



Supporting Information

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Origin of Non-Magnetic Kramers Doublet in the Ground State of Dysprosium

Triangles: Evidence for Toroidal Magnetic Moment^{**}

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SUPPORTING INFORMATION

Computational Details

Presently it is impossible to treat *ab initio* a polynuclear lanthanide complex as is. It is studied therefore in this work as separate mononuclear dysprosium fragments. In this connection the question arises to cut suitable mononuclear fragments from the molecule, which would not change significantly the energy structure on the magnetic centre. To have a good description of the 4f ligand-field states within a fragment one needs to take into account the influence of the neighboring dysprosium ions. They have been simulated by the closed-shell La^{3+} *ab initio* embedding model potentials (AIMP).¹

The second approximation concerned the coordination sphere. Cutting the distant atoms may have a crucial effect on the orientation of anisotropy axes. Therefore we took into account all distant atoms which are connected through chemical bonds to the dysprosium, with a small basis sets, thus making possible to take larger basis sets for other atoms. The only removed atoms are those connected to the La^{3+} AIMP from the opposite side of the molecule. The structure of the calculated fragments is shown in the Figure 1S. No geometry optimization on the fragments have been done, all atomic coordinates (except for added hydrogens) being taken from the crystal X-ray analysis.

For the electronic structure, the *ab initio* calculations were performed by means of MOLCAS-7.0 program.² The basis sets were atomic natural orbitals from the MOLCAS ANO-RCC library for dysprosium and the atoms from the first coordination sphere, while for the distant atoms the minimal relativistic atomic natural orbital basis sets developed by Tsuchiya (ANO-DK3 basis library) were used. The following contractions were used: [8s7p5d4f2g1h] for Dy, [3s2p1d] for O, [4s3p1d] for Cl, [2s1p] for H. Embedding potential $\text{La}^{3+}/\text{LaMnO}_3$ developed by de Graaf were used to simulate the influence of the neighbour Dy ions.³

The active space of the complete active space self consistent field (CASSCF) calculation included the Dy 4f orbitals (CAS (9 in 7)) since we are interested in the ligand field states only. The 4f orbitals are known to be localized, which allows us to consider the charge transfer states much higher in energy, thus being not relevant for the magnetism.

The number of roots to be calculates is also a good question. Since the lanthanides have a very strong spin-orbit coupling, a large number of roots should be included in the spin-orbit mixing within the restricted active space state interaction (RASSI-SO) procedure. To exclude all the doubts we calculated all the roots in the active space.

The second order multiconfigurational perturbation calculation (CASPT2) was not performed. It was only tested for the lowest 20-30 roots in order to estimate the average change in the energy differences. It came out that the CASPT2 relative energies do not differ much from the CASSCF ones, therefore the CASSCF energies were further used. The spin-orbit coupling was calculated by the RASSI program,³ but due to some internal limitations of the program itself, and also probably the hardware, it was possible to mix only the roots coming from the following atomic multiplets: ^6H , ^6F , and ^6P (all sextets); ^4I , ^4F , ^4M , ^4G , ^4K , ^4L , ^4D , ^4H , ^4P , ^4G , ^4F and ^4I (128 from 224 quadruplets); ^2L , ^2K , ^2P , ^2N , ^2F , ^2M , ^2H , ^2D , ^2G and ^2O (130 from 490 doublets). These are all the roots up to 50000 cm^{-1} . An important aspect of the lanthanide state interaction calculation is one should take into account all the states coming from an entire multiplet. Taking fewer roots than contained in a multiplet may induce strong deviations.

With the obtained spin-orbit multiplets, the powder susceptibility and the g-tensors for the lowest Kramers doublets of isolated fragments were further evaluated using the recently developed *ab initio* methodology.⁴ The basis of this approach is to calculate *ab initio* all angular moment matrix elements and then all magnetic moment matrix elements on the relevant spin-orbit multiplets obtained in CASSCF/CASPT2 calculations. These matrix elements are used in a separate routine to calculate (i) magnetic properties measured directly in experiment (temperature dependent Van Vleck susceptibility tensor and powder averaged function, field dependent magnetization for different temperatures and directions and the powder magnetization) and (ii) parameters of magnetic spin Hamiltonians for different spin-orbit multiplets and groups of spin states, described by the corresponding pseudospin, (g tensors, zero-field splitting tensors). In calculations of magnetic properties, all spin-orbit multiplets on the sites are usually taken into account, in particular, all ligand-field states in the case of transition metal ions (in the case of lanthanides and actinides the number of free spin states which are mixed in the RASSI-SO procedure is currently limited to 279). This is important for correct quantitative account of the effects of strong magnetic anisotropy and strong applied magnetic fields. Computationally, this routine (single_aniso) was interfaced with MOLCAS-7.0 program.

For the simulation of magnetic properties of polynuclear complexes we used an approach combining the calculated magnetic properties of individual metal fragments (CASSCF/CASPT2/RASSI-SO + single_aniso) with the description of anisotropic exchange interaction

between metal sites within the Lines model.⁵ The latter begins with the isotropic exchange interactions, which would be in the absence of spin-orbit coupling on metal sites. Diagonalizing the matrix of the corresponding Heisenberg Hamiltonian, written in the basis of spin-orbit multiplets of mononuclear metal fragments, obtained from quantum chemistry calculations, gives solutions corresponding to anisotropic exchange interactions between Kramers doublets of a given metal pair. The main advantage of the Lines model is that it uses one single parameter, corresponding to effective isotropic exchange interaction, to simulate the anisotropic exchange coupling. This allows avoiding of overparametrization of the simulations. In some cases, as in the present case of Dy₃ complex, the Lines model is completely adequate. The simulations have been done with a specially designed routine (poly_aniso), which was interfaced with the single_aniso routine treating individual metal fragments.

This ab initio based methodology has already been successfully applied for the treatment of the effects of strong magnetic anisotropy in polynuclear transition metal complexes. Thus it allowed to explain the origin of strong anisotropy in dinuclear Co(II) complex of calyx[8]arenes,⁶ to rationalize the magnetic data in Co-NC-W pairs of octacyanotungstate(V)-cobalt(II) three-dimensional networks,⁷ and to understand the complex magnetism in mixed-valent Co^{II}₃Co^{III}₄ heptanuclear wheel, in particular, the lack of SMM behaviour in this compound.⁸

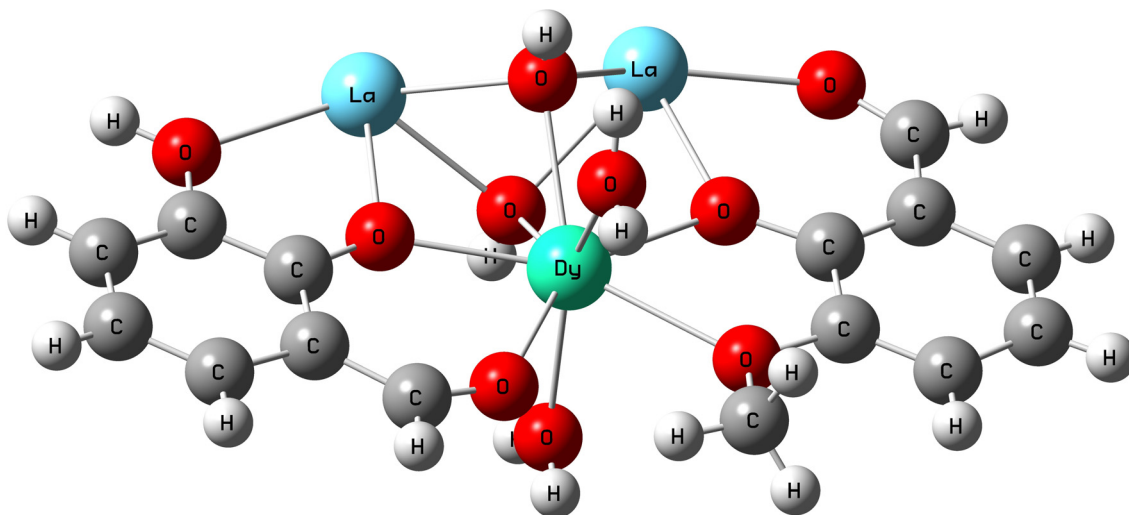


Figure 1S. The calculated fragments of centers 1 and 2. The center 3 has the same structure, except for the out of plane water molecules, which are replaced by chlorine ions.

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