

topic of research of several recent papers within the field of magneto-structural correlations. [1] Symmetry rules [2] give an explanation of the occurrence of ferro- or antiferromagnetic interactions in polynuclear compounds with transition metals; however the application of them to *f*-block elements is still unclear. The main advantage of the use of Gd(III) resides in its spin-only formalism, since its first excited state is well separated from its ground state. However the shielding of the inner electron orbits by the *f*-electrons promotes that the values of magnetic coupling are weak, which means that are hard to measure and easily confused with other interactions as the ligand field.

In the quest of clarify magneto-structural correlations in these complexes, we have synthesized three new digadolinium(III) complexes with hexa-, hepta- and octanoate ligands [caproate (cap), enanthate (ena) and caprylate (capy), respectively] of formulae $[\text{Gd}_2(\text{cap})_6(\text{H}_2\text{O})_4]$ (**1**), $[\text{Gd}_2(\text{ena})_6(\text{H}_2\text{O})_4]$ (**2**) and $[\text{Gd}_2(\text{capy})_6(\text{H}_2\text{O})_4]$ (**3**) and their structures have been determined by X-ray diffraction on single crystals. Their structures consist of neutral and isolated digadolinium(III) units, containing six monocarboxylate ligands and four coordinated water molecules, where the aliphatic tails pointing to the *a* direction in all cases. The hydrophobic character of this tails avoids the inclusion of any crystallographic water molecule. The bridging skeleton within the Gd(III) units is built by a $\mu\text{O}(1):\kappa^2\text{O}(1)\text{O}(2)$ framework where the values of the intramolecular Gd–Gd separation are 4.133(2) (**1**), 4.1150(13) (**2**) and 4.1378(7) (**3**) Å and those of the Gd–O–Gd angle are 113.69(15) (**1**), 113.2(2) (**2**) and 113.90(12) (**3**)°. This structural pattern has already been observed in previously reported complexes whose structure and magnetic properties were reported.[3]

Magnetic susceptibility measurements in the temperature range 1.9–300 K reveal the occurrence of a weak intramolecular antiferromagnetic interaction in **2** [$J = -0.042(2) \text{ cm}^{-1}$, the Hamiltonian being defined as $H = -JS_A \cdot S_B$] in contrast with the intramolecular ferromagnetic coupling which occurs in **1** and **3** [$J = +0.037(3)$ (**1**) and $+0.057(3) \text{ cm}^{-1}$ (**3**)]. The magneto-structural data of **1–3** indicates a suitable relation between the magnetic coupling between two gadolinium(III) ions and the geometrical parameters at the $\mu\text{O}(1):\kappa^2\text{O}(1)\text{O}(2)$ bridge.

[1] L. Cañadillas-Delgado, O. Fabelo, C. Ruiz-Pérez, J. Cano *Nova Science Publishers, Inc., New York*, **2010**, and references therein. [2] E. Ruiz, P. Alemany, S. Alvarez, J. Cano *J. Am. Chem. Soc.* **1997**, *119*, 1297-1303. [3] a) L. Cañadillas-Delgado, O. Fabelo, J. Cano, J. Pasán, F.S. Delgado, M. Julve, F. Lloret, C. Ruiz-Pérez, *CrystEngComm* **2009**, *11*, 2131-2142; b) L. Cañadillas-Delgado, O. Fabelo, J. Pasán, F.S. Delgado, M. Julve, F. Lloret, C. Ruiz-Pérez, *Dalton Trans* **2010**, *39*, 7286-7293.

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Telling “twin molecules” apart in the solid state world: charge density approach

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Chemical compounds that tend to form crystals with several independent species ($Z' > 1$, often pseudosymmetric) or exist as several polymorphic modifications are an evergreen challenge of the solid state world. Encountering these “twins” (molecules or crystals of the same chemical nature) significantly complicates the scientific efforts of many crystallographers. In the case of $Z' > 1$, however, they mostly have to go to the efforts of averaging, as such molecules are usually believed to be identical. Meanwhile, the self-association of these species, like the interactions between counterions, can cause the

electron density redistribution that makes them distinct. As a result, the crystal structures and thus the related properties cannot be predicted based on the quantum chemical calculations of an isolated molecule.

Theoretical methods were elaborated to rationalize the crystal structures with $Z' = 2$ [1], but many systems have more than two independent species; therefore, to assess the degree to which they are different and how it is related to the crystal environment can be a challenge difficult to overcome. The similar questions can be addressed to the polymorphic modifications. Judging whether a distinction between the “twins” is significant is still based mostly on the comparison of geometrical parameters; interconnecting a molecular or crystal structure with the physicochemical properties of the resulting materials (e.g., their stability), on some empirical principles of crystal formation (dense packing, strength of interactions between species, etc. [1]). These approaches are, however, too rough approximations of the complex situation in a real crystal and provide no quantitative information on the matter. Much more powerful is the topological analysis of the electron density distribution within the “atoms in molecules” theory [2]. It allows accurately evaluating the net properties of molecules (e.g., their charge) and the energy of interactions they form in a crystal (and so the energy of a crystal lattice), hence distinguishing the “twins” at both the molecular and supramolecular levels.

We tested this approach on a series of $Z' > 1$ crystals and polymorphs with intermolecular interactions of various strength: from classical H-bonds (as in paracetamol [3]) to weak van-der-Waals contacts (as in a sidone imine derivative [4]). It proved to be an effective tool to identify and quantify even subtle differences between the molecules and their crystal environments [4] and thus to correlate the charge transfer and mutual polarization due to the self-association with the interaction energy, while revealing some important implications for crystal engineering. In summary, $Z' > 1$ systems should be dealt with care, as neglecting even faint distinction between the independent species (those caused by the weakest interactions) can have measurable consequences; the “cost” for a crystal structure being sometimes high [5]. This approach also allowed estimating the stability of polymorphic modifications, the isoenergetic ones and those violating the “density rule”; in the latter case it helped to reveal the interactions that are responsible for this [3].

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[1] A. Gavezotti *CrystEngComm* **2008**, *10*, 389-398. [2] R.F.W. Bader *Atoms In molecules. A Quantum Theory* **1990**. [3] Yu. V. Nelyubina, I. V. Glukhov, M. Yu. Antipin, K. A. Lyssenko *Chem. Comm.* **2010**, *46*, 3469-3471. [4] Yu. V. Nelyubina, M. Yu. Antipin, I. A. Cherepanov, K. A. Lyssenko *CrystEngComm* **2010**, *12*, 77-81. [5] Yu. V. Nelyubina, I. L. Dalingler, K. A. Lyssenko, *Angew. Chem. Int. Ed.* **2011**, *50*, 2892-2894.

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Looking at nanoscale properties in macro-systems with x-ray diffraction imaging

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A feature of emerging nanotechnology is the development of novel materials based on the dispersion of nano-particles in a broad variety of matrices. Applications of such materials range from novel paints and coatings, to a new generation of light alloys, advanced photonics and telecommunication devices, cosmetics and novel biomedical