

Cerium (III) Complexes Modeling with Sparkle/PM3

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Abstract. The Sparkle/PM3 model is extended to cerium(III) complexes. The validation procedure was carried out using only high quality crystallographic structures (R factor < 0.05Å), for a total of thirty-seven Ce(III) complexes. The Sparkle/PM3 unsigned mean error, for all interatomic distances between the Ce(III) ion and the directly coordinating oxygen or nitrogen atoms, is 0.080Å, a level of accuracy equivalent to the Sparkle/AM1 figure of 0.083Å. 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.

Keywords: Cerium, Sparkle Model, PM3, Lanthanide.

1 Introduction

The motivation for research on Ce(III) has been mainly focused on developing materials for phosphor and scintillator applications [1].

Recently, we introduced Sparkle/AM1 [2], a new paradigm for semiempirical quantum chemical calculations on lanthanide complexes. Sparkle/AM1 lanthanides function as new elements to the semiempirical quantum chemistry molecular orbital model AM1 [3]. That is, when a lanthanide complex is calculated, the lanthanide is represented by a sparkle, whereas the ligands are modeled by AM1.

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 +3*e* 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.

Indeed, Sparkle/AM1 was mainly designed to predict 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 [4]. Besides, Sparkle/AM1 calculations are hundreds of times faster [2], and have been recently employed for the study of quantum yields of luminescence for some complexes [5]-[9].

PM3 [10],[11] was introduced in 1989 as a more accurate semiempirical model, giving lower average errors than AM1 [3], mainly for the enthalpies of formation. PM3 also became very popular [12]. More recently, Stewart completed the parameterization of PM3 to all non-radioactive elements of the main group, excluding the noble gases, thus largely amplifying its usefulness [13].

In order to broaden the range of applications of our sparkle model, we advance, in the present article, Sparkle/PM3 parameters for the calculation of Ce(III) complexes to complement the Sparkle/AM1 parameters that have already been published for Ce(III) ion [14].

2 Parameterization Procedure

The parameterization procedure used for Ce(III) was essentially the same as the one described in our previous work on Sparkle/AM1 for Ce(III)[14]. Accordingly, we only used high quality crystallographic structures (R-factor < 5%) taken from the "Cambridge Structural Database 2003" (CSD) [15]-[17], having found a total of 37 structures of complexes of Ce(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[14].

The Sparkle/PM3 parameters found for the cerium (III) ion are shown in Table 1.

Table 1. Parameters for the Sparkle/PM3 model for Ce(III)

	Sparkle/PM3 - Ce(III)
GSS	58.5701153062
ALP	2.5665085968
a ₁	1.8026688761
b ₁	7.5971870028
c ₁	1.8009003439
a ₂	0.1319892158
b ₂	9.6116040841
c ₂	3.0613741124
¹ EHEAT (kcal.mol ⁻¹)	944.7
AMS (amu)	140.1150

¹ The heat of formation of the Ce(III) ion in Sparkle/PM3 was obtained by adding to the heat of atomization of cerium, its first three ionization potentials.

3 Results and Discussion

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

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

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 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. Table S1 of the supplementary material presents the $UME_{(Ce-L)_S}$ and UMEs for both Sparkle/PM3 and Sparkle/AM1 for thirty-seven cerium (III) complexes.

Table 2 presents unsigned mean errors for both Sparkle/PM3 and Sparkle/AM1 for various types of distances in the Ce(III) complexes considered. Results indicate that the two models are essentially equivalent. Distances between the cerium (III) ion and its directly coordinated ligand atoms are predicted with higher accuracy than either the distances between two Ce(III) ions in dilanthanide compounds, or the distances between atoms of the faces of the coordination polyhedron. Luckily that is so, because radial lanthanide ion-ligand atom distances are far more important for luminescent complex design [18].

Table 2. Sparkle/AM1 and Sparkle/PM3 unsigned mean errors for all types of sets of distances involving the central cerium (III) ion, Ce, and the ligand atoms of the coordination polyhedron, L, for thirty-seven Ce(III) complexes considered

	Sparkle/AM1	Sparkle/PM3
Ce – Ce	0.212	0.212
Ce – O	0.081	0.078
Ce – N	0.073	0.067
L – L'	0.208	0.190
Ce – L and Ce – Ce	0.083	0.080
Ce-L, Ce – Ce and L-L'	0.174	0.155

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 $g(x; k, \theta)$, where $x > 0$ stands for the UMEs, $k > 0$ is the 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 [19] 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.

Figure 1 presents a gamma distribution fit of the $UME_{(Ce-L)}$ s for Sparkle/PM3. 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 fit for Sparkle/PM3 is 0.062, above the 0.05 value, thus attaching statistical significance to the fit and, by extension, to the Ce(III) Sparkle/PM3 model as well.

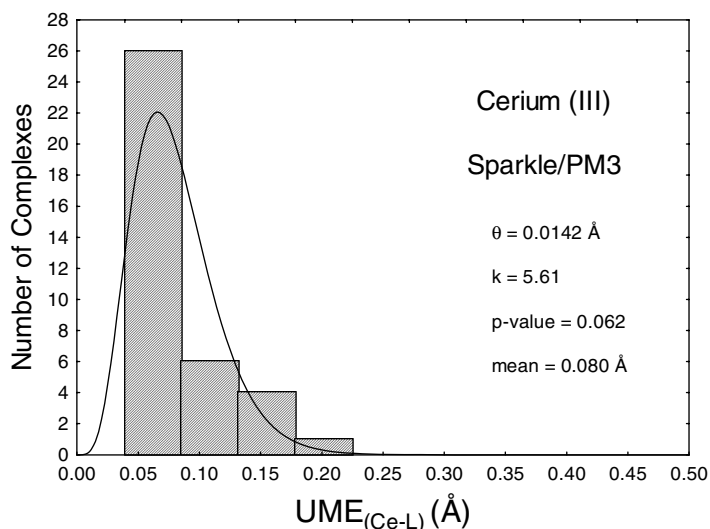


Fig. 1. Probability densities of the Gamma distribution fits of the $UME_{(Ce-L)}$ s for the Ce(III) Sparkle/PM3 model, superimposed to histograms of the same data for all 37 Ce(III) complexes considered; where k is the shape parameter and θ is the scale parameter of the gamma distribution; the **p-value** 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 37 $UME_{(Ce-L)}$ s

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 [4]. 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 notable 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.

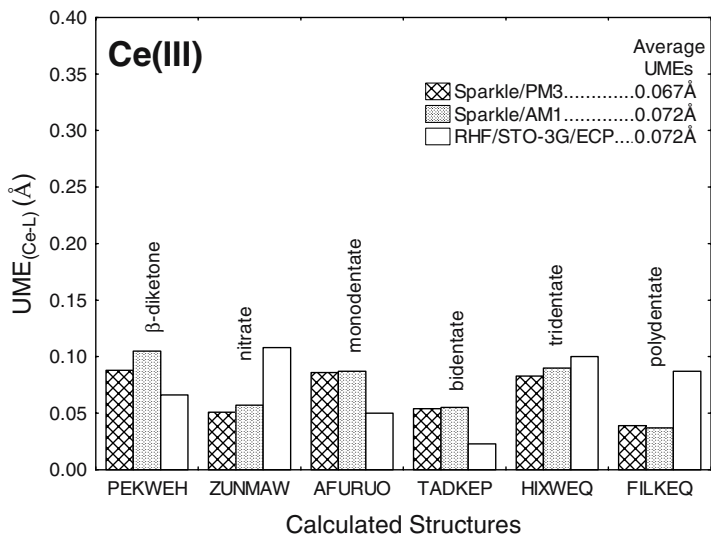


Fig. 2. Unsigned mean errors, $UME_{(Ce-L)}$ s, involving only the interatomic distances R_j between the cerium central ion and the atoms of the coordination polyhedron (in Å), obtained from the Sparkle/PM3, Sparkle/AM1 and RHF/STO-3G/ECP *ab-initio* calculations of the ground state geometries, for each of the six representative cerium(III) complexes, identified by their respective Cambridge Structural Database

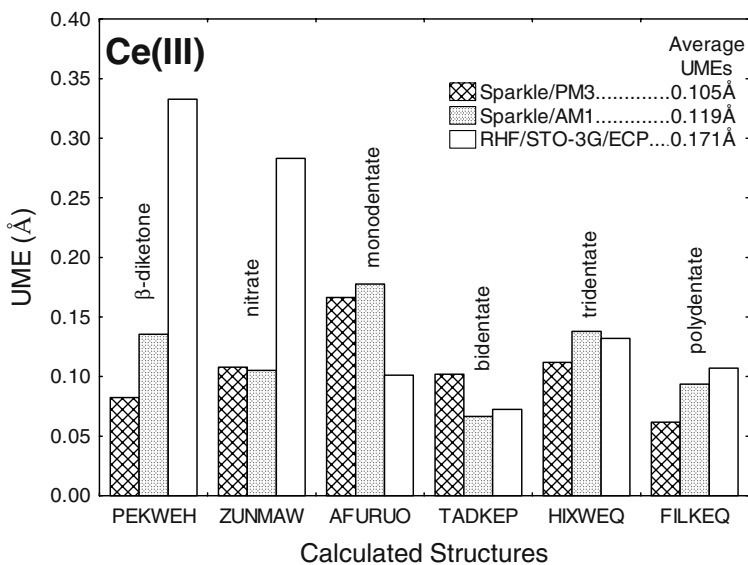


Fig. 3. Unsigned mean errors, $UME_{(Ce-L)}$ s, (in Å), between the cerium central ion and the atoms of the coordination polyhedron, as well as the interatomic distances R_j between all atoms of the coordination polyhedron obtained from the Sparkle/PM3, Sparkle/AM1 and RHF/STO-3G/ECP *ab-initio* calculations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

For Ce(III) we chose six of these complexes to have their geometries fully optimized with the model chemistry RHF/STO-3G/ECP. The chosen complexes were selected to be representative of the various classes of ligands (β -diketones, nitrates, monodentates, bidentates, tridentates, and polydentates) present in the validation set (see Fig. S2 in supplementary material).

Figure 2 and 3 presents the average $UME_{(Ce-L)}$ and UME values for Sparkle/PM3, Sparkle/AM1 and RHF/STO-3G/ECP full geometry optimizations of the six complexes considered. Clearly, all three model chemistries are comparable, with Sparkle/PM3 being in average slightly superior to Sparkle/AM1, which is, in turn, superior to RHF/STO-3G/ECP for the prediction of the geometries of the whole coordination polyhedra.

4 Conclusion

The most accurate ab initio effective core potential full geometry optimization calculations that can be nowadays carried out on cerium (III) 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 seemingly an accurate and statistically valid tool for the prediction of coordination polyhedra of lanthanide complexes.

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 complexes design research.

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Supplementary Material Available: Instructions and examples on how to implement the Ce(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 Ce(III). Examples of Mopac93r2 crystallographic geometry input (.dat) and optimized geometry summary output (.arc) files from Sparkle/PM3 calculations for the Ce(III) complex GIFCUT10 and for the dicerium complex XEXCUY. Tables of $UME_{(Ce-L)}$ s and $UMEs$ for both Sparkle/PM3 and Sparkle/AM1 for Ce(III). Figure with gamma distribution fits of the UME data for both Sparkle/PM3 and Sparkle/AM1 models.

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