

Note

AM1 Sparkle modeling of Er(III) and Ce(III) coordination compounds

Ricardo O. Freire ^a, Elizete V. do Monte ^b, Gerd B. Rocha ^a, Alfredo M. Simas ^{a,*}

^a Departamento de Química Fundamental, Universidade Federal de Pernambuco, Rua Prof. Luiz Freire s/n, CCEN, UFPE, 50590-470-Recife, PE, Brazil

^b Departamento de Química, Universidade Federal da Paraíba, CCEN, 58.059-970-João Pessoa, PB, Brazil

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Abstract

The recently defined Sparkle/AM1 model is now extended to Er(III) and Ce(III), using the same parameterization scheme. Thus, a set of fifteen complexes for each lanthanide ion, 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 twenty-two more complex structures for the Ce(III) ion and twenty-four more for the Er(III) ion, all of high crystallographic quality. For the thirty-seven cerium(III) complexes and thirty-nine erbium(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 0.08 and 0.06 Å, a level of accuracy comparable to present day ab initio/ECP geometries, while being hundreds of times faster. The Sparkle/AM1 model may thus prove useful for luminescent complex design.

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1. Introduction

Trivalent erbium displays an eye safe intra-4f¹¹ ⁴I_{13/2} → ⁴I_{15/2} rather sharp transition at 1.54 μm in the near infrared, which lies at the lowest attenuation and low dispersion window of standard silica based optical fibers. And it is due to the general availability of Er(III)-doped amplifiers, that optical telecommunications networks have developed as much [1]. On the other hand, motivation for research on Ce(III) has been mainly focused on developing materials for phosphor and scintillator applications [2].

As it happens with all trivalent lanthanide ions, the closed 5s²5p⁶ outer shell effectively screens the unfilled 4f orbitals. That is why the wavelength of the intra 4f sub-shell emission depends little on the actual host and is prac-

tically temperature independent, a technologically valuable property. However, the forbidden character of the transition within the 4f sub-shell makes direct excitation of the lanthanide ion difficult and requires that the excited state population of the emitting lanthanide ion be generated by energy transfer from the triplet state of the ligands, which function as an antenna. The complex thus formed then may act as an infrared photoactive center when incorporated into a suitable host matrix. Indeed, the first report of infrared electroluminescence at 1.54 μm was made for vacuum deposited films of an organic erbium complex: erbium (III) tris(8-hydroxyquinoline) [3].

Design of Er(III) complexes capable of exhibiting high luminescence quantum yields in the near infrared region is therefore of interest due to their possible technological applications in polymer based optical signal amplifiers for easy integration with existing components [4–8]. Such design is not simple because the designed complex should also be compatible with polymeric matrices [9].

To predict the luminescence quantum yield of a lanthanide complex, one usually starts by characterizing the

* Corresponding author. Tel.: +55 81 2126 8440; fax: +55 81 2126 8442/8440.

E-mail address: simas@ufpe.br (A.M. Simas).

interaction between the ligands and the central ion through the ligand field parameters, B_q^k , which can be calculated provided the coordination geometry is known. Within the simple overlap model [10,11], 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 ambience on the lanthanide ion $4f^n$ configuration. So, the ability to predict geometries of lanthanide ion complexes is therefore central to the process of luminescent complex design, and may also be useful for other applications, such as the design of erbium complexes as gas sensors [12].

In order to be able to predict geometries of lanthanide complexes, we had developed earlier the original Sparkle model [13,14], which we recently improved and called Sparkle/AM1 [15]. In the present paper, we extend Sparkle/AM1 to Er(III) and Ce(III). The Sparkle/AM1 model replaces the trivalent lanthanide ion by a Coulombic charge of $+3e$ superimposed to a repulsive exponential potential of the form $\exp(-\alpha r)$, which accounts for the size of the ion, and uses Gaussian functions in the core–core repulsion energy term. That is, Sparkle/AM1 assumes that the lanthanide trications behave like simple ions, without any angular steric properties – the angular effects of the f orbitals being negligible. As we previously mentioned [15], the good agreement between predicted and observed environments of the ions is strong evidence for the validity of this idea.

1.1. Parameterization procedure

The parameterization procedure used for Ce(III) and Er(III) ions 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) [17–19]. Fifteen different representative structures of Ce(III) and Er(III) complexes with nitrogen or oxygen as coordinating atoms, important for luminescence and telecommunications research, were chosen as the training set, with the following types of ligands: β -diketone, nitrate, monodentate, bidentate, tridentate, polydentate and dilanthanides. More than 60% of all Er(III) and Ce(III) complexes available at CSD, possess oxygen and/or nitrogen as directly coordinating atoms. 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 chemical sense.

2. Results and discussion

The Sparkle/AM1 parameters obtained for cerium(III) and erbium(III) are shown in Table 1.

In the validation procedure, we used a set of twenty-two more complexes for Ce(III) and twenty-four more complexes for Er(III), all of high crystallographic quality, yielding a total of thirty-seven and thirty-nine coordination compounds considered for Ce(III) and Er(III), respectively (Table 2).

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

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

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

Two cases have been examined: (i) UMEs involving the interatomic distances $R_{i,j}$ between the lanthanide central ion and the atoms of the coordination polyhedron, as well as the interatomic distances $R_{i,j}$ between all atoms of the coordination polyhedron, and (ii) $UME_{(L_n-L)}$ s involving only the interatomic distances $R_{i,j}$ between the lanthanide

Table 1
Parameters for the Sparkle/AM1 model for the Ce(III) and Er(III) ions

	Sparkle/AM1	
	Ce(III)	Er(III)
GSS	58.7223887052	58.0489423317
ALP	2.6637769616	3.6568232540
a_1	1.7507655141	0.7029401580
b_1	7.6163181355	8.7235009642
c_1	1.8064852538	1.7746084736
a_2	0.0093401239	0.1321261631
b_2	8.7664931283	8.3498075890
c_2	3.2008171269	3.0114806813
EHEAT (kcal mol ⁻¹) ^a	944.7	1016.15
AMS (amu)	140.115	167.26

^a The heats of formation of the Ce(III) and Er(III) ions in Sparkle/AM1 were obtained by adding to the heat of atomization of each respective lanthanide, their first three ionization potentials [16].

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

Ligand group number	Ligand type	Number of structures	
		Ce(III)	Er(III)
1	β -Diketone	4	2
2	Nitrate	7	11
3	Monodentate	4	6
4	Bidentate	1	6
5	Tridentate	7	0
6	Polydentate	10	9
7	Dilanthanide	4	5

central ion and the atoms of the coordination polyhedron, important in luminescent complex design.

The graphical representation of the UME and of the $UME_{(Ln-L)}$ s for both Ce(III) and Er(III) are shown in parts a and b of Figs. 1 and 2, respectively. Clearly, total UMEs

are larger than the $UME_{(Ln-L)}$ s. Indeed, whereas the maximum UMEs for Ce(III) and Er(III) are, respectively, 0.35 and 0.26 Å, their largest $UME_{(Ln-L)}$ s are, also, respectively, only 0.24 and 0.14 Å, indicating that both cerium and erbium ligand atom distances are more accurately

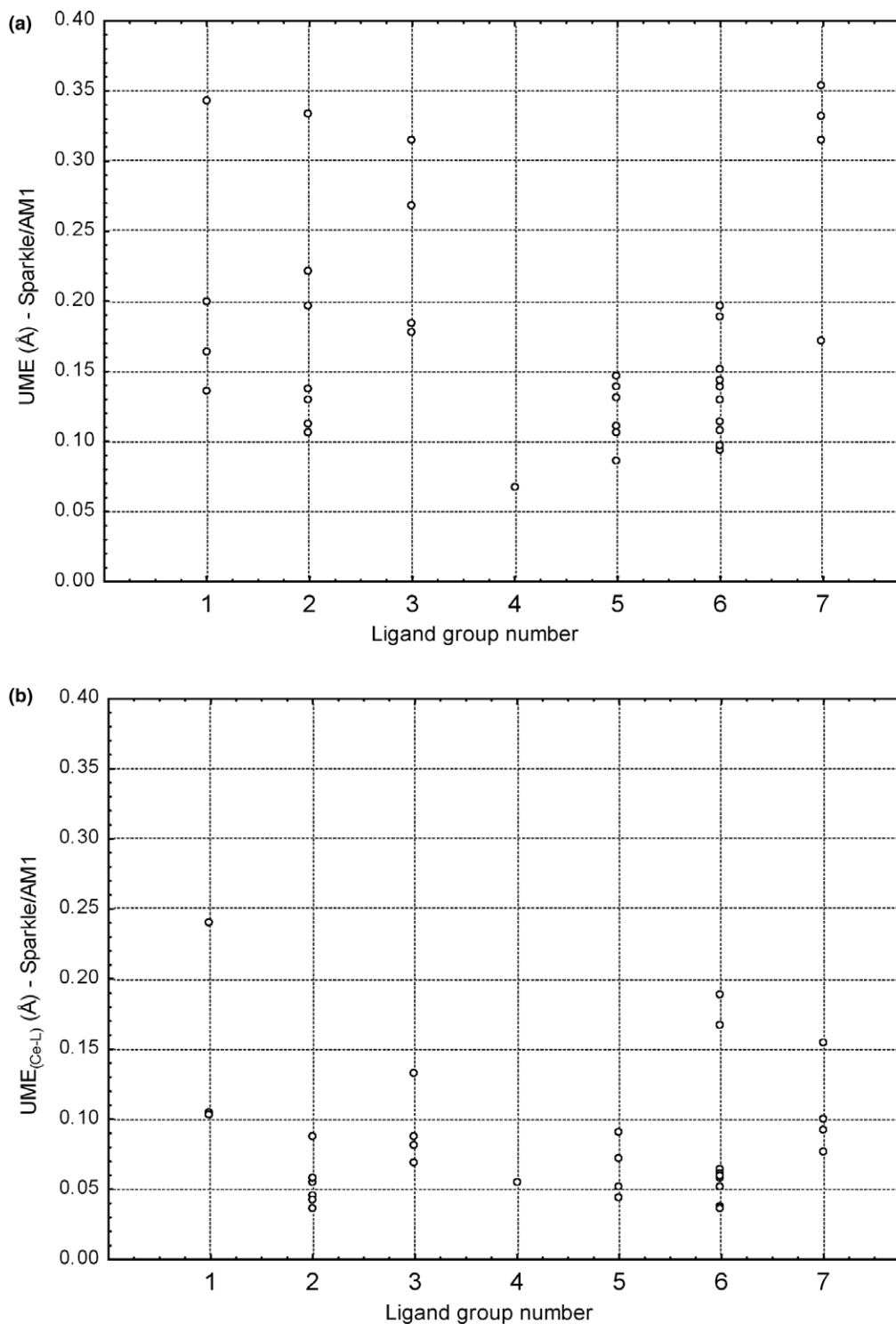


Fig. 1. Unsigned mean errors for each of the thirty-seven cerium(III) complexes, assembled according to the ligand group numbers defined in Table 2. (a) presents the UMEs and (b) presents the $UME_{(Ce-L)}$ s. The same scale has been used in both to facilitate comparison.

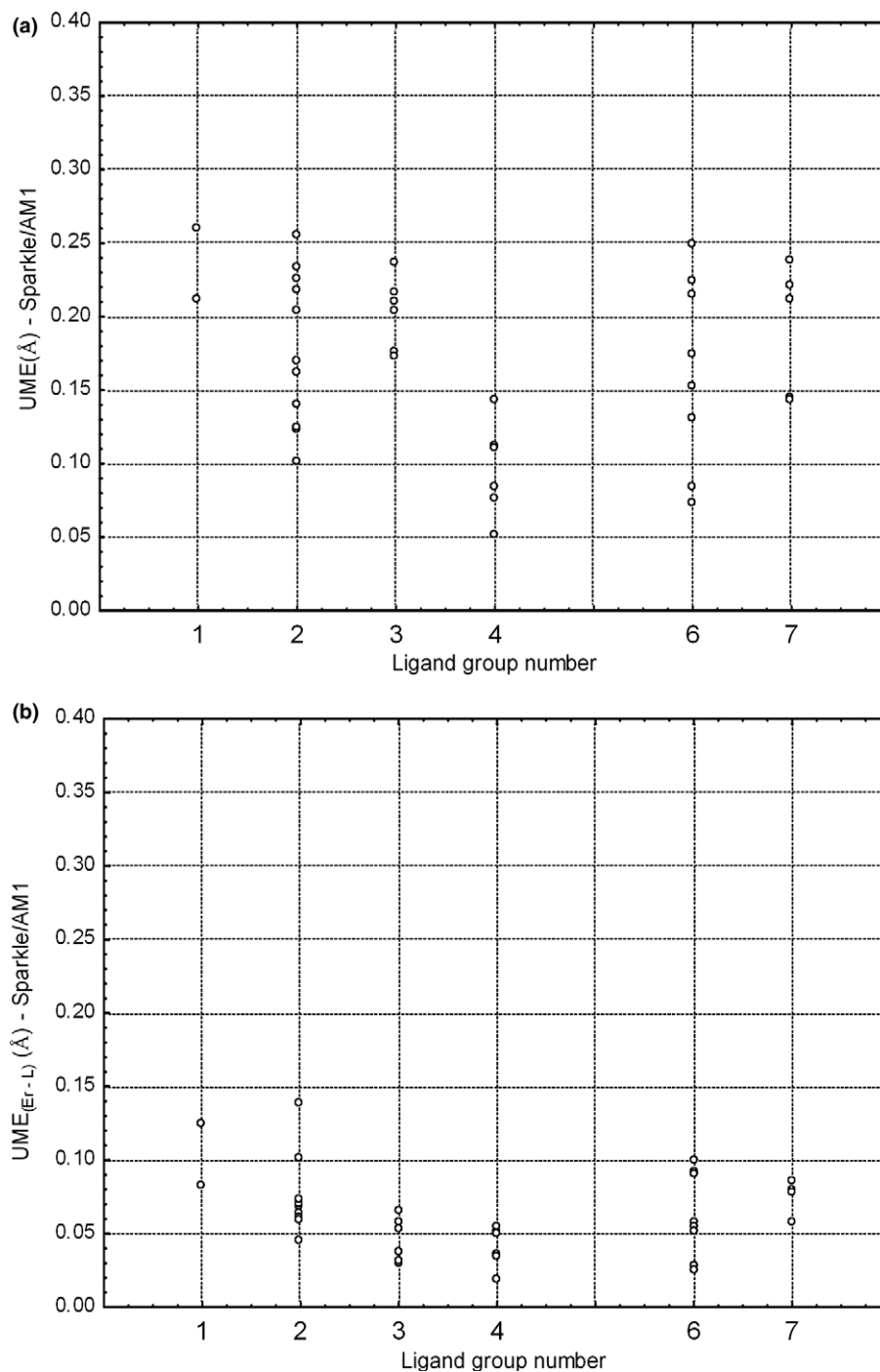


Fig. 2. Unsigned mean errors for each of the thirty nine erbium(III) complexes, assembled according to the ligand group numbers defined in Table 2. (a) presents the UMEs and (b) presents the UME_(Er-L)s. The same scale has been used in both to facilitate comparison.

described than the whole coordination polyhedron. And fortunately that is so, because for luminescent complex design, accurate description of distances between the directly coordinating atoms and the central lanthanide ion are exceedingly more important than the whole coordination polyhedron.

In Table 3 we present Sparkle/AM1 unsigned mean errors for specific types of bond distances, not only for

Ce(III) and Er(III), but also for the previously published Eu(III), Gd(III), Tb(III) [15], and Pr(III) [20]. Indeed, the same patterns that appear for previous ions are reproduced in the case of Ce(III) and Er(III), showing they are all comparable parameterizations.

Once again, the very important lanthanide ion–ligand atom distances are the most accurately predicted of all interatomic distances.

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) complexes; 70 Gd(III) complexes; 42 Tb(III) complexes; 48 Pr(III) complexes; all 37 Ce(III) complexes, and all 39 Er(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 [20]	0.2002	0.0813	0.0695	0.2332	0.0808	0.2032
Sparkle/AM1–Ce	0.2122	0.0809	0.0728	0.2077	0.0802	0.1826
Sparkle/AM1–Er	0.1374	0.0678	0.0360	0.2061	0.0638	0.1756

3. Conclusion

In conclusion, Sparkle/AM1 parameters for Ce(III) and Er(III) are here defined at the same level of quality of the previously introduced Sparkle/AM1 parameters for Eu(III), Gd(III), Tb(III) [15], and Pr(III) [20], and may be of value in complex design for applications to luminescence and/or telecommunications research. As we previously argued [20], Sparkle/AM1 may be a choice in combinatorial searches of optimum molecular architectures for certain applications, where dozens of structures must have their geometries fully optimized.

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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.2006.01.044](https://doi.org/10.1016/j.jorganchem.2006.01.044).

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