Note

Structure and magnetic properties of Ln$_2$[Cu(opba)]$_3$(DMSO)$_6$(H$_2$O) · (H$_2$O) compounds with Ln=La–Lu exhibiting ladder-like molecular motifs ☆

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Abstract

The reaction of Ln(III) ions with the precursor [Cu(opba)]$^{2-}$ in DMSO has afforded a series of isostructural compounds of general chemical formula Ln$_2$[Cu(opba)]$_3$(DMSO)$_6$(H$_2$O) · (H$_2$O), where Ln(III) stands for a lanthanide ion and opba stands for ortho-phenylenebis(oxamato). The crystal structure has been solved for the Gd(III) containing compound. It crystallizes in the orthorhombic system, space group *Pbn*2$_1$ (No. 33) with $a = 9.4183(2)$ Å, $b = 21.2326(4)$ Å, $c = 37.9387(8)$ Å and $Z = 4$. The structure consists of ladder-like molecular motifs parallel to each other. To the best of our knowledge, this is the first Ln(III)Cu(II) coordination polymer family exhibiting the same crystal structure over the whole lanthanide series. The magnetic properties of the compounds have been investigated and the magnetic behavior of the Gd(III) containing compound was studied in more detail.
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1. Introduction

The nature of the magnetic interaction between rare earth and other paramagnetic centers has been studied for several years. In molecular systems, the first paper describing an isolated molecule containing paramagnetic 3d and 4f ions appeared in the literature in the mid-seventies [1]. Unfortunately, neither the structural features nor the magnetic properties were fully characterized. Only 10 years later, the first fully characterized molecules were described [2]. Actually, this first molecular compounds containing Gd(III) ions coupled with Cu(II) ions had been found to be ferromagnetically coupled [2,3]. At that time, this result was rather surprising and aroused some great hope in the field of the design of molecular magnets. This observation was later confirmed [4,5] and extended to Gd(III)-organic radical systems [6]. An elementary semi-quantitative treatment involving spin polarization was suggested for explaining the ferromagnetic nature of the coupling [7–9] and the influence of the topology and the nature of the bridging ligand was studied [10,11]. More recently, several examples of antiferromagnetic coupling have been reported for Gd(III) complexes with organic radicals or with Cu(II) anionic complexes [12–14]. Simplified approaches have also been suggested for explaining the coupling between a non Gd(III) lanthanide ion and a Cu(II) ion [7,8,15]. A complete review of these problems was published recently [16]. Until now and despite great efforts,

the understanding of the magnetic interactions involving rare earth ions is still far from satisfactory. However, there is currently a renewal of activity in the field of the 4f/3d molecular systems as they could, for instance, present great interest for their non-linear optical properties [17] or as far high nuclearity metal complexes design is concerned [18,19]. For these reasons, we have decided to re-investigate the system Ln(III)/[Cu(opba)]$^{2-}$ in DMSO.

Indeed, several years ago some of us were working in the field of 3d-4f coordination polymers. Our objective at the time was to design extended molecular compounds incorporating both transition metal ions and rare earth ions, and to investigate and interpret their magnetic properties [8,20–27]. First, we focused on the system Ln(III)–[Cu(pba)]$^{2-}$ where pba stands for 1,3-propylene-bis(oxamato). Unfortunately, all these compounds crystallize with a large number of non-coordinated water molecules. Most of these crystallization water molecules were easily lost from the crystal lattice, leading to rather unstable compounds difficult to study. In order to improve the stability of the compounds, we decided to work with the precursor [Cu(opba)]$^{2-}$ where (opba) stands for orthophenylenebis(oxamato) which is represented in Scheme 1. Indeed, this Cu(II) precursor is readily soluble in polar organic solvents such as DMF or DMSO, and it has been successfully used to obtain several one-, two- and three-dimensional compounds [28–34]. In particular, in association with Ln(III) ions, this Cu(II) molecular precursor has led to mono- and bi-dimensional compounds [26,35].

One of these systems, already studied by some of us in the nineties, is known for leading to compounds presenting the same crystal structure over the whole lanthanide series. Unfortunately, at that time we did not succeed in structurally characterizing these compounds. This lack of structural data remained a problem, because this family of compounds has been used for characterizing the nature of the interaction between Ln(III) and Cu(II) [36] and because the Gd(III) containing compound has been found to exhibit a long range ferromagnetic ordering at a T_c of 1.75 K [34]. The crystal structure of these compounds has now been solved

and is described hereafter. Shortly, their magnetic properties will be studied as well.

2. Experimental

2.1. Synthesis

The copper(II) precursor Na$_2$[Cu(opba)] · 3H$_2$O was prepared as previously described [29]. The Ln$_2$[Cu(opba)]$_3$(DMSO)$_6$(H$_2$O) · (H$_2$O) compounds, where Ln stands for lanthanide ion, were prepared as follows according to the so-called vapor diffusion method: 1 mmol of Ln(III) nitrate and 1 mmol of Na$_2$[Cu(opba)] · 3H$_2$O were dissolved in DMSO. The resulting solution, intense blue in color, was filtered and placed in a tube which was sealed and kept at 70 °C in a water bath. After a few days, crystalline powder and/or single crystals appeared at the bottom of the tube. The chemical analysis of the Gd(III) containing compound was found to be compatible with the formula Gd$_2$[Cu(opba)]$_3$(DMSO)$_6$(H$_2$O) · (H$_2$O).

Anal. Calc. for Gd$_2$[Cu(opba)]$_3$(DMSO)$_6$(H$_2$O) · (H$_2$O): Gd, 18.0; Cu, 10.9; O, 23.8; H, 2.9; N, 4.8; S, 11.0. Found: Gd, 18.0; Cu 10.9; O, 23.5; H, 2.8; N, 5.0; S, 11.2%.

2.2. X-ray structure determinations

A single crystal of Gd$_2$[Cu(opba)]$_3$(DMSO)$_6$ (H$_2$O) · (H$_2$O) was sealed in a glass capillary for X-ray single crystal data collection. The crystal was mounted on a Nonius Kappa CCD diffractometer at room temperature with Mo Kα radiation ($\lambda = 0.71073$ Å). Preliminary cell constants were determined from reflections obtained on 10 frames (1°φ rotation per frame). For the data collection, a crystal-to-detector distance of 45.0 mm has been used and data collection strategy (determination and optimization of the detector and goniometer positions) has been performed with the help of the COLLECT program [37] to measure Bragg reflections of the asymmetric triclinic basal unit cell. The reflections have been indexed, Lorentz-polarization corrected and then integrated by the DENZO program of the Kappa CCD software package [38].

Structure determination has been performed with the solving programs SIR97 [39] and SHELXL97 [40] that revealed all the non-hydrogen atoms. All metallic and sulfur atoms of the molecular ladder-like entity were refined anisotropically using the SHELXL program. The other atoms were refined isotropically. Hydrogen atoms have not been localized.

Crystal data and structure refinement of the Gd(III) containing compound are listed in Table 1. The characterization of the obtained micro crystalline powders has been assumed on the basis of comparisons between
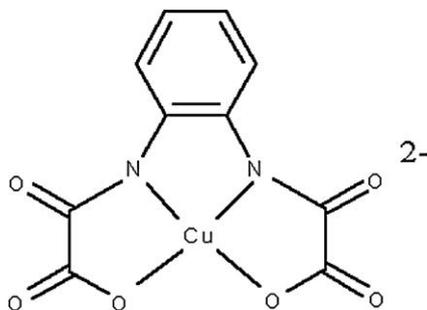
Scheme 1.

Table 1
Crystallographic data and final structure refinement for $Gd_2[Cu(opba)]_3(DMSO)_6(H_2O) \cdot H_2O$

Molecular formula	$Gd_2Cu_3H_{50}O_{26}N_6S_6C_{42}$
Formula weight	1752.36
Crystal dimensions (mm)	$0.045 \times 0.062 \times 0.070$
Temperature (K)	298
Crystal system	orthorhombic
Space group	$Pbn2_1$ (No. 33)
a (Å)	9.4183(2)
b (Å)	21.2326(4)
c (Å)	37.9387(8)
Z	4
D_{calc} (g cm^{-3})	1.534
$F_{(000)}$	3452
μ (mm^{-1})	2.784
Radiation	Mo Kα
hkl Range	$-12 \leqslant h \leqslant 8, -20 \leqslant k \leqslant 27,$ $-48 \leqslant l \leqslant 48$
θ Range (°)	$2.94 \leqslant \theta \leqslant 27.10$
Data collected	15 425
Observed data ($F_{obs} \geqslant 2\sigma(F_{obs})$)	6919
Parameters refined	396
Goodness-of-fit on F^2	0.972
Final R indices [$I > 2\sigma(I)$]	$R_1 = 11.04\%; wR_2 = 27.01\%$
Final shift/error	0.058
Residual density (e Å^{-3})	0.241 (in the vicinity of Gd)

experimental powder X-Ray diffraction diagrams and the calculated one from the crystal structure. The calculated XRD diagram has been performed using POW-DERCELL [41] software and compared with experimental one using WINPLOTR [42] software.

2.3. Magnetic measurements

Magnetic measurements were carried out with a Quantum Design MPMSXL squid magnetometer. All the samples were crystalline for insuring chemical purity and were prepared in a way to prevent the orientation of the microcrystallites within the applied magnetic field.

3. Results and discussion

3.1. Description of the structure

The asymmetric unit along with the atomic numbering scheme is depicted in Fig. 1. The crystalline structure can be described as the juxtaposition of infinite molecular ladder-like motifs spreading along the
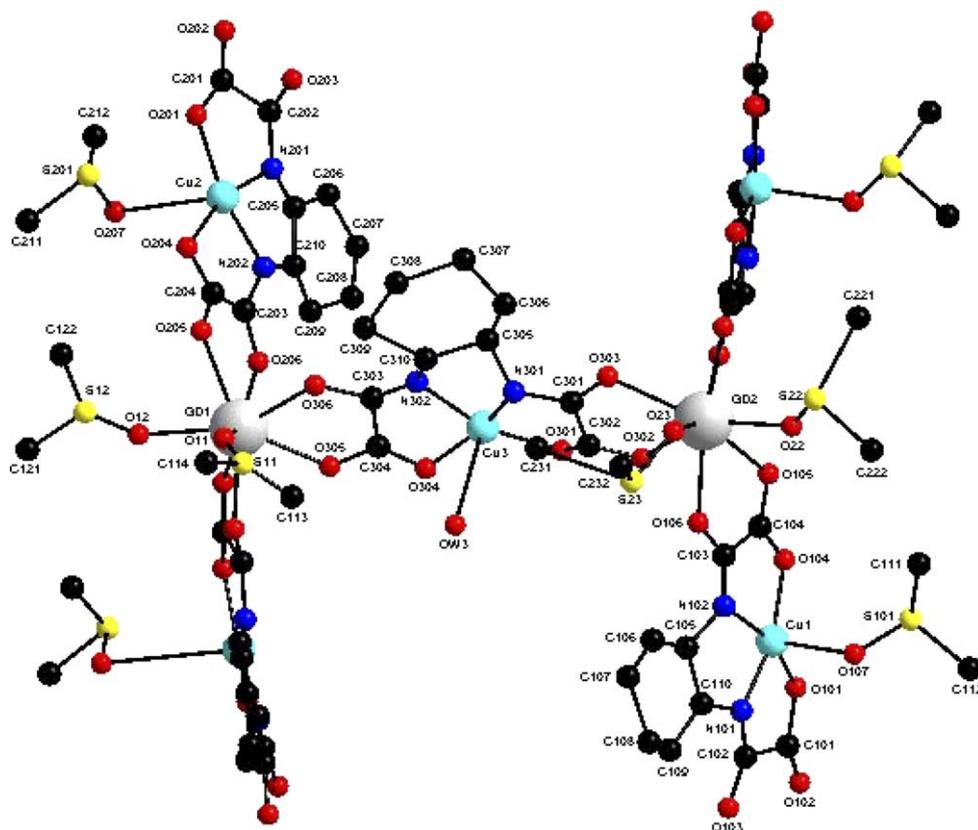

Fig. 1. Projection view of an extended asymmetric unit of $Gd_2[Cu(opba)]_3(DMSO)_6(H_2O) \cdot (H_2O)$. For clarity, crystallization molecules have been omitted.

(a)   **(b)**   **(c)**
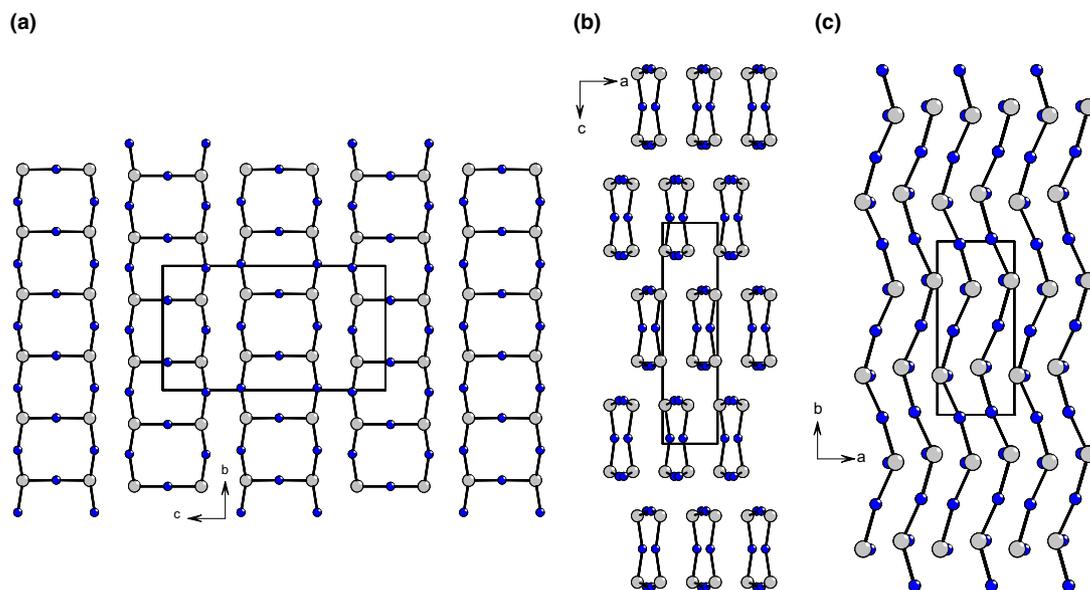
Fig. 2. Symbolic projection views of Gd$_2$[Cu(opba)]$_3$(DMSO)$_6$(H$_2$O) · (H$_2$O) along the crystallographic axis. For clarity, only metal ions have been drawn. Dark circles are symbolizing Cu(II) and light gray ones Gd(III).

$\vec{b}$-axis (see Fig. 2). The side pieces of the ladder consist of Gd[Cu(opba)] units. These side pieces are linked together by rungs made of [Cu(opba)] groups (see Fig. 3). The asymmetric unit contains two independent Gd(III) atoms and three Cu(II) atoms. Both Gd(III) atoms are eight coordinated by six oxygen atom from three [Cu(opba)] groups and two oxygen atoms from two coordination DMSO molecules so forming a distorted dodecahedral. All the three Cu(II) atoms are five coordinated by two oxygen atoms and two nitrogen atoms from an (opba) group in the basal plane and by one oxygen atoms from either a water molecule (Cu3 belonging to the rungs) or a DMSO molecule (Cu1 and Cu2 belonging to the side pieces) occupying the apical position. In all cases, the coordination polyhedral of the copper atoms can be depicted as a capped square pyramidal. For Cu3, the water molecule is disordered on two equiprobable positions localized on both sides of the basal plane. All the coordination DMSO molecules are pointing toward the intermolecular space so forming an intricate network of hydrogen bonds. The Gd–Cu distances across an oxamato bridge are in the range 5.72–5.5 Å, while the Gd–Gd distances of a [Cu(opba)] unit vary from 11.31 to 11.35 Å. The shortest distances between two Gd(III) atoms (9.01 Å) involve non-connected Gd(II) ions belonging to two side pieces from two neighboring ladders. The crystallization water molecule is located in the intermolecular space. This crystal structure is very similar to that of Ln$_2$[Cu-(opba)]$_3$ · xDMF · yH$_2$O ($x \approx 10$ and $y \approx 4$), where Ln stands for a lanthanide ion comprised between Tb and Lu [26].

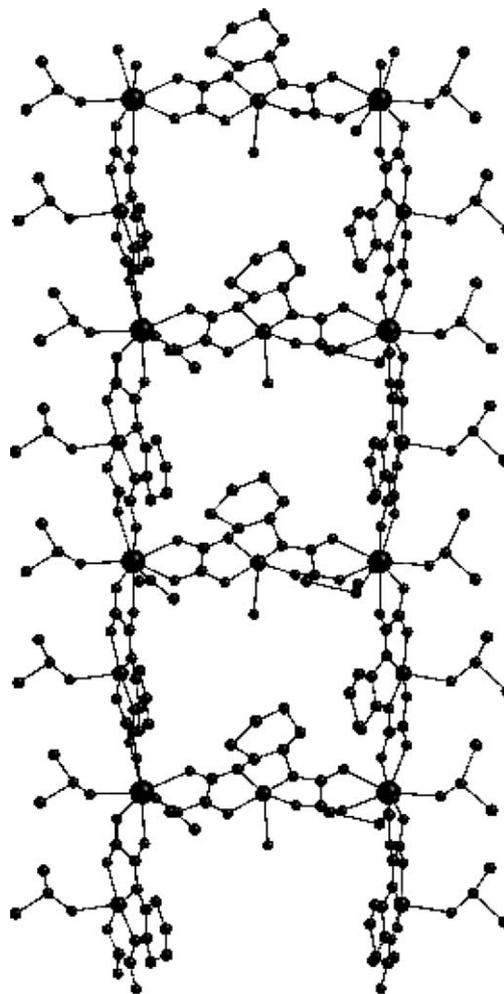Fig. 3. Perspective view of a molecular ladder-like motif in Gd$_2$[Cu(opba)]$_3$(DMSO)$_6$(H$_2$O) · (H$_2$O).

3.2. Magnetic properties

3.2.1. The Gd(III)–Cu(II) case

We have represented in Fig. 4 the temperature dependency of the $\chi_M T$ products of the compounds $Gd_2[Cu(opba)]_3(DMSO)_6(H_2O) \cdot H_2O$ (**1**) and $Lu_2[Cu(opba)]_3(DMSO)_6(H_2O) \cdot H_2O$ (**2**). The experimental susceptibilities have been corrected from the sample holder contribution and the core diamagnetism estimated from Pascal's tables. At room temperature $\chi_M T$'s are, respectively, equal to 15.2 and 1.1 emu K mol^{-1}. These values are slightly smaller than expected. Indeed, for (**1**) the Curie constant, considering a Zeeman factor $g = 2$ identical for all the magnetic centers, should be equal to 16.9 emu K mol^{-1} ($2 \times S = 7/2$[Gd(III)] + $3 \times S = 1/2$[Cu(II)]). Room temperature X-Band EPR measurement on a powdered of (**2**) gives a broad signal centered at $g = 2.08$ characteristic of isolated Cu(II). Therefore, the Curie constant should be equal to 1.12 emu K mol^{-1} for (**2**), the rare earth Lu(III) being diamagnetic. The difference between the measured and calculated values can reasonably be attributed to a deficit in solvating molecules onto the chemical formula. These features are rather common in the field of molecular magnetism. The molecular frames are often well defined by X-ray diffraction methods; however, the frames let appear small gaps which may be, or not, occupied by disordered solvent molecules.

The $\chi_M T$ product of (**2**) is constant in all the temperature ranges, which proves that there are no interactions between copper ions in the ladder. On the contrary, $\chi_M T$ for (**1**) increases continuously on lowering the temperature and reaches 53 emu K mol^{-1} at 2 K. The interactions are ferromagnetic between the Gd(III) and Cu(II) centers as expected [22,43,44]. Irrespective of the nature of the bridge between these two spin carriers, there are only few examples for which the interaction is found to be antiferromagnetic [13,45]. The magnitude of the superexchange parameters has been extracted from susceptibility measurements for other ladder type architectures with the same bridging ligands using a model developed by Georges et al. [23]. In all instances, they were found to be smaller than 1 K. We decided to employ the basic molecular field theory to analyze our data for (**1**) with one coupling constant J between Gd(III) and Cu(II) spins and unique Zeeman factor g. The coupling between two spins is described by the Heisenberg Hamiltonian $H = -JS_{Gd(III)} \cdot S_{Cu(II)}$. The best agreement between experience and theory in the temperature range 5–100 K is represented in the inset of Fig. 4 with $J = 1.02$ K and $g = 1.9$. The coupling parameter is in agreement with what has already been reported and, as expected, g is smaller than 2 because of the underestimation of the molecular mass. It must be noticed that the saturation magnetizations, M_S's, are smaller than expected for (**1**) and (**2**) (not represented).

3.2.2. The other Ln(III)–Cu(II) cases

The magnetic behavior of all the other $Ln_2[Cu(opba)]_3(DMSO)_6(H_2O) \cdot H_2O$ compounds has been re-explored on the basis of chemically pure crystalline samples. The qualitative results of these measurements are summarized in Scheme 2. From this table, it clearly appears that the very simple mechanism suggested by one of us some years ago [8], according to which the Ln(III)–Cu(II) interaction would be antiferromagnetic when the Ln(III) ion involved has less than seven 4f electrons and ferromagnetic otherwise, is not valid for interpreting the observed magnetic behavior. Indeed, on the basis of their $\chi T = f(T)$ curves, the $Ln_2[Cu(opba)]_3(DMSO)_6(H_2O) \cdot H_2O$ compounds can be classified in to three different families depending on the lanthanide ion involved.

The first family (**family 1.**) is constituted by the La(III), the Lu(III), and the Y(III) containing compounds. The $\chi T = f(T)$ curve follows a perfect Curie Law calculated for three copper(II) ions as expected, since these lanthanide ions are diamagnetic. To this family may be added the Eu(III) containing compound because its ground state is non-magnetic ($^7F_0$).

The second family (**family 2.**) is constituted by the Ce(III), Pr(III), Nd(III), Ho(III), Er(III), Tm(III) and Yb(III) containing compounds. The magnetic $\chi T = f(T)$ curves observed decrease continuously in the studied temperature range.

The third and last family (**family 3.**) is constituted by the Sm(III), the Tb(III) and the Dy(III) containing compounds. The $\chi T = f(T)$ curves decrease while the temperature is lowered, then reach a minimum, and increase again when the temperature is lowered further.
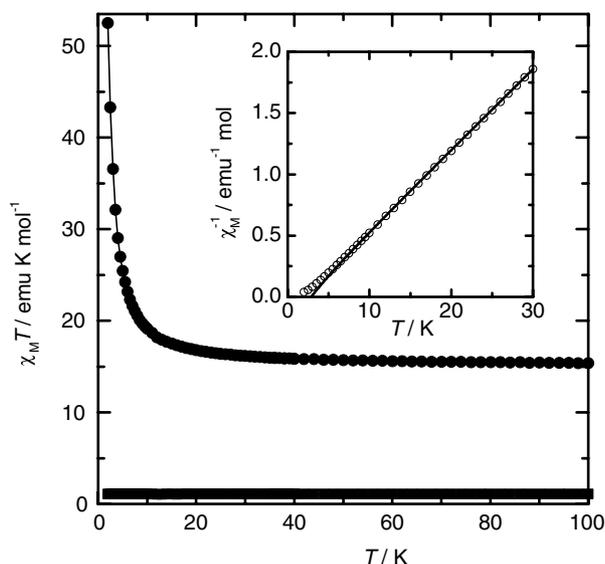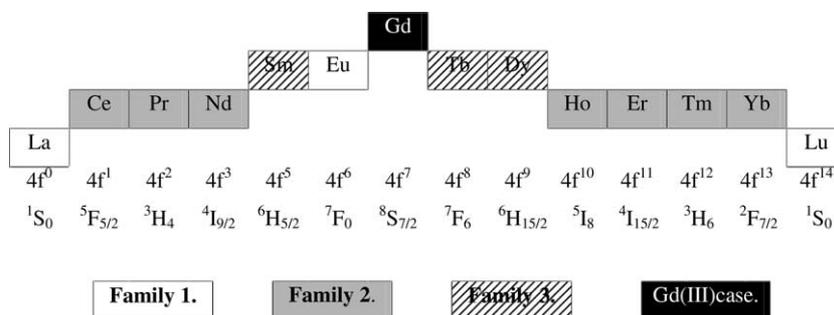

Fig. 4. Temperature dependence of the product $\chi_M T$ for compounds (**1**) (full circles) and (**2**) (full squares). Inset: thermal variation of χ_M^{-1} for (**1**) (open circles) with the best fitted curve (full line), see text for details.

Scheme 2.

From these qualitative results one can notice that, except in the Eu(III) containing compound, lanthanide ions with electronic configuration $[Xe]4f^n$ and $[Xe]4f^{14-n}$ exhibit the same magnetic behavior and belong to the same family. For the moment, we do not know what the scientific explanation is for this observation. Further work will have to be done on this.

4. Conclusions and outlook

The understanding of the magnetic interactions involving rare-earth ions in molecular magnets is still far from satisfactory. The key point is the role of the orbital contribution, which introduces many complications, in particular large anisotropies. We are convinced that this family of compounds presenting the same structure, irrespective of the lanthanide ion involved, will help us to understand the mechanism of the 4f–3d magnetic interactions more fully. This family of structurally characterized isostructural compounds is, to the best of our knowledge, the only one reported up to now. We are currently re-investigating their magnetic behavior in order to bring new insights on these still obscure mechanisms.

Appendix A. Supplementary materials

Full details of the X-ray structure determination of compound $Gd_2[Cu(opba)]_3(DMSO)_6(H_2O) \cdot (H_2O)$ have been deposited with the Cambridge Crystallographic Data Center under the depository number CCDC-245643 and can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 IEZ, UK; fax: (internat.) +44 1223/336 033; E-mail: deposit@ccdc.cam.ac.uk], on request, from the authors and the reference to this publication.

Crystallographic data in CIF format, anisotropic thermal parameters, complete list of bond lengths and angles, complete list of atomic coordinates and listing of calculated and observed structure factors can be obtained free of charge on request from the authors and the reference to this publication. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2004.11.048.

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