

# JCTC

## Journal of Chemical Theory and Computation

### Sparkle/AM1 Parameters for the Modeling of Samarium(III) and Promethium(III) Complexes

Ricardo O. Freire,<sup>†</sup> Nivan B. da Costa Junior,<sup>‡</sup> Gerd B. Rocha,<sup>†</sup> and  
Alfredo M. Simas<sup>\*,†</sup>

*Departamento de Química Fundamental, CCEN, UFPE, 50590-470 - Recife, PE,  
Brazil, and Departamento de Química, CCET, UFS, 49100-000 - Aracaju, SE, Brazil*

Received September 20, 2005

**Abstract:** The Sparkle/AM1 model is extended to samarium(III) and promethium(III) complexes. A set of 15 structures of high crystallographic quality ( $R$  factor  $< 0.05$  Å), with ligands chosen to be representative of all samarium complexes in the Cambridge Crystallographic Database 2004, CSD, with nitrogen or oxygen directly bonded to the samarium ion, was used as a training set. In the validation procedure, we used a set of 42 other complexes, also of high crystallographic quality. The results show that this parametrization for the Sm(III) ion is similar in accuracy to the previous parametrizations for Eu(III), Gd(III), and Tb(III). On the other hand, promethium is an artificial radioactive element with no stable isotope. So far, there are no promethium complex crystallographic structures in CSD. To circumvent this, we confirmed our previous result that RHF/STO-3G/ECP, with the MWB effective core potential (ECP), appears to be the most efficient ab initio model chemistry in terms of coordination polyhedron crystallographic geometry predictions from isolated lanthanide complex ion calculations. We thus generated a set of 15 RHF/STO-3G/ECP promethium complex structures with ligands chosen to be representative of complexes available in the CSD for all other trivalent lanthanide cations, with nitrogen or oxygen directly bonded to the lanthanide ion. For the 42 samarium(III) complexes and 15 promethium(III) complexes considered, the Sparkle/AM1 unsigned mean error, for all interatomic distances between the Ln(III) ion and the ligand atoms of the first sphere of coordination, is 0.07 and 0.06 Å, respectively, a level of accuracy comparable to present day ab initio/ECP geometries, while being hundreds of times faster.

### Introduction

Lanthanide complexes and supramolecular architectures have been employed in various areas such as sensors,<sup>1</sup> liquid crystalline materials,<sup>2</sup> electroluminescent devices,<sup>3</sup> luminescent labels for specific biomolecule interactions,<sup>4</sup> and powerful catalysts for various organic transformations.<sup>5</sup> Luminescent lanthanide chelates have been widely used because of their advantages over traditional organic fluorophores: a long decay-time luminescence, large Stokes' shift, narrow emission band, and negligible concentration quenching.

Samarium metal is easily magnetized and difficult to demagnetize.<sup>6</sup> Furthermore, since samarium also has the smallest magnetic moment of all of the paramagnetic lanthanides, it has been used in chiral shift reagents where it presents a greatly reduced line broadening, thereby increasing the reliability of the empirical assignment of the absolute configuration of compounds.<sup>7</sup>

So far, ligand design has mainly produced structures that encapsulate the samarium ion, such as macrocycles and cryptates, creating bulkiness around the metal ion. Since the early 1980s, however, assemblies with two samarium ions facing each other have been discovered<sup>8</sup> and are now appearing in larger numbers.

There is a lack of theoretical methodologies that would permit the a priori design of samarium ligands for various

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

<sup>†</sup> Departamento de Química Fundamental, CCEN.

<sup>‡</sup> Departamento de Química, CCET.

applications. The ability to efficiently and accurately model all of these samarium molecular systems and interactions is, therefore, an open area of research. More specifically, modeling the influence of the chemical ambience on the  $4f^n$  configuration is of significance in the investigation of magnetic and spectroscopic properties of samarium compounds. For example, the description of ligand field effects is central to the design of new ligands capable of forming stable and highly luminescent complexes,<sup>9,10</sup> where the aim is to achieve strong ligand-to-metal energy transfer rates and intense metal-centered emission. The characterization of the interaction between the ligands and the central ion can be done through the ligand field parameters,  $B_q^k$ , which can be calculated provided the coordination geometry is known. Within the simple overlap model,<sup>10–12</sup> the values of  $B_q^k$  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 ligand–lanthanide interatomic distances, thus amplifying any inaccuracies. Such interatomic distances are the most sensitive geometric variables impacting upon the description of the effect of the surrounding chemical scenery on the lanthanide ion  $4f^n$  configuration. Therefore, a method to accurately predict the geometries of lanthanide complexes from theoretical calculations would be of great advantage. Predicting such geometries may be even more pertinent in light of the fact that obtaining single crystals of lanthanide complexes of appropriate size and optical quality for crystallographic structure determinations may be difficult.<sup>13–16</sup> Reliable, accurate, and fast quantum chemical models for predicting geometries of samarium complexes are urgently needed.

Promethium does not possess any stable isotopes. However, some of them find a variety of uses, such as the activation of zinc sulfide phosphor with  $\beta$  radiation of  $^{147}\text{Pm}$ , which provides self-sustaining light sources and is widely used in nocturnal illumination devices.<sup>17</sup> Complexes of promethium radionuclides, mainly  $^{147}\text{Pm}$  and  $^{149}\text{Pm}$ , have been used in bioresearch, such as in rat age-dependent permeation through skin in vitro,<sup>18</sup> in the development of receptor-based radiopharmaceuticals,<sup>19</sup> and in the radiotherapy of cancer.<sup>20</sup> Radiometals show some significant differences in tumor uptake and retention, physical half-lives, and  $\beta$ -particle path lengths, which may become important determinants of dosimetry and the therapeutic efficacy of pretargeted radioimmunotherapy with these radiolanthanides. The choice of therapeutic radionuclide depends on various factors, such as disease type, stage, and tumor burden; there is not a single ideal radionuclide for cancer therapy.  $^{149}\text{Pm}$ , especially, must always be considered as an option because of its  $\alpha$  and  $\beta$  energies for the targeted radiotherapy of cancer, low energy, and low-abundance  $\gamma$  emissions, suitable for tracking radiopharmaceuticals in vivo and estimating absorbed radiation doses.<sup>20</sup> Hence, the availability of a fast and accurate a priori quantum chemical model for the prediction of structures of Pm(III) coordination compounds could be of help in the design of promethium complexes exhibiting high thermodynamic, kinetic, and in vivo stabilities.

Ab initio calculations of lanthanide complexes have been sparsely appearing in the literature using various types of

effective core potentials, ECPs.<sup>21–27</sup> ECPs replace the chemically inert core electrons of the lanthanide with a potential acting on the valence electrons, which can also be derived to take into account relativistic effects. However, such ECP calculations still demand a large amount of CPU time, rendering high-quality calculations on systems of real chemical interest impractical. Indeed, samarium ab initio/ECP calculations are exceedingly rare.

To make possible the AM1<sup>28</sup> semiempirical calculation of lanthanide complexes, we recognized that the 4f orbitals are contracted toward the nucleus and shielded from fields outside the ion by the outermost 5s and 5p closed shells and introduced the Sparkle model<sup>29</sup> in which we represent the lanthanide ion by a sparkle, that is, 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. We further introduced into the model Gaussian functions in the core–core repulsion energy term to make it compatible with AM1.<sup>30</sup> Recently,<sup>31</sup> we explicitly included sparkle–sparkle core–core interactions to allow the calculation of dilanthanide compounds and defined a new paradigm, Sparkle/AM1, designed to possess geometry prediction accuracies for lanthanide complexes comparable to present day ab initio/ECP calculations, while being hundreds of times faster. Initially, we presented parametrizations for Eu(III), Gd(III), and Tb(III).<sup>31</sup> In the present paper, we extend Sparkle/AM1 to samarium(III) and promethium(III) complexes.

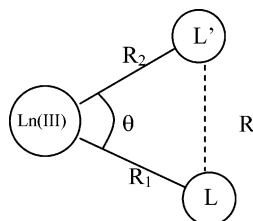
### Sparkle/AM1 for Samarium(III)

The parametrization procedure is a nonlinear minimization of an eight-dimension response function. We used a combination of Simplex and Newton–Raphson methods, aimed at finding one of its local minima, which ideally should both be the global minimum and make chemical sense.

The experimental crystallographic structures of the samarium complexes used were all taken from the Cambridge Structural Database 2004.<sup>32–34</sup> The traditional figure of merit for crystal structures is the crystallographic R factor, which provides a measure of how well the refined structure agrees with the experimental model. In the present study, only structures of high quality were considered, that is, structures with R factors less than 5%. For the current work, 15 different structures of complexes for the samarium(III) ion were also considered for parametrization. The response function,  $F_{\text{resp}}$ , was thus defined as

$$F_{\text{resp}} = \sum_{i=1} \left\{ \sum_{j=1} [100(R_{ij}^{\text{CSD}} - R_{ij}^{\text{calcd}})]^2 + \sum_{k=1}^2 \left[ \frac{2}{3} (\theta_{i,k}^{\text{CSD}} - \theta_{i,k}^{\text{calcd}})^2 \right] \right\} \quad (1)$$

where index  $i$  runs over all different complexes, 100 and  $2/3$  are coefficients taken from the response function originally used to parametrize MNDO,<sup>35</sup> index  $j$  runs over all distances ( $R$ ) of the samarium(III) ion to each of the directly coordinated atoms from the ligands, superscripts CSD and calcd refer to experimental and calculated quantities, and index  $k$  runs over all  $\theta$  angles formed by all combinations of two of the directly coordinated atoms from the ligands



**Figure 1.** Drawing representing the main variables used in the response function: Ln(III)–L interatomic distances and L–Ln(III)–L' bond angles. Ln stands for the central lanthanide ion, and L and L' are ligand atoms of the coordination polyhedron.

**Table 1.** Number of Samarium(III) and Promethium(III) Complexes in the Validation Sets, Classified into Each Ligand Group by Cluster Analysis

ligand group number	ligand type	number of structures	
		Sm(III)	Pm(III)
1	$\beta$ -diketonates	5	2
2	nitratates	7	2
3	monodentates	7	2
4	bidentates	4	2
5	tridentates	5	2
6	polydentates	8	4
7	dilanthanides	6	1

with the samarium(III) ion in its vertex, as in Figure 1. By adjusting  $R_1$ ,  $R_2$ , and the  $\theta$  angle, in Figure 1, the L–L' interatomic distance, which belongs to the coordination polyhedron, was indirectly adjusted.

The next step was to define the set of samarium complex structures to be used in the parametrization procedure, a set we called the samarium parametrization set. It is not simple to classify dozens of structures into smaller representative groups, from which to sample one or two structures to include in the parameter set. Thus, a cluster analysis of all the complexes available in the CSD for samarium was done. The cluster analysis was run with Statistica 6.0 software, using the Euclidean distances with complete linkage to cluster the complexes. As variables, the number of atoms directly coordinated to the lanthanide ion for each of the following types of ligands was used:  $\beta$ -diketonate, nitrate, monodentate, bidentate, tridentate, and polydentate. The disamarium complexes were considered a separate group. Only ligands with either or both nitrogen and oxygen as coordinating atoms were considered, since these are the most important ligating atoms for luminescence and most applications.

Moreover, the average unsigned mean error for each complex  $i$ ,  $UME_i$ , was defined as

$$UME_i = \frac{1}{n} \sum_{j=1}^n |R_{ij}^{CSD} - R_{ij}^{calcd}| \quad (2)$$

where  $n$  is the number of ligand atoms directly coordinating the lanthanide ion.

A set of 15 structures of high crystallographic quality ( $R$  factor  $< 0.05$  Å), with ligands chosen to be representative of all complexes in the CSD, with nitrogen or oxygen directly

**Table 2.** Sparkle/AM1 Parameters for the Sm(III) and Pm(III) Ions

	Sparkle/AM1 Sm(III)	Sparkle/AM1 Pm(III)
GSS	56.993 514 482 0	59.424 970 551 9
ALP	4.175 850 901 0	3.105 983 364 7
$a_1$	0.959 288 507 0	1.734 767 115 8
$b_1$	6.479 992 447 0	9.246 422 636 0
$c_1$	1.738 140 224 0	1.753 341 948 5
$a_2$	0.026 100 421 0	0.257 101 725 8
$b_2$	9.739 195 223 0	7.879 344 526 7
$c_2$	2.888 117 670 0	3.049 816 294 0
EHEAT (kcal mol <sup>-1</sup> ) <sup>a</sup>	974.4	976.9
AMS (amu)	150.36	145.0

<sup>a</sup> The heat of formation of the Sm(III) and Pm(III) ions in Sparkle/AM1 was obtained by adding to the heat of atomization of each lanthanide its first three ionization potentials.<sup>38</sup>

**Table 3.** Values of the Coordination Numbers, CNs, and UMEs for Sparkle/AM1, as Compared to the Respective Experimental Crystallographic Values, Obtained from the Cambridge Structural Database 2004,<sup>32–34</sup> for Each of the 42 Samarium(III) Complexes of the Validation Set

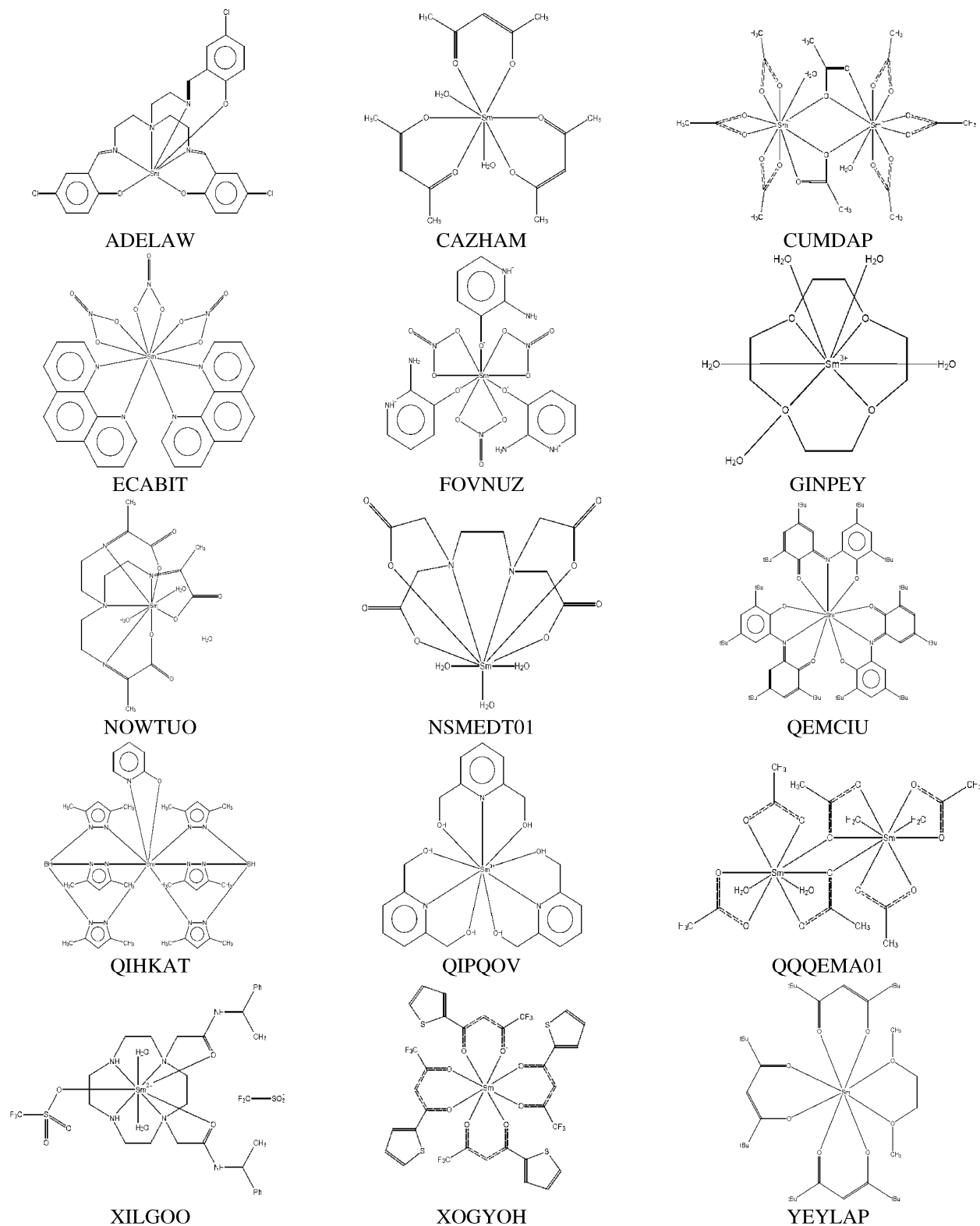
structure <sup>a</sup>	CN	UME (Å)		structure <sup>a</sup>	CN	UME (Å)	
		Sparkle/AM1				Sparkle/AM1	
ADELAW	7	0.1052		NSMEDT01	9	0.3283	
BUVWUK01	9	0.2659		QALFAK	9	0.3233	
CAZHAM	8	0.2472		QIHKAT	8	0.1278	
CORKEZ	9	0.2588		QIPQOV	9	0.2618	
ECABIT	10	0.1187		QOCKIC	8	0.0908	
FINDOV	6	0.0541		QQQEMA01	9	0.2129	
FUHQOO	9	0.0762		SMNICD	8	0.2563	
FUJYEO	8	0.1925		SOXKAR	9	0.2898	
GINPEY	9	0.1365		WIGVOX	7	0.1368	
GUPHUU	8	0.1523		WOCNIL	4	0.0871	
HAWMUN	8	0.1117		XAGVOQ	5	0.0561	
JAQNOE	8	0.1312		XAXYAW	7	0.1293	
JIZVOD	11	0.1571		XEPLAF	8	0.2742	
KIWROX	10	0.1964		XEXJAL	7	0.0683	
KUYBAH	9	0.2448		XILGOO	9	0.1034	
LIXDUR	9	0.1469		XIVFIR	8	0.1669	
LUHFEZ	10	0.0904		XOGYOH	8	0.0997	
MEWGOK	9	0.1300		XOWGAR	9	0.2875	
MOXJEO	9	0.3295		YENHOO	9	0.2641	
NAFKIO	5	0.1905		YUBPAM	8	0.1388	
NOWTUO	9	0.1905		ZALDUL	5	0.2466	

<sup>a</sup> The structures are identified by their respective codes of reference from the Cambridge Structural Database 2004.<sup>32–34</sup>

bonded to the samarium ion, was used as a training set (Figure 2). In the validation procedure, we used a set of 42 complexes, also of high crystallographic quality.

Seven molecular groups can be identified from Figure 3. Table 1 describes the molecular clusters and the number of structures found in each.

As previously mentioned, the parametrization procedure used for samarium(III) complexes was identical to the one we successfully used to obtain Sparkle/AM1 parameters for Eu(III), Gd(III), and Tb(III)<sup>31</sup>. The validation procedure has been performed by using, as a measure, the UME, eq 2, this time summing up over all 42 complexes of the validation set.



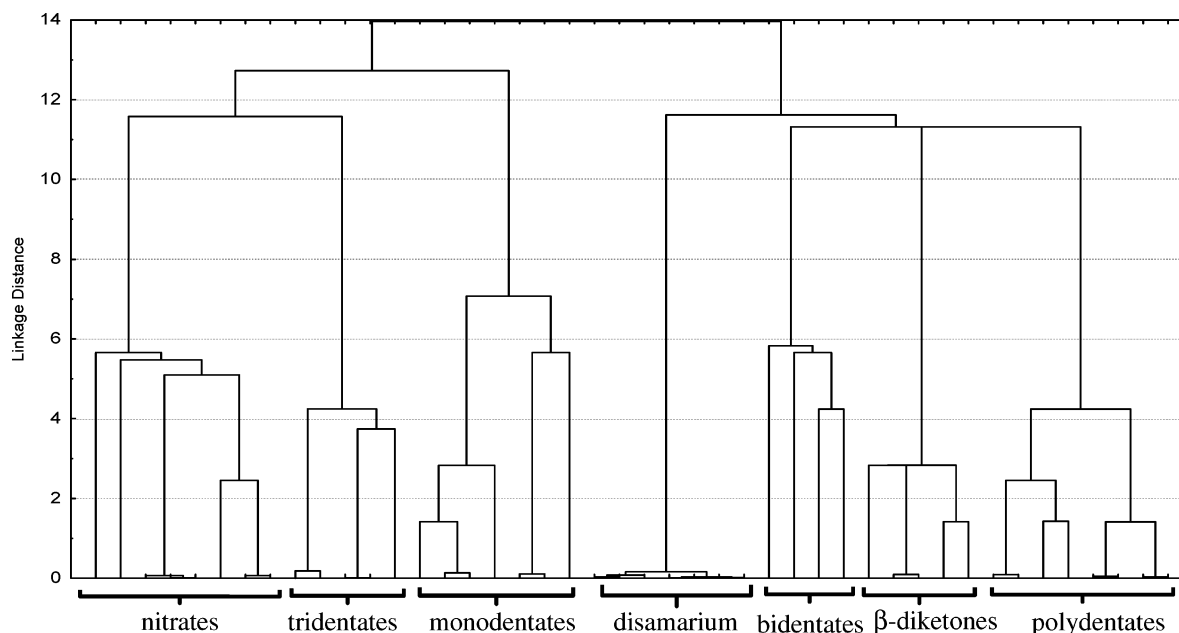
**Figure 2.** Schematic two-dimensional representations of the samarium(III) complexes that constitute the parametrization training set, obtained from the Cambridge Structural Database 2004.<sup>32–34</sup>

Sparkle/AM1 model calculations have been carried out using the MOPAC93r2 package<sup>36</sup> for the geometry optimization of samarium(III) complexes. MOPAC keywords used in all Sparkle/AM1 calculations were GNORM = 0.25, SCFCRT = 1.D-10 (in order to increase the SCF convergence criterion), and XYZ (the geometry optimizations were performed in Cartesian coordinates).

The best parameter set found that defines the Sparkle/AM1 model for the samarium(III) ion is presented in Table 2.

Our objective, which was to guarantee that Sparkle/AM1 for Sm(III) was as accurate as Sparkle/AM1 for Eu(III), Gd(III), and Tb(III),<sup>31</sup> was achieved. In Table 3, we present the UMEs for all 42 complexes used in the validation test.





**Figure 3.** Cluster analysis of all 42 samarium(III) complexes, in terms of both the UMEs and the number of atoms directly coordinated to the lanthanide ion, for each of the various types of ligands. The UMEs are calculated for each complex as the sum of all absolute values of differences between experimental and calculated interatomic distances, involving all atoms of the coordination polyhedron as well as these and the central samarium(III) ion.

If we observe the UMEs in Figure 4 for each of the 42 complexes, grouped according to the cluster analysis shown in Figure 3, where the UME was calculated considering all interatomic distances of the coordination polyhedron, we can see that only three complexes, MOXJEO, NSMEDT01, and QALFAK, present UMEs above 0.3 Å. In the three cases, the high UMEs of 0.330, 0.328, and 0.323 are mainly due to problems in the description of L–L distances, where L is an atom of the ligand directly coordinating the samarium ion. The errors caused by the L–L distances correspond to 82%, 87%, and 92% of the total UMEs, respectively.

However, by analyzing only the distances involving the Sm(III) ion, Figure 4b, we can observe that most of the structures show a UME below 0.20 Å. Table 4 shows UMEs separated by more specific types of bonds and angles. As mentioned before, distances between samarium(III) and oxygen or nitrogen ligand atoms are the most important for the design of luminescent complexes, their UMEs being 0.064 and 0.095, for Sm(III)–O and Sm(III)–N, respectively.

### Sparkle/AM1 for Promethium (III)

The fact that there are no crystallographic structures of promethium complexes available, although promethium complexes are being used in bioresearch, makes it even more useful to have a semiempirical model for them, a model that could be of help in their design.

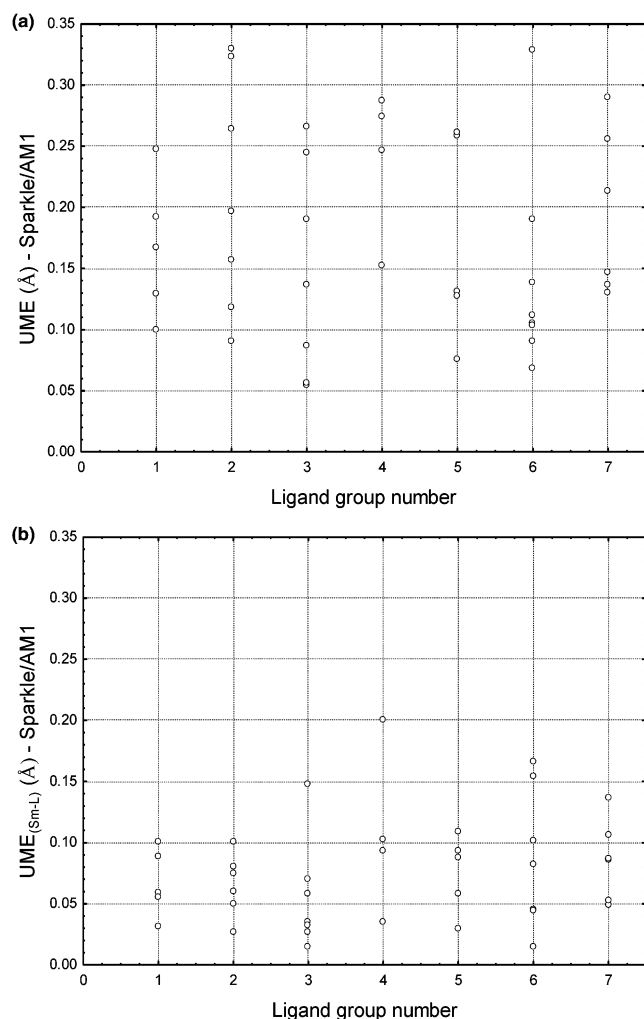
Accordingly, we then decided to investigate the possibility of parametrizing Sparkle/AM1 for promethium from results of *ab initio*/ECP calculations using only the quasirelativistic ECP for promethium(III) ions, developed by Dolg et al.<sup>22</sup> and implemented in Gaussian 98 as the MWB50 ECP,<sup>37</sup> together with its related [5s4p3d] – GTO valence basis sets.

This ECP includes  $46 + 4f^n$  electrons in the core, leaving the outermost 11 electrons to be treated explicitly.

Recently,<sup>31</sup> we presented evidence that either enlarging the basis set or including correlation, or both, in the calculations, does not necessarily lead to higher accurate lanthanide complex coordination polyhedron predictions. Actually, in many cases, it even worsened their geometries.<sup>31</sup> Our previous results further indicated that RHF/STO-3G/ECP or RHF/3-21G/ECP results are seemingly equivalent in accuracy,<sup>31</sup> when we compare MWB52 ECP calculations carried out on seven different Eu(III) complexes.

Therefore, we decided to investigate this fact in greater detail in order to be able to arrive at a reasonable *ab initio* standard, from which Sparkle/AM1 for promethium could be parametrized. We started with one of the simplest samarium complexes, the isolated cation of nona-aqua-samarium(III) tris(trifluoromethanesulfonate),  $[\text{Sm}(\text{H}_2\text{O})_9]^{3+}$ , of CSD code BUVWUK01 (Figure 5), and concentrated on determining which *ab initio* model chemistry with the MWB51 ECP would more accurately predict its coordination polyhedron only. First, we carried out a series of RHF calculations with basis sets of increasing size. Our results are presented in the two top graphs of Figure 6. Both the UME of the whole coordination polyhedron and the  $\text{UME}_{(\text{Sm}-\text{L})}$  of the samarium ion ligand distances only considerably worsened as the basis set increased. Actually, these errors more than doubled by going from STO-3G to 6-31G\*.

We then decided to fix the basis set at STO-3G and studied the effect of improving the model by the inclusion of electron correlation, both by means of the B3LYP functional and by many-body perturbation theory at the MP2 level. Again, by adding correlation, the predicted coordination polyhedron became worse, as can be clearly seen in the two graphs in



**Figure 4.** Unsigned mean errors for each of the 42 Sm(III) complexes, assembled according to the ligand group numbers defined in Table 1. Part a presents the UMEs, and part b presents the  $UME_{(Sm-L)}$  values. The same scale has been used in both parts to facilitate comparison.

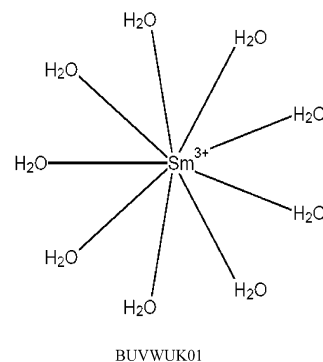
the middle of Figure 6. However, the effect of including electron correlation was much smaller than the basis set effect and affected the whole coordination polyhedron more than the europium–ligand atom distances only. Finally, we decided to examine both factors together, by increasing the basis set size together with including electron correlation. The same trend cropped up, and the two bottom graphs of Figure 6 confirm that RHF/STO-3G is seemingly the most accurate ab initio model for lanthanide complex coordination polyhedron crystallographic geometry prediction from isolated lanthanide complex ion calculations.

We then decided to confirm that RHF/STO-3G/ECP full geometry optimizations of a few representative samarium complexes of known crystallographic geometries would yield coordination polyhedra errors comparable to those of Sparkle/AM1 for the same complexes, thus justifying the use of promethium RHF/STO-3G/ECP calculations to obtain Sparkle/AM1 parameters for promethium. Figure 7 presents the seven samarium complexes chosen, one from each of the clusters of Figure 3, including the largest of all, the disamarium complex of CSD code MEWGOK, with 116 atoms.

**Table 4.** Values of the Coordination Numbers, CNs, and UMEs for Each of the 15 Promethium(III) Complexes of the Validation Set, for Sparkle/AM1, as Compared to Their Respective Fully Optimized RHF/STO-3G/ECP Geometries<sup>a</sup>

structure <sup>1</sup>	CN	UME (Å) Sparkle model
BUVWUK01{Pm}	9	0.1612
CAZHAM{Pm}	8	0.2043
FINDOV{Pm}	6	0.0826
FUHQOO{Pm}	9	0.1582
FUJYEO{Pm}	8	0.1548
GUPHUU{Pm}	8	0.1276
KUYBAH{Pm}	9	0.2133
LUHFEZ{Pm}	10	0.1422
NOWTUO{Pm}	9	0.1389
NUQYUT{Pm}	6	0.0844
QALFAK{Pm}	9	0.2044
QIPQOV{Pm}	9	0.1328
SOXKAR{Pm}	9	0.2594
XEXJAL{Pm}	7	0.1121
XILGOO{Pm}	9	0.1380

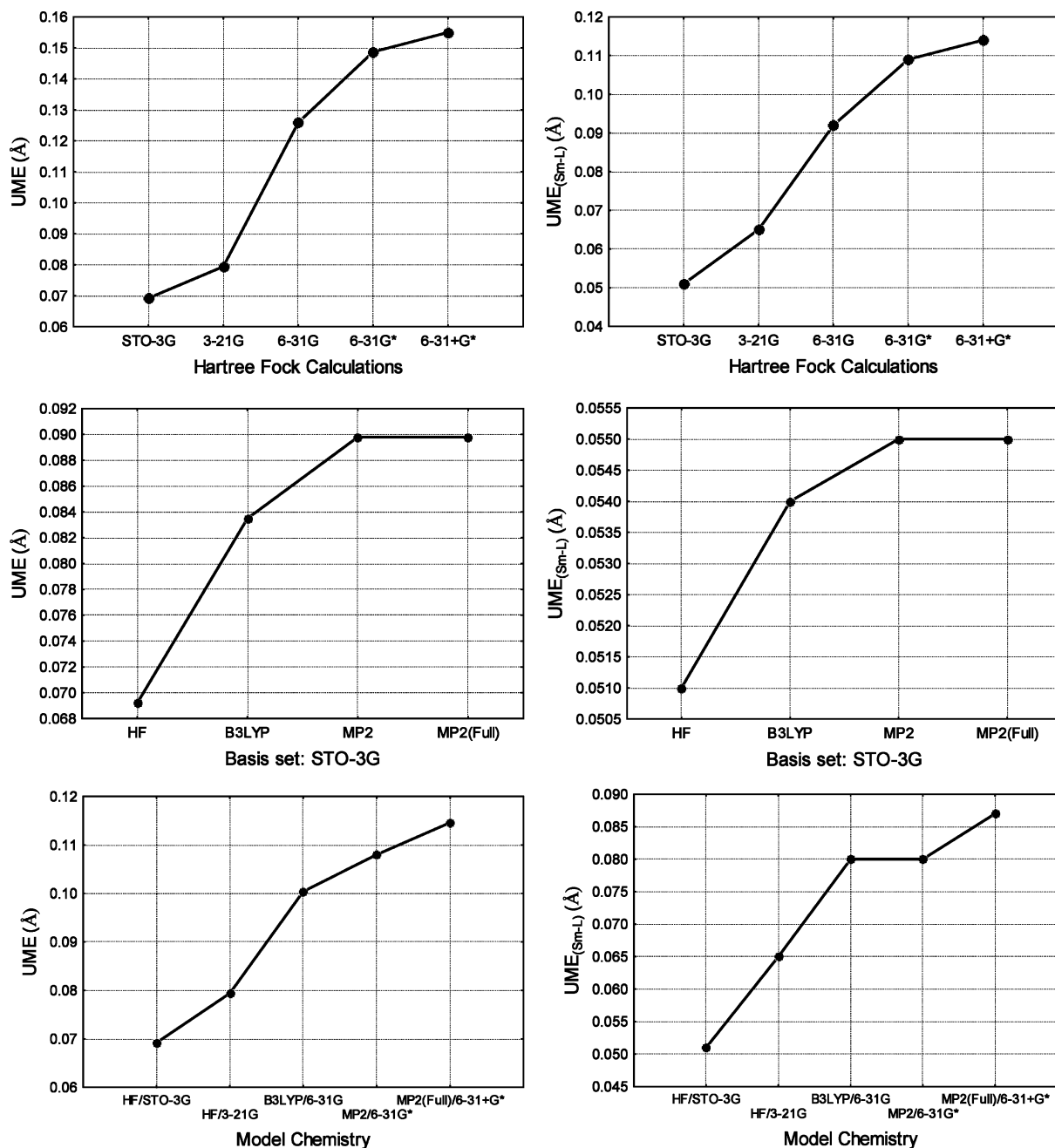
<sup>a</sup> These geometries were obtained by using, as starting points, the geometries of the respective samarium complexes obtained from the Cambridge Structural Database 2004<sup>32–34</sup> and by replacing samarium with promethium. For example, XILGOO{Pm} represents the samarium XILGOO complex, with Pm instead of Sm.



**Figure 5.** Schematic representation of the structure of the cation nona-aqua-samarium(III) obtained from the Cambridge Structural Database 2004.<sup>32–34</sup>

Figure 8 shows UMEs and the  $UME_{(Sm-L)}$  for these complexes for both Sparkle/AM1 and RHF/STO-3G/ECP, where one can clearly see that the errors are comparable and trend similarly across the complexes. The results indicate that the Sm(III) parametrization of the Sparkle/AM1 model is capable of predicting coordination polyhedra for most structures with an accuracy equivalent to that of ab initio RHF/STO-3G/ECP. Only for the complex with a polydentate ligand, XEXJAL, was the ab initio RHF/STO-3G/ECP methodology more accurate than the Sparkle/AM1 model. However, the coordination polyhedron UME obtained by Sparkle/AM1 and ab initio RHF/STO-3G/ECP are both low and very close: 0.075 Å and 0.079 Å, respectively.

Consider the ratios in CPU time spent in the complete geometry optimization of the seven structures selected for this analysis between ab initio RHF/STO-3G/ECP and Sparkle/AM1 model calculations. These ratios indicate how fast the Sparkle/AM1 calculation is when compared to the



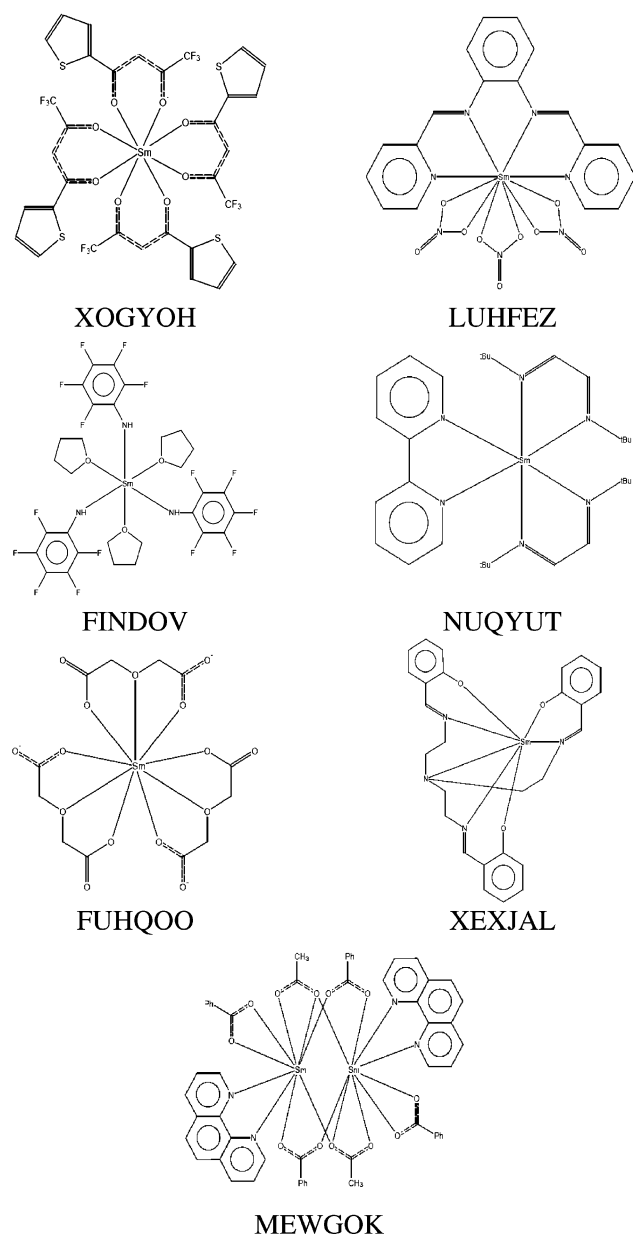
**Figure 6.** UMEs and  $UME_{(Sm-L)}$  for the cation nona-aqua-samarium(III) for various model chemistries, all using the quasirelativistic ECP of Dolg et al.,<sup>22</sup> and all compared to the Cambridge Structural Database 2004<sup>32–34</sup> crystallographic geometry.  $UME_{(Sm-L)}$  considers only samarium–ligand atom distances, and UME further includes all distances within the coordination polyhedron.

ab initio one. All have been performed on a Pentium IV 3.0 GHz computer with 2 GB of RAM memory (DDR- 400). For this set of complexes, Sparkle/AM1 calculations ranged from 26 s up to 19 min and were from 115 to 1839 times faster than the corresponding ab initio calculations.

Presently, we do not know the root cause of why RHF/STO-3G/ECP using MWB ECP appears to be the most efficient ab initio model chemistry for coordination polyhedron crystallographic geometry predictions from isolated lanthanide complex ion calculations. But, fortunately, that is so, because the usage of RHF/STO-3G/ECP with MWB ECPs leads to relatively fast ab initio calculations. This finding is warranted only for predictions of coordination polyhedron crystallographic geometries of lanthanide com-

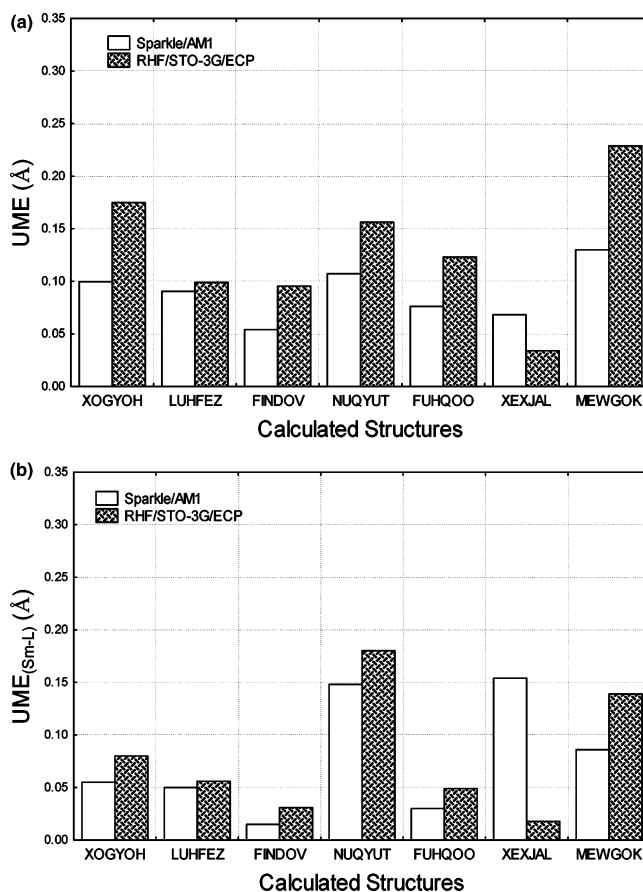
plexes using MWB ECPs. Thus, we cannot assume that this finding would hold true, either for other ECPs or for the geometries of the remaining parts of the molecule. And most likely, this finding will not hold true for the prediction of other properties. However, as we already mentioned, coordination polyhedron geometries are the most sensitive geometric variables impacting upon the description of the effect of the surrounding chemical scenery on the lanthanide ion  $4f^n$  configuration.

To obtain the 15-complex promethium parametrization set, we followed the procedure previously used for Eu(III), Gd(III), and Tb(III),<sup>31</sup> and for Sm(III), and chose another set of samarium complexes with ligands representative of the seven types shown in Table 1. Then, as starting points, we



**Figure 7.** Schematic two-dimensional representations of the structures of samarium(III) complexes, used for comparison between *ab initio* model geometries and their crystallographic counterparts, identified by their respective Cambridge Structural Database 2004<sup>32–34</sup> codes. The *ab initio* calculations have been performed using the Hartree–Fock method with the STO-3G basis set for all atoms, except for the samarium(III) ion, in which case we used the quasirelativistic ECP of Dolg et al.<sup>22</sup>

used the geometries of these samarium complexes, replaced samarium with promethium, and fully optimized the geometries with RHF/STO-3G/ECP. We defined a special code for the promethium parametrization set: XILGOO{Pm}, for example, would be the samarium XILGOO complex with Pm instead of Sm. Figure 9 shows the 15 complexes of the promethium parametrization set. The best parameter set found that defines the Sparkle/AM1 model for the promethium(III) ion is also presented in Table 2. Table 4 presents the errors between the promethium Sparkle/AM1 and RHF/



**Figure 8.** Unsigned mean errors, obtained from Sparkle/AM1 and *ab initio* RHF/STO-3G/ECP calculations of the ground-state geometries, for each of the seven representative samarium(III) complexes, identified by their respective Cambridge Structural Database 2004<sup>32–34</sup> codes and using the quasirelativistic ECP of Dolg et al.<sup>22</sup> (a) UME includes all distances within the coordination polyhedron and central samarium ion, and (b) UME<sub>(Sm–L)</sub> considers only samarium–ligand atom distances.

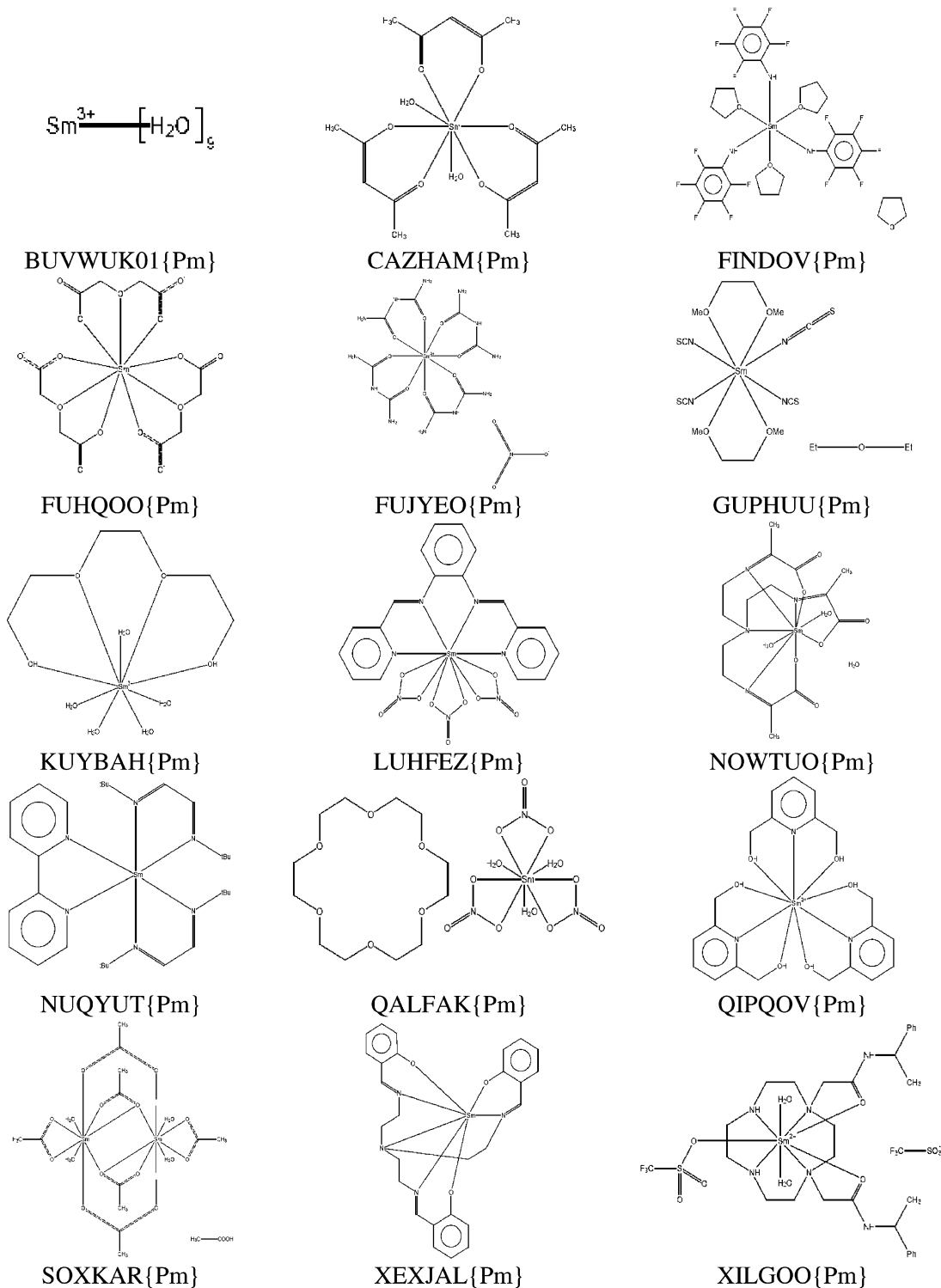
STO-3G/ECP results for the 15-complex set, and Table 5 shows the UMEs broken into more specific types of bonds and angles. The figures clearly indicate that results for promethium are, therefore, comparable to results for europium, gadolinium, terbium, and samarium, and the use of the present parametrization for promethium seems warranted until experimental crystallographic structures appear in the literature. As we already indicated, it is precisely when there are no experimental data that theoretical calculations may prove more useful.

## Conclusions

Sparkle/AM1 for samarium(III) predicts both lanthanide–ligand distances and distances involving any two atoms in the coordination polyhedron, at the same level of accuracy of the Sparkle/AM1 models as that for Eu(III), Gd(III), and Tb(III) ions. Besides, Sparkle/AM1 accuracy is competitive with, and sometimes better than, *ab initio* geometries, while being hundreds of times faster.

In conclusion, our results indicate that, for geometry prediction purposes, the Sparkle/AM1 model for Sm(III) is





**Table 5.** Sparkle/AM1 Unsigned Mean Errors for All Distances Involving the Central Lanthanide Ion, Ln, and the Ligand Atoms of the Coordination Polyhedron, L, for 96 Eu(III) Complexes, 70 Gd(III) Complexes, 42 Tb(III) Complexes, All 42 Sm(III) Complexes, and All 15 Pm(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, and L–L'	Ln–Ln, and L–L'
Sparkle/AM1, Eu	0.1624	0.0848	0.0880	0.2170	0.0900	0.1900
Sparkle/AM1, Gd	0.1830	0.0600	0.0735	0.2082	0.0658	0.1781
Sparkle/AM1, Tb	0.2251	0.0754	0.0440	0.2123	0.0746	0.1823
Sparkle/AM1, Sm	0.1381	0.0644	0.0960	0.2158	0.0745	0.1851
Sparkle/AM1, Pm <sup>a</sup>	0.3376	0.0561	0.0591	0.1977	0.0589	0.1681

<sup>a</sup> For promethium, instead of crystallographic geometries as a reference, we used fully optimized RHF/STO-3G/ECP geometries as described in the text.

**Acknowledgment.** The authors acknowledge the financial support of CNPq, CAPES, FACEPE (Brazilian agencies), PRONEX, Instituto do Milênio de Materiais Complexos, and “Programa Primeiros Projetos” for financial support and CENAPAD (Brazilian institution) for having made available to us their computational facilities. Finally, we gratefully acknowledge the Cambridge Crystallographic Data Centre for the Cambridge Structural Database 2004.

**Supporting Information Available:** Instructions and examples on how to implement the Sm(III) and Pm(III) Sparkle/AM1 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 Sm(III) and Pm(III). Examples of Mopac93r2 reference geometry input (.dat) and optimized geometry summary output (.arc) files from Sparkle/AM1 calculations for (i) the Sm(III) complexes XAGVOQ and QQQEMA01 and (ii) the Pm(III) complexes XEXJAL{Pm} and SOXKAR{Pm}. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) Gameiro, C. G.; da Silva, E. F., Jr.; Alves, S., Jr.; de Sá, G. F.; Santa-Cruz, P. A. *Mater. Sci. Forum* **1999**, *315*, 249.
- (2) Binnemans, K.; Görller-Walrand, C. *Chem. Rev.* **2002**, *102*, 2303.
- (3) Kido, J.; Okamoto, Y. *Chem. Rev.* **2002**, *102*, 2357.
- (4) Thunus, L.; Lejeune, R. *Coord. Chem. Rev.* **1999**, *184*, 125.
- (5) Molander, G. A.; Romero, J. A. C. *Chem. Rev.* **2002**, *102*, 2161.
- (6) Scholz, W.; Fidler, J.; Schrefl, T.; Suess, D.; Matthias, T. J. *Appl. Phys.* **2002**, *91*, 8492.
- (7) Inamoto, A.; Ogasawara, K.; Omata, K.; Kabuto, K.; Sasaki, Y. *Org. Lett.* **2000**, *2*, 3543.
- (8) Mital, S. P.; Singh, R. V.; Tandon, J. P. *Synth. React. Inorg. Met.-Org. Chem.* **1982**, *12*, 269.
- (9) de Sá, G. F.; Malta, O. L.; Donega, C. M.; Simas, A. M.; Longo, R. L.; Santa-Cruz, P. A.; da Silva, E. F., Jr. *Coord. Chem. Rev.* **2000**, *196*, 165.

- (10) Faustino, W. M.; Rocha, G. B.; Silva, F. R. G.; Malta, O. L.; de Sá, G. F.; Simas, A. M. *THEOCHEM* **2000**, *527*, 245.
- (11) Malta, O. L. *Chem. Phys. Lett.* **1982**, *87*, 27.
- (12) Malta, O. L. *Chem. Phys. Lett.* **1982**, *88*, 353.
- (13) Ronda, C. R. *J. Alloys Compd.* **1995**, *225*, 534.
- (14) Bünzli, J.-C. G.; Pighet, C. *Chem. Rev.* **2002**, *102*, 1897.
- (15) Thompson, L. C. In *Handbook on the Physics and Chemistry of Rare-Earths*; Gschneider, K. A., Eyring, L., Eds.; North-Holland: Amsterdam, 1979.
- (16) Mondry, A.; Bukietyńska, K. *J. Alloys Compd.* **2004**, *374*, 27.
- (17) Ravi, S.; Mathew, K. M.; Seshadri, N. K.; Subramanian, T. K. *J. Radioanal. Nucl. Chem.* **2001**, *250*, 565.
- (18) Kassai, Z.; Koprda, V.; Bauerová, K.; Harangozó, M.; Bendová, P.; Bujnová, A.; Kassai, A. *J. Radioanal. Nucl. Chem.* **2003**, *258*, 669.
- (19) Li, W. P.; Smith, C. J.; Cutler, C. S.; Ketrings, A. R.; Jurisson, S. S. *J. Nucl. Med.* **2000**, *41* (5), 246.
- (20) Lewis, M. R.; Zhang, J. L.; Jia, F.; Owen, N. K.; Cutler, C. S.; Embree, M. F.; Schultz, J.; Theodore, L. J.; Ketrings, A. R.; Jurisson, S. S.; Axworthy, D. B. *Nucl. Med. Biol.* **2004**, *31* (7), 973.
- (21) Dolg, M.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1989**, *90*, 1730.
- (22) Dolg, M.; Stoll, H.; Savin, A.; Preuss, H. *Theor. Chim. Acta* **1989**, *75*, 173.
- (23) Cundari, T. R.; Stevens, W. J. *J. Chem. Phys.* **1993**, *98*, 5555.
- (24) Ross, R. B. *J. Chem. Phys.* **1994**, *100*, 8145.
- (25) Dolg, M. In *Modern Methods and Algorithms of Quantum Chemistry*; Grotendorst, J., Ed.; John von Neumann Institute for Computing: Jülich, Germany, 2000; NIC series, Vol. 1, p 479.
- (26) Tsuchiya, T.; Nakajima, T.; Hirao, K.; Seijo, L. *Chem. Phys. Lett.* **2002**, *361*, 334.
- (27) Cao, X.; Dolg, M. *THEOCHEM* **2002**, *581*, 139.
- (28) Dewar, M. J. S.; Zebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.
- (29) de Andrade, A. V. M.; da Costa, N. B., Jr.; Simas, A. M.; de Sá, G. F. *Chem. Phys. Lett.* **1994**, *227*, 349.
- (30) Rocha, G. B.; Freire, R. O.; da Costa, N. B., Jr.; de Sá, G. F.; Simas, A. M. *Inorg. Chem.* **2004**, *43*, 2346.
- (31) Freire, R. O.; Rocha, G. B.; Simas, A. M. *Inorg. Chem.* **2005**, *44*, 3299.
- (32) Allen, F. H. *Acta Crystallogr., Sect. B* **2002**, *58*, 380.
- (33) Bruno, I. J.; Cole, J. C.; Edgington, P. R.; Kessler, M.; Macrae, C. F.; McCabe, P.; Pearson, J.; Taylor, R. *Acta Crystallogr., Sect. B* **2002**, *58*, 389.
- (34) Allen, F. H.; Motherwell, W. D. S. *Acta Crystallogr., Sect. B* **2002**, *58*, 407.
- (35) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.
- (36) Stewart, J. J. P. *MOPAC 93.00 Manual*; Fujitsu Limited: Tokyo, Japan, 1993.
- (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) Lide, D. R. *Handbook of Chemistry and Physics* [CD-ROM]; CRC Press: New York, 2002.

CT050236Z