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Modeling lanthanide coordination compounds: Sparkle/AM1 parameters for praseodymium (III)

Ricardo O. Freire [a], Nivan B. da Costa Jr. [b], Gerd B. Rocha [a], Alfredo M. Simas [a,*]

[a] *Departamento de Química Fundamental, CCEN, Universidade Federal de Pernambuco, UFPE, Av. Prof. Luiz Freire sn, 50590-470 Recife, PE, Brazil*
[b] *Departamento de Química, CCET, UFS, 49100-000 Aracaju, SE, Brazil*

Abstract

The Sparkle/AM1 model, recently defined for Eu(III), Gd(III) and Tb(III) [R.O. Freire, G.B. Rocha, A.M., Simas, Inorg. Chem. 44 (2005) 3299] is now extended to Pr(III), using the same parameterization scheme. Thus, a set of 15 complexes, with various representative ligands of high crystallographic quality (R-factor < 0.05 Å) and which possess oxygen and/or nitrogen as coordinating atoms, was used as the training set. In the validation procedure we used a set of 33 more structures, also of high crystallographic quality. For the 48 complexes, the Sparkle/AM1 unsigned mean error, for all interatomic distances between the Pr(III) ion and the ligand atoms of the first sphere of coordination, is 0.08 Å, again comparable to present day ab initio/ECP calculations, while being hundreds of times faster.
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The two electrons in the 4f subshell of the trivalent praseodymium ion, cause a series of multiplets leading to luminescence in an organic medium in the ultraviolet, visible and infrared regions. However, when compared to luminescence research on Eu(III) and Tb(III), relatively less work has been committed to Pr(III). Nonetheless, quantum efficiencies above 100% have been reported for Pr(III) when excited by 185 nm light [1], opening perspectives of significant improvements of the quantum efficiencies of electroluminescent devices by using Pr(III) as an emitter [2]. Ligands of interest to lanthanide ion luminescence research, almost entirely coordinate through oxygen or nitrogen, and nitrogen-based ligands have been increasingly used, to the point that 65% of all Pr(III) complexes whose structures have been deposited in the Cambridge Structural Database belong to this category. Other subjects of interest involving Pr(III) are chemiluminescence [3] and intensities in absorption spectra, since these are quite sensitive to the structural features of its environment, more especially so when the ion is coordinated [4].

On the other hand, self-assembling molecular architectures with incorporated lanthanide ions may find potential applications due to their magnetic and luminescent properties. For example, fabrication of multidimensional coordination polymers by the self-assembly process may be important for the design of lanthanide-based devices such as light converters [5]. Indeed, many topological structures can be, at least in principle, visualized by assembling lanthanide ions and multifunctional ligands. However, design of such coordination compounds poses a challenge because, due to

* Corresponding author. Tel.: +55 81 2126 8447; fax: +55 81 2126 8442.
E-mail address: simas@ufpe.br (A.M. Simas).

their intrinsic characteristics, lanthanide ions possess a lack of stereochemical preference, a handful of high coordination numbers and small energy variations among their various coordination geometries.

Recently, there has been some research effort towards constructing Pr(III) complexes with biologically active ligands such as thiosemicarbazones [6], picrates [7], and tetracyclins [8]. Difficulties are enormous in the case of the Pr(III) tetracycline complex: there is disagreement about the metal–ligand sites in complexes of this ligand [8] and no single crystals of this compound could be prepared for X-ray diffraction, and even powder X-ray diffraction patterns failed to yield acceptable unit cell parameters and structures. Moreover, it had been shown that tautomerism is crucial for the understanding of the chemical behavior of tetracycline, 64 being the total number of tautomers that must be considered [9]. Hence, a general molecular modeling technique that can rapidly and accurately predict the geometries of Ln(III) coordination compounds, coupled with a molecular orbital description of the ligands in the complex, is urgently needed. Even more so because lanthanide ions, in view of their electronic configuration and size are also often used as surrogates for calcium(II) ions to function as spectroscopic probes in studies of biological systems and as diagnostic agents in clinical medicine [10]. In that direction, Stewart [11] has developed the MOZYME algorithm, which has permitted semiempirical calculations on systems as large as 20,000 atoms. Recently, Anikin et al. [12], developed a truly linear scaling technique for semiempirical methods, called LocalSCF [12], which now allows AM1 calculations on systems as large as 120 000 atoms on a personal computer.

The semiempirical description of lanthanide ions was made possible with our original Sparkle model [13,14], which was recently improved and called Sparkle/AM1 [15], and that can be programmed to be used with MOPAC or MOZYME. The Sparkle/AM1 model replaces the trivalent lanthanide ion by a Coulombic charge of $+3e$ superimposed on a repulsive exponential potential of the form $\exp(-\alpha r)$, which accounts for the size of the ion, and uses Gaussian functions in the core–core repulsion energy term. That is, Sparkle/AM1 assumes that the lanthanide tricarions behave like simple ions, without any angular steric properties – the angular effects of the f orbitals are assumed to be negligible. Until now, Sparkle/AM1 had been only parameterized for Eu(III), Gd(III) and Tb(III) [15]. In the present communication, we extend Sparkle/AM1 to Pr(III).

The parameterization procedure used for Pr(III) was essentially the same as the one described in our previous work on Eu(III), Gd(III) and Tb(III) [15], and will not be repeated here. Accordingly, we only used high quality crystallographic structures (*R*-factor < 5%) taken from the "Cambridge Structural Database 2003" (CSD) [16–18]. Fifteen different representative structures of

Pr(III) complexes with nitrogen or oxygen as coordinating atoms, important for luminescence research, were chosen as the training set, with β-diketone, nitrate, monodentate, bidentate, tridentate, polydentate ligands, as well as dipraseodymium complexes. Such complexes constitute approximately 65% of all Pr(III) present in the CSD. To find the parameters, we carried out a non-linear minimization of an eight-dimension response function, using a combination of Newton–Raphson and Simplex methods, aimed at finding one of its local minima, which ideally should be the global minimum and make sense chemically. The Sparkle/AM1 parameters obtained for Pr(III) are shown in Table 1. Implementation of Pr(III) Sparkle/AM1 model in MOPAC93r2 is easy: general instructions can be found in Supplementary materials.

In the validation procedure, we used a set of 33 more complexes, also of high crystallographic quality, for a total of 48 coordination compounds considered (Table 2). Interestingly, in CSD, there are more high quality Pr(III) crystallographic structures with nitrate type ligands than any other category.

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

Table 1
Parameters for the Sparkle/AM1 model for the Pr(III) ion

	Sparkle/AM1–Pr(III)
GSS	58.9017644267
ALP	2.6104229985
a_1	1.7515391427
b_1	7.6039742620
c_1	1.8084677103
a_2	0.0097057032
b_2	8.7264195205
c_2	2.9111890014
EHEAT[a] (kcal mol^{-1})	952.9
AMS (amu)	140.9077

[a] The heat of formation of the Pr(III) ion in Sparkle/AM1 was obtained by adding to the heat of atomization of praseodymium, its first three ionization potentials [21].

Table 2
Number of praseodymium (III) complexes in the validation set, classified into each ligand group

Ligand group number	Ligand type	Number of structures
1	β-Diketone	7
2	Nitrate	17
3	Monodentate	8
4	Bidentate	1
5	Tridentate	3
6	Polydentate	4
7	Dipraseodymium	8

$$\mathrm{UME}_i = \frac{1}{n_i} \sum_{j=1}^{n} |R_{i,j}^{\mathrm{CSD}} - R_{i,j}^{\mathrm{calc}}|, \qquad (1)$$

where n_i is the number of ligand atoms directly coordinating the lanthanide ion. As total UME, we preferred not to use the average of the individual complexes UMEs because different complexes may have different

coordination numbers. As such, as total UME, we preferred to use the average of the errors of all considered distances of all complexes. Two cases have been examined: (i) UMEs involving the interatomic distances R_j between the praseodymium central ion and the atoms of the coordination polyhedron, as well as the interatomic distances R_j between all atoms of the coordination polyhedron and (ii) $\mathrm{UME}_{\mathrm{(Pr–L)}}$s involving only the interatomic distances R_j between the praseodymium central ion and the atoms of the coordination polyhedron.

Fig. 1(a) and (b) shows a graphical representation of the UME and of the $\mathrm{UME}_{\mathrm{(Pr–L)}}$s for the 48 complexes of the validation set. The most evident conclusion upon inspection of both drawings is that the interatomic distances between the praseodymium ion and the directly coordinated atoms are more accurately described than the whole coordination polyhedron. These distances are the most important variable for the calculation of the luminescence quantum yield through the ligand field parameters, B_q^k, via the simple overlap model [19,20]. Indeed, the ability to predict geometries of Pr(III) complexes is therefore central to the process of luminescent complex design. On the other hand, the ability to correctly describe the coordination polyhedron is useful for other supramolecular applications. And the errors in the coordination polyhedron, displayed in Fig. 1(a), are of the same size as the errors obtained from present day ab initio effective core potential calculations as discussed before [15]. In Table 3, we present Sparkle/AM1 unsigned mean errors for specific types of bond distances, not only for Pr(III) but also for the previously published Eu(III), Gd(III) and Tb(III) ions just to reinforce the fact that the Pr(III) parameters are at the same level of quality of the previous Eu(III), Gd(III) and Tb(III) Sparkle/AM1 parameters.

Therefore, Sparkle/AM1 calculations, which are hundreds of times faster than ab initio/ECP calculations, are not only able to produce research grade geometries, but also may be a choice in combinatorial searches of optimum molecular architectures for particular applications, where hundreds of structures must have their geometries optimized.
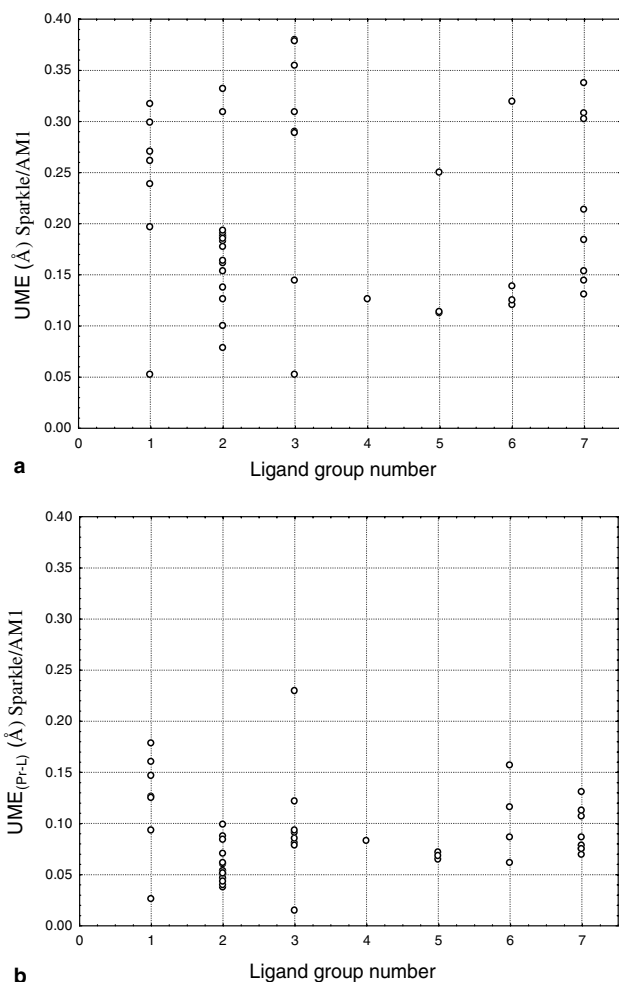

Fig. 1. Unsigned mean errors for each of the 48 praseodymium (III) complexes, assembled according to the ligand group numbers defined in Table 2; (a) presents the UMEs and (b) presents the $\mathrm{UME}_{\mathrm{(Pr-L)}}$s. The same scale has been used in both to facilitate comparison.

Table 3
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) [15] complexes; 70 Gd(III) [15] complexes; 42 Tb(III) [15] complexes, and all 48 Pr(III) complexes considered

Model	Unsigned mean errors for specific types of distances (Å)					
	Ln–Ln	Ln–O	Ln–N	L–L′	Ln–L and Ln–Ln	Ln–L, Ln–Ln and L–L′
Sparkle/AM1–Eu [15]	0.1624	0.0848	0.0880	0.2170	0.0900	0.1900
Sparkle/AM1–Gd [15]	0.1830	0.0600	0.0735	0.2082	0.0658	0.1781
Sparkle/AM1–Tb [15]	0.2251	0.0754	0.0440	0.2123	0.0746	0.1823
Sparkle/AM1–Pr	0.2002	0.0813	0.0695	0.2332	0.0808	0.2032

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Appendix A. Supplementary materials

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.06.001.

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