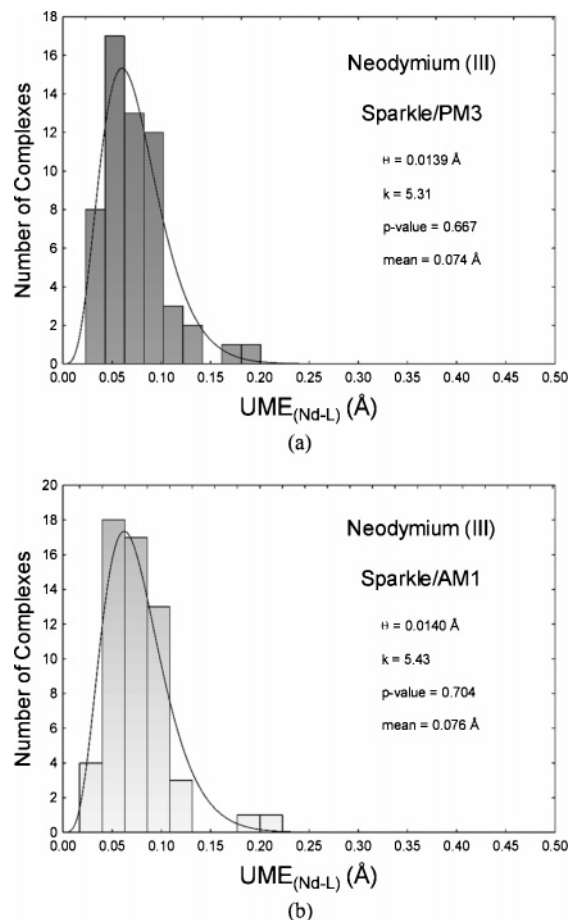


Figure 1. Probability densities of the Gamma distribution fits of the $UME_{(Ln-L)}$ s for the Nd(III) Sparkle/PM3 and Sparkle/AM1 models, superimposed to histograms of the same data for all 57 Nd(III) complexes considered; where k is the shape parameter, and θ is the scale parameter of the gamma distribution; 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 57 $UME_{(Ln-L)}$ s.

Figures 2 and 3 present, each, a gamma distribution fit of the respective $UME_{(Ln-L)}$ for the present Sparkle/PM3 as well as for previously published Sparkle/AM1 models for promethium and samarium. In all cases the respective p -values were well above the critical value of 0.05, ranging from 0.911 to 0.968, thus validating the usage of the sparkle model for both PM3 and AM1 for the prediction of lanthanide complexes geometries.

Equivalent analysis for the whole UMEs, with similar conclusions, can be found in Figures S1–S3 of the Supporting Information.

Comparison with *ab Initio*/ECP Calculations

Repeated studies by our research group^{1,3,4} have confirmed the unanticipated fact 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

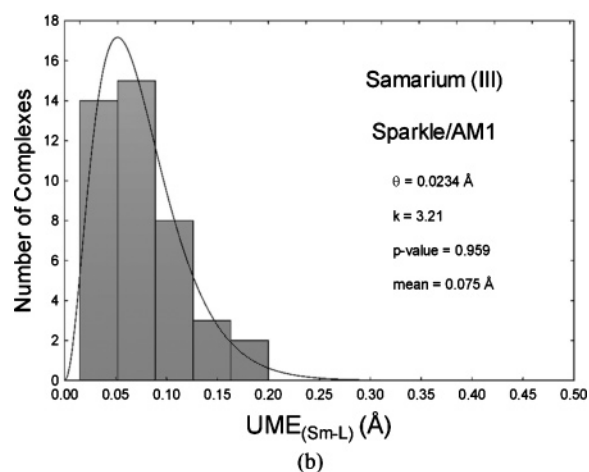
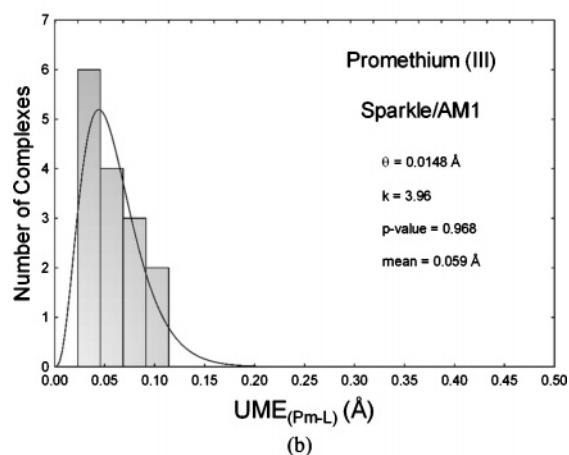
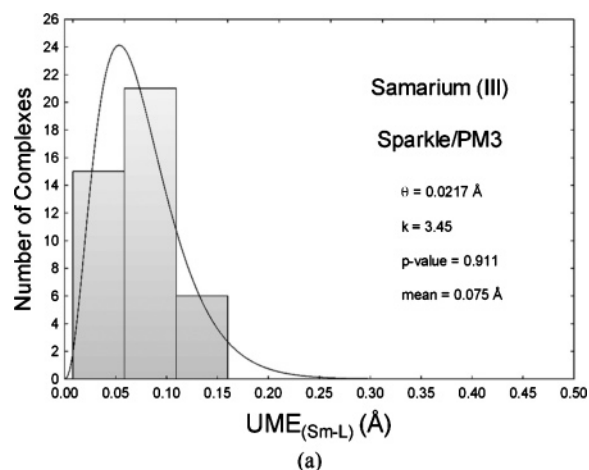
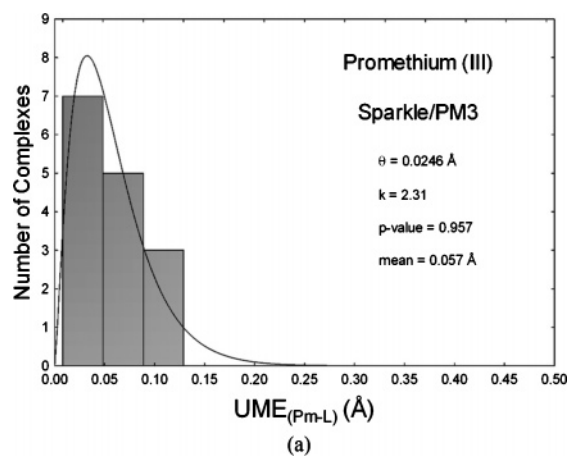


Figure 2. Probability densities of the Gamma distribution fits of the $UME_{(Ln-L)}$ s for the Pm(III) Sparkle/PM3 and Sparkle/AM1 models, superimposed to histograms of the same data for all 15 Pm(III) complexes considered; where k is the shape parameter, and θ is the scale parameter of the gamma distribution; 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 15 $UME_{(Ln-L)}$ s.

augmented the deviations and impaired the quality of the predicted coordination polyhedron geometries.

In the Sm(III) Sparkle/AM1 paper,³ we presented RHF/STO-3G/ECP full geometry optimizations of seven representative samarium complexes of known crystallographic geometries, including a disamarium, of CSD code MEWGOQ. We are therefore in a position to compare the accuracy of Sparkle/PM3 with Sparkle/AM1 and RHF/STO-3G/ECP for the same set.

Figure 4 presents the average $UME_{(Sm-L)}$ and UME values for Sparkle/PM3, Sparkle/AM1, and RHF/STO-3G/ECP full geometry optimizations of the complexes presented in Figure 7 of ref 3. Clearly, all three model chemistries are comparable, with Sparkle/AM1 being on average slightly superior to both Sparkle/PM3 and to RHF/STO-3G/ECP.

Since there are no reports of ab initio full geometry optimization of neodymium(III) complexes, we chose seven of these complexes to have their geometries fully optimized with the model chemistry RHF/STO-3G/ECP. The chosen complexes, shown in Figure 5, were selected to be representative of the various classes of ligands (β -diketones,

Figure 3. Probability densities of the Gamma distribution fits of the $UME_{(Ln-L)}$ s for the Sm(III) Sparkle/PM3 and Sparkle/AM1 models, superimposed to histograms of the same data for all 42 Sm(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.

nitrates, monodentates, bidentates, tridentates, polydentates, and dilanthanides) present in the validation set.

Figure 6 presents the average $UME_{(Nd-L)}$ and UME values for Sparkle/PM3, Sparkle/AM1, and RHF/STO-3G/ECP full geometry optimizations of the complexes presented in Figure 5. Clearly, all three model chemistries are comparable, this time, with Sparkle/PM3 being on average slightly superior to both Sparkle/AM1 and to RHF/STO-3G/ECP. Indeed, $UME_{(Nd-L)}$ s of the order of 0.056 Å are small enough to be useful to the luminescent neodymium complex design.

Geometry Prediction Coherence

The variational theorem applies to Sparkle model calculations simply because the semiempirical models AM1 and PM3 retain the algebraic structure of the Hartree–Fock method. However, since the Sparkle model parameters are the result of a sophisticated fit of experimental values, in principle there are no guarantees that a minimized sparkle model geometry will function as an estimate of the true experimental

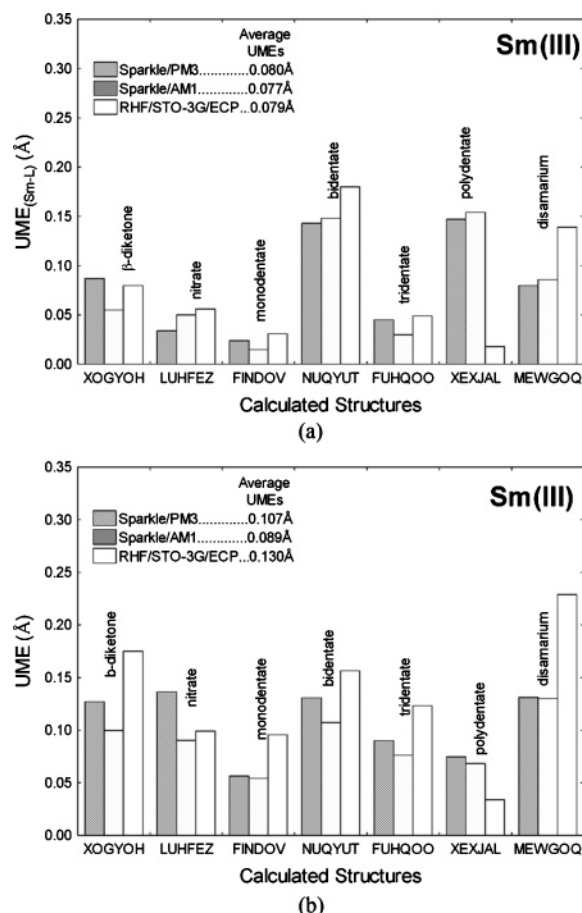


Figure 4. Unsigned mean errors, $UME_{(Ln-L)}$ s (in Å), between the samarium central ion and the atoms of the coordination polyhedron and between the samarium central ion and the atoms of the coordination polyhedron as well as all the interatomic distances R_i between all atoms of the coordination polyhedron, obtained from Sparkle/PM3, Sparkle/AM1, and ab initio RHF/STO-3G/ECP calculations of the ground-state geometries, for each of the representative Sm(III) complexes, identified by their respective Cambridge Structural Database 2004 codes.

geometry. By extension, in principle, there are also no guarantees that a sparkle model global minimum geometry will be closer to the experimental geometry than any of the other sparkle model local minima found.

On the other hand, the sparkle model was parametrized from experimental geometries as input data, and its parameters have been thoroughly minimized to lead to optimized geometries with the lowest deviations possible from the starting geometries. Thus, we can reasonably conjecture that the sparkle model optimized geometry that can be obtained starting from the experimental geometry should be the sparkle model global minimum or at least very close to it. And if this conjecture is true, then trying to find the geometry corresponding to the global minimum in the sparkle model nuclear potential energy hypersurface for an arbitrary complex whose experimental geometry is unknown is a legitimate procedure.

In order to verify in a preliminary manner this conjecture, a samarium(III) complex, of CSD code QIPQOV, was selected as a case study.

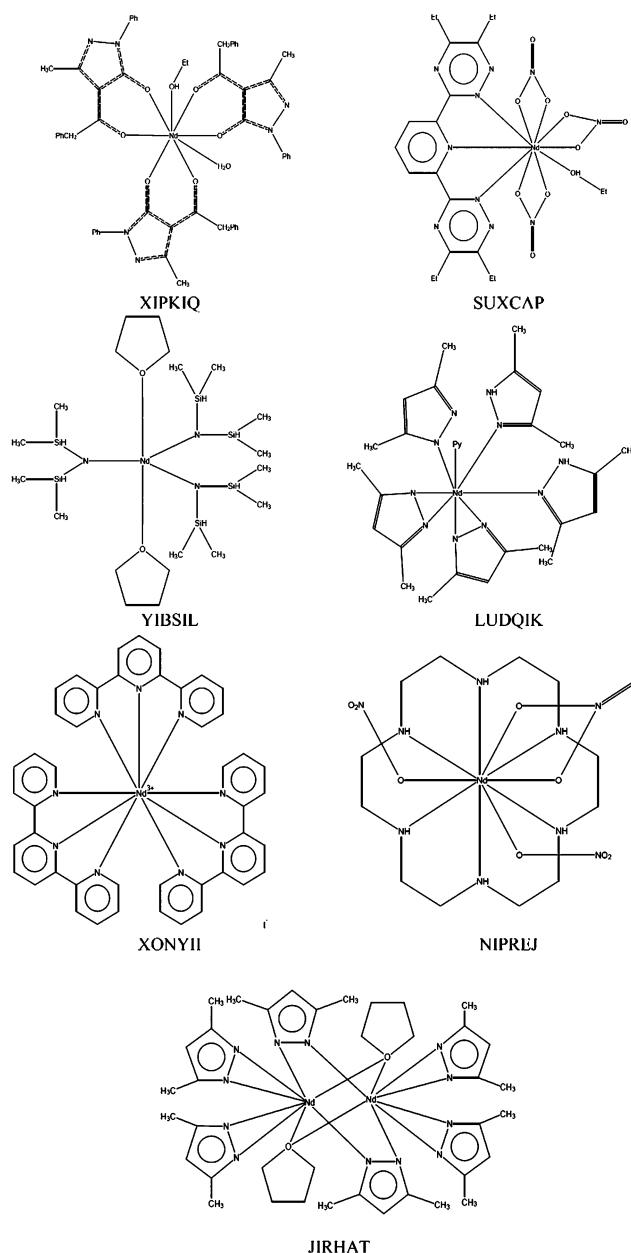


Figure 5. Schematic two-dimensional representation of the structures of neodymium(III) complexes, used for comparison between ab initio model geometries and their crystallographic counterparts, identified by their respective Cambridge Structural Database 2004. The ab initio calculations have been performed using the Hartree–Fock method with the STO-3G basis set for all atoms, except for the neodymium(III) ion, in which case we used the quasirelativistic ECP of ref 46.

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 samarium 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 axes of this Cartesian coordinate system; (iii) we rotated the ligand

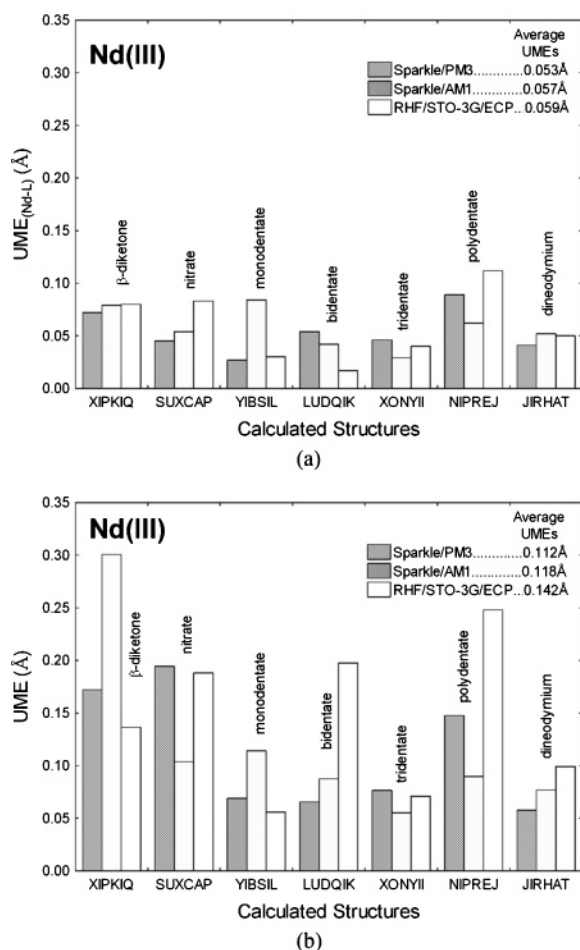


Figure 6. Unsigned mean errors, $UME_{(Ln-L)}$ s (in Å), between the neodymium central ion and the atoms of the coordination polyhedron and between the neodymium central ion and the atoms of the coordination polyhedron as well as all the interatomic distances R_i between all atoms of the coordination polyhedron, obtained from Sparkle/PM3, Sparkle/AM1, and ab initio RHF/STO-3G/ECP calculations of the ground-state geometries, for each of the representative Nd(III) complexes, identified by their respective Cambridge Structural Database 2004 codes.

around this chosen axis by a random angle belonging to the interval $[+30^\circ, -30^\circ]$; (iv) subsequently, one of the atoms of the ligand, we called atom R, was randomly chosen to define the axis connecting it to the samarium ion; and (v) a random translation, in the direction of this axis, was finally applied to the whole ligand—the magnitude of this translation belonging to the interval $[-15\%, +15\%]$ of the interatomic distance between the samarium ion and atom R of the ligand.

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 samarium atom that the corresponding Sparkle/PM3 geometry optimizations converged to one or more uncoordinated ligands. A total of 45 of the outputs were then discarded for this reason.

First, consider $UME_{(Ln-L)}$ s as accuracy measure. As can be clearly seen in Figure 7a, the 155 remaining output geometries grouped into 5 clusters. The cluster with the

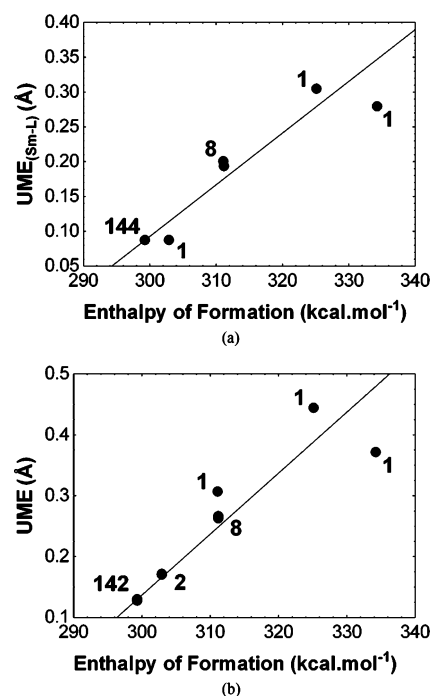


Figure 7. Clusters of output geometries obtained from Sparkle/PM3 full geometry optimizations of random input geometries for the samarium complex of CSD code QIPQOV, showing that the group of clusters with the highest enthalpies of formation was also the group of clusters with the highest $UME_{(Sm-L)}$ s and UME. The number of optimized geometries comprising each group of clusters is also shown. The trendline is present just to guide the eye.

lowest energy also has 144 essentially identical output geometries. And this cluster also has the smallest value of $UME_{(Ln-L)}$. And considering that 200 random initial geometries is a reasonable number, likely the geometry corresponding to the 144 outputs cluster is also the global minimum.

Now consider UMEs as the accuracy measure. Figure 7b shows that in this case the geometries grouped into six clusters, the one with the lowest energy, with 142 essentially identical output geometries, being also the one with the lowest UME.

The trendlines in both parts a and b of Figure 7 are present just to guide the eye and to make it easy to confirm that trying to find the geometry corresponding to the global minimum, in the sparkle model nuclear potential energy hypersurface for an arbitrary complex whose experimental geometry is unknown, is warranted.

Moreover, apparently, it is not hard to find the geometry corresponding to the global minimum of this lanthanide complex. Indeed, out of 155 attempts, 144 arrived at the $UME_{(Sm-L)}$ minimum, a 93% chance; and 142 arrived at the UME minimum, a 92% chance. So, at least in this case, a few different input geometries should be enough to arrive to the global minimum with a high degree of certainty.

Conclusion

Sparkle/PM3 presents a level of accuracy equivalent to Sparkle/AM1 and also to the most accurate ab initio full

geometry optimization calculations that can be nowadays carried out on complexes of a size large enough to be of relevance to complex design.

Besides, both Sparkle/PM3 and Sparkle/AM1 seem to have captured the deterministic aspects involved in the prediction of the geometries of the complexes, as indicated by the statistically significant gamma distribution fits of the unsigned mean errors data.

The preliminary results presented in this article unveiled a significant trend: that more accurate geometry local minima do tend to cluster at lower total energies. And, as the energies of the local minima increase, their $UME_{(Sm-L)}S$ or UMEs also tend to increase.

This trend adds to the validity of Sparkle/PM3 as a trustworthy lanthanide complexes geometry prediction tool.

Finally, the decision of which of the equivalent models to use either Sparkle/PM3 or Sparkle/AM1 rests with the user who must choose based on an appraisal of the influence of either AM1 or PM3 on the quantum chemical description of the specific ligands under investigation and the likely ensuing impact of this choice on the property of interest.

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Supporting Information Available: Instructions and examples on how to implement the Nd(III), Pm(III), and Sm(III) Sparkle/PM3 model in Mopac93r2; parts of the codes of subroutines Block.f, Calpar.f, and Rotate.f that need to be changed as well as their modified versions for Nd(III), Pm(III), and Sm(III); examples of Mopac93r2 crystallographic geometry input (.dat) and optimized geometry summary output (.arc) files from the Sparkle/PM3 calculations for the Nd(III) complex XONYII, for the dineodymium complex JIRHAT, for the Pm(III) complex XEXJAL{Pm}, for the dipromethium complex SOXKAR{Pm}, for the Sm(III) complex XAGVOQ, and for the disamarium complex QQQEMA01; tables of $UME_{(Ln-L)}S$ and UMEs for both Sparkle/PM3 and Sparkle/AM1 for Nd(III), Pm(III), and Sm(III), respectively; figures with gamma distribution fits of the UME data for both Sparkle/PM3 and Sparkle/AM1 models for Nd(III), Pm(III), and Sm(III); and table with UMEs for various types of distances involving the lanthanide ion and the ligand atoms, for both Sparkle/PM3 and Sparkle/AM1, for all complexes, and for each of the ions considered in this article. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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