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Sparkle Model for AM1 Calculation of Lanthanide Complexes: Improved Parameters for Europium[†]

Gerd B. Rocha,[‡] Ricardo O. Freire,[‡] Nivan B. da Costa, Jr.,[§] Gilberto F. de Sá,[‡] and Alfredo M. Simas*,[‡]

Departamento de Química Fundamental, Universidade de Federal de Pernambuco UFPE,
50.590-470 Recife, Pernambuco Brazil, and Departamento de Química,
Universidade Federal de Sergipe UFS, 49.000-100 Aracaju, Sergipe Brazil

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In the present work, we sought to improve our sparkle model for the calculation of lanthanide complexes, SMLC, in various ways: (i) inclusion of the europium atomic mass, (ii) reparametrization of the model within AM1 from a new response function including all distances of the coordination polyhedron for tris(acetylacetonate)(1,10-phenanthroline) europium(III), (iii) implementation of the model in the software package MOPAC93r2, and (iv) inclusion of spherical Gaussian functions in the expression which computes the core–core repulsion energy. The parametrization results indicate that SMLC II is superior to the previous version of the model because Gaussian functions proved essential if one requires a better description of the geometries of the complexes. In order to validate our parametrization, we carried out calculations on 96 europium(III) complexes, selected from *Cambridge Structural Database 2003*, and compared our predicted ground state geometries with the experimental ones. Our results show that this new parametrization of the SMLC model, with the inclusion of spherical Gaussian functions in the core–core repulsion energy, is better capable of predicting the Eu–ligand distances than the previous version. The unsigned mean error for all interatomic distances Eu–L, in all 96 complexes, which, for the original SMLC is 0.3564 Å, is lowered to 0.1993 Å when the model was parametrized with the inclusion of two Gaussian functions. Our results also indicate that this model is more applicable to europium complexes with β-diketone ligands. As such, we conclude that this improved model can be considered a powerful tool for the study of lanthanide complexes and their applications, such as the modeling of light conversion molecular devices.

Introduction

In 1994, we developed a semiempirical model for the computation of ground state properties for lanthanide complexes.[1] This model, named *Sparkle Model for the Calculation of Lanthanide Complexes*, SMLC, was successfully applied to some coordination compounds and served as an entry point for the calculation of their electronic and optical properties. M. T. Benson et al. have applied this model for 10-coordinate gadolinium complexes and found good results for the description of their molecular properties.[2] T. R. Cundari et al. have used the SMLC model for Gd(III) for the calculation of many Gd(III) coordination complexes and Gd(III) trihalides. For the last ones, they observed that the SMLC model predicts a wrong D_{3h} geometry instead of the correct C_{3v} due to its intrinsic electrostatic character.[3] This behavior was reported by us[1] and by ab initio studies using various effective core potentials, ECPs.[4] Recently, R. Puchta et al. have published a paper named “Exploring {2}-metallacryptands and {2}-metallacryptates with quantum chemical methods—When (not only) computer chemists’

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* Corresponding author. E-mail: simas@ufpe.br.

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[‡] UFPE.

[§] UFS.

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dreams come true" where they also used the sparkle model for transition metals.[5] They have obtained good results for geometries and thermodynamic properties of gallium and iron cryptand and cryptate compounds.

In our research group, the sparkle model has been applied in an intense way to calculate and predict some spectroscopic properties, such as singlet and triplet energy positions, electronic spectra of lanthanide complexes, etc.[6−7] With these quantities, we have built rate equations that involve energy transfer mechanisms to determine quantum yields and luminescence efficiencies for these complexes. In a recent paper,[8] we presented a first proposition of a highly luminescent europium complex based on calculated results only. This designed europium complex is formed either by three benzoyltrifluoroacetylimide anion ligands or by three benzoylacetylimide ligands plus one 2,2′-bipyridine. Through sparkle model calculations, we have obtained quantum yields from Eu(III) $^5D_0$ level of 65.1% for the first complex and 67.0% for the second complex. Syntheses of these complexes are being attempted in our laboratories. A review paper shows many of these results for various lanthanide complexes.[9]

This semiempirical model assumes that the lanthanide ion 4f orbitals do not have a significant contribution to the chemical bond between the atoms of the first coordination sphere of the larger ligands and the lanthanide ion.[10] In other words, the overlap between the lanthanide ion 4f orbitals and orbitals of the ligand atoms is very small, conferring to the chemical bond a largely electrostatic behavior. Therefore, we postulate that the lanthanide ion could be satisfactorily represented by the Coulombic potential corresponding to a point of charge of value identical to its oxidation state, superimposed by a repulsive exponential potential, both centered in the position of the nucleus of the lanthanide ion. Such representation is called sparkle and was originally introduced in the program MOPAC 6.0.[11] The sparkles in MOPAC possess nuclear charges $+2e$, $+1e$, $-1e$, and $-2e$. They are "elements" that represent pure ionic charges: no orbitals, no associated masses, zero heats of atomization, no ionization potentials, and ionic radii of approximately 0.7 Å. They were intended to be used as surrogates for alkaline ions, sulfates, or ammonium ions, among others. In short, sparkles were created with the intent of simulating the behavior of counterions. Accordingly, the sparkle is a charge in the center of a repulsive spherical exponential potential of the form $\exp(-\alpha x)$, where α is the parameter that represents its hardness.

The first version of the SMLC model[1] was as follows: replacement of the sparkle $+2e$ charge by a $+3e$ charge to represent the lanthanide ion Eu^{3+}, inclusion of the heat of formation of gaseous Eu^{3+} in the variable EHEAT (1005.3 kcal mol^{-1}), obtained from the sum of the heat of atomization of the neutral europium atom, plus its first three ionization potentials,[12] and, finally, optimization of the parameters AM and ALP for inclusion in the semiempirical method AM1 in the MOPAC 6.0 code. The optimization was made through a modified simplex[13] in order to minimize the response function: the sum of the squares of the differences between the calculated and experimental distances of the atoms of the coordination polyhedron of the complex tris(acetylacetonate)(1,10-phenanthroline)−europium(III). Only the coordination polyhedron is involved in the parametrization of the sparkle, because the semiempirical methods already describe well the geometries of the organic ligands.

Tris(acetylacetonate)(1,10-phenanthroline)−europium(III) possesses a coordination number equal to eight: the six oxygen atoms of three β-diketones, plus two nitrogen atoms belonging to 1,10-phenanthroline. So, according to the crystallographic data,[14] the coordination polyhedron for this complex presents the geometry of a square-antiprism (Figure 1).

The parametrization results of the original SMLC model are α_{core} (Eu) for AM1 = 2.0 and $G_{SS}/27.21$ for AM1 = 2.0.[1]

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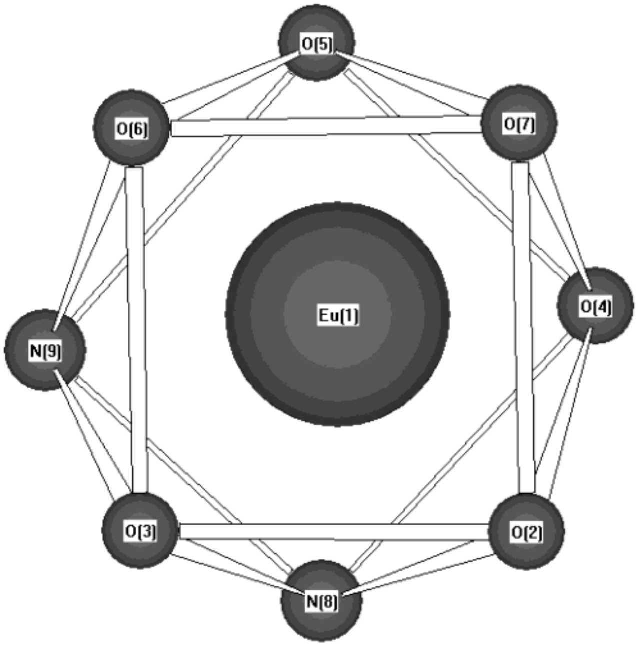

Figure 1. Coordination polyhedron from the crystallographic structure of the complex tris(acetylacetonate)(1,10-phenanthroline)−europium(III).

The importance of knowing the ground state geometries of the complexes is the subsequent possibility of calculating many other properties essential to inorganic chemists, in particular to spectroscopists.

In the present work, we sought to improve the SMLC model in various ways: (i) inclusion of the europium atomic mass, (ii) reparametrization of the model within AM1[15] for a new form for the response function which, this time, includes all distances of the coordination polyhedron of tris(acetylacetonate)(1,10-phenanthroline)−europium(III), (iii) implementation of the model in the software package MOPAC93r2,[16] and, finally, (iv) inclusion of two spherical Gaussian functions in the expression which computes the core−core repulsion energy.

The simple inclusion of the europium atomic mass in the SMLC model allowed the calculation of the moments of inertia for molecules and the calculation of their force constants. Now, it is possible to calculate, among others, spectroscopic properties in the infrared region, their absorption intensities and frequencies, as well as their normal modes of vibration. Indeed, we can now calculate rotational and vibrational partition functions and determine the thermodynamic properties, such as enthalpy, entropy, free energy, heat capacity, and kinetics properties, such as rate constants, activation energies, reaction mechanisms through its intrinsic coordinates. Also, we can determine transition states for these reactions and also the activation energies involved in the chemical reactions. Besides, it is also possible to calculate these properties at various temperatures and to observe their behavior when the temperature is varied. See, for example, the reactions of lanthanide complexation.[17] We can further calculate nonlinear optical properties through the methodology TDHF (time dependent Hartree−Fock).[18] For the calculation of the hyperpolarizability tensors through this methodology, program MOPAC93r2 first, for convenience, reorients the molecule according to its moments of inertia, which can now be computed due to the inclusion of the europium mass in the model.

Table 1. Adjusted Parameters for the SMLC II Model Parameterized for the Eu(III) Ion

	parameter values (spi)	
	SMLC I	SMLC II
GSS	54.420000	55.553560
ALP	2.000000	2.049424
a_1		0.145870
b_1		7.202259
c_1		1.712893
a_2		0.004508
b_2		7.911483
c_2		2.340541

The modification carried on in the response function has the purpose of including all interatomic distances between the atoms that compose the coordination polyhedron of the complexes used in the reparametrization. The original version[1] took into account only 24 of the 36 possible distances for the tris(acetylacetonate)(1,10-phenanthroline)−europium(III) complex. The form of the function has also been changed, and the response function used in this paper is the sum of the squares of the deviations between the experimental and calculated distances divided by the corresponding experimental distances in each point of the simplex. We call the version of SMLC reported in this paper version II.

Implementation of the SMLC II Model in the MOPAC93r2 Package

To implement the SMLC II model in the package MOPAC93r2, it was necessary to modify the block.f and calpar.f subroutines. The block.f subroutine was changed in the same way as the original article.

In the MOPAC93r2 package, position 103 of its various arrays is used to define the original MOPAC $+2e$ sparkle. We decided to use it to define our sparkle representing the Eu(III) ion. As such, we changed its charge, CORE(103), from $+2e$ to $+3e$. We also used the value of 1005.3 kcal mol^{-1} for the heat of formation of the europium(III) ion in EHEAT(103).[1] Finally, we introduced the optimized europium(III) parameters for AM1 semiempirical method, which are listed in Table 1.

In the MNDO semiempirical method, the expression to calculate the core−core repulsion energy has different forms depending on the pair of involved atoms. For N−H and O−H, this is

$$E_{\mathrm{N}}(\mathrm{A,B}) = Z_{\mathrm{A}} Z_{\mathrm{B}} \langle s_{\mathrm{A}} s_{\mathrm{A}} | s_{\mathrm{B}} s_{\mathrm{B}} \rangle (1 + R_{\mathrm{AB}} e^{-\alpha_{\mathrm{B}} R_{\mathrm{AB}}} + e^{-\alpha_{\mathrm{H}} R_{\mathrm{AB}}}) \quad (1)$$

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and for the other atoms, this is

$$E_N(A,B) = Z_A Z_B \langle s_A s_A | s_B s_B \rangle (1 + e^{-\alpha_A R_{AB}} + e^{-\alpha_B R_{AB}}) \quad (2)$$

Here, Z_A and Z_B are core charges associated to nuclei A and B, respectively. The α parameter represents the hardness of atomic nucleus, and R_{AB} is the interatomic distance between atom A and atom B.

The basic difference between MNDO semiempirical method and both AM1 and PM3 methods is the presence of two summations of the Gaussian functions, centered in each atom, in the expression to calculate the core−core repulsion energy. Originally, in AM1 semiempirical method, these Gaussian functions were added in order to correct for long-range interactions in the core−core repulsion integrals. Then, for AM1 method, the expression for this core−core integral, $E_N(A,B)$, is

$$E_N(A,B) = E_N^{MNDO}(A,B) + \left(\frac{Z_A Z_B}{R_{AB}}\right)\left(\sum_{k=1}^{ng_A} a_{k_A} e^{-b_{kA}(R_{AB}-c_{kA})^2} + \sum_{k=1}^{ng_B} a_{k_B} e^{-b_{kB}(R_{AB}-c_{kB})^2}\right) \quad (3)$$

where $E_N^{MNDO}(A,B)$ is the core−core repulsion energy for the MNDO method and is defined in eqs 1 and 2; Z_A and Z_B are the core charges for the A and B cores; R_{AB} is the interatomic nuclear distance between nuclei A and B; a_k, b_k, and c_k are, respectively, the intensity, width, and position of the kth Gaussian function, and, finally, ng_A and ng_B are the number of Gaussian functions centered in atoms A and B, respectively.

For the present second version of SMLC model, SMLC II, we have just added two spherical Gaussian functions to our first version of the sparkle model for the AM1 semiempirical method, each one containing three adjustable coefficients a_k, b_k, and c_k.

Finally, in MOPAC93r2, the monocentric bieletronic integrals $\langle ss|ss \rangle$ are given by both arrays GSS (in eV) and by AM (in Hartrees) in block.f. As such, the instruction, AM(103)=GSS(103)/ENRGY, must be placed in subroutine calpar.f after the end of the DO instruction of number 40, the variable ENRGY being set equal to 27.21.

Results

The best parameters found which define SMLC II model are presented in Table 1.

With the purpose of testing and validating this parametrization version of the sparkle model, we tried to reproduce the coordination polyhedra for the ground state geometries of a group of europium(III) complexes. We called this group "test set" and we used the crystallographic database *Cambridge Structural Database 2003* (CSD)[19−21] in order to select europium(III) complexes' crystallographic structures. In our searches, we found 590 structures, of which only 275 had their 3D coordinates available. After a detailed analysis of each one of the structures, we were able to choose the 96 most representative ones in order to build our test set.

Table 2. Interatomic Distances of the Coordination Polyhedron of the Tris(acetylacetonate)(1,10-phenanthroline)−Europium(III): Experimental Crystallographic Values and Both SMLC and SMLC II Calculated Values and Their Signed Deviations

no.	atoms	expt (Å)	SMLC (Å)	signed deviation (Å)	SMLC II (Å)	signed deviation (Å)
1	Eu1−O2	2.4097	2.3423	0.0674	2.3608	0.0489
2	Eu1−O3	2.3884	2.1715	0.2169	2.3273	0.0611
3	Eu1−O4	2.3555	2.3402	0.0153	2.3605	−0.0050
4	Eu1−O5	2.3606	2.1733	0.1873	2.3273	0.0333
5	Eu1−O6	2.3799	2.3619	0.0180	2.3551	0.0248
6	Eu1−O7	2.3719	2.1466	0.2253	2.3146	0.0573
7	Eu1−N8	2.6463	2.6117	0.0346	2.5297	0.1166
8	Eu1−N9	2.6371	2.7210	−0.0839	2.6170	0.0201
9	O2−O3	2.8246	2.5562	0.2684	2.6126	0.2120
10	O2−O4	3.1176	2.8154	0.3022	2.9389	0.1787
11	O2−O5	4.5950	4.2701	0.3249	4.4623	0.1327
12	O2−O6	4.1187	4.3623	−0.2436	4.3127	−0.1940
13	O2−O7	2.9884	3.0645	−0.0761	3.1300	−0.1416
14	O2−N8	3.2187	2.9520	0.2667	2.9341	0.2846
15	O2−N9	4.6275	4.4513	0.1762	4.4025	0.2250
16	O3−O4	4.4597	4.2566	0.2031	4.4482	0.0115
17	O3−O5	4.4467	4.1369	0.3098	4.4310	0.0157
18	O3−O6	2.9468	2.9056	0.0412	3.0010	−0.0542
19	O3−O7	4.0775	3.3192	0.7583	3.5887	0.4888
20	O3−N8	3.0281	3.2930	−0.2649	3.3436	−0.3155
21	O3−N9	2.9729	2.9517	0.0212	2.9576	0.0153
22	O4−O5	2.8013	2.5560	0.2453	2.6163	0.1850
23	O4−O6	4.4971	4.3831	0.1140	4.3519	0.1452
24	O4−O7	3.1531	3.0952	0.0579	3.1495	0.0036
25	O4−N8	2.9514	2.9341	0.0173	2.9147	0.0367
26	O4−N9	4.0409	4.4147	−0.3738	4.3606	−0.3197
27	O5−O6	2.9286	2.9113	0.0173	3.0136	−0.0850
28	O5−O7	3.1076	3.2929	−0.1853	3.5135	−0.4059
29	O5−N8	4.0805	3.3569	0.7236	3.4348	0.6457
30	O5−N9	3.0004	2.9458	0.0546	2.9534	0.0470
31	O6−O7	2.8283	2.5953	0.2330	2.6369	0.1914
32	O6−N8	4.6922	4.6136	0.0786	4.5890	0.1032
33	O6−N9	3.2661	3.0216	0.2445	2.9986	0.2675
34	O7−N8	4.8258	4.6358	0.1900	4.6939	0.1319
35	O7−N9	4.8150	4.6151	0.1999	4.6734	0.1416
36	N8−N9	2.7254	2.8091	−0.0837	2.8028	−0.0774

We calculated all interatomic distances of the coordination polyhedron for each complex, using their crystallographic geometries as starting points and by optimizing the ground state geometry applying SMLC II model. The MOPAC keywords used in all SMLC II calculations were the following: GNORM = 0.25 (in order to guarantee the energy minimum), SCFCRT = 1.D-10 (in order to increase the SCF convergence criteria), and XYZ (the geometry optimizations were performed in Cartesian coordinates). The unsigned mean error, UME, was calculated by the sum of all absolute values of differences between experimental (R_{exp}) and calculated interatomic distances (R_{calc}), eq 4.

$$\mathrm{UME} = \frac{1}{N}\sum_{i=1}^{N} |R_{exp} - R_{calc}| \quad (4)$$

Table 2 shows results for the distances between all the atoms of the coordination polyhedron of tris(acetylacetonate)-(1,10-phenanthroline)−europium(III) complex and their re-

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Table 3. Values of the Coordination Numbers, CNs, and Unsigned Mean Errors, UMEs, for Both SMLC and SMLC II, as Compared to the Respective Experimental Crystallographic Values, for Each of the Complexes of the Test Set Used[a]

		UME (Å)				UME (Å)	
structure[1]	CN	SMLC	SMLC II	structure[1]	CN	SMLC	SMLC II
ABOFOM[22]	9	0.331	0.116	MASJUL[66]	8	0.134	0.054
ACPNEU[23]	8	0.106	0.046	MASKAS[67]	8	0.278	0.029
AFTBEU[24]	8	0.372	0.090	MAXDIY[67]	9	0.216	0.188
BEKWUJ[25]	11	0.663	0.544	MTXPVE[68]	7	0.300	0.031
BIWFUI[26]	10	0.730	0.261	NAMZUW[69]	9	0.280	0.200
CEXKUL[27]	9	0.345	0.158	NOHLOL[70]	9	0.040	0.038
CIRKET[28]	8	0.219	0.035	NOHLUR[71]	9	0.295	0.163
DIWNOM[29]	10	0.609	0.127	NOJMII[72]	8	1.219	0.503
DOTZAN[30]	8	0.289	0.237	NOJMOO[72]	8	0.800	0.524
ECABOZ[31]	10	0.525	0.518	NOJMOO01[45]	8	0.799	0.522
EGOBEH[32]	9	0.141	0.110	PADDAZ[73]	10	0.364	0.295
EUACAC10[33]	8	0.358	0.274	PIEUAC01[74]	8	0.130	0.026
EUBZAC10[34]	8	0.201	0.027	PIEUAC20[34]	8	0.191	0.023
FOCQOD[35]	9	0.202	0.048	PUGKIL[75]	8	0.203	0.033
FOCREU[35]	9	0.358	0.270	QHDOEU[76]	7	0.126	0.021
GACJOJ[36]	10	0.811	0.516	QIGJAR[77]	9	0.118	0.034
GAPRUK[37]	8	0.045	0.040	QIMREJ[78]	10	0.759	0.629
GEBYAN[38]	9	0.771	0.667	RITFIJ[79]	10	0.515	0.576
HAFROV[39]	7	0.101	0.035	SAZXOG[80]	8	0.657	0.579
HANBIH[40]	9	0.052	0.044	SIYKAM[81]	10	0.456	0.357
HANDUV[40]	9	0.130	0.087	SOLNAI[82]	10	0.236	0.200
HANMOY[41]	9	0.024	0.023	TEBHOX[83]	9	0.617	0.335
HAZGAQ[42]	8	0.200	0.166	TMHPEU10[84]	8	0.079	0.036
HIHFIN[43]	9	0.497	0.107	TMUNEU[85]	9	0.670	0.637
HIKWIH[44]	8	2.008	0.521	TOGHUS[86]	8	0.136	0.062
HILVED[45]	8	0.091	0.045	TPYREU01[87]	9	0.058	0.050
HIZGUS[46]	7	0.291	0.206	VAQDIA[88]	8	0.230	0.015
HXDZEU10[47]	10	0.683	0.177	VEQFAY[89]	7	0.196	0.120
JAKVIA[48]	7	0.269	0.191	VIGPAC[90]	7	0.471	0.295
JAXXOV[49]	8	0.090	0.034	WOMCIK[91]	9	0.630	0.309
JEWHUO[50]	8	0.412	0.057	XAWWIB[88]	9	0.051	0.043
JEYTEM[51]	7	0.111	0.053	XICHIA[92]	8	0.160	0.095
JOSQUD[52]	8	0.202	0.168	XICHOG[92]	8	0.088	0.086
JOSTEQ[53]	8	0.212	0.178	XIWPIC[93]	9	0.197	0.040
JUGBUI[53]	10	0.590	0.483	XIWTUS[94]	8	0.115	0.037
KAKKEM[54]	8	0.289	0.133	YATHOQ[95]	8	0.500	0.431
KAKPAN[55]	8	0.483	0.151	YEGYEO[96]	8	0.222	0.034
KAYGUM[56]	10	0.723	0.278	YEZFAK[97]	8	0.197	0.060
KIFKOZ01[57]	9	0.481	0.266	YITPIA[98]	9	0.164	0.080
KIFKOZ02[58]	9	0.474	0.257	YODYIZ[99]	8	0.385	0.147
KIHSEZ[59]	10	0.412	0.089	YOJDIK[100]	8	0.080	0.029
KITFOI[60]	9	0.191	0.114	YUXREO[101]	9	0.443	0.217
LIFJAL[61]	10	0.416	0.202	ZACXAC[102]	9	0.373	0.075
LOPDAV[62]	9	0.090	0.102	ZIPPAP[103]	8	0.662	0.582
LOWBEE[63]	10	0.350	0.296	ZODXIZ[104]	9	0.194	0.167
LOZVAX[64]	9	0.396	0.091	ZOJTAT[105]	8	0.196	0.154
MAJZIG[65]	8	0.072	0.020	ZUCCIJ[106]	8	0.179	0.097
MAJZOM[65]	8	0.092	0.027	ZUVLAD[107]	10	0.543	0.510

[a] The structures are identified by their respective codes of reference from the *Cambridge Structural Database 2003*.[22−107]

spective deviations from the experimental ones, calculated with both SMLC[1] and SMLC II models. For the interatomic distances between Eu(III) ion and the atoms of the first coordination sphere (Eu−L, distances 1−8), the SMLC II absolute errors are almost all smaller than 0.1 Å, while, for the original version of the SMLC model, we detected many errors larger than 0.1 Å. These results indicate that the inclusion of Gaussian functions is important, mainly for the description of the Eu−L bonds (UME for SMLC is 0.1923 Å and UME for SMLC II is 0.1506 Å).

In Table 3, we show the UME for all test set structures. To make comprehensive Table 3 interpretations, we have

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performed a cluster analysis in order to know the predictive power of our SMLC model for the calculation of europium complexes and to be able to answer the following question: for what type of europium(III) coordination compound is this new sparkle model parametrization more appropriately applicable?

The cluster analysis was performed with *Statistica 6.0* software, and we have used the Euclidean distances with single linkage criteria to cluster the complexes. We have used the following variables: UME for Eu−L distances (in Å), number of β-diketone ligands, number of nitrate ligands, number of monodentate ligands, number of bidentate ligands, number of tridentate ligands, number of polydentate ligands,

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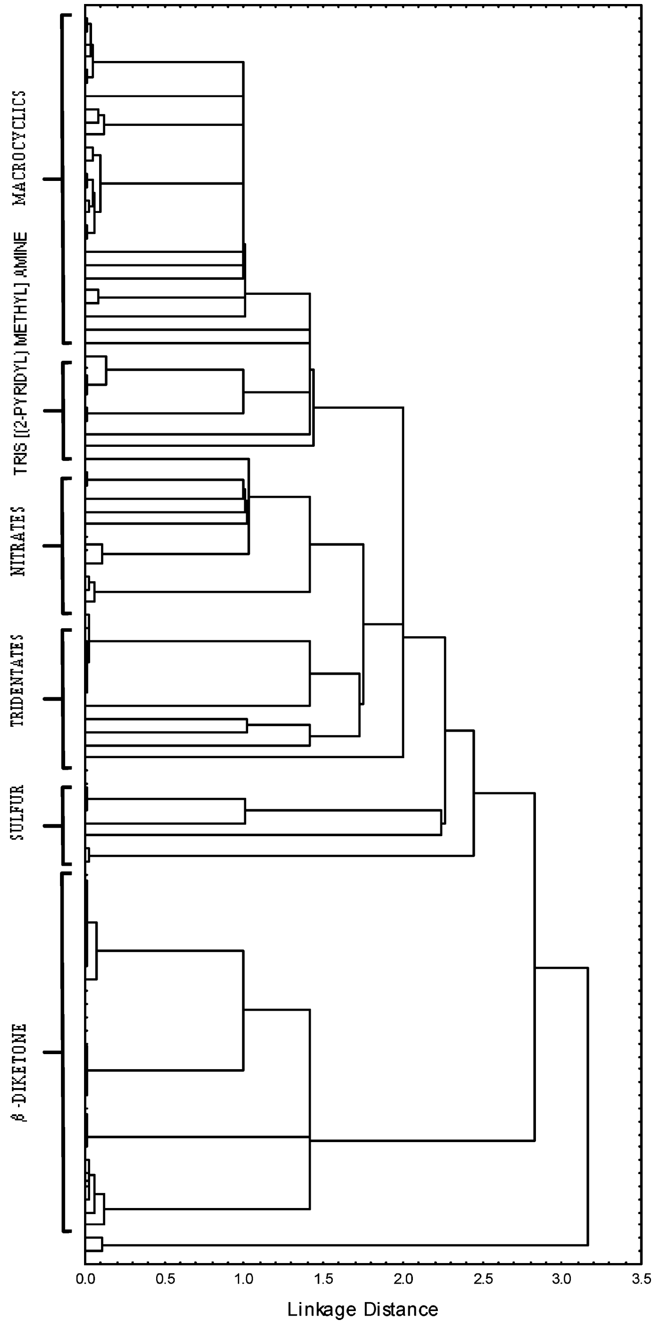

Figure 2. Cluster analysis of all 96 complex test structures in terms of their unsigned mean error (UME) calculated by the sum of all absolute values of differences between experimental and calculated interatomic distances involving the europium(III) ion.

number of ligands with sulfur atoms bonded to Eu(III), and coordination number of the complex.

We were able to detect the formation of seven different groups in Figure 2. Six groups were formed by ligand similarity in the complexes: group 1, with *β*-diketone ligands (28 structures); group 2, with nitrate ligands (16 structures); group 3, with ligands similar to tris[(2-pyridyl)-methyl] amine (8 structures); group 4, with tridentate ligands (8 structures); group 5, with polydentate ligands (26 structures); and, finally, group 6, with coordinating sulfur atom (6 structures) ligands. A seventh group was created with the inclusion of all other complexes. For this, we have collected complexes with monodentate and bidentate ligands that are not similar to *β*-diketones.

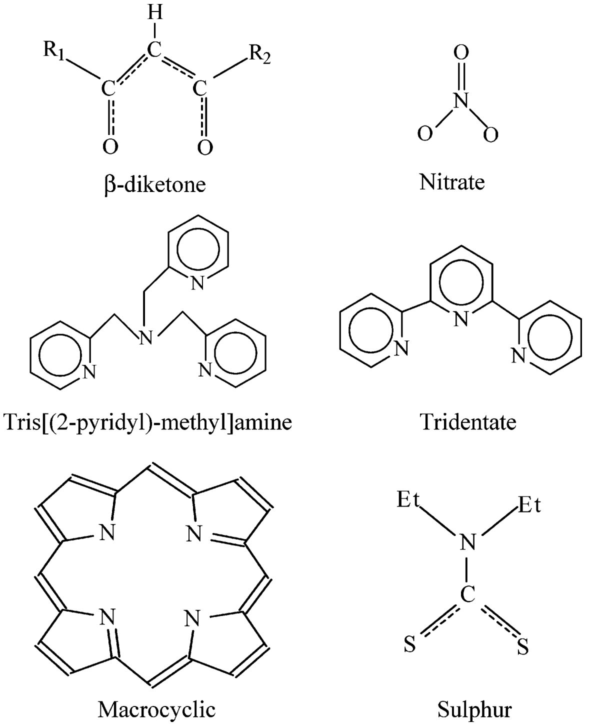

Figure 3. Examples of ligands of each cluster from the cluster analysis presented in Figure 2.

In Figure 3, we show the UME for Eu−L distances for all complexes, divided in groups, from 1 to 7 for both versions of the sparkle model. Thus, we were able to point out which complexes are more correctly predicted via this new parametrization of the sparkle model, SMLC II.

We were capable of detecting significant reductions in UME for complexes in all groups by looking at the SMLC II deviations and by comparing them with the ones from the original version, presented, respectively, in Figure 3b,a. More specifically, for complexes of groups 5 and 6, we detected the largest reductions on the UMEs.

Our results show that all group 1 complexes present a small UME. This group is formed by europium(III) complexes with *β*-diketone ligands, similar to the complex used in the parametrization procedure. One exception is the Diaqua−tris(acetylacetonate)−europium(III) monohydrate complex that has UME = 0.2740 Å, because, SMLC II predicts an incorrect structure for its coordination polyhedron. In this case, one water molecule is placed 3.8452 Å away from the europium(III) ion, resulting in a coordination number of seven. However, except for this fact, the Eu−L distances for group 1 complexes are predicted with the lowest UME in comparison with complexes of other six groups. Most structures of the group 1 show UME below 0.0600 Å.

We can point out that SMLC II model predicts the Eu−L distances for some europium(III) complexes inserted in other groups in good agreement with the experimental ones. As examples, consider Eu(III) complexes with tridentate (group 4) and macrocyclic ligands (group 5).

The UME value for the complexes of group 5, calculated with SMLC II model, ranged from 0.040 Å (GAPRUK) to

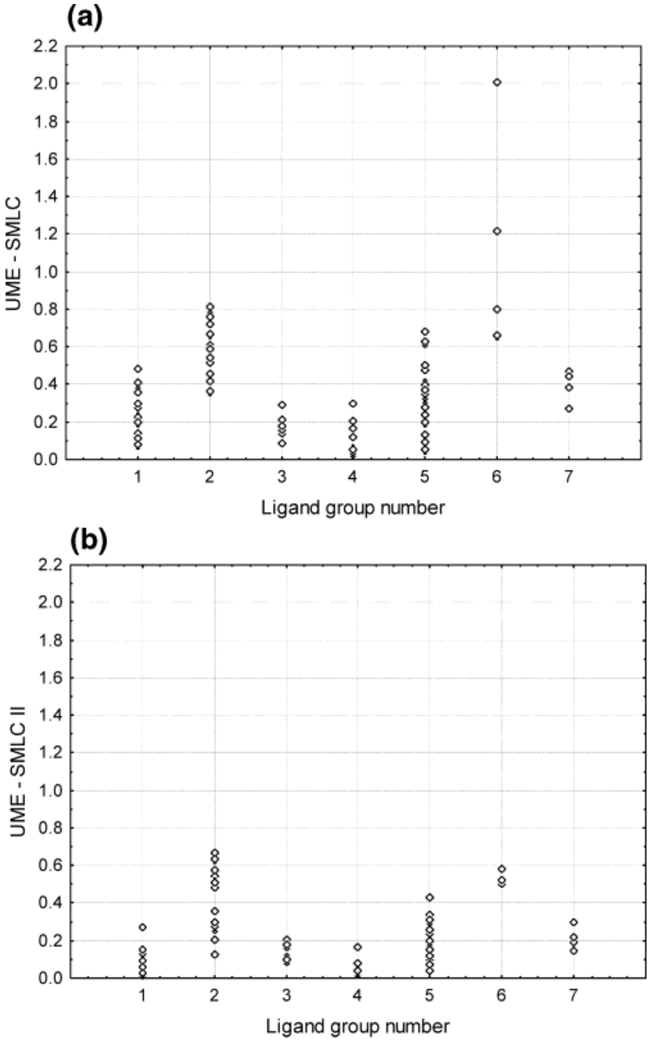

Figure 4. Unsigned mean errors (UMEs), calculated by the sum of all absolute values of differences between experimental and calculated interatomic distances involving the europium(III) ion, for each of the 96 test complexes, grouped according to the cluster analysis shown in Figure 3: (a) calculated with the original SMLC model, and (b) calculated with the present SMLC II model.

0.431 Å (YATHOQ). The reason for this long interval is the presence of monodentate ligands, see Figure 5. Analyzing all the structures of this group, we notice that complexes with a macrocyclic ligand plus water molecules bonded to Eu(III) ion are well predicted by this version of the sparkle model. However, complexes with other monodentate ligands, such as chlorine or isothiocyanatos, bonded to europium(III) ion, are not as well predicted by SMLC II.

We can observe in Figure 4 that the ground state geometries for Eu(III) complexes with nitrate ligands (group 2) and Eu(III) complexes with ligands having one or more coordinating sulfur atoms (group 6) are not as well predicted by this new parametrization nor by the original sparkle model. Especially, for the complexes of group 6, comparison of two versions of the sparkle model reveal larger deviations in the Eu−L distances calculated with the previous version of SMLC model than the ones found with the model presented in this paper.

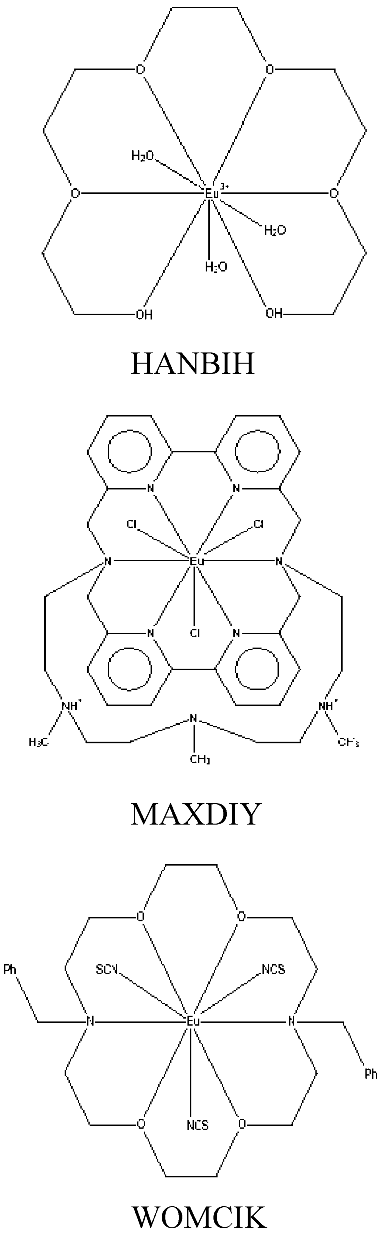

Figure 5. Some macrocyclic ligands present in the test set of 96 complexes.

For group 2, the reason for larger deviations is because both parametrizations of the sparkle model are not able to correctly predict the coordinate arrangement for the nitrate group in these Eu(III) complexes. Instead of the nitrate group coordinating to the central ion with the two oxygen atoms (bidentate form), SMLC II and SMLC predict the nitrate group coordinated by only one oxygen atom, increasing the UME by 0.5 Å, approximately, in both cases.

Finally, the UME for all 825 Eu−L distances in all 96 Eu(III) complexes, which is 0.3564 Å for the original version of the sparkle model, is lowered to 0.1993 Å in this new SMLC II parametrization, a reduction of 44.08% when compared to the original version of the sparkle model. In Table 3, we can count 62 europium(III) complexes with UME below 0.1993 Å, and this represents almost two-thirds of all calculated complexes.

Conclusions

This new parametrization of the SMLC model, SMLC II, reveals a better statistical adjustment than the original version of the model. Clearly, the Gaussian functions are very important, mainly for the description of the sparkle−atom distances of the first coordination sphere.

In conclusion, we can say that our SMLC model is capable of predicting in a satisfactory way the ground state geometries of Eu(III) complexes with ligands that present mainly coordinated (and partially charged) oxygen atoms. For these cases, this parametrization is more applicable, such as in the cases of β-diketones and salicylates. For complexes with ligands that have nitrogen atoms coordinated to the lanthanide ion, our results indicate that if these atoms are partially charged, the Eu−N distances are better predicted.

Our results show that this parametrization indeed predicts the crystallographic structures of the ground state geometries of europium complexes with tridentate and macrocyclic ligands to useful accuracy.

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