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Sparkle model for AM1 calculation of neodymium(III) coordination compounds

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Abstract

The Sparkle/AM1 model, the only available semiempirical quantum chemical model for the calculation of complexes of lanthanide ions, recently defined for Eu(III), Gd(III) and Tb(III), is now extended to Nd(III). Accordingly, all 57 Nd(III) complexes of high crystallographic quality (*R*-factor < 0.05 Å), possessing oxygen or nitrogen as directly coordinating atoms, present in the Cambridge Structural Database 2003, were considered. A subset of 15 structures was chosen by cluster analysis to constitute the parameterization training set. All 57 complexes were considered back in the validation part, and the Sparkle/AM1 unsigned mean error, for all interatomic distances between the Nd(III) ion and the ligand atoms of the first sphere of coordination, was found to be 0.07 Å, a level of accuracy useful for luminescent complex design and comparable to present day rare earth complex ab initio/ECP calculations, while being hundreds of times faster.

Keywords: Sparkle model; AM1; Neodymium; Lanthanide; Rare earth; Coordination compounds

1. Introduction

Much attention has been devoted recently to near infrared luminescence of trivalent lanthanide ions, such as Nd(III), because several lanthanides show luminescence in the telecommunication low-loss near infrared regions of standard silica based optical fibers [1]. The excitation spectrum of neodymium in solution shows three main bands at 880, 1055 and 1330 nm—the 1050 nm being the most intense and detectable. In particular, neodymium has been used within polymeric wave-guides to amplify signals at 1060 nm [2]. Due to its particular energy level structure, neodymium is ideal for the laser transition, and Nd–Yttrium–aluminum–garnet, Nd:YAG, is well known as a laser source for various purposes.

Since transitions within the 4f subshell of lanthanide ions are Laporte forbidden, luminescence can happen by coordinating the Nd(III) ion with suitable organic chromophore ligands—that is, ligands that can absorb energy and, subsequently, transfer the energy to the lanthanide ion via mechanisms which partially mix the configurations, making the f–f transitions partially allowed [3]. Sharp luminescence is then observed, although with a lifetime that is somewhat long, because the f–f transitions are still partially forbidden. However, since Nd(III) is a near infrared emitter it has lower-energy emissive states, and thus possesses a relatively small energy gap. Thus, contrary to Eu(III) and Er(III), which need chromophores that absorb in the ultraviolet, Nd(III) may be combined with a far wider range of chromophoric ligands which absorb visible light, eliminating any competitive excitation by biological molecules and offering the potential for improved detection limits in bioassays [4].

However, the near infrared luminescence of Nd(III) can be much more easily quenched by non-radiative energy transfer by high energy vibrations, usually stretching vibrations of nearby or coordinated solvent molecules, than visible light emitters such as Eu(III) or Tb(III) [5]. In fact, observation of near infrared luminescence of lanthanide complexes doped in a hybrid sol–gel material, for example, is severely limited by quenching of the excited states. Another major problem of most powerful luminescent lanthanide complexes is that they

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do not dissolve well in water and in most starting solutions for the synthesis of sol–gel glasses [6].

Chromophoric ligand design has therefore many facets and is an open area of research.

Another topic which has received much attention recently is the application of coordination compounds of lanthanide ions with biologically active ligands.

For example, complexes of lanthanide ions, neodymium(III) included, with coumarin derivatives have been demonstrated to possess: anti-proliferative activity on various cancer cell lines [7]; good anticoagulant action [8]; and, more recently, that they are potent cytotoxic agents [9].

However, both chromophoric ligand design as well as studies on quantitative structure-biological activity relationships on such complexes are somewhat compromised, due to a lack of fast and accurate quantum chemical models to treat coordination compounds of lanthanide ions. It is indeed common for papers to report ab initio calculations of the isolated ligands only. That is because, so far, scientists have been unable to efficiently treat the complex as a whole, even though it is perfectly possible to do so through ab initio effective core potential calculations [10] (ab initio/ECP)—the drawback being that these calculations are presently so much time consuming that usually they are not even considered.

The sparkle model for the calculation of lanthanide complexes was originally created in 1994 for the AM1 prediction of geometries of lanthanide complexes [11]. At the time it was very simple: it replaced the lanthanide ion by a point of charge +3e superimposed to a repulsive potential of the form $\exp(-\alpha r)$ to mimic the size of the ion, and was parameterized using only one typical europium complex of coordination number 8: tris(acetylacetonate)-(1,10-phenantroline) of europium(III). The original sparkle accuracy was qualitative, but it had the merit of being an easy choice then available which allowed insights on the structure of Eu(III) complexes. In 2000, high quality density functional calculations confirmed that the f electrons do not participate in the lanthanide–ligand bond [12].

In 2004 [13], to make the sparkle model compatible with AM1, two Gaussian functions were added to the core–core repulsion term to make it consistent with AM1; and the europium atomic mass was also included to allow Sparkle calculation of vibrational spectra of the complexes. And, recently, a much more statistically sound technique of parameterization was introduced, which defined a new paradigm, Sparkle/AM1 [14], designed to possess crystallographic geometry prediction accuracies comparable to present day ab initio effective core potential calculations for lanthanide complexes with nitrogen or oxygen directly coordinated to the lanthanide ion. Such complexes constitute about 60% of all Nd(III) complexes with structures deposited in the CSD. Sparkle/AM1 parameters are already available for Eu(III), Gd(III) and Tb(III) [14]. In the present work, we extend the Sparkle/AM1 model to Nd(III) complexes.

1.1. Parameterization procedure

The parameterization procedure used for Nd(III) was essentially the same as the one described in our previous work which defined the Sparkle/AM1 paradigm for Eu(III), Gd(III) and Tb(III) [14]. Accordingly, we used all 57 high quality crystallographic structures (R-factor < 5%) with nitrogen or oxygen as coordinating atoms, important for luminescence and telecommunications research, taken from the "Cambridge Structural Database 2003" (CSD) [15–17]. A cluster analysis of all these complexes was then performed, which resulted in 15 different representative structures of Nd(III) complexes chosen to constitute the training set, with the following types of ligands: β-diketone, nitrate, monodentate, bidentate, tridentate, and polydentate, as well as dineodymium complexes where the two Nd(III) ions face each other directly, and are displayed in Fig. 1. To find the parameters, we carried out a non-linear minimization of the 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 or very close to it, and make chemical sense.

In the validation procedure, we added back the other 42 complexes, and evaluated the accuracy measures for all 57 complexes structures of high crystallographic quality, which were classified by the same cluster analysis according to their predominant ligand group, as indicated in Table 1.

The sparkle parameters that were optimized, are all related to the core–core repulsion energy between atoms A and B, $E_N(\mathrm{A,B})$, which, in the semiempirical method AM1, is [18]:

$$E_N(\mathrm{A,B}) = Z_\mathrm{A} Z_\mathrm{B} \langle S_\mathrm{A} S_\mathrm{A} | S_\mathrm{B} S_\mathrm{B} \rangle (1 + \mathrm{e}^{-\alpha_\mathrm{A} R_\mathrm{AB}} + \mathrm{e}^{-\alpha_\mathrm{B} R_\mathrm{AB}}) + \left(\frac{Z_\mathrm{A} Z_\mathrm{B}}{R_\mathrm{AB}}\right) \left(\sum_{k=1}^{n_\mathrm{gA}} a_{k_\mathrm{A}} \mathrm{e}^{-b_{k_\mathrm{A}} (R_\mathrm{AB} - c_{k_\mathrm{A}})^2} + \sum_{k=1}^{n_\mathrm{gB}} a_{k_\mathrm{B}} \mathrm{e}^{-b_{k_\mathrm{B}} (R_\mathrm{AB} - c_{k_\mathrm{B}})^2} \right) \quad (1)$$

where $\langle S_\mathrm{A} S_\mathrm{A} | S_\mathrm{B} S_\mathrm{B} \rangle$ is parameter GSS; α_A or α_B are ALP, a parameter representing the hardness of the lanthanide ion core; Z_A and Z_B are CORE, the core charges associated to nuclei A and B, respectively; R_AB is the interatomic distance between atoms or sparkles A and B; a_k, b_k and c_k

Table 1
Number of neodymium(III) complexes in the validation set, classified into each ligand group

Ligand group number	Ligand type	Number of structures
1	β-Diketone	2
2	Nitrate	18
3	Monodentate	9
4	Bidentate	6
5	Tridentate	7
6	Polydentate	12
7	Dineodymium	3

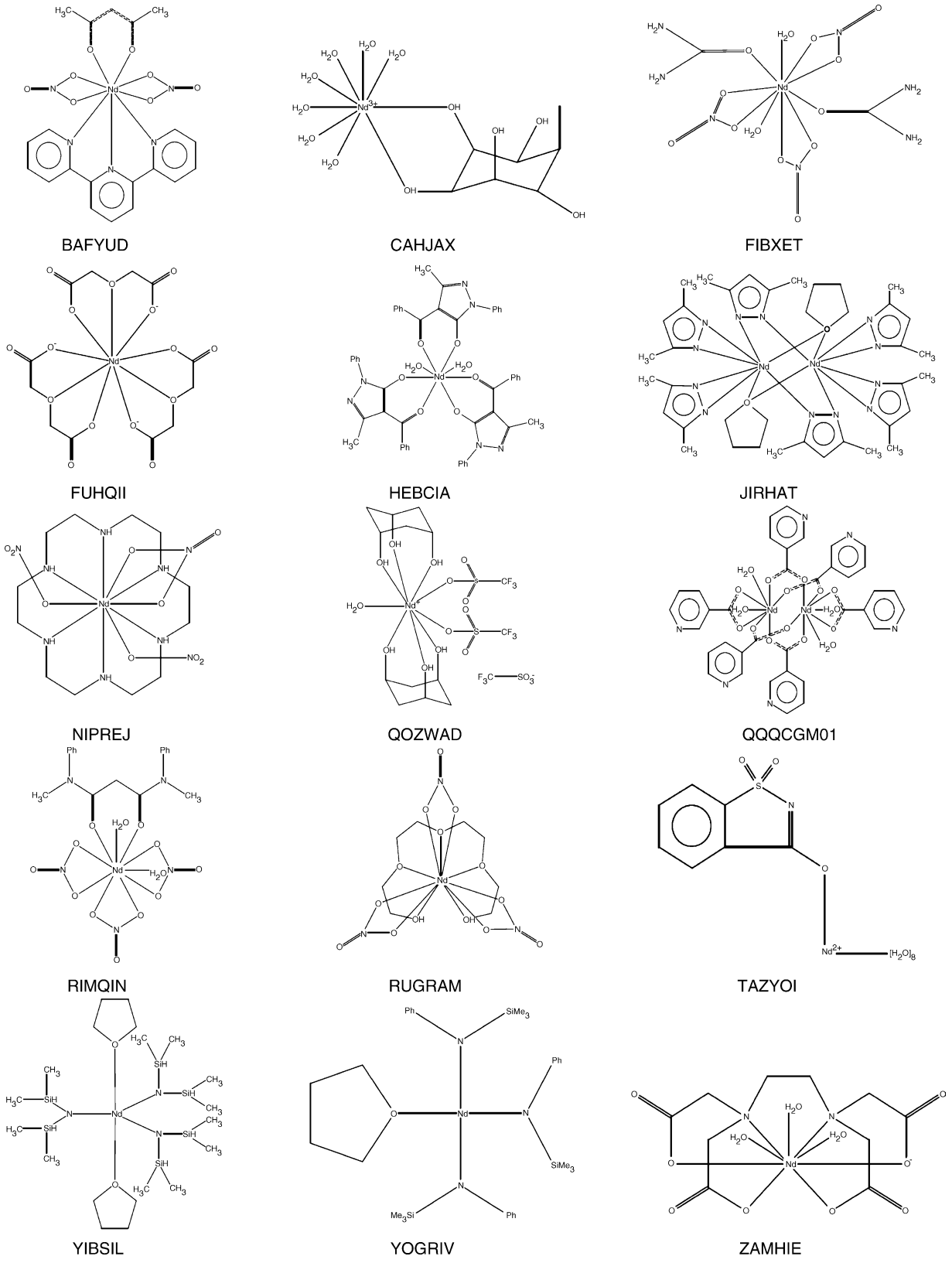

Fig. 1. Schematic two-dimensional representations of the neodymium(III) complexes, that constitute the parameterization training set, obtained from the Cambridge Structural Database [15–17].

are, respectively, the intensity, width and position of the kth Gaussian function, and, finally, n_{gA} and n_{gB} are the number of Gaussian functions centered in atoms A and B, respectively.

2. Results and discussion

The Sparkle/AM1 parameters obtained for neodymium(III) are shown in Table 2.

As for the case of Eu(III), Gd(III) and Tb(III), as accuracy measure, we used the average unsigned mean error for each complex i, UME_i, defined as:

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

where n_i is the number of ligand atoms directly coordinating the lanthanide ion. The total UME is obtained by running the summation of UME_is over all 57 complexes. Two cases have been examined: (i) UMEs involving the interatomic distances

Table 2
Parameters for the Sparkle/AM1 model for the Nd(III) ion

	Sparkle/AM1–Nd(III)
GSS	4.5002951307
ALP	57.6242766015
a_1	1.1206946050
b_1	6.8295606379
c_1	1.7859049866
a_2	0.1070369350
b_2	10.7894804795
c_2	3.1628661485

Table 3
Values of the coordination numbers, CNs, and unsigned mean errors, UMEs, for Sparkle/AM1, as compared to the respective experimental crystallographic values, obtained from the Cambridge Structural Database [15–17], for each of the 57 neodymium(III) complexes

Structure[a]	CN	UME (Å) sparkle model	Structure[a]	CN	UME (Å) sparkle model
ANTNND10 [23]	9	0.1676	OFONUS [51]	6	0.1161
BAFYUD [24]	9	0.1501	QAJHEO [52]	9	0.1518
BAWDIM10 [25]	10	0.1513	QAYWOC [53]	4	0.2849
BEXQIE [26]	11	0.2155	QOZVIK [54]	9	0.1990
BILSIY [27]	9	0.1229	QOZWAD [54]	9	0.1496
BUVWOE01 [28]	9	0.2833	QQQCGM01 [55]	8	0.1867
CAHJAX [29]	9	0.2714	QUBWOZ [56]	10	0.1540
CANBOI [30]	10	0.1769	RAMXAE [57]	9	0.2584
DODVAT [31]	10	0.1402	RICNOG [58]	11	0.1972
DUCMAP [32]	10	0.2244	RIJSEI [59]	5	0.2272
FAHFID [33]	10	0.2820	RIMQIN [60]	10	0.2306
FIBXET [34]	10	0.2843	RUGRAM [61]	11	0.1722
FUHQII [35]	9	0.1714	SOKBAV [62]	10	0.1655
GUHJAU [36]	10	0.1982	SOTXEE [63]	10	0.3352
HEBCIA [37]	8	0.3179	SUCRIR [64]	10	0.3000
HERWAC [38]	9	0.1843	SUXCAP [65]	9	0.1039
HOXNND01 [39]	12	0.1295	TAZYOI [66]	9	0.2657
JIRHAT [40]	8	0.0767	TUPYOS [67]	9	0.1907
KIHSAV [41]	10	0.0178	WEFVUY [68]	9	0.0769
LEJSUO [42]	8	0.3078	XIFMAA [69]	9	0.2089
LUDQIK [43]	8	0.0874	XIPKIQ [70]	8	0.3009
LUHSOW [44]	9	0.0198	XONYII [71]	9	0.0550
MINLIE [45]	7	0.1642	YENKOR [72]	9	0.2362
MIPTIO [46]	7	0.1254	YIBSIL [73]	5	0.1140
NATPAZ01 [47]	9	0.3045	YODYEV [74]	10	0.2101
NAVCIW [48]	8	0.1184	YOGRIV [75]	4	0.2205
NIPREJ [49]	10	0.0897	YURMUT [76]	11	0.1766
OBELUC [50]	9	0.1427	ZAMHIE [77]	9	0.3148
OFONIG [51]	6	0.1249			

[a] The structures are identified by their respective codes of reference from the Cambridge Structural Database 2003 [15–17].

Table 4
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, and all 57 Nd(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 [14]	0.1624	0.0848	0.0880	0.2170	0.0900	0.1900
Sparkle/AM1–Gd [14]	0.1830	0.0600	0.0735	0.2082	0.0658	0.1781
Sparkle/AM1–Tb [14]	0.2251	0.0754	0.0440	0.2123	0.0746	0.1823
Sparkle/AM1–Nd	0.1076	0.0781	0.0505	0.2141	0.0723	0.1858

Table 5
Sparkle/AM1 optimized geometry[a] of complex 1,4,7,10,13,16-hexa-azacyclo-octadecane-bis(nitrato-O)-(nitrato-O,O′)-neodymium, coded as NIPREJ in the Cambridge Structural Database [15–17]

Atom	*X*	*Y*	*Z*
Nd(III)	−0.0159433	0.0060842	−0.0133275
O	2.4922804	−0.0603331	−0.0592499
O	1.6704020	1.8627154	0.0688571
O	−1.9814357	−0.4703499	−1.4837155
O	−1.7410124	−1.0936868	1.4247633
N	−1.6500861	1.8015109	1.0054393
N	−0.6605779	1.9994808	−1.6093589
N	0.9581684	−0.0835102	−2.4764893
N	0.1653610	−2.4095476	−1.0453095
N	0.9553288	−1.8486045	1.5846227
N	0.5562481	0.7559783	2.4632809
O	3.7884092	1.6297364	0.0206576
O	−2.4049819	−2.0896942	−2.7576063
O	−3.6501865	−0.3536544	−2.7790521
O	−2.8400110	−2.3856290	2.6896521
O	−3.2186779	−0.2829604	2.6832849
N	2.6934705	1.1624312	0.0104212
N	−2.7181331	−0.9866749	−2.3572169
N	−2.6383478	−1.2717916	2.2823449
C	−2.2627222	2.7734009	0.0855054
C	−1.2563818	3.1947551	−1.0073099
C	0.3038173	2.3293599	−2.6599165
C	0.7547015	1.0494350	−3.3942477
C	0.7852152	−1.3517184	−3.2049062
C	0.9617067	−2.5607029	−2.2716079
C	0.4333535	−3.5300728	−0.1293905
C	1.4183038	−3.0999306	0.9795062
C	1.8433496	−1.3864262	2.6525090
C	1.2174329	−0.1816685	3.3857031
C	−0.4880900	1.5071219	3.1802280
C	−1.2246063	2.4758028	2.2403665
H	−2.6109015	3.7030423	0.6142219
H	−3.1620101	2.2980362	−0.4025118
H	−1.8012928	3.8247599	−1.7636325
H	−0.4273909	3.8109678	−0.5600803
H	1.1853985	2.8325851	−2.1703326
H	−0.1226269	3.0337956	−3.4272170
H	−0.0418566	0.7742974	−4.1434790
H	1.6945183	1.2894712	−3.9648553
H	1.5216418	−1.4492359	−4.0497320
H	−0.2592475	−1.3749037	−3.6346899
H	0.6637169	−3.4796894	−2.8507988
H	2.0436440	−2.6626053	−1.9752799
H	0.8728810	−4.4200409	−0.6583614
H	−0.5376909	−3.8564480	0.3433394
H	1.4895294	−3.9347676	1.7303957
H	2.4419213	−2.9206903	0.5468624
H	2.8235819	−1.0926332	2.1802774
H	2.0467383	−2.1868563	3.4171915
H	0.4544914	−0.5724758	4.1183357
H	2.0303192	0.3265939	3.9751078
H	−0.0597116	2.1025613	4.0331556
H	−1.2344303	0.7683733	3.5967014
H	−2.1016613	2.8952506	2.8091514
H	−0.5445014	3.3276896	1.9565931
H	−1.4121634	1.4581546	−2.0224457
H	1.9082054	−0.0545727	−2.1409670
H	−2.3434876	1.1025386	1.2491960
H	−0.8161085	−2.4254687	−1.3008194
H	0.0384291	−2.0216445	1.9819326
H	1.2411216	1.4220669	2.1419462

[a] The following quantities present in the MOPAC93r2 output may also be useful for checking purposes when validating the implementation of the Nd(III) Sparkle/AM1 model as explained in the appendix: heat of formation = −288.308 kcal mol^{-1}; electronic energy = −61107.640 eV; core–core repulsion = 54371.0870 eV; dipole = 10.338 D; and HOMO LUMO energies (eV) which are −10.881 and −0.157, respectively.

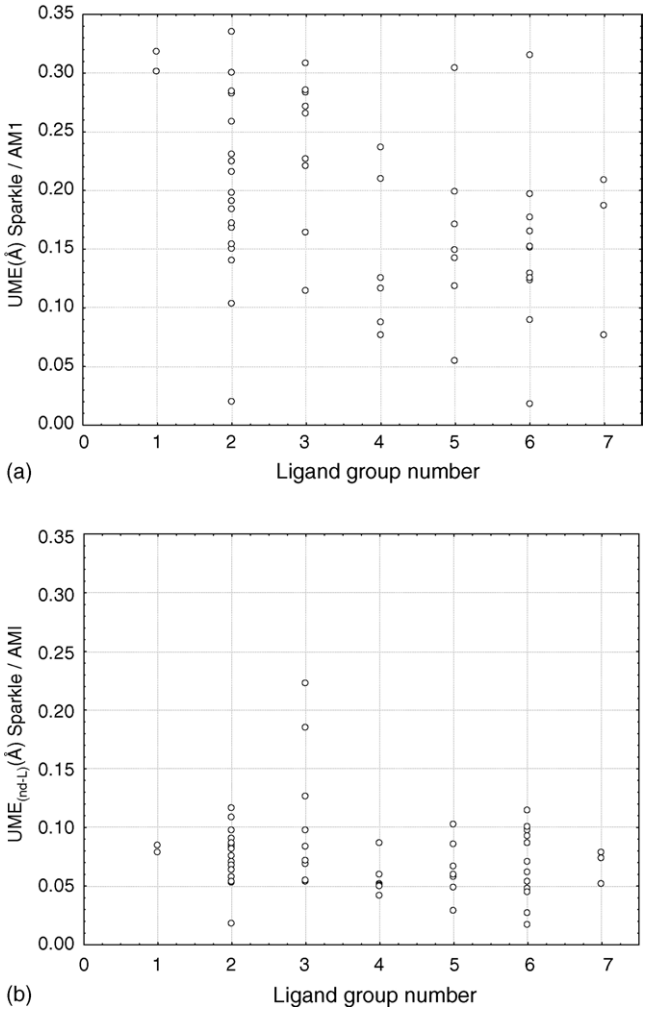

Fig. 2. Unsigned mean errors for each of the 57 neodymium(III) complexes, assembled according to the ligand group numbers defined in Table 1: (a) presents the UMEs and (b) presents the $UME_{(Nd–L)}$s. The same scale has been used in both to facilitate comparison.

R_j between the neodymium 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) $UME_{(Nd–L)}$s involving only the interatomic distances R_j between the neodymium central ion and the atoms of the coordination polyhedron, important to luminescent complex design.

Table 3 shows individual UMEs for all 57 complexes, and parts a and b of Fig. 2 show graphical representations of the UMEs and of the $UME_{(Nd–L)}$s for each of the complexes, grouped in each ligand group cluster defined by Table 1. As with Eu(III), Gd(III) and Tb(III), the lanthanide–ligand atom distances (Fig. 2, part b), important for luminescence research, are more accurately described than the whole coordination polyhedron, lanthanide included (Fig. 2, part a). And while part a presents a scattered plot up to 0.35 Å, part b indicates that most deviations fall below 0.10 Å. The average UME is 0.19 Å while the average $UME_{(Nd–L)}$ is 0.07 Å.

Table 4 presents Sparkle/AM1 unsigned mean errors for specific types of bond distances, not only for Nd(III) complexes but also for the previously published Eu(III), Gd(III) and Tb(III) complexes. Indeed, the same patterns that appear for previous ions are reproduced in the case of Nd(III), showing they are all comparable parameterizations.

Implementation of the Sparkle/AM1 model in MOPAC93r2 is relatively simple. In the appendix we explain how to modify the computer codes of the relevant subroutines. As a test case, we present in Table 5 the Sparkle/AM1 optimized geometry of the polydentate complex 1,4,7,10,13,16-hexa-azacyclo-octadecane-bis(nitrato-*O*)-(nitrato-*O*,*O*′)-neodymium, coded as NIPREJ in the Cambridge Structural Database [15–17], and shown in Fig. 1. To validate an implementation of the Sparkle/AM1 model for Nd(III) in mopac93r2, simply run a full geometry optimization of NIPREJ and confirm that the results are equal to those of Table 5.

3. Conclusion

Sparkle/AM1 assumes that the trivalent lanthanides behave like simple ions, with no stereochemical preference, and no angular effects from the f orbitals. The agreement between the predicted and observed complex coordination polyhedra strongly corroborates the soundness of this concept.

A quantum mechanical semiempirical model of lanthanide coordination compounds, now extended to Nd(III), is potentially very useful to all applications mentioned in the introduction. For structure–activity relationships, it is now possible to compute, for example, a series of reactivity indices [19], charges, bond orders, and so forth. In luminescence research, the energy levels of the lowest triplet states of the ligand system, in the complex, can be computed via INDO/S-CI [20–22]. Moreover, frequencies of the normal modes can also be calculated, and may prove useful in the assessment of possibilities of quenching. Moreover, Sparkle/AM1 calculations are indeed much faster than ab initio/ECP calculations: a few hundred times faster than STO-3G/ECP, one thousand times faster than STO-3G/3-21G, and several thousand times faster than 6-31G*/ECP [14]. And the accuracy of the ab initio/ECP coordination polyhedron is indeed comparable to the Sparkle/AM1 ones [14]. In short, many possibilities open up for scientists involved in complex design when, sometimes, it may be important to evaluate a series of different ligands in a combinatorial manner, which Sparkle/AM1 now makes feasible.

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Appendix A

To implement the sparkle model for Nd(III) in the software package MOPAC93r2, we followed a procedure previously described in the supplementary information of Freire et al. [14], where only one lanthanide ion is implemented at a time via modifications in subroutines block.f, calpar.f and rotate.f. Since position 103 of MOPAC's various arrays is used to define the original MOPAC +2e sparkle, we decided to use it to define our sparkle representing the Neodymium ion: Nd(III). As such, we changed the sparkle core charge, CORE(103), from +2e to +3e.

The heat of formation of the neodymium(III) ion was obtained by adding to the heat of atomization of neodymium [78], its first three ionization potentials, yielding 962.8 kcal mol^{-1}, which was assigned to EHEAT(103). Finally, the atomic mass of Nd(III) was set at 144.24 amu [78], which was assigned to AMS(103).

In order to facilitate the implementation, we will present below the parts of subroutines Block.f, Calpar.f and Rotate.f, both before and after the changes that need to be made to implement the Nd(III) sparkle, together with both dat and arc files for two representative complexes.

Upon implementing the code, simply use the geometry present in Table 5 for the Nd(III) complex NIPREJ as input data. Since this geometry is already optimized, reoptimizing it should not alter it significantly, serving as an indication that the Nd(III) Sparkle/AM1 implementation is correct.

Appendix B. Relevant parts of the original Mopac93r2 subroutines

Block.f (original)

```
      BLOCK DATA
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      COMMON /NATORB/ NATORB(107)
     ...
     9 'Au','Hg','Tl','Pb','Bi','Po','At','Rn',
     1 'Fr','Ra','Ac','Th','Pa',' U','Np','Pu','Am','Cm','Bk','Cf','XX',
     2 'Fm','Md','Cb','++',' +','--',' -','Tv'/
C
C   NATORB IS THE NUMBER OF ATOMIC ORBITALS PER ATOM.
     ...

     4196.9665D0, 200.5900D0, 204.3700D0, 207.2000D0, 208.9804D0,
     518*0.000D0,   1.0079D0, 5*0.000D0/
C
C   CORE IS THE CHARGE ON THE ATOM AS SEEN BY THE ELECTRONS
     ...

     1 3.D0,4.D0,5.D0,6.D0,7.D0,0.D0,
     2  15*0.D0,1.D0,2.D0,1.D0,-2.D0,-1.D0,0.D0/
C
C     ENTHALPIES OF FORMATION OF GASEOUS ATOMS ARE TAKEN FROM \ANNUAL
     ...

************************************************************
*               DATA FOR THE SPARKLES                      *
************************************************************
*                               DATA FOR THE " ++ " SPARKLE
      DATA EHEAT(103)    / 0.0D0/
      DATA VS(103)       /10.0D0/
   ...
      DATA GSSPM3(102)/      12.8480000D0/
      DATA HSPPM3(102)/       0.1000000D0/
      END
```

Calpar.f (original)

```
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      COMMON /ONELEC/ USS(107),UPP(107),UDD(107)
     ...
   40 CONTINUE
      EISOL(1)=USS(1)
      AM(1)=GSS(1)/ENRGY
      AD(1)=AM(1)
     ...
   60    FORMAT(1H ,1X,'OUTPUT INCLUDES DEBUG INFORMATION',//)
   70    CONTINUE
      RETURN
      END
```

Rotate.f (original)

```
      SUBROUTINE ROTATE (NI,NJ,XI,XJ,W,KR,E1B,E2A,ENUC,CUTOF2)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
    ...

         IF(NATORB(NJ).GT.3) THEN
            E2A(2) = -CSP2 *X(1)
            E2A(3) = -CPPS2*XX11-CPPP2*YYZZ11
            E2A(4) = -CSP2 *X(2)
            E2A(5) = -CPPS2*XX21-CPPP2*YYZZ21
            E2A(6) = -CPPS2*XX22-CPPP2*YYZZ22
            E2A(7) = -CSP2 *X(3)
            E2A(8) = -CPPS2*XX31-CPPP2*ZZ31
            E2A(9) = -CPPS2*XX32-CPPP2*ZZ32
            E2A(10)= -CPPS2*XX33-CPPP2*ZZ33
         END IF
         IF(ABS(TORE(NI)).GT.20.D0.AND.ABS(TORE(NJ)).GT.20.D0) THEN
C SPARKLE-SPARKLE INTERACTION
            ENUC=0.D0
            RETURN
         ELSEIF (RIJ.LT.1.D0.AND.NATORB(NI)*NATORB(NJ).EQ.0) THEN
            ENUC=0.D0
            RETURN
         ENDIF
         SCALE = EXP(-ALP(NI)*RIJ)+EXP(-ALP(NJ)*RIJ)
C
         IF (NI.EQ.24.AND.NJ.EQ.24) THEN
            SCALE = EXP(-ALPTM(NI)*RIJ)+EXP(-ALPTM(NJ)*RIJ)
         ENDIF
   ...

         IF(NATORB(NI)*NATORB(NJ).EQ.0)KI=0
         KR=KR+KI
      ENDIF
      RETURN
      END
```

Appendix C. Sparkle/AM1 model modified subroutines for Nd(III)—modifications in bold

Block.f for Nd(III)

```
      BLOCK DATA
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      COMMON /NATORB/ NATORB(107)
    ...

     9 'Au','Hg','Tl','Pb','Bi','Po','At','Rn',
     1 'Fr','Ra','Ac','Th','Pa',' U','Np','Pu','Am','Cm','Bk','Cf','XX',
     2 'Fm','Md','Cb','++',' +','--',' -','Tv'/
C
C   NATORB IS THE NUMBER OF ATOMIC ORBITALS PER ATOM.
    ...

     4196.9665D0, 200.5900D0, 204.3700D0, 207.2000D0, 208.9804D0,
     518*0.000D0,   1.0079D0, 144.2400D0, 4*0.000D0/
C
C   CORE IS THE CHARGE ON THE ATOM AS SEEN BY THE ELECTRONS
    ...

     1 3.D0,4.D0,5.D0,6.D0,7.D0,0.D0,
     2  15*0.D0,1.D0,3.D0,1.D0,-2.D0,-1.D0,0.D0/
C
C     ENTHALPIES OF FORMATION OF GASEOUS ATOMS ARE TAKEN FROM \ANNUAL
    ...

************************************************************
*               DATA FOR THE SPARKLES                      *
************************************************************
*                              DATA FOR THE " ++ " SPARKLE
      DATA EHEAT(103)    / 962.8D0/
      DATA VS(103)       /10.0D0/
   ...

       DATA ALPAM1(103)   / 4.5002951307D0/
       DATA GSSAM1(103)  / 57.6242766015D0/
       DATA GUESA1(103,1) / 1.1206946050D0/
       DATA GUESA2(103,1) / 6.8295606379D0/
       DATA GUESA3(103,1) / 1.7859049866D0/
       DATA GUESA1(103,2) / 0.1070369350D0/
       DATA GUESA2(103,2) / 10.7894804795D0/
       DATA GUESA3(103,2) / 3.1628661485D0/
   ...

      DATA GSSPM3(102)/      12.8480000D0/
      DATA HSPPM3(102)/       0.1000000D0/
      END
============================================================
```

Calpar.f for Nd(III)

```
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      COMMON /ONELEC/ USS(107),UPP(107),UDD(107)
    ...
   40 CONTINUE
      EISOL(1)=USS(1)
      AM(103)=GSS(103)/ENRGY
      AM(1)=GSS(1)/ENRGY
      AD(1)=AM(1)
     ...
   60    FORMAT(1H ,1X,'OUTPUT INCLUDES DEBUG INFORMATION',//)
   70    CONTINUE
      RETURN
      END
```

Rotate.f for Nd(III)

```
      SUBROUTINE ROTATE (NI,NJ,XI,XJ,W,KR,E1B,E2A,ENUC,CUTOF2)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
    ...
         IF(NATORB(NJ).GT.3) THEN
            E2A(2) = -CSP2 *X(1)
            E2A(3) = -CPPS2*XX11-CPPP2*YYZZ11
            E2A(4) = -CSP2 *X(2)
            E2A(5) = -CPPS2*XX21-CPPP2*YYZZ21
            E2A(6) = -CPPS2*XX22-CPPP2*YYZZ22
            E2A(7) = -CSP2 *X(3)
            E2A(8) = -CPPS2*XX31-CPPP2*ZZ31
            E2A(9) = -CPPS2*XX32-CPPP2*ZZ32
            E2A(10)= -CPPS2*XX33-CPPP2*ZZ33
         END IF
         If (ni.eq.103 .and. nj.eq.103) goto 39
         IF(ABS(TORE(NI)).GT.20.D0.AND.ABS(TORE(NJ)).GT.20.D0) THEN
C SPARKLE-SPARKLE INTERACTION
            ENUC=0.D0
            RETURN
         ELSEIF (RIJ.LT.1.D0.AND.NATORB(NI)*NATORB(NJ).EQ.0) THEN
            ENUC=0.D0
            RETURN
         ENDIF
39       Continue
         SCALE = EXP(-ALP(NI)*RIJ)+EXP(-ALP(NJ)*RIJ)
         IF (NI.EQ.24.AND.NJ.EQ.24) THEN
            SCALE = EXP(-ALPTM(NI)*RIJ)+EXP(-ALPTM(NJ)*RIJ)
         ENDIF
    ...
         IF(NATORB(NI)*NATORB(NJ).EQ.0)KI=0
         KR=KR+KI
      ENDIF
      RETURN
      END
```

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