

# RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

## ARTICLE

## RM1 Modeling of Neodymium, Promethium, and Samarium Coordination Compounds

Cite this: DOI: 10.1039/x0xx00000x

Manoel A. M. Filho<sup>a</sup>, José Diogo L. Dutra<sup>a,c</sup>, Gerd B. Rocha<sup>b</sup>, Alfredo M. Simas<sup>c</sup>, and Ricardo O. Freire<sup>a,\*</sup>

Received 00th January 2012,  
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

[www.rsc.org/](http://www.rsc.org/)

The RM1 model is parameterized for the prediction of geometries of Nd(III), Sm(III), and Pm(III) complexes. By adding the lanthanides to RM1 with a set of 5d, 6s, and 6p orbitals, the model is now capable of accurately describing direct coordinations to the lanthanide trication, not only by oxygen and nitrogen, but also by other atoms, such as carbon, sulfur, chlorine and bromine. Overall, the accuracy of the RM1 model for interatomic distances between the lanthanide ion and other directly coordinated atoms is 0.06 Å for both Nd(III) and Sm(III), and 0.05 Å for Pm(III). The RM1 model for Nd(III), Sm(III), and Pm(III) is indeed a more general model than the previous sparkle models, and may be used for any complex of these trivalent lanthanide ions. More importantly, if the Nd(III), Sm(III), or Pm(III) complex of interest contains coordinated atoms which are neither oxygen nor nitrogen, then the RM1 model advanced in this article must be the semiempirical model of choice.

### Introduction

Lanthanide complexes display a wide array of applications, as light conversion molecular devices<sup>1</sup>, in thermochromic materials in temperature indicating devices<sup>2</sup>, as emission layers in OLED (organic light-emitting diode) devices<sup>3</sup>, etc. One of the most important applications of neodymium complexes is that they can be long-lived near infrared emitters with an essentially monochromatic emission profile free from “environmentally emissive pollution”<sup>4</sup> in the range of 1064 nm, which also lies within the telecommunications window of silica photonic crystal fibers. Another important application of light emitting neodymium complexes is to *in vivo* imaging, since biological tissues are relatively more transparent to near infrared radiation<sup>5</sup>.

However, such complexes may present thermal instability, photo-instability, and low mechanical strength. As such, the ability to model them theoretically with the intent of developing new, more stable and much stronger complexes, for all their possible myriad of applications, is of considerable value.

Likewise, samarium complexes are used for several different purposes. There is even a complex of a radioisotope of samarium, <sup>153</sup>Sm, (Samarium-153-ethylene diamine tetramethylene phosphonate, trade name Quadramet)<sup>6</sup> which is used for the treatment of cancers that have spread to the bones and helps alleviate the associated pain. Samarium complexes may also behave as light converters, by emitting orangish light when illuminated with ultra-violet light. Moreover, they can also be used as coordination polymerization catalysts<sup>7, 8</sup>. In addition, thermal stability is also an issue when developing luminescent samarium complexes<sup>9</sup>.

On the other hand, the most stable of the nuclei of the various synthetic promethium atoms <sup>145</sup>Pm has a half-life of about 17.7 years; and another technologically important one is <sup>147</sup>Pm, used as a beta radiation source, with a half-life of about 2.6 years. Hence, there is not a voluminous body of work on Pm complexes, although a few applications have been presented, such as: complexes of promethium with ligands such as DTPA, DOTA, and DTPA-Octreotide as receptor-based radiopharmaceuticals<sup>10</sup>; hydroxyquinolates of promethium<sup>11</sup>; complexes of promethium with ethylenediaminetetraacetic, diethylenetriaminepentaacetic and nitrilotriacetic acids<sup>12</sup>; extraction studies using acetylacetonate complexes of promethium<sup>13</sup>, etc. This paucity of data and interest might change in the future if a novel application for promethium complexes is discovered, in which case, it would be even more important to be able to theoretically model promethium coordination compounds so that the experiment can be previously designed and carried out with a greater probability of success.

In this article, we extend the parameterization of our RM1 (Recife Model 1)<sup>14</sup> semiempirical model for lanthanides<sup>15, 16</sup> for the trivalent ions Nd(III), Pm(III), and Sm(III). Unlike our previous Sparkle Models, however, we now include atomic orbitals in the lanthanide cation, rendering RM1 a much more general model, capable of accurately modeling coordination bonds of these metals, not only with oxygen and nitrogen, but also with other atoms such as carbon, sulfur, chlorine, and bromine.

## Previous Semiempirical Parameterizations for Nd, Pm, and Sm

Chemical bonds between a lanthanide central ion and the directly coordinating atoms of the ligands lack directionality, with the complexes displaying a large array of coordination numbers, usually from eight to ten. This is commonly attributed to the fact that the contribution of the occupied 4f orbitals to the electron density is buried inside the ion core and does not significantly sustain a presence in the region associated with the valence shell. Thus, these chemical bonds possess a character, which can be regarded as essentially electrostatic. Based on this conceptualization, the original Sparkle Model<sup>17, 18</sup> represented the lanthanide ion by a point charge of value +3e superimposed to a repulsive potential of the form  $\exp(-\alpha r)$  in order to assign a size to the metal ion. Since the model was regarded as useful<sup>19-24</sup>, it was subsequently and significantly improved by adding Gaussian functions to the semiempirical core-core repulsion<sup>25</sup> and was then fully parameterized within AM1<sup>26, 27</sup>, PM3<sup>28, 29</sup>, PM6<sup>30</sup>, PM7<sup>31</sup>, with an emphasis on solid state calculations, and RM1<sup>32</sup>.

## The RM1 Model for the Lanthanides

Most lanthanide complexes display lanthanide ions directly coordinated to oxygen or nitrogen atoms of the ligands, ideal situations that are effectively modeled by the Sparkle Model. Nevertheless, a lesser but still significant number of complexes possess ligands with atoms such as C, S, Cl, and Br directly coordinated to the lanthanide trication. For these cases, the sparkle model is no longer enough - the description of such bonds requires the presence of semiempirical atomic orbitals at the lanthanide trication center. Consequently, we recently introduced a new approach we called the RM1 model for the lanthanides<sup>15, 16</sup>, which regards the lanthanide in the semiempirical calculation as an atom with a core depicting  $[\text{Xe}4f^n]$ , where  $n = 3, 4, \text{ and } 5$ , for Nd(III), Pm(II), and Sm(III), respectively; while assigning to its semiempirical valence shell, three electrons and the following set of semiempirical atomic orbitals: 5d 6s 6p. Although the lanthanide initially enters the calculation as a neutral species, this parameterization is expected to work only for trications. Indeed, dications would require a different core,  $[\text{Xe}4f^{n+1}]$ , and two electrons in the valence shell, although the same set of nine atomic orbitals, 5d 6s 6p, could also be used. Hence, in the present article we will concern ourselves with RM1 model for the lanthanide parameters for the trications of Nd, Pm, and Sm only.

## Parameterization

The first step in a parameterization procedure is to collect all high quality crystallographic structures (R-factor < 5%) of complexes of neodymium and samarium from the Chemical Structural Database, CSD<sup>33-35</sup>. For neodymium we found 88 structures and, for samarium, 76. Of course, unlike in the parameterizations of the previous Sparkle Models, we did not restrict ourselves to only ligands with oxygen and/or nitrogen directly coordinating atoms. This time, we accepted all currently existing complexes in CSD regardless of the type of ligands. For promethium, due to the paucity of experimental data, we proceeded as before<sup>26, 29-32</sup> and generated from ab initio MSW relativistic pseudopotentials a data set of 20 promethium complexes.

It would be unfeasible to parameterize the new model for all CSD available complexes for each lanthanide. In addition, in the universe of complexes there are many repetitive types of bonds, which could be overrepresented in the parameterization set, if all were taken into account, deforming the model. Hence, a need for smaller samplings of the universe of complexes that can balance the diversity of bonds while guaranteeing representativity of the smaller samplings vis-à-vis the universe. For that purpose, as before<sup>31, 32</sup>, we used the hierarchical clustering divisive analysis DIANA<sup>36</sup> to cluster the complexes according to the following metric:

$$R_i = \sum_j \sum_k \frac{1}{\sigma_j^{dist}} \left| d_{i,j,k}^{CSD} - d_{i,j,k}^{Calc} \right| + \sum_l \frac{1}{\sigma_l^{angle}} \left| \theta_{i,l}^{CSD} - \theta_{i,l}^{Calc} \right| \quad (1)$$

where  $R_i$  is a value associated to each complex  $i$ ;  $j$  runs over all types of bonds, e.g. Ln-N, Ln-O, Ln-C, Ln-S, Ln-P, etc;  $k$ , runs over all bonds of type  $j$ ;  $\sigma_j^{dist}$  is the standard deviation of all crystallographic bond lengths of type  $j$  for all complexes of the universe;  $d_{i,j,k}^{CSD}$  is the crystallographic  $k^{\text{th}}$  bond distance of type  $j$  for complex  $i$ ;  $d_{i,j,k}^{Calc}$  is the Sparkle/AM1<sup>26, 27</sup> calculated value of the same bond;  $\sigma_l^{angle}$  is the standard deviation of all crystallographic bond angles of the type A-Ln-B, with A,B = O, N, C, S, Cl, and Br;  $\theta_{i,l}^{CSD}$  is the crystallographic  $l^{\text{th}}$  bond angle of complex  $i$ ; and  $\theta_{i,l}^{Calc}$  is its Sparkle/AM1<sup>26, 27</sup> calculated counterpart. We only used experimental data to calculate the standard deviations used to make sure that the summations in Eq. (1) add comparable terms. From this analysis, we defined two parameterization sets for each of the lanthanides: one we called the small set, and the other we called the big set. Using a combination of Simplex and GSA algorithms, we minimized the sum of  $R_i$  for all complexes of the small set. However, this time, calc in Eq. 1 refers to calculations using the intermediary parameters of the parameterization procedure. After the parameterization procedure converged to the small set, we then amplified it to the large set and ran the procedure again. When this second parameterization converged, we declared the procedure terminated and collected the converged set of parameters, which we present in Table 1.

## Validation of the Parameters

In order for the parameters to be useful, they must lead to accurate geometries for new complexes of Nd, Pm, and Sm. And that can only be counted upon to the extent that the new structures do not deviate substantially from those present in the universe set from which the parameterization sets were taken as representative. That is the reason why we assembled the universe set from all structures of high crystallographic quality (R-factor < 5%) we could find in the CSD<sup>33-35</sup>. Not only that, for a parameterized model to have stable predictive value, the deviations of the predicted distances from their crystallographic counterparts, calculated for the universe set of complexes per lanthanide ion, should be random around a mean, implying that the associated mean error can serve as an accuracy measure of the model. As accuracy functions, we used unsigned mean errors for each complex  $i$ ,  $\text{UME}_i$ s, defined as:

$$UME_i = \frac{1}{n} \sum_{j=1}^n |R_{i,j}^{CSD} - R_{i,j}^{RM1}| \quad (2)$$

where  $n$  is the number of distances,  $R_{i,j}^{CSD}$  is the CSD value for distance  $j$  of complex  $i$ ; and  $R_{i,j}^{RM1}$  is the RM1 model for lanthanides value for the same distance.

**Table 1.** Parameters for the RM1 model for the trications of Nd, Pm and Sm.

RM1		Nd <sup>3+</sup>		Sm <sup>3+</sup>
Parameters*	Unit		Pm <sup>3+</sup>	
$U_{ss}$	eV	-14.63358576	-15.49364118	-16.50932392
$U_{pp}$	eV	-7.04786329	-7.10121188	-7.01802973
$U_{dd}$	eV	-19.64139071	-19.42342210	-18.87325201
$\zeta_s$	bohr <sup>-1</sup>	1.45828951	1.06553607	1.29391374
$\zeta_p$	bohr <sup>-1</sup>	1.57051639	1.84692454	1.73865631
$\zeta_d$	bohr <sup>-1</sup>	1.51356096	1.42404921	1.52137784
$\beta_s$	eV	-7.92937324	-7.98225667	-8.07790225
$\beta_p$	eV	0.96436908	0.97790850	0.93933043
$\beta_d$	eV	-3.81235096	-3.92556510	-4.01938912
$F_{sd}^0$	eV	7.67339141	7.98507005	7.99982834
$G_{sd}^2$	eV	4.13487169	4.12901400	4.16372927
$\rho_{core}$	bohr	1.71382705	1.75646078	1.73942317
$\square$	Å <sup>-1</sup>	1.28977046	1.39327199	1.30770515
$\zeta_s'$	bohr <sup>-1</sup>	0.80945985	0.74640624	0.66348032
$\zeta_p'$	bohr <sup>-1</sup>	1.44135558	1.46778967	1.49230342
$\zeta_d'$	bohr <sup>-1</sup>	0.99725490	0.76914732	0.85315362
$a_{11}$	none	0.39689242	0.34756381	0.25388371
$b_{21}$	Å <sup>-2</sup>	7.70668519	7.68360060	7.71382635
$c_{31}$	Å	1.58918037	1.64949482	1.73109300
$a_{12}$	none	0.02699990	0.06530230	0.03775390
$b_{22}$	Å <sup>-2</sup>	10.32264526	9.91730194	10.01336548
$c_{32}$	Å	3.23690696	3.11782729	3.21008569

\*Parameters are  $s$ ,  $p$ , and  $d$  atomic orbital one-electron one-center integrals  $U_{ss}$ ,  $U_{pp}$  and  $U_{dd}$ ; the  $s$ ,  $p$ , and  $d$  Slater atomic orbital exponents  $\zeta_s$ ,  $\zeta_p$ , and  $\zeta_d$ ; the  $s$ ,  $p$ , and  $d$  atomic orbital one-electron two-center resonance integral terms  $\beta_s$ ,  $\beta_p$ , and  $\beta_d$ ; the core-core repulsion term  $\alpha$ ; the two-electron integrals  $F_{sd}^0$ ,  $G_{sd}^2$ ; and the additive term  $\rho_{core}$  needed to evaluate core-electron and core-core nuclear interactions; the second set of exponents to compute the one-center integrals  $\zeta_s'$ ,  $\zeta_p'$ , and  $\zeta_d'$ ; and the six parameters for the two Gaussian functions.

As before<sup>37</sup>, two types of functions were considered. The first one is  $UME_{(Ln-L)_i}$  which sums all distances from the lanthanide ion to the directly coordinating atoms of the ligands. The second is the one we simply call  $UME_i$  where, to the distances already considered in  $UME_{(Ln-L)_i}$ , we further add all distances between any two of the atoms belonging to the coordination polyhedron of the complex. Tables S1-S3 of the supplementary information display  $R_i$  values for all complexes, where we indicate, with different colors in the CSD codes, which ones of the complexes were chosen to participate in the small and large parameterization sets.

The statistical validation step seeks to ensure that the deviations of the UMEs behave randomly around a mean. In addition,

since UMEs can only have positive values, they should follow a gamma distribution function parameterized to reproduce exactly the mean and variance of the UME for each of two sets of UMEs, for each one of the three lanthanide ions being considered. If the gamma distribution thus obtained adjusts the data within a 95% confidence interval, then the mean and variance are statistically justified to be used as accuracy measures of the model. And this can be verified from the  $p$ -value of the one-sample nonparametric Kolmogorov-Smirnoff test, which must be above 0.05<sup>38</sup>. Figures 1 and 2 show these values for both  $UME_{(Nd-L)}$  and  $UME$  for all Neodymium ion complexes considered. The equivalent figures (Figs S1 to S4) for Samarium and Prometium are presented in Supplementary Information.

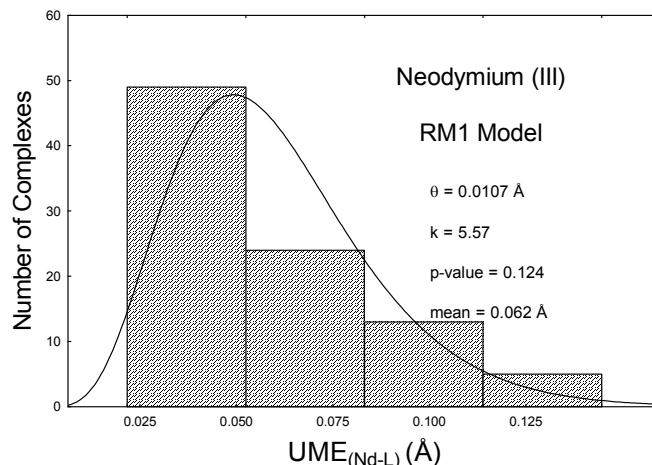


Figure 1: Histogram of the  $UME_{(Ln-L)}$ s for all 88 complexes of Nd(III) optimized via the RM1 model being advanced in this article. The shape  $k$  and scale  $\theta$  are parameters of the fitted gamma distribution, and the mean is equal to  $k\theta$ . The  $p$ -value of the one-sample nonparametric Kolmogorov-Smirnoff is also shown. This value is above 0.05, and therefore the data can be considered adjusted to the fitted gamma distribution within a 95% confidence interval.

Clearly, the histograms follow the underlying distributions and the  $p$ -values are all satisfactory, indicating that the corresponding means and variances can be indeed taken as accuracy measures of the models. The robustness of this parameterization approach of ours has already been verified for our previous Sparkle Models, when a German research group independently checked their accuracies by optimizing the geometries of 650 different lanthanide complexes and concluded that Sparkle/AMI is “surprisingly accurate” for the estimation of average bond lengths of the type Ln-OH<sub>2</sub>. Moreover, they verified to their satisfaction that the geometrical deviations found “can be described by normal distributions”<sup>39</sup>.

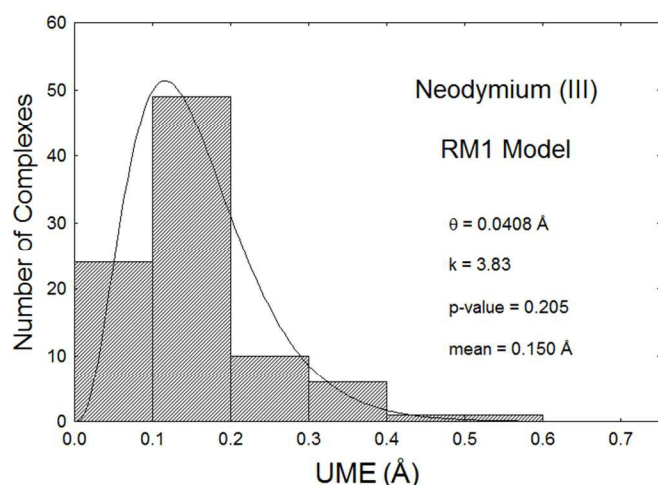


Figure 2: Histogram of the UMEs for all 88 complexes of Nd(III) optimized via the RM1 model being advanced in this article. The shape  $k$  and scale  $\theta$  are parameters of the fitted gamma distribution, and the mean is equal to  $k\theta$ . The  $p$ -value of the one-sample nonparametric Kolmogorov-Smirnov is also shown. This value is above 0.05, and therefore the data can be considered adjusted to the fitted gamma distribution within a 95% confidence interval.

## Discussion

The main motivation of the RM1 Model for the Lanthanides was to extend the accuracy of the semiempirical modeling of complexes for coordination bonds other than those by oxygen or nitrogen, that are already so well described by the previous Sparkle Models.

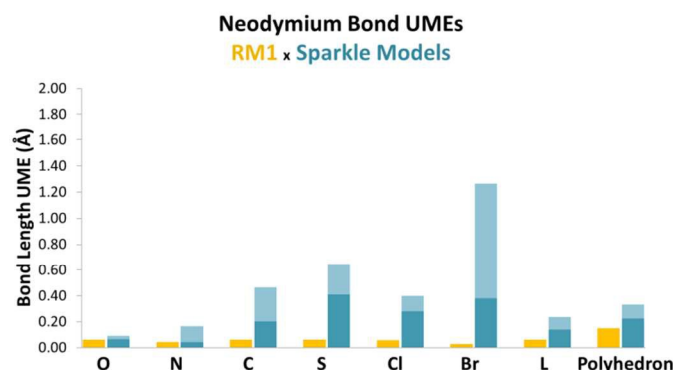


Figure 3. Comparison between the accuracy measures, UMEs, of the RM1 model for Nd(III), being advanced in this article (amber bars) and of the various Sparkle models (two-lightness bars) for the various types of directly coordinated bonds, indicated in the horizontal axis by the atom directly coordinated to the metal ion: either O, N, C, S, Cl, or Br. L refers to the sum of the UMEs of all these atoms, plus UMEs for Nd-Nd bonds. And Polyhedron refers to the sum of all UMEs in L plus the sum of all UMEs between any two atoms of the coordination polyhedron. The top of the top light blue bar indicates the UME of the least accurate of the Sparkle models, and the bottom of the top light blue bar (corresponding to the top of the dark blue bar) indicates the UME of the least accurate of the Sparkle models. Raw data used to draw this figure can be found in the supplementary information

Accordingly, Figures 3, 4 and 5 show UMEs for all different types of distances for the complexes of Nd(III), Pm(III), and Sm(III) respectively, which are indicated by the symbol of the atom being directly coordinated to the lanthanide ion.  $UME_{(Ln-L)_S}$  are also shown in Figures 3, 4 and 5 as the last set of two bars, above the word “polyhedron”. The amber bars represent the unsigned mean errors in the RM1 model for the lanthanides, which is being advanced in this article. On the other hand, the two-lightness or two-toned bars represent the unsigned mean error ranges in the previous Sparkle models - the top of the bar indicating the UME or  $UME_{(Ln-L)}$  error for the least accurate Sparkle model, whereas the bottom of the light colored top bar indicates the UME or  $UME_{(Ln-L)}$  error for the most accurate Sparkle model.

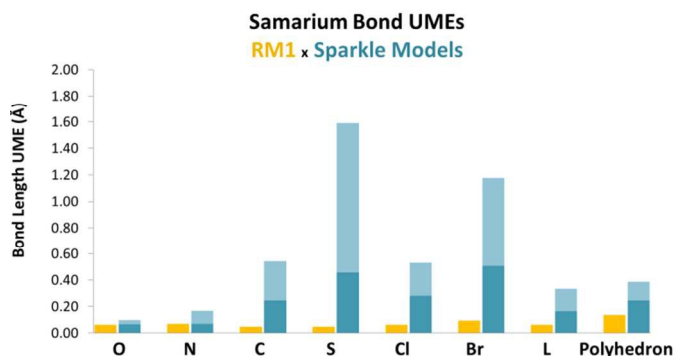


Figure 4. Comparison between the accuracy measures, UMEs, of the RM1 model for Sm(III), being advanced in this article (amber bars) and of the various Sparkle models (two-lightness bars) for the various types of directly coordinated bonds, indicated in the horizontal axis by the atom directly coordinated to the metal ion: either O, N, C, S, Cl, or Br. L refers to the sum of the UMEs of all these atoms, plus UMEs for Sm-Sm bonds. Polyhedron refers to the sum of all UMEs in L plus the sum of all UMEs between any two atoms of the coordination polyhedron. The top of the top light blue bar indicates the UME of the least accurate of the Sparkle models, and the bottom of the top light blue bar (corresponding to the top of the dark blue bar) indicates the UME of the least accurate of the Sparkle models. Raw data used to draw this figure can be found in the supplementary information

For example, let us consider the case of Nd(III)-S coordination bonds. The UME for the present RM1 model is  $0.0630\text{Å}$  and is represented by the top of the amber bar. The least accurate Sparkle model in this case is Sparkle/PM7 with a value of  $0.6476\text{Å}$ , and the most accurate Sparkle model is Sparkle/RM1 with a value of  $0.4103$ . All other Sparkle model UMEs lie in between these extreme values, as  $0.4280\text{Å}$  for Sparkle/AM1,  $0.4265\text{Å}$  for Sparkle/PM3, and  $0.5552$  for Sparkle/PM3. Raw data used to build Figures 3, 4 and 5 can be found in Tables S4, S5 and S6 of the Supplementary Information.

Clearly, from Fig. 3, the UMEs for Ln-Ln, Ln-O and Ln-N bonds are stable throughout the models, and are reproduced well by the RM1 model for the lanthanides. The UMEs for Nd-O bonds, for example, are about  $0.08\text{Å}$  for the Sparkle Models and  $0.06\text{Å}$  for RM1 for Nd(III). The corresponding numbers for Pm(III) are about  $0.06\text{Å}$  and  $0.05\text{Å}$  (see Fig.4); and, for Sm(III),  $0.08\text{Å}$  and  $0.06\text{Å}$  (see Fig.5). Numbers for Ln-N distances follow the same pattern.

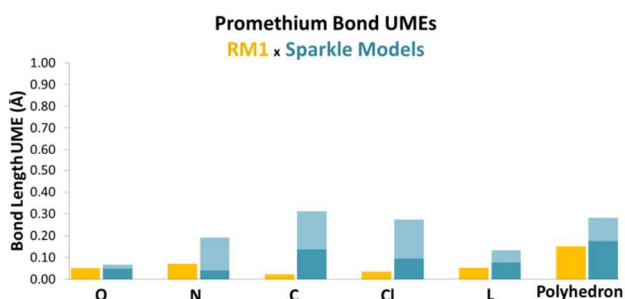


Figure 5. Comparison between the accuracy measures, UMEs, of the RM1 model for Pm(III), being advanced in this article (amber bars) and of the various sparkle models (two-lightness bars) for the various types of directly coordinated bonds, indicated in the horizontal axis by the atom directly coordinated to the metal ion: either O, N, C, or Cl. L refers to the sum of the UMEs of all these atoms, plus UMEs for Pm-Pm bonds. Polyhedron refers to the sum of all UMEs in L plus the sum of all UMEs between any two atoms of the coordination polyhedron. The top of the top light blue bar indicates the UME of the least accurate of the sparkle models, and the bottom of the top light blue bar (corresponding to the top of the dark blue bar) indicates the UME of the least accurate of the sparkle models. Raw data used to draw this figure can be found in the supplementary information

The accuracy novelty of the RM1 Model for the Lanthanides being introduced here for Nd(III), Pm(III), and Sm(III) complexes lies in the description of the other types of bonds. Indeed, take, for example, the next most important type of coordination bonds: Ln-C bonds, which comprise ~30% of both Nd-L and Sm-L bonds. While the average UME for the Sparkle Models is 0.27Å for Nd(III), 0.24Å for Pm(III), and 0.36Å for Sm(III), the corresponding numbers of the RM1 Model for the Lanthanides drop dramatically to 0.06Å for Nd(III), to 0.02Å for Pm(III), and to 0.05Å to Sm(III). This trend occurs for all other types of bonds other than Ln-O and Ln-N ones.

## Conclusions

For complexes with only directly coordinating oxygen or nitrogen atoms, either RM1 or any of the other sparkle models may be used as they yield comparable accuracies. The decision of which of the sparkle models will be the one of choice, thus rests on the specific manner by which each of the underlying semiempirical models, AM1, PM3, PM6, PM7, or RM1, describes the organic part of the complex.

However, the present RM1 model for Nd(III), Pm(III), and Sm(III) is the most accurate of all and can be used for any complex of these trivalent lanthanide ions.

More importantly, if the Nd(III), Pm(III), or Sm(III) complex of interest contains directly coordinating atoms which are neither oxygen nor nitrogen, then usage of the RM1 model for Nd(III), Pm(III), and Sm(III) complexes, being advanced in this article, is mandatory.

## Acknowledgements

We appreciate the financial support from the following Brazilian agencies and institutions: FAPITEC/SE, FACEPE(PRONEX), CNPq, CAPES and INCT-INAMI.

## Notes and references

<sup>a</sup> Pople Computational Chemistry Laboratory, Departamento de Química, Universidade Federal de Sergipe, 49.100-000 – São Cristóvão, SE, Brazil.

<sup>b</sup> Departamento de Química, CCEN, Universidade Federal da Paraíba, 58.059-970 – João Pessoa, PB, Brazil.

<sup>c</sup> Departamento de Química Fundamental, Universidade Federal de Pernambuco, 50.740-540, Recife, PE, Brazil.

Electronic Supplementary Information (ESI) available: Instructions on how to run the Nd(III), Pm(III), and Sm(III) RM1 model for the Lanthanides in Mopac2012; additional tables and figures; Mopac sample input (.mop) and optimized geometry summary output (.arc) files.

1. J. M. Lehn, *Angew. Chem.-Int. Edit. Engl.*, 1990, **29**, 1304.
2. T. G. Cherkasova, V. S. Cherkasov and E. S. Tatarinova, *Zh Neorg Khim+*, 1994, **39**, 1483.
3. A. de Bettencourt-Dias, *Dalton T*, 2007, 2229.
4. J.-C. G. Bunzli and S. V. Eliseeva, *Chemical Science*, 2013, **4**, 1939.
5. W. Z. Li, J. Y. Li, H. F. Li, P. F. Yan, G. F. Hou and G. M. Li, *J Lumin*, 2014, **146**, 205.
6. I. G. Finlay, M. D. Mason and M. Shelley, *The Lancet Oncology*, 2005, **6**, 392.
7. G. Erker and R. Aul, *Chem Ber*, 1991, **124**, 1301.
8. D. Y. Chen, J. H. Zou, W. X. Li, B. Xu, Q. Y. Li, G. W. Yang, J. Wang, Y. M. Ding, Y. Zhang and X. F. Shen, *Inorg Chem Commun*, 2014, **40**, 35.
9. Y. R. Ni, J. Tao, J. Y. Jin, C. H. Lu, Z. Z. Xu, F. Xu, J. M. Chen and Z. T. Kang, *J Alloy Compd*, 2014, **612**, 349.
10. W. Li, C. Smith, C. Cutler, A. Ketrings and S. Jurisson, *Journal of Nuclear Medicine*, 2000.
11. T. Ishimori, *Bulletin of the Chemical Society of Japan*, 1955, **28**, 203.
12. K. Chmutov, P. Nazarov, G. Masslova and V. Sheptunov, *Journal of Chromatography A*, 1971, **59**, 415.
13. J. Rydberg and Y. Albinsson, *Solvent Extraction and Ion Exchange*, 1989, **7**, 577.
14. G. B. Rocha, R. O. Freire, A. M. Simas and J. J. P. Stewart, *J Comput Chem*, 2006, **27**, 1101.
15. M. A. Filho, J. D. L. Dutra, H. L. Cavalcanti, G. B. Rocha, A. M. Simas and R. O. Freire, *J Chem Theory Comput*, 2014, **10**, 3031.
16. M. A. M. Filho, J. D. L. Dutra, G. B. Rocha, A. M. Simas and R. O. Freire, *PLoS ONE*, 2014, **9**, e86376.
17. A. V. M. de Andrade, N. B. da Costa, A. M. Simas and G. F. de Sa, *Chem Phys Lett*, 1994, **227**, 349.
18. A. V. M. de Andrade, N. B. da Costa, A. M. Simas and G. F. de Sa, *J Alloy Compd*, 1995, **225**, 55.
19. W. M. Faustino, G. B. Rocha, F. R. G. E. Silva, O. L. Malta, G. F. de Sa and A. M. Simas, *J Mol Struct-Theochem*, 2000, **527**, 245.
20. N. B. da Costa, R. O. Freire, M. A. C. dos Santos and M. E. Mesquita, *J Mol Struct-Theochem*, 2001, **545**, 131.
21. R. O. Freire, R. Q. Albuquerque, S. A. Junior, G. B. Rocha and M. E. de Mesquita, *Chem Phys Lett*, 2005, **405**, 123.
22. R. O. Freire, F. R. G. E. Silva, M. O. Rodrigues, M. E. de Mesquita and N. B. D. Junior, *J Mol Model*, 2005, **12**, 16.
23. S. Biju, M. L. P. Reddy and R. O. Freire, *Inorg Chem Commun*, 2007, **10**, 393.
24. J. D. L. Dutra, T. D. Bispo and R. O. Freire, *J Comput Chem*, 2014, **35**, 772.
25. G. B. Rocha, R. O. Freire, N. B. da Costa, G. F. de Sá and A. M. Simas, *Inorg Chem*, 2004, **43**, 2346.
26. R. O. Freire, N. B. da Costa, G. B. Rocha and A. M. Simas, *J Chem Theory Comput*, 2006, **2**, 64.
27. C. C. Bastos, R. O. Freire, G. B. Rocha and A. M. Simas, *J Photoch Photobio A*, 2006, **177**, 225.
28. R. O. Freire, G. B. Rocha and A. M. Simas, *J Brazil Chem Soc*, 2009, **20**, 1638.
29. R. O. Freire, N. B. da Costa, G. B. Rocha and A. M. Simas, *J Chem Theory Comput*, 2007, **3**, 1588.

30. R. O. Freire and A. M. Simas, *J Chem Theory Comput*, 2010, **6**, 2019.
31. J. D. L. Dutra, M. A. M. Filho, G. B. Rocha, R. O. Freire, A. M. Simas and J. J. P. Stewart, *J Chem Theory Comput*, 2013, **9**, 3333.
32. M. A. M. Filho, J. D. L. Dutra, G. B. Rocha, R. O. Freire and A. M. Simas, *Rsc Adv*, 2013, **3**, 16747.
33. F. H. Allen, *Acta Crystallogr B*, 2002, **58**, 380.
34. F. H. Allen and W. D. S. Motherwell, *Acta Crystallogr B*, 2002, **58**, 407.
35. I. J. Bruno, J. C. Cole, P. R. Edgington, M. Kessler, C. F. Macrae, P. McCabe, J. Pearson and R. Taylor, *Acta Crystallogr B*, 2002, **58**, 389.
36. L. Kaufman and P. J. Rousseeuw, *Finding groups in data: an introduction to cluster analysis*, John Wiley & Sons, 2009.
37. R. O. Freire, G. B. Rocha and A. M. Simas, *Inorg Chem*, 2005, **44**, 3299.
38. R. O. Freire, G. B. Rocha and A. M. Simas, *Chem Phys Lett*, 2006, **425**, 138.
39. M. Seitz and N. Alzakhem, *J Chem Inf Model*, 2010, **50**, 217.