

# Dalton Transactions

Accepted Manuscript



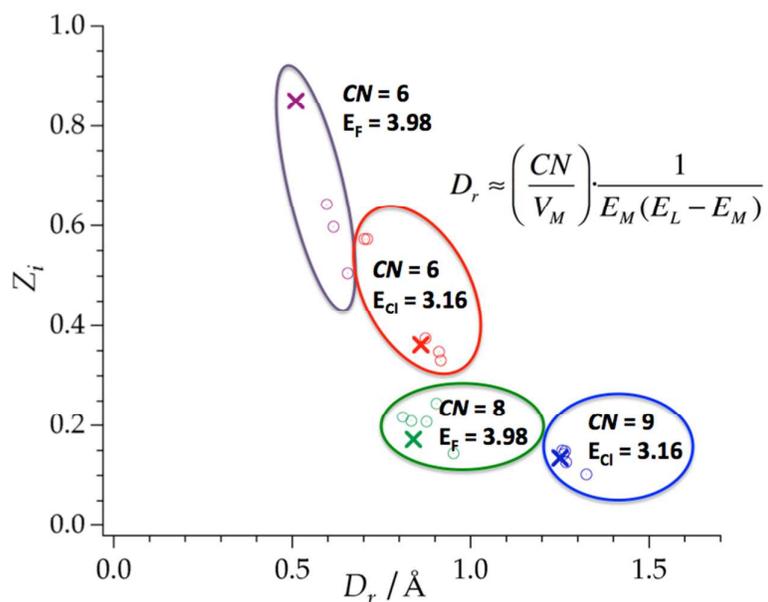
This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*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. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it 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.

The Radial Effective Charge model has proven useful in the study of the magnetic properties of lanthanide single ion magnets. But do its effective charge parameters have any physical meaning? Here we relate radial displacement ( $D_r$ ) and effective charge ( $Z_i$ ) with chemical factors such as coordination numbers  $CN$ , valence  $V_M$  and electronegativities  $E_M, E_L$ .





## Modeling the magnetic properties of lanthanide complexes: relation of the REC parameters with Pauling electronegativity and coordination number

Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

José J. Baldoví,<sup>a</sup> Alejandro Gaita-Ariño<sup>a,\*</sup> and Eugenio Coronado<sup>a</sup>

www.rsc.org/

**In a previous work, we introduced the Radial Effective Charge (REC) model to study the magnetic properties of lanthanide single ion magnets. Now, we perform an empirical determination of the effective charges ( $Z_i$ ) and radial displacements ( $D_r$ ) of this model using spectroscopic data. This systematic study allows us to relate  $D_r$  and  $Z_i$  with chemical factors such as the coordination number and the electronegativities of the metal and the donor atoms. This strategy is being used to drastically reduce the number of free parameters in the modeling of the magnetic and spectroscopic properties of  $f$ -element complexes.**

The unique spectroscopic and magnetic properties of lanthanide ions have excited researchers for decades.<sup>1</sup> These systems present a more complex and intricate spectra than those of transition metals, which are characterized by a few broad bands. In this context, crystal-field theory is essential to analyze and simulate the energy level schemes of  $f$ -element complexes,<sup>2</sup> providing an accuracy level of about  $10 \text{ cm}^{-1}$ .<sup>3,4,5</sup> The determination of the crystal field parameters (CFPs) is a fundamental problem in solid state physics materials. The CFPs can be deduced from a direct fit of UV/visible spectroscopic experimental data.<sup>6</sup> Also, information about the lower lying magnetic levels can be obtained from the far infrared (FIR)<sup>7</sup> or from inelastic neutron scattering (INS) spectra.<sup>8</sup> In any case, the fitting procedures need a trial set of non-zero CFPs, while the rest of the CFPs are set to zero because of the idealized symmetry of the complex, this strategy is valid for simple salts. However, when dealing with molecular systems, this strategy requires the determination of a large number of CFPs, resulting in overparametrization. In these cases, the idealization of the chemical structure is often unreasonable and this constitutes an open problem. Since such procedures involve a function of many variables which have to be fitted, starting from a good trial set of CFPs is necessary in order to

reach good convergence with a minimum of error.<sup>9</sup> This initial set of CFPs can be calculated from the real structure of the compounds using Complete Active Space *ab initio* calculations<sup>10</sup> or, more inexpensively, by a simple point-charge electrostatic model (PCEM).<sup>11</sup> This latter approach, due to its inherent limitations, was subsequently improved by several *semiempirical* models.<sup>12,13,14,15,16,17</sup>

In this context, we developed the Radial Effective Charge (REC) model in 2012, modeling the effect of the ligating atom through an effective charge situated along the lanthanoid-donor atom axis.<sup>18</sup> The REC model has become very useful for quick predictions of the magnetic properties and for obtaining an initial set of CFPs and has been applied with success to a large variety of  $f$ -element complexes with interesting optical<sup>19</sup> and magnetic properties<sup>20</sup>. This approximation also needs parameterization to provide a more realistic description of the properties. By taking into account covalency, it relies on two parameters, namely the radial displacement ( $D_r$ ) and the effective charge ( $Z_i$ ), that are obtained from a direct fit of the experimental spectroscopic and/or magnetic properties. The predictive power of this approach was recently demonstrated in a series of isostructural polyoxometalates,<sup>21</sup> suggesting the idea of the utility of building a general library for the inexpensive rationalization of the properties of rare earth compounds. Nevertheless, it is not clear whether these effective parameters really are transferrable between different complexes, independently of the coordination number.

In this communication, we perform a systematic application of the REC model to a series of later lanthanide ions in crystal hosts. We have chosen four families that present a lanthanoid ion coordinated by halides: fluorides and chlorides, as model systems. The spectroscopic studies<sup>22</sup> and the CFPs determination that have been carried out on these systems permit us to obtain reliable  $D_r$  and  $Z_i$  parameters. The general formula of the studied lanthanide ions in crystal hosts are:  $\text{Cs}_2\text{NaYCl}_6\cdot\text{Ln}^{3+}$  (Cl6),  $\text{LaCl}_3\cdot\text{Ln}^{3+}$  (Cl9) and  $\text{LiYF}_4\cdot\text{Ln}^{3+}$  (F8), where Ln = Tb, Dy, Ho, Er and Tm, and the isostructural family,  $\text{Cs}_2\text{NaYF}_6\cdot\text{Ln}^{3+}$  (F6), in which the data of Ho and Er compounds is used in the fit. We extract the REC parameters using two

<sup>a</sup> Instituto de Ciencia Molecular (ICMol), Universidad de Valencia, C/Catedrático José Beltrán 2, E-46980 Paterna, Spain.

† Footnotes relating to the title and/or authors should appear here. Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

different procedures in modified versions of the SIMPRE package.<sup>23</sup> The first one consists on the fitting of the ground multiplet energy level scheme for each lanthanoid. For the description of the whole series, a second step is the collective fit: we obtain the best combination of  $D_r$  and  $Z_i$  with minimum mean squared error. In addition, the phenomenological CFPs of each lanthanide complex involved in this study are directly fitted. Results of the calculations concerning CFPs and energy levels are compared with the phenomenological CFPs and spectroscopic energy levels and reported as Supporting Information.

The results of every individual fit, taken together with the collective fits for each family, reveal at first glance some trends that can be related both with the Pauling electronegativities of the ligands and with the coordination numbers (see fig. 1). For instance, for a given coordination number (CN), e.g.  $CN=6$ ,  $D_r$  is higher for the ligand with a lower electronegativity ( $E_{Cl} < E_F$ ). Additionally, for a given donor atom,  $D_r$  is higher for a higher coordination number. This is verified both for  $F^-$  and  $Cl^-$ . This means that as far as the coordination number increases, the effective charge is placed closer to the lanthanoid. On the other hand, a more electronegative donor atom will retain the effective charge a bit further respect to the rare earth ion, resulting in a less covalent coordination bond.

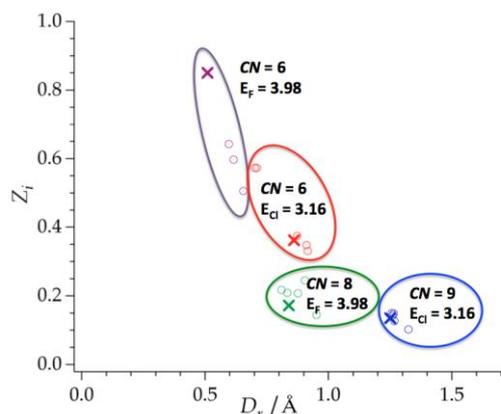


Figure 1.  $D_r$  and  $Z_i$  parameters obtained for each CFPs individual fit (open circles), collective fitting of the energy levels (cross) for the families Cl6 (red), F8 (green), Cl9 (blue) and F6 (purple).

Previous efforts in this field (see for example ref. 17) attempted to find relatively simple relations between some kind of effective charge parameters and chemical concepts such as the coordination number or the electronegativity. In the light of present data, a careful analysis of the collective fit numerical data results in the following approximate relation between the radial displacement ( $D_r$ ), the coordination number (CN), the valence of the metal ( $V_M$ ) and the Pauling electronegativities of the ligand and of the metal ( $E_L$  and  $E_M$ , respectively):

$$D_r \approx \left( \frac{CN}{V_M} \right) \frac{1}{E_M(E_L - E_M)} \quad (1)$$

We have arrived to this expression taking advantage of the fact that  $E_L - E_M$  is inversely related to the degree of covalency

of a chemical bond. Table 1 allows a comparison between the approximation offered by equation 1 and the collective fit of the ground multiplet energy level scheme of each family. The thus calculated energy levels, which is the standard and recommended procedure of the REC model, are compared with the experiment in figs. SI6-SI9. The diagonal calculated CFPs are compared with the phenomenological ones, which are extracted from the experiment, in figs. SI10-SI12. Also, in Table 1, the averages of the  $D_r$  obtained within the individual fits of the four families, based on ground multiplet energy levels and crystal field parameters, are reported.

Table 1.  $D_r$  estimated either from equation 1, by a collective fit of each family or as an average of the individual fits of the energy levels and of the CFPs. (\*): see text.

	$D_r$ (Å)			
	Eq. 1	Collective fit	Fit energy levels (ave.)	Fit CFPs (ave.)
F6	0.6	0.51 (*)	0.57 (*)	0.57 (*)
F8	0.8	0.84	0.81	0.88
Cl6	0.85	0.86	0.90	0.85
Cl9	1.28	1.25	1.24	1.27

As can be observed, the agreement is reasonable for the four families. Note that for the F6 family, marked with (\*) in Table 1, the collective fit uses only the data of  $Ho^{3+}$  and  $Er^{3+}$ , and this value is expected to change if we take into account more derivatives.

Regarding the obtained effective charges of these complexes, an inverse proportional relation respect to the  $D_r$  values may be observed in both fluoride and chloride-based families (fig. 2 and SI5). This is indeed a general trend in all the systems fitted using this model: as far as the effective charge is getting closer to the lanthanoid ion, its value decreases (figs. SI1-SI4). The reason for this is obvious: if a solution is already in the right parameter region, pushing the charges closer to the metals and simultaneously rising their effective values will produce a completely incorrect total CF splitting. In fig. 2, we have plotted the individual  $D_r$  and  $Z_i$  values obtained when fitting the ground multiplet CF splitting, the ones obtained when fitting the CFPs directly and the lowest relative error combination that describes the ground multiplet energy levels of the whole series. As an approximation, the following relation can be extracted:

$$f_{X,CN} = D_r \cdot Z_i \quad (2)$$

where  $f$  is a factor which depends on the coordination number and on the coordinated atom (X).

The resulting values of  $f_{X,CN}$  are calculated using the REC parameters of the collective fit. Such values are:  $f_{F,6}$  ( $CN=6$ ) = 0.434,  $f_{F,8}$  ( $CN=8$ ) = 0.144,  $f_{Cl,6}$  ( $CN=6$ ) = 0.311 and  $f_{Cl,8}$  ( $CN=9$ ) = 0.169. For the two families coordinated by chlorides, the relation  $Z_i = f_{Cl} / D_r$  is calculated keeping the averaged  $f_{Cl} = (f_{Cl,6} + f_{Cl,9}) / 2$  constant. This function is represented by the dashed black line in fig. 2. For F6 and F8, the function  $Z_i = f_F / D_r$  is plotted in fig. SI5.

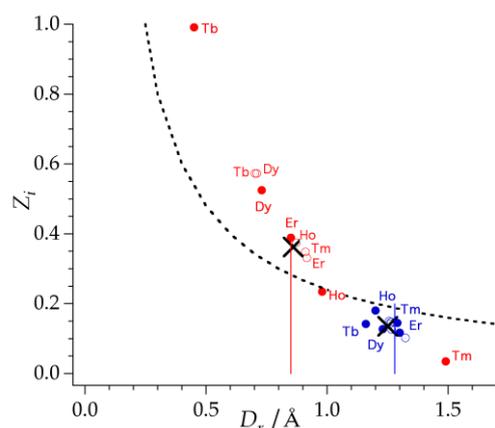


Figure 2. Radial displacement ( $D_r$ ) and effective charge ( $Z_i$ ) values obtained fitting the ground multiplet energy levels (circles) and crystal field parameters (open circles);  $\text{Cs}_2\text{NaYCl}_6\text{:Ln}^{3+}$  (red) and  $\text{LaCl}_3\text{:Ln}^{3+}$  (blue). Collective fit (black cross). Dashed line: function  $Z_i = f_c/D_r$ ; vertical lines:  $D_r$  from equation 1.

The relations 1 and 2 presented in this communication allow an initial estimation of the CFPs, energy levels, magnetic and optical properties for homoleptic later lanthanide complexes. They can be especially useful to obtain an initial trial of CFPs for spectroscopic studies in  $f$ -element complexes using the full hamiltonian. Also, the REC parameters obtained can be used as initial values for  $D_r$  and  $Z_i$  in the fitting procedures when modeling the properties of this kind of systems in an inexpensive way.

For perspective, let us compare the approximations presented in equations 1 and 2 with previous efforts towards this direction. There are several similarities between the estimation of the effective charge of ref. 17, where a modified point-charge model is presented, and the present one, namely, the effective charge:

- is directly proportional to the valence of the metal
- is inversely proportional to the number of ligands
- goes to zero as the electronegativity of the ligand approaches the electronegativity of the metal
- can be written as a negative number plus a term that depends linearly on the electronegativity of the ligand.

Furthermore, in a recent work by Tanner et al.,<sup>24</sup> (c) is exactly true and (d) is approximately true if one considers small differences in electronegativity, as one then can look at the linear approximation of a negative Gaussian function. As ref. 24 considers a constant radius depending only on the metal ion, it also supports the proportionality between  $D_r$  and  $CN$ : crystallographic radii increase with the coordination number, thus a rising radial displacement is needed to compensate for this if an invariant effective radius is to be obtained.

In summary, we have used 18 different compounds, grouped in four isostructural families, to extract two equations that allow an estimation of the Radial Effective Charge model parameters. These equations not only give satisfactory parameters for the halide complexes presented in this work, they have already been used in two challenging systems where the lanthanoid ion is coordinated by oxygen<sup>25</sup> and nitrogen<sup>26</sup> atoms. Thus, they are expected to be a very useful tool to address the widespread need for an inexpensive estimation of

a starting parameter set in more sophisticated CF determinations, as well as a route for an inexpensive qualitative prediction of the magnetic properties of  $f$ -block compounds.

## Acknowledgements

The present work has been funded by the EU (ERC Advanced Grant SPINMOL and ERC Consolidator Grant DECRESIM), the Spanish MINECO (grant MAT2011-22785, MAT2014-56143-R, CTQ2014-52758-P), and the Generalitat Valenciana (Prometeo and ISIC Programmes of excellence). A.G.-A. acknowledges funding by the MINECO (Ramón y Cajal contract). J.J.B. thanks the Spanish MINECO for an FPU predoctoral grant.

## Notes and references

- J.-C. G. Bünzli, *Acc. Chem. Res.*, **2006**, *39*(1),53–61
- D. J. Newman, *Advances in Physics*, 1971, *20*(84), 197-256.
- Morrison, C.A., & Leavitt, R.P. (1982). *Spectroscopic properties of triply ionized. Handbook on the physics and chemistry of rare earths*, *5*, 461-692
- C.-K. Duan, P.A. Tanner, *J. Phys. Chem. A* 2010, *114*, 6055-6062
- K.A. Schoene, J.R. Quagliano, F.S. Richardson, *Inorg. Chem.* 1991, **30**, 3803-3812
- W.T. Carnall, P.R. Fields and B.G. Wybourne, *J. Chem. Phys.* 1965, *42*, 3797.
- R. Marx, F. Moro, M. Dörfel, L. Ungur, M. Waters, S. D. Jiang, M. Orlita, J. Taylor, W. Frey, L. F. Chibotaru and J. van Slageren, *Chem. Sci.*, 2014, **5**, 3287-3293.
- K. S. Pedersen, L. Ungur, M. Sigrist, A. Sundt, M. Schau-Magnussen, V. Vieru, H. Mutka, S. Rols, H. Weihe, O. Waldmann, L. F. Chibotaru, J. Bendix and J. Dreiser, *Chem. Sci.*, 2014, **5**, 1650-1660.
- J. van Leusen, M. Speldrich, H. Schilder and P. Kögerler, *Coord. Chem. Rev.* 2014, DOI:10.1016/j.ccr.2014.10.011.
- L. F. Chibotaru and L. Ungur, *J Chem Phys*, 2012, 137.
- H. Bethe, *Ann. Phys.-Berlin*, 1929, **3**, 133-208.
- P. Porcher, M. C. Dos Santos and O. Malta, *Phys. Chem. Chem. Phys.*, 1999, **1**, 397-405.
- W. Urland, *Chem. Phys.*, 1976, **14**, 393-401.
- C. K. Jorgensen, R. Pappalardo and H. H. Schmidtke, *J. Chem. Phys.*, 1963, **39**, 1422-1430.
- O. L. Malta, *Chem. Phys. Lett.*, 1982, **87**, 27-29.
- O. L. Malta, *Chem. Phys. Lett.*, 1982, **88**, 353-356.
- Z. Zolnierak, *J. Phys. Chem. Solids*, 1984,*45*(5), 523-528
- J. J. Baldoví, J. J. Borrás-Almenar, J. M. Clemente-Juan, E. Coronado and A. Gaita-Ariño, *Dalton T.*, 2012, **41**, 13705-13710.

- 19 M.A. Hughes, M.A. Lourenço, J.D. Carey, B. Murdin, K.P. Homewood, *Optics express*, 2014, 22(24), 29292-29303.
- 20 (a) J.J. Baldoví, S. Cardona-Serra, J.M. Clemente-Juan, E. Coronado, A. Gaita-Ariño, *Chem. Sci.*, 2013, 4 (3), 938-946; (b) J.J. Baldoví, J.M. Clemente-Juan, E. Coronado, A. Gaita-Ariño *Polyhedron*, 2013, 66, 39-42; (c) J.J. Baldoví, E. Coronado, A. Gaita-Ariño, C. Gamer, M. Giménez-Marqués, G. Mínguez Espallargas, *Chem. Eur. J.*, 2014, 20(34), 10695-10702; (d) B. Monteiro, J.T. Coutinho, C.C.L. Pereira, L.C.J. Pereira, J. Marçalo, M. Almeida, J.J. Baldoví, E. Coronado, A. Gaita-Ariño, *Inorg. Chem.*, 2015, 54 (4), 1949-1957; (e) K.Qian, J.J. Baldoví, S.-D. Jiang, A. Gaita-Ariño, Y.-Q. Zhang, J. Overgaard, B.-W. Wang, E. Coronado, S. Gao, *Chem. Sci.*, 2015, *Accepted manuscript*.
- 21 J.J. Baldoví, J.M. Clemente-Juan, E. Coronado, Y. Duan, A. Gaita-Ariño and C. Giménez-Saiz, *Inorg. Chem.*, 2014, 53(18), 9976-9980.
- 22 (a) C.K. Jayasankar, F.S. Richardson and M.F. Reid, *J. Less-Common Metals*, 1989, 148, 289-296; (b) C.K. Jayasankar, M.F. Reid and F.S. Richardson, *Phys. Stat. Sol.*, 1989, 155, 559; (c) G.K. Liu, W.T. Carnall, R.P. Jones, R.L. Cone, J. Huang, *J. Alloys and Compounds*, 1994, 207/208, 69-73; (d) P.A. Tanner, V.V. Ravi Kanth Kumar, C.K. Jayasankar, M.F. Reid, *J. Alloys and Compounds*, 1994, 215, 349-370; (e) P.A. Tanner, M.D. Faucher, X. Zhou, *J. Phys. Chem. A*, 2011, 115, 2557-2567; (f) X. Zhou, P.A. Tanner, M.D. Faucher, *J. Phys. Chem. C*, 2007, 111, 683-687; (g) P.A. Tanner, M.D. Faucher, *Chem. Phys. Lett.*, 2007, 445, 183-187.
- 23 (a) J. J. Baldoví, S. Cardona-Serra, J. M. Clemente-Juan, E. Coronado, A. Gaita-Ariño and A. Palii, *J Comput Chem*, 2013, 34, 1961-1967. (b) J. J. Baldoví, J. M. Clemente-Juan, E. Coronado, A. Gaita-Ariño and A. Palii, *J Comput Chem*, 2014, 35(26), 1930-1934.
- 24 P.A. Tanner, L. Ning, *J. Phys. Chem. A*, 2013, 117, 1503-1507
- 25 J.J. Baldoví, Y. Duan, R. Morales, A. Gaita-Ariño, E. Ruiz, E. Coronado, *submitted*
- 26 M.A. Antunes, J.T. Coutinho, I.C. Santos, J. Marçalo, L.C.J. Pereira, M.Almeida, J.J. Baldoví, A. Gaita-Ariño, E. Coronado, *submitted*