

Critical evaluation of ambiguities in computational modelling of zero-field splitting parameters – case study: trigonal and triclinic dinuclear Gd^{3+} complexes

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Streszczenie

The symmetry aspects permeate studies of transition ions in coordination compounds, profoundly affecting spectroscopic and magnetic properties, yet are not adequately recognized in literature. To investigate these aspects, two structurally similar dinuclear Gd^{3+} complexes were synthesized as potential molecular nanomagnets (MNMs): $[Gd_2(L^1)_3](NO_3)_3$ (**1** symmetric; trigonal C_3 site symmetry) and $[Gd_2(L^2)_3](NO_3)_3$ (**2** dissymmetric; triclinic C_1). Using various structural datasets, the zero-field splitting parameters (ZFSPs) are modelled for Gd^{3+} centers employing superposition model and ab initio MOLCAS code. The symmetry issues in ZFSP modelling are categorized and crucial notions defined. The intertwined symmetry and magnetism issues in ab initio computations are expounded. Existence of infinite number of numerically distinct, yet physically equivalent, parameter sets for low site symmetry necessitates using standardization for valid direct comparison of ZFSPs, whereas invariant quantities for quantifying the degree of physical equivalence of modelled ZFSPs. Analysis of symmetry aspects inherent in the modelled ZFSP sets reveals that: (i) the SHAPE-generated structural datasets are unsuitable for ZFSP modelling; (ii) the triclinic symmetry inherent in MOLCAS-computed ZFSPs for **1** is merely *apparent*, not *actual*. The importance of the symmetry and magnetism aspects for proper interpretation of computational and experimental results is demonstrated. By expounding these aspects encountered at the interface between diverse methodologies, this in-depth study may improve researchers' knowledge and diminish proliferation of incorrect interpretations of compounds' properties. This paper has a broader character as a critical evaluation of ambiguities in interpretation of the modelled ZFSP sets reported in literature, which are related to symmetry and magnetism aspects.

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