XXI Brazilian Meeting on Inorganic Chemistry
X Brazilian Meeting on Rare Earths
III Workshop on Theoretical Bioinorganic Chemistry
Belo Horizonte, September 12 - 15th 2024

Lessons on magnetic anisotropy from lanthanide-chalcogen complexes

José Severiano C. Neto,[1] Lucas G. Fachini,[1] Diego E. L. Seckler,[1] Francielli S. Santana,[1] Arsen Raza,[2] Matteo Briganti,[1] Mauro Perfetti,[2] Jaísa F. Soares[1]

[1]Departamento de Química, Universidade Federal do Paraná, Curitiba-PR, Brazil
[2] Dipartimento di Chimica "Ugo Schiff", Università degli Studi di Firenze, Firenze, Italy
E-mail: joseseveriano@ufpr.br

Thematic Area: Rare-Earths

Keywords: Lanthanide-chalcogen complexes, Single-Molecule Magnets, *Ab initio*

Lanthanide complexes exhibit high magnetic anisotropy, which can be tuned by appropriate molecular design. In the present work, dichalcogenoimidodiphosphinate ligands, $N(EPPh_2)_2^-$ (*E* = O, S, and Se),[1] produced six crystalline $[Ln\{N(EPPh_2)_2\}_3]$ complexes (Ln = Dy or Er, Fig. 1a) characterized by structural, spectroscopic, and magnetometric analyses. Changing the chalcogen donor atoms led to significant structural changes in the resulting complexes, with a relevant impact on magnetic properties. Six and nine-coordinate Ln^{3+} ions were observed with the lighter chalcogens (*O* and *S,* respectively), while Se gave rise to seven-coordinate products. For the former, the short Ln-chalcogen bond distances and crowded coordination spheres led to fast magnetic relaxation due to high rhombicity, confirmed by *ab initio* calculations. Conversely, in $[Dy\{N(SePPh_2)_2\}_3]$, the additional coordination of one nitrogen atom led to a uniquely favorable Dy–N axis corresponding to the easy anisotropy axis of the structure. *Ab initio* calculations revealed for this complex a perfectly axial ground state mainly composed by the highest m_J projection (m_J = ±15/2; g ≈ [0, 0, 20]) and a first excited state at higher energy than in all other complexes in the series (Fig. 1b). AC magnetic susceptibility measurements confirmed the theoretical findings, revealing slow magnetic relaxation for $[Dy\{N(SePPh_2)_2\}_3]$ in both zero and applied static fields. These results highlight the importance of tailored syntheses in fine-tuning magnetic properties.

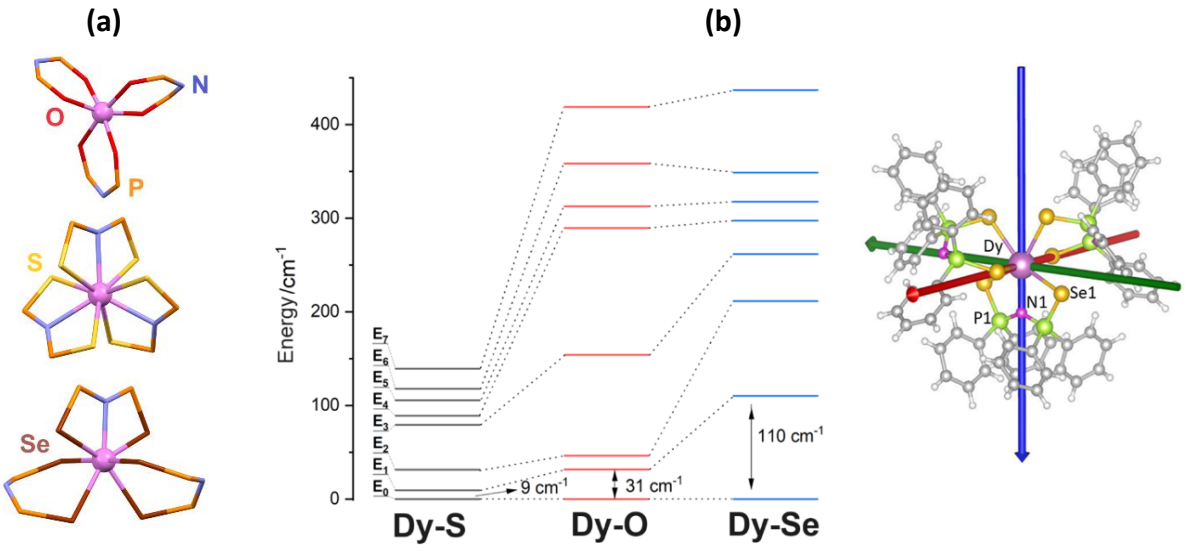

Figure 1: (a) Representation of the $[Ln\{N(EPPh_2)_2\}_3]$ coordination geometries. (b) Left: Calculated energies of the $^6H_{15/2}$ Kramer's doublets (E_n) in the Dy^{3+} complexes. Right: Structure of $[Dy\{N(SePPh_2)_2\}_3]$, emphasizing the easy magnetization axis in the ground state (blue).

Acknowledgments: UFPR/PROEX-Capes/CNPq/ERC-ELECTRA

References: [1] P. B. Hitchcock *et al.,* Inorg. Chim. Acta, **96**, 77 (1985); (b) F. T. Wang *et al.,* Synth. React. Inorg. Met. Org. Chem., **8**, 119 (1978).