Inorganic Chemistry
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Molecular Anisotropy Analysis of Single-Ion Magnets Using an Effective Electrostatic Model

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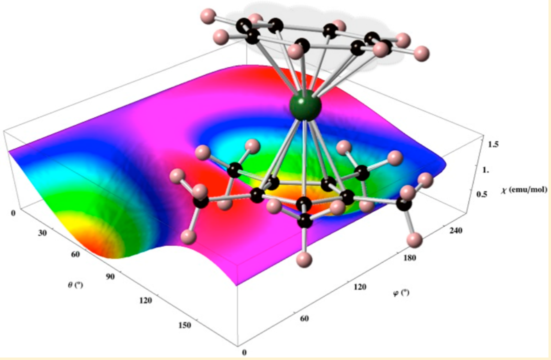
S Supporting Information

ABSTRACT: Simple electrostatic models have been shown to successfully rationalize the magnetic properties of mononuclear single molecule magnets based on f-elements and even to predict the direction of the magnetic anisotropy axis in these nanomagnets. In this Article, we go a step forward by showing that these models, conveniently modified to account for the covalency effects, are able to predict not only the easy axis direction but also the three components of the magnetic anisotropy. Thus, by using a lone pair effective charge (LPEC) model we can fully reproduce the angular dependence of the magnetic susceptibility in single crystals of pentamethylcyclopentadienyl-Er-cyclooctatetraene single-ion magnet. Furthermore, the parametrization of the ligands obtained in this study has been extrapolated to successfully reproduce spectroscopic data of a set of mononuclear lanthanoid complexes based on the same kind of ligands, thus emphasizing the predictive character of this model.



■ INTRODUCTION

For more than two decades single molecule magnets (SMMs) have been a hot topic in the field of molecular magnetism due to their rich physical behavior.[1] These systems are among the most complex magnetic entities, showing slow relaxation of the magnetization and magnetic hysteresis at low temperatures, together with quantum phenomena like quantum tunneling of the magnetization,[2] quantum coherence, or quantum interference.[3] A remarkable advance in this field appeared in 2003 when the possibility of observing such features in mononuclear lanthanoid complexes was demonstrated by Ishikawa et al. in a family of complexes of general formula $[Ln(Pc)_2]^-$, in which a lanthanoid ion is sandwiched between two phthalocyanine moieties.[4] Since 2008, when we published the second family of mononuclear SMMs,[5] also known as single-ion magnets (SIMs), the impact of this class of molecular nanomagnets dramatically increases, and now hundreds of SIMs have been reported.[6−8]

In contrast with the classical polynuclear SMMs, whose properties are governed by exchange interactions, in lanthanide-based molecular nanomagnets magnetic exchange is usually irrelevant. In this case, the electronic spectrum and thus the magnetic properties depend primarily on the magnetic anisotropy resulting from the crystal field splitting, and secondarily on hyperfine coupling. As a consequence, a fairly complex crystal field Hamiltonian (H_{CF}) must be properly defined for a full theoretical description of these systems. To rationalize the magnetic behavior we recently developed a general theoretical approach that determines the effect of the crystal field on both the splitting of the J ground state and the mixing of the resulting magnetic levels, providing at the same time an indication of the leading anisotropy parameters that control such a splitting/mixture.[9] A realistic description of the lowest energy sublevels and their wave functions with extrapolable ligand effect parameters may help in describing their magnetic properties and guiding the discovery of new derivatives. Moreover, such a description will permit researchers to deal with the potential application of these systems as spin qubits in quantum computing.[10]

For the study of the CF splitting in lanthanide-based nanomagnets, there are currently several alternatives. The original method of Ishikawa employed both powder susceptibility and ^{1}H NMR data, thus ensuring the correct orientation of the anisotropy axis, but was later applied to other systems relying merely on χT data.[11] It is now widely recognized that a major shortcoming of this approach was to assume a linear dependence of the diagonal parameters on the number of f-electrons. Post-Hartree−Fock calculations have been the default option for the theoretical charaterization of SIMs. The great strength of *ab initio* calculations is the possibility of progressively and objectively improving the quality of the method. Thus, the systematic procedure of increasing the quality of the basis set, enlarging the embedding and the active space (up to a reasonable limit), and, most importantly, including more correlation effects (CASPT2 over CASSCF) should consistently produce a convergent set of results. Still, it is difficult to use this method to establish intuitive trends that may help in the design of new systems. A possible way to solve this problem is the use of *semiempirical* effective electrostatic

Received: August 19, 2014
Published: October 1, 2014

dx.doi.org/10.1021/ic5020253 | *Inorg. Chem.* 2014, 53, 11323−11327

models that relate the molecular structure to the spectroscopic/magnetic properties. In this context, in 2012, we used a classical point charge electrostatic model (PCE model),[12] to extract the CF parameters in different coordination environments. This allowed the establishment of useful trends for the rational design of f-element molecular nanomagnets[9] based on the molecular geometry. A qualitative effort in the same direction was reported by Rinehart and Long.[13] The classical electrostatic model was improved by distinguishing between different kinds of donor atoms to allow the modeling of the magnetic properties, with the development of both the *semiempirical* radial effective charge (REC) and the lone pair effective charge (LPEC) models.[14] In a second step, Chilton et al. demonstrated very recently that, at least in Dy(III) complexes, the orientation of the magnetic anisotropy axis can be reliably determined simply by a purely electrostatic approach.[15] The present work represents a third step along this line, where we show that intuitive effective electrostatic models can successfully analyze the molecular anisotropy of mononuclear lanthanide complexes reproducing the angular dependence of the magnetic susceptibility in a quantitative way. Additionally, the aim of the present work is to addres the two main challenges addressed by these approaches, namely: (1) Can an effective point charge description realistically describe the CF effects of covalent ligands? (2) Can the results of the ligand parametrization in one complex be extrapolated to a different complex with similar kind of ligands?

For that, we have chosen the Cp*ErCOT single-ion magnet, where Cp* = pentamethylcyclopentadiene anion (C_5Me_5) and COT = cyclooctatetraene dianion ($C_8H_8^{2-}$).[16] This organometallic complex is of particular complexity because of the presence of two different crystallographic orientations, each occupied by two different conformers. The main features that make the study of this system an excellent opportunity to verify this effective model are the following: (i) The complex is based on aromatic rings, which are eminently covalent. (ii) A detailed study of the angular dependence of the magnetic susceptibility of Cp*ErCOT was recently reported by Sessoli and coworkers,[17] thus permitting the comparison with the predicted molecular anisotropy of the system using the calculated crystal-field parameters (CFPs), without the introduction of any extra-parameter. (iii) High quality spectroscopic information is available on the crystal field splitting on a series of independent complexes with Cp* and COT rings combined with trispyrazolylborate (Tp$^-$) ligands, which were previously parametrized by our models.[18] This third point is the most exciting one because it paves the way toward the building of a general library of ligands to which effective radial and charge parameters can be associated. Such information could be very useful to predict the properties of different complexes in different crystal fields.

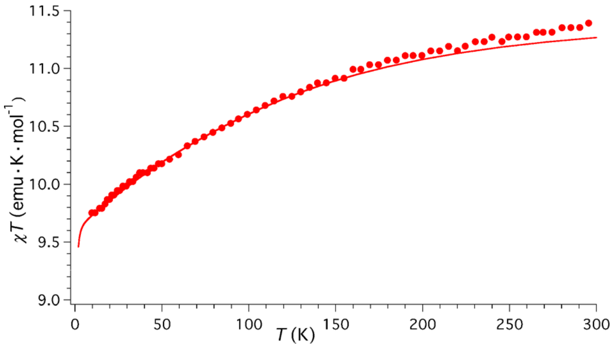


Figure 1. Fitting of the experimental χT product of Cp*ErCOT from 10 to 300 K using the LPEC model in the SIMPRE package with the structure measured at 10 K. Notation: experimental (dots), from ref 17; theoretical (solid line), average of the two conformers.

■ RESULTS AND DISCUSSION

Herein, we apply the LPEC model (see the theoretical approach section in Supporting Information) to the organometallic mononuclear single-molecule magnet Cp*ErCOT, where the erbium cation is sandwiched between two aromatic rings: Cp* and COT (Supporting Information Figure S1 and ref 16). Following the procedure described in the Supporting Information, an excellent agreement ($E = 4.4 \times 10^{-6}$) with the experimental magnetic behavior (powder data) was obtained (Figure 1 red solid line) with the following set of parameters: $D_v = 0.98$ Å, $D_r = 0.26$ Å, and Z_i(Cp*) = 0.4. Since Z_i (COT) is related with Z_i (Cp*) through the equation Z_i(COT) = 1.25Z_i(Cp*), the resulting value of Z_i(COT) is equal to 0.5. A study of the shape and depth of the minimum in parameter space is provided in the Supporting Information (Figures S2, S3, and S4). As the angular dependence of the susceptibility was measured between 2 and 10 K,[17] we used the crystal data obtained at 10 K for all our calculations. Nevertheless, as a common problem with theoretical modeling is not knowing the effects in the properties of a structural change with temperature, we verified that only minor deviations in the χT product depend on the structure determined at different temperatures (10, 20, and 120 K) as shown in Supporting Information Figure S5.

According to our calculations, the ground state for both conformers of Cp*ErCOT is dominated by the highest M_J value (Ising-type). The contribution of $M_J = \pm 15/2$ is of 96% (95%) for conformer 1 (2). The first excited state is placed at 156 cm^{-1} in the first conformer and 125 cm^{-1} in the second one. This description is fully compatible with the observed slow relaxation of the magnetization in this organometallic single-ion magnet.

At this point, it is interesting to examine the effect of the π-cloud displacement that we simulate via the vertical displacement (D_v) of the effective charges. To determine the influence of D_v, we performed the calculations using the classical PCE model placing formal charges on the crystallographic positions of the carbon atoms. The χT product curve represented in Supporting Information Figure S5 gives clear and expected evidence that a minimalistic PCE model is not able to predict a comparable magnetic behavior (with deviations on the order of 10% at 20 K). As we know that fitting a single susceptibility curve to a number of free parameters often can lead to different solutions and that powder data is not very sensitive to anisotropy, this is a necessary but not sufficient condition to give a satisfactory answer to challenge 1, i.e., the validity of a point charge description to describe the CF effects of a covalent ligand. Thus, we need to validate the parametrization by predicting, without further fittings, independent properties of the same compound, and, if possible, also of different compounds, in order to test the validity of the three *semiempirically* determined parameters. By doing so, we will also address challenge 2.

First, we will use the model we obtained from the powder susceptibility data together with the crystal structure to predict the magnetic anisotropy that has been determined experimentally in ref 17. We used the real coordinates modified by

D_v and D_r (from the powder χT LPEC fit) and simulate the experimental rotations labeled Rot1 and Rot2 performed by Sessoli et al.[17] Such rotations are depicted in Figure 2 where the magnetic field is vertically oriented in the paper plane and the crystal rotates around an axis perpendicular to the plane.

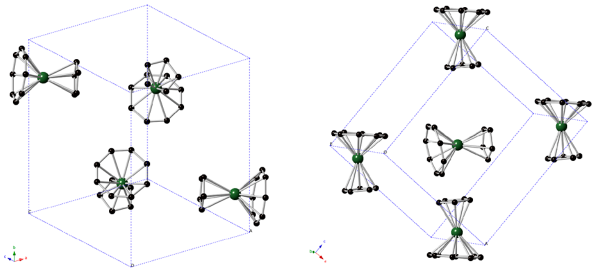


Figure 2. Orientation of the molecules in the two experimental rotations performed by Sessoli et al. in ref 17: Rot1 (left) and Rot2 (right).

The predicted spherical angular dependence of the magnetic susceptibility at 10 K is plotted versus θ and φ in Supporting Information Figures S6 and S7. For a comparison between the theoretical calculations using the LPEC and the PCE models, and the experimental results, the angular dependence of the magnetic susceptibility of the two rotations is represented in Figure 3. Note that single-crystal experimental data needed to be scaled by a factor of 0.81 to be consistent with the experimental powder data reported in ref 17 at 10 K. The theoretical prediction is superimposed in Figure 3 without the use of any extra-parameter.

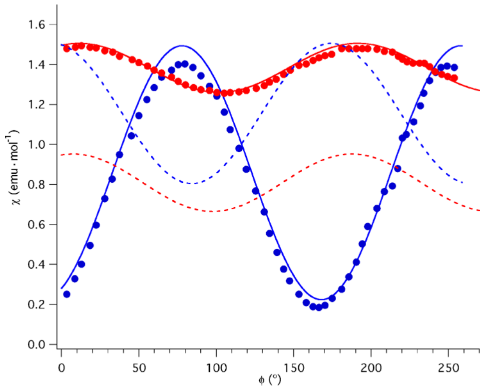


Figure 3. Angular dependence of magnetic susceptibility performed on a single crystal at H = 1 kOe for Rot1 (blue) and Rot2 (red) at 10 K measured in ref 17. A scaling factor of 0.81 needs to be applied in order to match the single-crystal experimental data with the powder data. Solid line plots the theoretical prediction (no extra-parameters) using the LPEC model. Dashed line corresponds to the theoretical prediction with a minimal PCE model.

An almost perfect agreement in both phase and intensity for the two experimentally available rotations is obtained using the parameters obtained from the χT fit. As for the powder χT curve, the theoretical curve results from the weighted average of the signals of the two different crystallographic orientations, each occupied by two different conformers (Figure 3). The angular dependence of magnetic susceptibility for Rot1 and Rot2 of each conformer on each crystallographic orientation is available in the Supporting Information section (Figures S8–S9); this allows a better understanding of how the actual magnetic anisotropy works in each single Er-ion frame. It is remarkable that a three-parameter LPEC model, which uses as sources of information the powder χT data and the low temperature crystallographic data, is enough to match, without any additional parameter, the magnetic anisotropy of this complex system. On the other hand, it is also important to notice that a minimal electrostatic model would be utterly unable to predict the experimental angular dependence of the magnetic susceptibility. The PCE model provided a ground state mainly determined by $M_J = \pm^1/_2$ (more than 99%) in the experimentally determined direction of the main axis of anisotropy for each conformer. As can be seen in Figure 3, neither the phase nor the intensity are compatible with the observed behavior measured in ref 17 (Figure 3 and also Supporting Information Figure S10). These results underline the severe limitations of this simple electrostatic model to determine the easy axis in those cases in which the ligands have lone pairs (or π-clouds) which are not pointing directly toward the lanthanoid ion. From our experience applying the REC and LPEC models in other systems, we suggest that this correction is necessary to determine the easy axis of the magnetization when dealing with rigid polyhapto ligands such as aromatic rings, including phthalocyaninato anions.

Subsequently, the angular dependence of χ for both rotations at different temperatures was calculated and plotted for comparison with the experimental results (Figure 4). Again, the experimental curves have been closely reproduced by the LPEC model without any further fitting. From Figure 4 (left) we are able to detect some kind of experimental deviation of the maximum position from around 80° to 67.5° in the data at 5 K. We can safely discard that this originates from a structural transition. It is more probably connected with the hysteretic effects experimentally detected below this temperature.[17] The fact that such deviation of the maximum χ is not observed for Rot2 [Figure 4 (right)] supports this assumption.

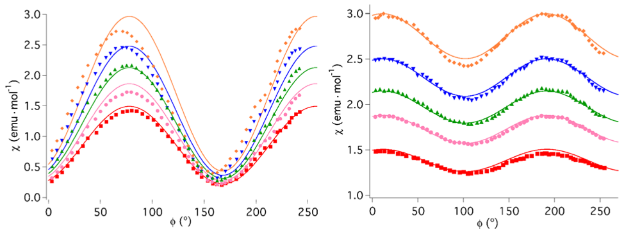


Figure 4. Angular dependence of the magnetic susceptibility at different temperatures for Rot1 (left) and Rot2 (right) at H = 1 kOe. From top to bottom: 5, 6, 7, 8, and 10 K. Comparison between experiment: data from ref 17 (solid circles) and theory (solid lines).

The second challenge we mentioned in the Introduction is arguably the most exciting. Has this model a predictive character? Can we extrapolate the specific parameters for each kind of ligand to other compounds coordinated by the same ligands? This possibility is related to the spectrochemical and nephelauxetic series of ligands, distinguishing quantitatively between "weak" and "strong" field ligands for lanthanoid complexes. In this work, we want to link this challenge to yet another open problem in this field, namely the reliable estimation of the total CF splitting, i.e., the CF strength of the ligands. Using the LPEC model, the calculated total splitting for both conformers is Δ = 630 and 513 cm^{-1} (Figure 5 and Supporting Information Tables S2–S3).

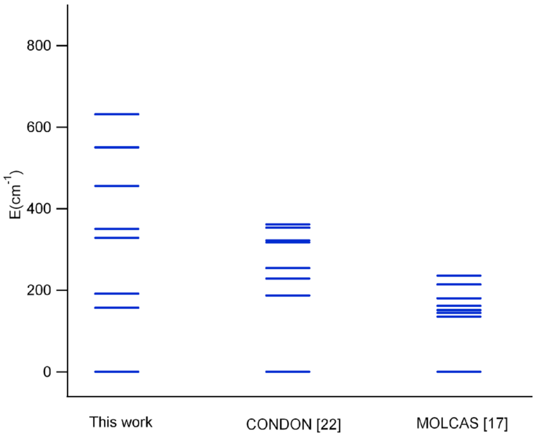


Figure 5. Calculated energy level scheme for Cp*ErCOT (conformer 1) in this work and previous calculations reported in refs 17 (MOLCAS using DFT optimized structure) and 22 (CONDON).

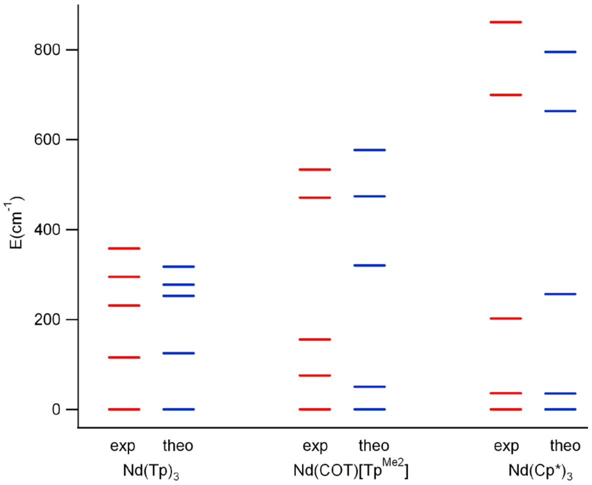


Figure 6. Experimental and calculated energy level scheme for $NdTp_3$ (fit), $\{Nd(COT)[HB(3,5\text{-}Me_2pz)_3]\}$ (prediction), and $Nd(Cp^*)_3$ (prediction).

These rather large Δ-values are in full agreement with the expected behavior, as aromatic rings are known to produce very strong CF splitting and they are placed at the right of the spectrochemical series. In particular, spectroscopic isometallic results by Amberger et al. have indicated $\Delta = 861$ cm^{-1} for $Nd(Cp^*)_3$,[19] $\Delta = 533$ cm^{-1} for $\{Nd(COT)[HB(3,5\text{-}Me_2pz)_3]\}$,[20] and $\Delta = 358$ cm^{-1} for $NdTp_3$.[21] These results provide evidence that Δ is higher in compounds that are coordinated by aromatic rings than for those coordinated by nitrogenated ligands such as pyrazolylborate.[18b] This is logically expected according to the ligand position in the spectrochemical series, ordered from weak to strong field ligands. It is to be noted that the other available models are unable to predict this strong CF splitting in the study of this complex. Thus, for the reported system, a previous fit using the CONDON software yielded a total CF splitting $\Delta \sim 380$ cm^{-1} (Figure 5),[22] whereas the CASSCF/RASSI model estimated Δ values of 276 and 308 cm^{-1} when using the crystallographic structure, and 235 cm^{-1} for both conformers with the DFT optimized structures.[17]

Given that different theoretical tools strongly disagree in the values of Δ, we test the predictions based on this *semiempirical* effective electrostatic model in cases where spectroscopic data are available. We check the calculated energy levels using the effective charge description of ligands: Tp^-,[18b] Cp* and COT (present work), against the real electronic structure determined by spectroscopy for $\{Nd(COT)[HB(3,5\text{-}Me_2pz)_3]\}$ and $Nd(Cp^*)_3$. For comparison with a direct fit using the REC model, in Figure 6 these energy level schemes are plotted together with the one reported for $Nd(Tp)_3$.[18b] The fitting of the spectroscopic energy levels by Amberger et al. gave a ground state wave function $M_J = \pm{}^5/_2$. Taking into account the crystal structure of these complexes, we obtain a ground state formed by $0.54|\pm{}^5/_2\rangle + 0.46|\mp{}^7/_2\rangle$, $0.69|\pm{}^5/_2\rangle + 0.19|\mp{}^5/_2\rangle$, and $0.89|\pm{}^5/_2\rangle + 0.11|\mp{}^7/_2\rangle$ for $Nd(Tp)_3$, $\{Nd(COT)[HB(3,5\text{-}Me_2pz)_3]\}$, and $Nd(Cp^*)_3$, respectively. With this result, we encourage experimentalists working on molecular magnetism to measure the magnetic properties of both $\{Nd(COT)[HB(3,5\text{-}Me_2pz)_3]\}$ and $Nd(Cp^*)_3$, because the M_J contributions to the ground state wave functions are completely compatible with SMM behavior. This is the first time where the evolution of the total CF splitting of a series of rare earth complexes has been successfully predicted using the contributions of each ligand taken into account separately. As we can see in Figure 6, the accuracy of the predicted total CF splitting is striking, but there is clearly room for improvement in the fine details, especially in $\{Nd(COT)[HB(3,5\text{-}Me_2pz)_3]\}$. Such an improvement is expected with the full study using the spectroscopic data of multiple families.[23]

■ CONCLUDING REMARKS

In this study the crystal field effect created by the Cp* and COT ligands is modeled by a *semiempirical* effective electrostatic model that has been corrected to account for the π-cloud effects. This is done by a fit of the temperature dependence of the powder magnetic susceptibility of the compound Cp*ErCOT. To verify this model, a zero-parameter fit is performed that quantitatively reproduces an experimental full magnetic anisotropy analysis recently reported,[17] i.e., two perpendicular rotations of the crystal in the presence of a magnetic field at temperatures ranging from 5 to 10 K. Subsequently, the obtained parametrization for Cp* and COT ligands, together with analogous results for Tp^- from a previous study, is used for a zero-parameter fit of the spectroscopically determined crystal field splitting and magnetic properties of two further complexes, $Nd(COT)[Tp^{Me2}]$ and $Nd(Cp^*)_3$. The quantitative agreement of the prediction of the CF splitting demonstrates the predictive character of this elegant and simple approach.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of the theoretical model, fitting procedure, further anisotropy information, and energy levels and wave functions of the two conformers. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

†This manuscript is part of the Ph.D. thesis of José J. Baldoví.

Funding

The present work has been funded by the EU (Project ELFOS and ERC Advanced Grant SPINMOL), the Spanish MINECO

(Grants MAT2011−22785 and the CONSOLIDER project on Molecular Nanoscience CSD 2007−00010 with FEDER cofinancing), 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 MECD for FPU predoctoral grant.

Notes

The authors declare no competing financial interest.

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