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Mesoxalate as Cu(II)-Ln(III) linker in the construction of MOFs in DMSO/water medium†

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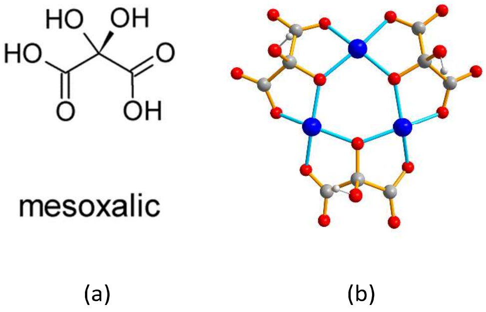
Five new heterometallic 3d-4f metal-organic frameworks with general formula $[Ln(H_2O)_zCu_3(Hmesox)_3DMSO]\cdot xH_2O\cdot yDMSO$ (Ln(III) = La, Ce, Pr, Nd and Eu; H_4mesox = mesoxalic or dihydroxymalonic acid; and DMSO= dimethylsulfoxide) have been prepared by crystal growth in agarose gel in a mixed solvent DMSO/water medium. The **LaCu3**, **CeCu3**, **PrCu3** and **NdCu3** yield prismatic well-formed chiral crystals whereas **EuCu3** produces laminar and bad-shaped crystals. The structural analysis shows cubic neutral chiral (10,3)-a networks for the former four compounds. On the other hand, the **EuCu3** yields neutral chains with lower connectivity crystallizing in a monoclinic space-group. The magnetic susceptibility study reveals antiferromagnetic coupling among the copper(II) ions through the mesoxalate-alkoxo exchange path-way. Theoretical DFT studies agree with the magnetic susceptibility investigations and show a correlation between the intensity of the magnetic coupling and the bridging Cu-O-Cu angles.

Introduction

The design and synthesis of 3d-4f heterometallic metal-organic frameworks (MOFs) is a very active field of research because of the potential applications of these materials in catalysis,[1, 2] magnetism,[3-9] luminescence,[10] proton conduction[11] or molecular absorption.[12]. One of the most difficult issues in the synthesis of those heterometallic 3d-4f compounds resides in the design of a ligand with the appropriate sites capable of coordinating both ions. We have found that the mesoxalate ligand (the conjugate base of the mesoxalic acid, H_4mesox) as a good choice for such a purpose (Scheme 1). The mesoxalate ligand yields triangular anionic copper(II) complexes, $[Cu_3(Hmesox)_3]^{3-}$, which can work as secondary building units (SBUs) in the construction of polymetallic assemblies or metal-organic frameworks.[13-16] Most of previous studies were done with divalent paramagnetic 3d ions as counterions and the compounds showed interesting properties such as chirality, long-range magnetic ordering, as well as proton-conduction.[15-19] However, this trinuclear unit has a very interesting configuration wherein the carboxylate groups are also able to join to the 4f ions (Scheme 1).

In a pure aqueous medium, only the La(III) derivatives $[La(H_2O)_3Cu_3(Hmesox)_3(H_2O)_5]\cdot 8H_2O$ and $[La(H_2O)_2Cu_3(Hmesox)_3(H_2O)_3]\cdot 7H_2O$ are obtained,[20] meanwhile the remaining lanthanoid(III) ions produced the corresponding lanthanoid(III) mesoxalates, $[Ln_2(H_2mesox)_3]$, which are more insoluble than the heterometallic compound.[21, 22]



Scheme 1. (a). Mesoxalic acid (H_4mesox). (b). $[Cu_3(Hmesox)_3]^{3-}$ unit. Colour code: Cu, blue; C, dark grey; O, red; H, light grey.

Conversely, raising the medium solubility, using a DMSO/H_2O mixed solvent medium, and adding a gelling agent (agarose), resulted in an improvement in the crystal growing process which allowed us the isolation of the 3d-4f heterometallic compounds with general formula $[Ln(H_2O)_zCu_3(Hmesox)_3DMSO]\cdot xH_2O\cdot yDMSO$, (Ln(III) = La, Ce, Pr, Nd and Eu, hereinafter referred to as **LaCu$_3$**, **CeCu$_3$**, **PrCu$_3$**, **NdCu$_3$** and **EuCu$_3$**, respectively). The trivalent Ln(III) ions and the trinegative copper(II) triangular complexes combine together to give rise to neutral heterometallic metal-organic frameworks yielding in most cases highly-crystalline materials. In this study we investigate the synthesis, the crystal structure and their magnetic properties by single-crystal X-ray diffraction, magnetic susceptibility measurements and theoretical DFT calculations.

Experimental

Materials and methods

Basic copper(II) carbonate $CuCO_3.Cu(OH)_2$, mesoxalic acid disodium salt, copper(II) nitrate hexahydrate, lithium hydroxide hydrate and hydrated lanthanoid(III) nitrates were acquired from commercial sources and were used as received. Elemental analyses (C, H and S) were performed on an EA 1108 CHNS-O microanalytical analyser. IR spectra (400-4000 cm-1) were recorded on a Thermo Nicollet avatar 360 FT-IR spectrometer with the sample prepared as KBr disks. Magnetic susceptibility measurements on polycrystalline samples were carried out by means of a Quantum Design SQUID MPMS XL magnetometer. The dc measurements were performed in the temperature range 1.9-300 K at applied magnetic fields of 1000 Oe for T < 15 K, and 10.000 Oe for T ≥ 10 K. Diamagnetic corrections of the constituent atoms were estimated from Pascal's constants and experimental susceptibilities were also corrected for the temperature-independent paramagnetism and the magnetization of the sample holder. Powder X-ray diffraction patterns on polycrystalline samples were collected with a PANanalytical X'pert X-ray diffractometer (Cu Kα radiation = 1.54184 Å) at room temperature.

Synthetic procedures

The $[Ln(H_2O)_zCu_3(Hmesox)_3DMSO]\cdot xH_2O\cdot yDMSO$ compounds with Ln(III) = La, Ce, Pr, Nd, and Eu, **$LaCu_3$**, **$CeCu_3$**, **$PrCu_3$**, **$NdCu_3$** and **$EuCu_3$**, respectively, were prepared following a similar procedure. A cation exchange resin (Amberlite IR-120, 15.4 g) was added to a suspension of mesoxalate disodium salt (1.98 g, 11 mmol) in 14 mL of water and filtered through a Buchner funnel (porosity 25-50μm) into a round-bottom flask and was allowed to react under stirring with basic copper(II) carbonate (1.210 g, 11 mmol) for 20 minutes at 30ºC. Then the solution was cooled, filtered and the pH adjusted to 2.5 by the addition of the appropriate amount of a solution of lithium hydroxide in water (~1M). To the resultant solution, 20 mL of dimethylsulfoxide (DMSO) and 10 mL of an aqueous solution of copper(II) nitrate (200 mg, 0.70 mmol) were added under stirring, and the pH was adjusted to 3.5 by the addition of some more aqueous solution of lithium hydroxide.

Then, the 55 mL of $[Cu_3(Hmesox)_3DMSO]^{3-}$ precursor solution were divided into 11 aliquots of 5mL each, which were placed in 11 test tubes containing 1 mmol Cu^{2+}. Gelation of each aliquot was achieved by adding 45 mg of agarose to each tube and rising temperature to 80°C in a water bath until the solution became completely clear (without grains of agarose). Then, the tubes were allowed to cool to room temperature and gelation occurred (1-2 hours). Once gelation was completed, 0.33 mmol of the corresponding lanthanoid(III) nitrates (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er, Yb; *ca.* 145 mg) in 4mL of 50/50 water/DMSO, were slowly added to each test tube. The tubes were allowed to stand undisturbed at room temperature. Fig. 1 shows a test tube with crystals of **$LaCu_3$** growing in the agarose gel.

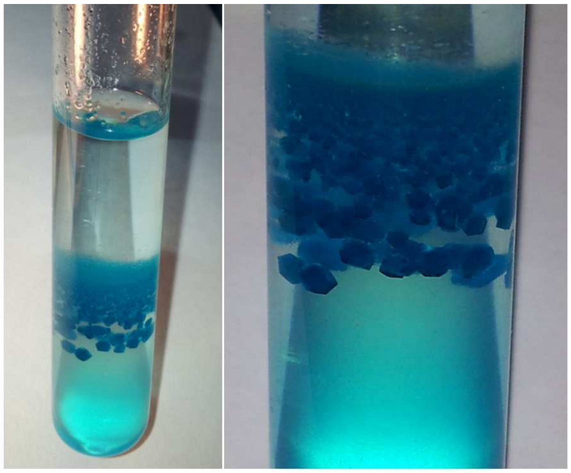


Fig. 1 Test tubes with crystals of **$LaCu_3$** growing in the agarose gel

Following this procedure X-ray-suitable single-crystals were obtained for **$LaCu_3$**, **$CeCu_3$**, **$PrCu_3$** and **$NdCu_3$** within a few days. **$EuCu_3$** corresponding crystals were obtained within two months. Anal. calcd. for $C_{12.4}H_{21.2}S_{1.7}O_{23.7}LaCu_3$: C, 15.95; H, 2.27; S, 5.83; found C, 16.01; H, 2.29; S, 5.78. Anal. calcd. for $C_{13}H_{19}S_2O_{22}CeCu_3$: C, 16.94; H, 2.06; S, 6.94; found: C, 16.83; H, 2.03; S, 6.95. Anal. calcd. for $C_{14}H_{28}S_{2.5}O_{25.5}PrCu_3$: C, 16.55; H, 2.76; S, 7.88; found: C, 16.39; H, 2.75; S, 7.87; Anal. calcd, for $C_{15.8}H_{37.4}S_{3.4}O_{28.4}NdCu_3$: C, 16.85; H, 3.32; S, 9.67; found: C, 16.87; H, 3.47, S, 9.90. IR spectra as well as powder X-ray diffraction patterns are shown in Electronic Supplementary Information (ESI).

Just a few single-crystals of **$EuCu_3$** were obtained which did not allow us to be able to carry out the elemental analyses, to obtain IR spectrum or to measure the magnetic properties. The corresponding test tubes for the other cations (Gd, Tb, Dy, Er and Yb) afforded low-crystallinity materials which did not allow the determination of the structure and preclude us from any magnetic measurements.

Crystallography

Data Collection

Single-crystal XRD data were collected at 100(2) K for **$LaCu_3$** and at 239(2)K for the remaining compounds using an Agilent SuperNova diffractometer with micro-focus X-ray on Cu-Kα radiation (λ = 1.5418 Å) for **$LaCu_3$** and **$EuCu_3$** and on Mo-Kα (λ = 0.71073Å) for **$CeCu_3$**, **$PrCu_3$**, **$NdCu_3$**.

CrysalisPro software was used to collect, index, scale and to apply analytical absorption correction based on Gaussian method.[23] Details of the refinement can be found in Table 1.

Table 1 Crystallographic data and structure refinement summary for **LaCu$_3$**, **CeCu$_3$**, **PrCu$_3$**, **NdCu$_3$** and **EuCu$_3$**.

Compound	**LaCu$_3$**	**CeCu$_3$**	**PrCu$_3$**	**NdCu$_3$**	**EuCu$_3$**
Empirical formula	$LaCu_3C_{12.4}H_{21.2}S_{1.7}O_{23.7}$	$CeCu_3C_{13}H_{19}S_2O_{22}$	$PrCu_3C_{14}H_{28}S_{2.5}O_{25.5}$	$NdCu_3C_{15.8}H_{37.4}S_{3.4}O_{28.4}$	$EuCu_3C_{11}H_{13}S_1O_{21}$
M / g mol^{-1}	933.53	922.14	1016.01	1125.72	855.86
Temperature / K	100(2)	293(2)	293(2)	293(2)	293(2)
λ / Å	1.54184	0.71073	0.71073	0.71073	1.54185
Crystal system	Cubic	Cubic	Cubic	Cubic	Monoclinic
Space group	$P2_13$	$P2_13$	$P2_13$	$P2_13$	C12/c1
a / Å	17.5235(11)	17.6180(2)	17.580(2)	17.5154(4)	20.2355(9)
b / Å	17.5235(11)	17.6180(2)	17.580(2)	17.5154(4)	27.1206(9)
c / Å	17.5235(11)	17.6180(2)	17.580(2)	17.5154(4)	23.3255(8)
α / °	90.00	90.00	90.00	90.00	90.00
β / °	90.00	90.00	90.00	90.00	109.709(4)
γ / °	90.00	90.00	90.00	90.00	90.00
V / Å^3	5381.0(6)	5468.52(11)	5433.2(11)	5373.5(2)	12051.1(8)
Z	4	4	4	4	8
Dcalc / g/cm^3	1.152	1.120	1.242	1.391	1.887
μ / mm^{-1}	8.437	2.091	2.192	2.321	18.423
Theta range / º	3.57-76.68	2.83-31.99	4.18-28.61	3.29-33.04	3.83-73.02
Unique reflections	119625	29436	4671	28229	41844
R(int)	0.0980	0.0787	0.0843	0.0816	0.1036
GOF on F^2	1.082	0.996	0.998	1.004	0.991
$R_1[I>2\sigma(I)]^a$	0.0742	0.0490	0.0841	0.0681	0.1441
$wR_2[I>2\sigma(I)]^b$	0.2191	0.1106	0.2221	0.1668	0.3517
Flack Parameter	-0.020(5)	-0.013(26)	0.015(72)	-0.120(58)	

$^aR_1 = [\Sigma(\|F_o\|-\|F_c\|)/\Sigma\|F_o\|]$; $^bwR_2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$

Structure Analysis and Refinement

Despite the excellent and well diffracting single-crystals obtained for **LaCu$_3$**, **CeCu$_3$**, **PrCu$_3$** and **NdCu$_3$**, it did not correspond to the same quality of structure resolution and the structure of these compounds proved difficult to elucidate. After measuring different set of crystals for each compound and trying to solve their structure, not only in lower but also in higher symmetry space-groups, we found that the model that best fitted the data and had a reasonable symmetry was the cubic $P2_13$ space group. We think that the variable amount of disordered water and DMSO molecules filling the large voids left by the neutral cubic three-dimensional network, randomly displaces the atoms from their ideal positions resulting in large standard deviations and in high *R* values. This occurs even if the well-shaped single-crystals just separated from their mother liqueurs are measured at low temperatures (100 K). Moreover, the apical position of the trinuclear copper entities can either be occupied by water or DMSO molecules, which also induces a random distortion of the structure. These two facts together with the presence of large amount of disordered crystallization solvent molecules, made it difficult to increase the quality of the fit. However, it is important to note that there is a perfect match between the experimental powder diffraction patterns for each compound and its corresponding simulation from the cif files of the single-crystals. Thus, we can conclude that despite the disorder, the structure of the metal-ligand network has been determined unambiguously.

The structures were solved by direct methods *(SHELXS-97)*,[24, 25] and refinement was done by full-matrix least squares on F^2 using the *SHELXL-97* program suite.[24, 25] All non-hydrogen positions were refined with anisotropic temperature factors, with the exception of some atoms which were refined isotropically since they destabilized the refinement (Compound **LaCu$_3$**: O1S, O2S, O3S, S2S, S3S, C1S, C2S,C3S, C4S, C5S, C6S; Compound **CeCu$_3$**: C1S; Compound **PrCu$_3$**: C1S, C2S; Compound **NdCu$_3$**: O1W, O1S, S1, C1S, C2S; Compound **EuCu$_3$**: O4C, O4F).

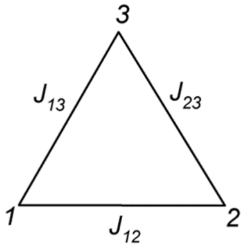
LaCu$_3$, **CeCu$_3$**, **PrCu$_3$** and **NdCu$_3$** DMSO coordination molecules were found and refined for all the compounds with DFIX commands for their S-O, S-C and C-C distances. The oxygen atom of the coordination DMSO molecules bridging the three copper atoms, locates in the trigonal axe, but there appears to be three sites for the S atom related to 3-fold rotation axes which sustains the low intensity of the peaks for this atom, also partial substitution of DMSO by water would have the same result. Crystallization DMSO molecules were found for **LaCu$_3$**, but they are highly disordered (even at 100(2) K) with partial occupation of 0.27 and 0.23. These two DMSO partial occupied molecules are not supposed to interact with the copper atoms through the S atom, due to their large Cu-S distances (3.15-3.25 Å). Attempts to identify DMSO crystallization molecules failed for compounds **CeCu$_3$**, **PrCu$_3$** and **NdCu$_3$** since these structures were highly disordered at 293(2) K. Nevertheless, new sets of *F^2(hkl)* values were obtained by the SQUEEZE procedure included in PLATON.[26-28] Hydrogen atoms of the water molecules and mesoxalate OH groups were neither found nor calculated. Attempts to locate and refine them destabilized the refinement because of the high disorder of the structures. Nevertheless, they were included in the unit card for calculation of the correct sum formula, density and F(000).

Because of the bad quality of the **EuCu$_3$** crystals, the data acquisition had to be carried out with seven different crystals before having a suitable data collection, all of them giving high absorption coefficients which made difficult the resolution of the structure and explains the high refinement coefficient *R* obtained. The hydrogen atoms of the water molecules bound to the europium atoms of compound **EuCu₃** were found by difference of electronic density maps, but could not located since a suitable tetrahedral geometry around the oxygen atom was not encountered. The central oxygen atom of hydroxyl group of mesoxalate ligands exhibits two different positions with an overall occupation of 1. Hydrogen atoms of the central OH groups were neither founded nor calculated. Hydrogen atoms of the methyl group of the DMSO coordination molecules were positioned geometrically (C−H=0.96Å) and refined using a riding model (AFIX 33) with U_{iso}(H)=1.5 U_{eq}(C). After assigning all peaks, the residual electron density is high, but attempts to distinguish solvent molecules were not successful due to the high disorder present in the structure. This fact can be explained in terms of the high atom number of the asymmetrical unit and the bad quality of the crystals, which were laminar 0.11 x 0.08 x 0.04 mm. This electron residual density is mainly located in the space between layers and confirms that almost all this electron density is due to the disorder of water and DMSO crystallization molecules which could not be found nor refined. Also for this compound, new sets of F^2*(hkl)* values were obtained by the SQUEEZE procedure contained in PLATON.[26-28] The H atoms have been included in the unit card for calculation of the correct sum formula, density and F(000). Details of the refinement can be found in Table 1. CCDC reference numbers for **LaCu₃**, **CeCu₃**, **PrCu₃**, **NdCu₃** and **EuCu₃** are 1402451, 1402452, 1402453, 1402454 and 1402455, respectively.

DFT calculations

Spin-unrestricted DFT calculations were performed at the B3LYP level by means of the *Gaussian09* code (Revision A.02) for the different $[Cu_3(Hmesox)_3\mu_3\text{-}DMSO]^{3-}$ triangles found in all the compounds.[29] A triple-ξ all-electron Gaussian basis set (TZVP) was used for all elements.[30]

The general zero-field Hamiltonian for a triangular system can be written as $\boldsymbol{H} = -J_{12}(\boldsymbol{S}_1\boldsymbol{S}_2) - J_{13}(\boldsymbol{S}_1\boldsymbol{S}_3) - J_{23}(\boldsymbol{S}_2\boldsymbol{S}_3)$, where 1, 2 and 3 refer to the three copper(II) centres and J_{12}, J_{13}, and J_{23} correspond to the magnetic coupling constants between two adjacent copper(II) centres (Scheme 2). Single-point calculations were performed for the quartet $S = 3/2$ (HS), with $S^2 \approx 3.75$ and the broken-symmetry $S = ½$ doublet states ↑↓↑, ↑↑↓, and ↓↑↑ (LS1, LS2 and LS3, respectively) with $S^2 \approx 1.75$. The atomic positions of the trinuclear units $[Cu_3(Hmesox)_3\mu_3\text{-}DMSO]^{3-}$ were taken from the cif files without minimization. We also calculated the energies of the $[Cu_3(Hmesox)_3\mu_3\text{-}H_2O]^{3-}$ with the atomic positions of the **LaCu₃** compound in order to investigate the effect of the water molecule in the apical position. For the case of the equilateral triangles (**LaCu₃**, **CeCu₃**, **PrCu₃** and **NdCu₃**) the LS states are degenerated and the magnetic coupling constants are equivalent $J = J_{12} = J_{13} = J_{23}$ thus the magnetic coupling constant value can be obtained from the difference between the energies of the HS and any of the LS states: $E(LS) - E(HS) = 2J$.[31, 32] For the case of the scalene triangles (**EuCu₃**) the values of the magnetic coupling constants are obtained from these differences, E(HS)−E(LS1)= $-J_{12}-J_{23}$, E(HS)−E(LS2)= $-J_{23}-J_{13}$ and E(HS)−E(LS3)= $-J_{12}-J_{13}$.



	Copper(II)		
States	1	2	3
HS	↑	↑	↑
LS1	↑	↓	↑
LS2	↑	↑	↓
LS3	↓	↑	↑

Scheme 2 Notation of the triangle and magnetic coupling constants (left). Magnetic states (HS, LS1, LS2 and LS3) and spin values in the respective Cu(II) ions. ↑ = 1/2; ↓ = −1/2 (right).

Results and discussion

Synthesis of $[Ln(H_2O)_zCu_3(Hmesox)_3DMSO]\cdot xH_2O \cdot yDMSO$, ($H_4$mesox= mesoxalic acid, Ln(III) = La, Ce, Pr, Nd and Eu. LaCu₃, CeCu₃, PrCu₃, NdCu₃ and EuCu₃)

Aqueous solution reaction of copper(II) carbonate with mesoxalic acid (H_4mesox) in the 30-40ºC temperature range yields a clear blue solution in which the trinuclear $[Cu_3(Hmesox)_3]^{3-}$ complex is formed.[17-20] The mesoxalate ligand in the trinuclear complex is triply deprotonated. Thus, two carboxylate and one alcohol hydrogen-ions need to be removed from the original mesoxalic acid (H_4L). For such a purpose, LiOH is added to increase the pH to favour the formation of $[Cu_3(Hmesox)_3]^{3-}$. In the same way, some excess of copper(II) (provided as copper(II) nitrate) is desired as it also decreases the amount of free mesoxalate species and displaces the equilibrium to the formation of the trinuclear complex.[15] Moreover, the DMSO/water mixed solvent medium increases medium solubility and all these conditions together avoid the precipitation of the Ln(III) mesoxalates, $[Ln_2(H_2mesox)_3]$.[21]

The crystal-growing process in agarose gel resulted in a slow mixing of the components yielding pure and high-quality crystals suitable for single-crystal X-Ray analysis.[33] Therefore, the control of the reaction conditions and the crystal growing process led to the isolation of the compounds.

Thermogravimetric study

Thermogravimetric analyses (TGA) (Fig. S1) show mass loss percentages between 21-25% in the temperature range 25°C-160°C corresponding to the loss of 4 H_2O and 1.7 DMSO; 2 H_2O and 2 DMSO; 5 H_2O and 2 DMSO; and 7 H_2O and 2 DMSO crystallization and weakly coordinated water and dimethylsulfoxide molecules, for compounds **LaCu₃**, **CeCu₃**, **PrCu₃**, and **NdCu₃**, respectively. The relative amount of water and DMSO has been calculated in relation to the elemental analyses. A progressive weight loss occurs upon further heating that corresponds to the degradation of the organic part of the material and the loss of the rest of the DMSO or water molecules.

The thermogravimetric study reveals two important features of these compounds which will have very important consequences in the structure determination. The compounds contain up to 25% of the total mass as crystallization molecules. These molecules are very disordered and constitute a source of uncertainty which results in bad agreement parameters in crystal structure refinement. Moreover, the crystallization molecules are lost at room temperature and during the X-ray data acquisition process there can be a change in the total amount of solvent and this will also result in bad quality data set.

Crystal Structure of [Ln(H_2O)Cu_3($Hmesox)_3$DMSO]·xH_2O ·yDMSO, Ln (III) = La, Ce, Pr and Nd.

LaCu$_3$, **CeCu$_3$**, **PrCu$_3$** and **NdCu$_3$** are isostructural and their structure arise from the neutralization of [Cu_3($Hmesox)_3$DMSO]$^{3-}$ anionic metalloligands by Ln(III) cations to yield infinite three-dimensional neutral networks with general compositions of [Ln(H_2O)Cu_3($Hmesox)_3$DMSO] (with Ln (III)= La, Ce, Pr and Nd) and x water and y DMSO crystallization molecules (Fig. 2). (The total amount of crystallization water and DMSO has been determined from elemental analyses. Thus, the x and y values are: 3, 0.7; 1, 1; 4, 1.5; and 6, 2.4; for **LaCu$_3$**, **CeCu$_3$**, **PrCu$_3$** and **NdCu$_3$**, respectively. The formula weight shown in Table 1 also agrees with these values).

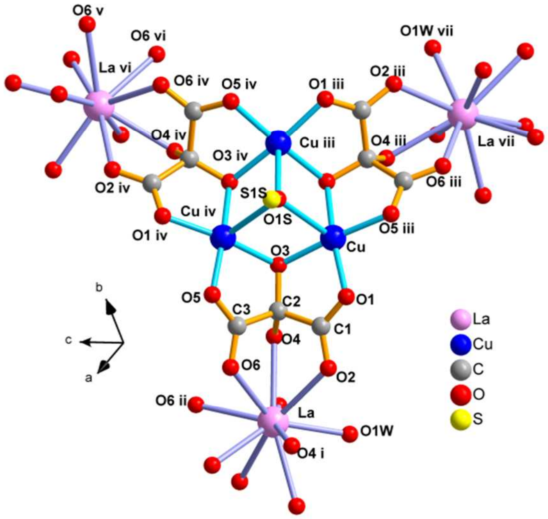
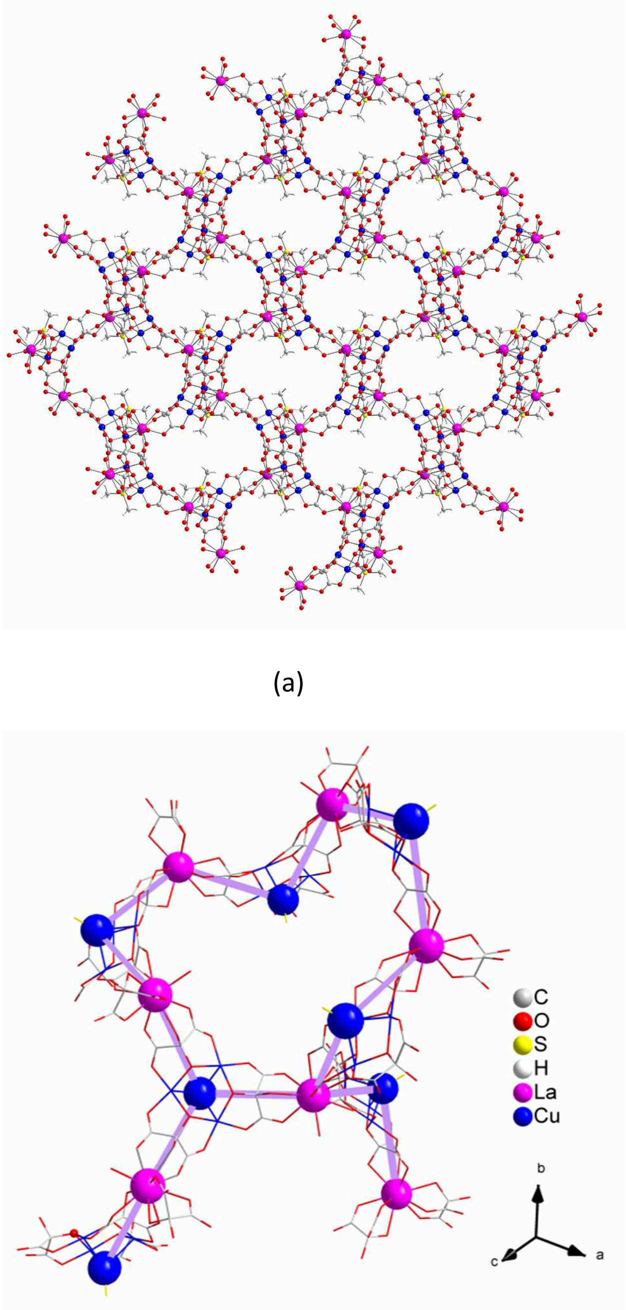


Fig. 2 [Cu_3($Hmesox)_3$DMSO]$^{3-}$ unit surrounded by three La(III) ions in **LaCu$_3$**, methyl groups of DMSO are not shown for clarity. (i) y, z, x; (ii) z, x, y; (iii) -0.5+y, 0.5-z, -x; (iv) -z, 0.5+x, 0.5-y; (v) -x, 0.5+y,0.5-z; (vi) –y, 0.5+z,0.5-x; (vii) -0.5+z, 0.5-x,-y.

The asymmetric unit contains one Ln(III) ion, one copper(II), one mesoxalate (3-) ligand, one coordination DMSO and one coordination water molecule. In the structure of **LaCu$_3$**, **CeCu$_3$**, **PrCu$_3$**, and **NdCu$_3$** the Ln(III) ions and the [Cu_3($Hmesox)_3$DMSO]$^{3-}$ units work as three-connecting nodes (Fig. 3) resulting in a cubic (10,3)-a network which is known as the default network of the combination of triangles.[34, 35] This network is homochiral and if one traces the four-membered helices, one finds the same handedness within a (10,3)-a net (Fig. 3).[17, 22, 36-46]



(a)

(b)

Fig. 3 (a). Three-dimensional structure of **LaCu$_3$**. (b). detail of the (10,3)-a network, the copper(II) trinuclear unit and the Ln(III) ions work as three-connectors

The crystallization of **LaCu₃**, **CeCu₃**, **PrCu₃**, and **NdCu₃** proceeds enantioselective to give chiral crystals with either right-handed (*P*) or left-handed (*M*) (10,3)-a nets. Nevertheless, the batch of crystals contains both enantiomorphs and the overall crystal mixture is expected to be racemic. However, the helices of the measured crystals of **LaCu₃** are all left-handed, *M* and the measured crystals of **CeCu₃**, **PrCu₃**, and **NdCu₃** exhibited left-, right- and left-handedness, respectively. The chirality of the (10,3)-a network arises from the Δ or Λ environment of the Ln atom (Fig. 4).[35] The measured crystals of **LaCu₃** and **PrCu₃** have Δ configuration, whereas those of **CeCu₃** and **NdCu₃** have Λ configuration. Flack parameters confirm their correct absolute structure (Table 1).[47-51]

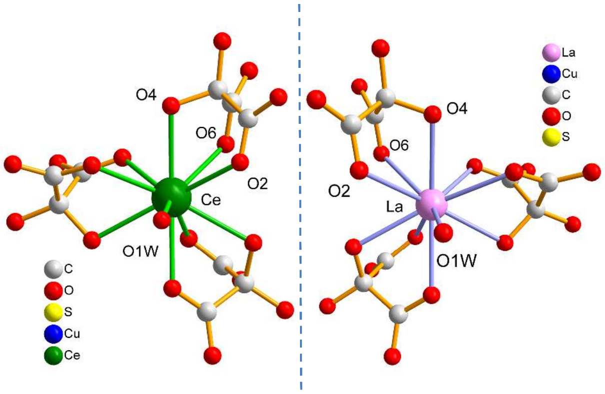


Fig. 4 Λ and Δ configuration of the Ce(II) and La(III) ions respectively in **CeCu₃** and in **LaCu₃**.

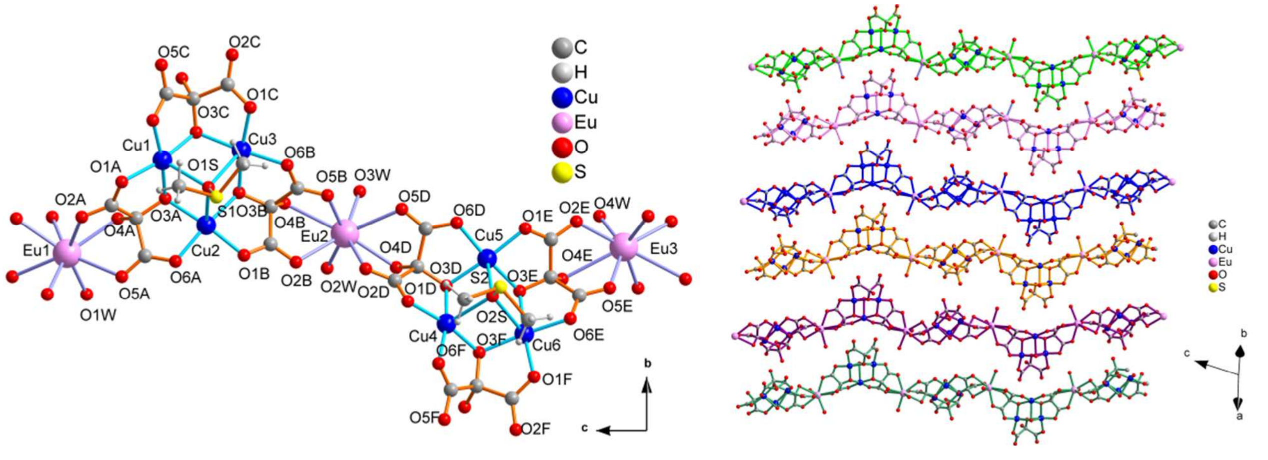
$[Eu(H_2O)_2Cu_3(Hmesox)_3DMSO]$ crystallizes in a monoclinic C1 2/c 1 space group with two trinuclear copper entities, in an idealized isosceles triangular arrangement, and two Eu(III) cations found in the asymmetric unit. The structure consist of neutral infinite chains of $[Eu(H_2O)_2Cu_3(Hmesox)_3DMSO]$ in which the Eu(III) ions and the $[Cu_3(Hmesox)_3DMSO]^{3-}$ metalloligands work as two-connecting nodes (Fig. 5).

In all the **LnCu₃** compounds the mesoxalate ligands are tri-anionic, i.e. $C_3HO_6^{3-}$ ($Hmesox^{3-}$) with the two carboxylate groups and one hydroxyl group deprotonated and they are bound to copper(II) ions to yield the $[Cu_3(Hmesox)_3DMSO]^{3-}$ anionic units in which the copper atoms are in the vertices of an equilateral (in **LaCu₃**, **CeCu₃**, **PrCu₃**, and **NdCu₃**) or almost-isosceles (in **EuCu₃**) triangle. Besides, all the mesoxalate ligands in **LaCu₃**, **NdCu₃**, **PrCu₃** and **NdCu₃** link two copper(II) ions with one Ln(III) ion in a μ_3-η^1:η^2:η^1:η^1:η^1:η^1 fashion acting as bidentate towards the copper(II) ions and tridentate towards the Ln(III). As result of this bridging behaviour of the mesoxalate all the trinuclear units function as three connectors leading to the (10,3)-a three-dimensional network (Fig. 3). On the other hand, one of the three mesoxalate ligands of the trinuclear units in **EuCu₃** works as μ_2-η^1:η^2:η^1 bridge linking only the two copper(II) ions resulting in a two connector behaviour of the trinuclear unit which leads to the one-dimensional network structure in **EuCu₃** (Fig. 5).

Each copper(II) ion is chelated by two mesoxalate ligands to a five-membered chelate ring in which the metallic ion exhibits a square pyramidal environment with a DMSO molecule bridging three copper(II) ions filling the apical position of the three copper(II) ions at the same time with a μ_3-*κO* bridging mode (Fig. 2). As an example, the basal Cu-O distances range between 1.929(5) and 1.944(6) Å in **LaCu₃**, and the apical Cu-O distance is 2.471(8) Å. Ln(III) ions in compounds **LaCu₃**, **CeCu₃**, **PrCu₃**, and **NdCu₃** exhibit coordination number 10 with an oxygen atom of a water molecule and nine oxygen atoms of three mesoxalate ligands working as tridentate (with one oxygen atom from a hydroxyl and two from two carboxylate groups) coordinate the Ln(III) ions in a sphenocorona polyhedron environment (Fig. 4). Main distances and angles are shown in Tables S1-S4.

The copper(II) ions in **EuCu₃** exhibit distorted square-pyramidal environment (Fig. 5) which arises from the coordination of four carboxylate-oxygen atoms of the mesoxalate ligands and the oxygen atom of a dimethylsulfoxide molecule which fills the apical site (Cu-O distances ranging from 1.94 to 1.98 the basal and from 2.32 to 2.59 Å the apical). Main distances and angles are shown in Table S5. The Europium (III) ions exhibit coordination number 8 with a square antiprism geometry: two water molecules and two tridentate mesoxalate ligands, through a hydroxyl-oxygen and two carboxylate-oxygen atoms, fill the coordination sphere of the Eu(III) ions.

The main structural difference between **LaCu₃**, **CeCu₃**, **PrCu₃**, and **NdCu₃** with **EuCu₃** results from the different coordination number of the Ln(III) ion. **LaCu₃**, **CeCu₃**, **PrCu₃**, and **NdCu₃** exhibit coordination number 10 for the lanthanoid(III) ion which result in a three-connecting node behaviour. On the other hand, Eu(III) exhibits coordination number 8 with only two trinuclear units around it which results in a two-connecting node behaviour that yields the chain structure. This change in the coordination number is related to the lanthanoid contraction. Another consequence of the reduction of the dimensionality of the network is the change in the habit (or facie) of the crystals. **LaCu₃**, **CeCu₃**, **PrCu₃**, and **NdCu₃** give rather big hexagonal-prismatic crystals which are good for X-Ray single crystal measurements. However, crystals of **EuCu₃** (and also the rest of the heavier lanthanoids) are small, laminar, usually twinned and obtained with very low yield which makes difficult to solve the structure and precludes the measurement of the magnetic properties.



(a) (b)

Fig. 5 (a). Molecular structure of the **EuCu₃** compound. The trinuclear unit and the Eu(III) ions work as two-connectors. (b). Packing of the chains formed.

Magnetic Properties

The temperature dependence of the $\chi_M T$ product for **LaCu₃** is shown in Fig. 6. The value observed at room temperature, 1.18 emu mol^{-1} K, is slightly lower to that expected for three non-interacting copper(II) ions (expected $\chi_M T=3x(N\beta^2g^2/3k)S(S+1)$ = 1.23 emu mol^{-1} K with g~2.1 and S =1/2) and, on lowering temperature, it shows a continuous decrease to reach 0.38 emu mol^{-1} K at 2 K. Because of the diamagnetic character of the La(III), the magnetic properties of the compound are only related to the copper(II) ions and this behaviour is indicative of the occurrence of a weak antiferromagnetic coupling among the copper(II) ions through the μ_2-O-alkoxide bridge of the mesoxalate ligands. The magnetization isotherm also points to an antiferromagnetic coupling with a S = ½ magnetic ground state. Owing to the equilateral triangular structure of the copper(II) trinuclear units the magnetic properties should be studied by means of the isotropic Heisenberg-Dirac-Van Vleck Hamiltonian formalism in the form of eq (1)

$$\hat{H}_{HDVV} = -J(\hat{S}_1\hat{S}_2 + \hat{S}_1\hat{S}_3 + \hat{S}_2\hat{S}_3) \qquad (1)$$

in which J is the exchange coupling constant and $\hat{S}_i$ the spin operator of the centre i. The equilateral triangular system is described by two degenerated spin doublets and a spin quartet separated by an energy gap of 3J/2. The analytical expression for the susceptibility is then given in eq (2)[52]

$$\chi_M=\left(N\beta^2g^2/4kT\right)\left[1+5\exp\left(-3J/2kT\right)/1+\exp\left(-3J/2kT\right)\right] \qquad (2)$$

N, g, β and k have their usual meaning. Best fit to this model gives (red line) $J = -45(1)$ cm^{-1}, $g = 2.09(1)$, $\Theta = 0.1(1)$ K and $R = 2.81x10^{-3}$. A Weiss parameter, Θ, was introduced to consider the magnetic coupling among copper(II) ions through the diamagnetic lanthanum(III). R is the agreement factor defined as $\Sigma_i[(\chi_M T)_{obs}(i)-(\chi_M T)_{calc}(i)]^2/\Sigma_i[(\chi_M T)_{obs}(i)]^2$.

Although the magnetic data follow the trend of the theoretical law, it is evident that the model doesn't reproduce the experimental values. The deviation is somewhat surprising since the compound is obtained as well formed and highly-pure crystals. As a result of this unexpected behaviour we have considered other effects such as the distortion towards lower symmetry of the equilateral triangle (isosceles or scalene) or the occurrence of antisymmetric exchange interactions (ASE).

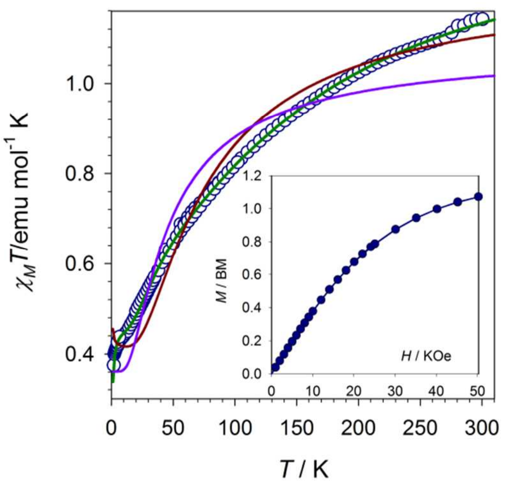


Fig. 6 Temperature dependence of the $\chi_M T$ product for **LaCu₃**. Red line, best fit to equation 2. Purple line, best fit to the model considering ASE. Green line, best fit to model shown in equation 3. The insert shows the Magnetization isotherm at 2 K.

Equilateral triangular complexes with antiferromagnetic interactions have a degenerated ground state and, as Jahn-Teller effects explains, this degeneration is unstable and distortion appears in order to remove the degeneracy. We have analysed the data with the isosceles triangular model, but the fit did not show any improvement, so the distortion from the equilateral triangle, if it occurs, it is not enough to explain the behaviour observed. [best fit to the isosceles triangular model: $J = -45.1$ cm^{-1}, $j = -45.2$, $g = 2.09(1)$, $\Theta = 0.1(1)$ K and $R = 2.81\text{x}10^{-3}$; the plot almost overlap that of the equilateral triangle].[52]

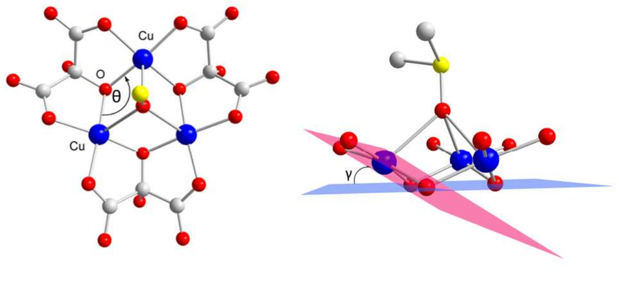
Antiferromagnetically coupled trinuclear complexes may exhibit spin frustration and these systems are candidates to show antisymmetric exchange interactions (ASE). The antisymmetric exchange parameter, G, can reach values in the order of 0.17-0.19 times J. The data were analysed by means of the analytical expression proposed by Ferrer *et al.*[52] with no special improvement of the fit. This is somewhat as expected since the deviation not only occurs in the low temperature region where the ASE interactions are operative. [Best fit parameters $J = -13.9$cm^{-1}, $j = -12.9$cm^{-1}, g_{par}=2.20, g_{per}=2.00 and $G = -1.4\text{x}10^{-3}$ cm^{-1} and $R = 6.26\text{x}10^{-3}$].

The distortion of the triangle and the occurrence of antisymmetric exchange interactions did not improve the quality of the fit, so we started to think that the compound could behave as containing more than one copper(II) triangle. Having in mind that the compound is obtained from a mixed solvent water and DMSO solution, the apical position of the three copper(II) ions of the trinuclear unit can be randomly filled either by water or DMSO molecules. It has been recently observed that a copper(II) tartronate derivative $Rb_3[Cu_3(tar)_3(H_2O)]$ has a coordination water molecule in the apical positon of the three copper(II) ions.[15] The effect of this alternation of water and DMSO in the apical position would result in the random alternation of triangles with somewhat different structural parameters and therefore the magnetic data would deviate from the single triangle model. This fact could also explain the rather high R values obtained in the structure refinement. An isotropic spin Hamiltonian for such a system with two equilateral triangles would then be described by

$$\hat{H} = -(1-\rho)J_1(\hat{S}_1\hat{S}_2 + \hat{S}_1\hat{S}_3 + \hat{S}_2\hat{S}_3) - \rho J_2(\hat{S}_4\hat{S}_5 + \hat{S}_5\hat{S}_6 + \hat{S}_4\hat{S}_6) \tag{3}$$

with the symbol ρ as the mole fraction of water in the apical position which can take values from 0 to 1 ($\rho = 0 \Rightarrow$ 100% DMSO; $\rho = 1 \Rightarrow$ 100% H_2O). The best fit parameters for such a model are $J_1 = -65(1)$cm^{-1} $J_2 = -15.5(3)$cm^{-1}, $g = 2.20(1)$, $\Theta = -0.50(2)$ K, $\rho = 0.33$ and $R = 3.29x10^{-5}$ with an almost perfect match of the magnetic data to the theoretical plot. As a result of the magnetic study we think that some of the apical positions are occupied by coordination water molecules (33%) and others by DMSO molecules with both slightly different structural parameters and therefore with different antiferromagnetic couplings. However, we cannot assign unambiguously any of the couplings to any of the molecules from the magnetic susceptibility measurements.

Because of the diamagnetic character of the lanthanum(III), the magnetic properties of **LaCu₃** are only associated with the copper(II) ions and the antiferromagnetic coupling observed in the $\chi_M T$ plot is related to the copper(II)-copper(II) interaction through the mesoxalate alkoxo bridging oxygens. The magnetic orbital of the copper(II) ions in square-planar environment is of the $d_{x^2-y^2}$ character and mainly located in the plane defined by the four basal oxygens. (The magnetic coupling through the apical exchange-pathway, where the nonmagnetic d_{z^2} orbital is defined, is very pour). It is well known that alkoxo- and hydroxo-bridged planar copper(II) complexes with Cu-O-Cu bridging angles (Fig. 7, θ) larger than 98º exhibit antiferromagnetic couplings with larger antiferromagnetic couplings for larger angles.[53, 54] However, **LaCu₃** displays a moderate antiferromagnetic coupling with Cu-O-Cu bridging angles of 114.45º, for which a strong antiferromagnetic coupling is expected.[17, 18] Nevertheless, we have observed other copper(II) mesoxalate trinuclear species displaying ferromagnetic couplings between copper(II) ions with Cu-O-Cu bridging angles around 114º. The reason of this unexpected ferromagnetic or weak antiferromagnetic coupling is the large deviation from the planarity that these compounds display. The μ_3-apical ligand in the trinuclear unit rise the copper(II) ions above the plane formed by the three bridging mesoxalate-alkoxide oxygens yielding a large hinge distortion (γ = 30.98º, Fig. 7) which results in a reduction of the antiferromagnetic contribution, leading to weak antiferromagnetic, or even to ferromagnetic couplings, at Cu-O-Cu bridging angles for which strong antiferromagnetic couplings are expected.[17, 55-57] Fig. 7 shows the deviation of the copper(II) ions from the plane of the bridging mesoxalate alkoxo-oxygens. This deviation reduces the efficiency of the alkoxo-oxygens in the mediation of the antiferromagnetic coupling.



(a) (b)

Fig. 7 (a). Cu-O-Cu bridging angle in the trinuclear units, θ. (b). deviation from the planarity of the basal plane of the copper atoms from the plane formed by the three bridging mesoxalate oxygens, hinge distortion γ. Color code: Cu, blue; O, red; S, yellow; C, grey. Hydrogen atoms omitted for clarity.

The temperature dependence of the $\chi_M T$ product for the **CeCu₃**, **PrCu₃**, and **NdCu₃** compounds is shown in Fig. 8. The values observed at room temperature are 2.01, 1.78 and 2.34 emu mol^{-1} K, respectively, which are somewhat lower than those expected for three isolated copper(II) ions ($\chi_M T$ expected for three copper(II) ions = 1.2 emu mol^{-1} K) *plus* the corresponding for the Ln(III) ion (0.81, 1.60 and 1.64 emu mol^{-1} K for Ce(III), Pr(III) and Nd(III), respectively).[54]

The $\chi_M T$ product continuously decreases on lowering temperature, which is indicative of the occurrence of dominant antiferromagnetic interactions. A quantitative analysis of the magnetic behaviour of these compounds, if possible, is much more complicated than that of compound **LaCu₃**. The Ce(III), Pr(III) and Nd(III) ions are paramagnetic and in addition to the Cu(II)···Cu(II) interactions the Cu···Ln(III) interactions also occur. Moreover, the lanthanoids exhibit their characteristic Stark effect for the 4f ions and the simultaneous consideration of these three effects is very complicated.[58, 59] Nevertheless, the magnetic coupling among the copper(II) ions in these triangles is calculated by DFT methods in the next section. The magnetic susceptibility study for the **EuCu₃** compound could not performed since the compound is obtained in very low yield and as laminar single crystals which are very difficult to separate from the agarose gel.

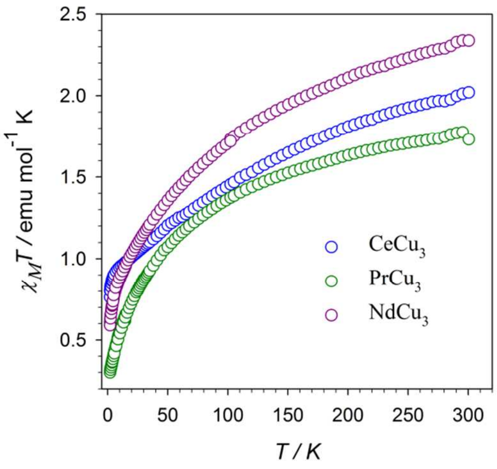


Fig. 8 Temperature dependence of the $\chi_M T$ product for the **CeCu$_3$**, **PrCu$_3$**, and **NdCu$_3$** compounds

DFT Study

The structural and magnetic studies in these compounds have shown copper(II) triangles in which different structural parameters and bridging apical groups are found. However, the magnetic coupling among the copper(II) ions in the **CeCu$_3$**, **PrCu$_3$**, **NdCu$_3$** and **EuCu$_3$** compounds could not be investigated because of the Ln(III)···Cu(II) magnetic interaction, the Stark effect of the Ln(III) ion or the pour quality of the material. Nevertheless, the Cu(II)···Cu(II) magnetic interaction in the [Cu$_3$(Hmesox)$_3$μ$_3$-DMSO]$^{3-}$ trinuclear units can be investigated by means of the DFT calculations.

Table 2 Hinge distortion, CuOCu bridging angle and theoretical magnetic coupling constants in the **LaCu$_3$**, **CeCu$_3$**, **PrCu$_3$** and **NdCu$_3$** copper(II) triangles

Triangle in compound	Cu-O-Cu/°	γ/°	J_{theo}/cm^{-1}
LaCu$_3$(μ$_3$-H$_2$O)	114.5(1)	31.3(1)	−50.4
LaCu$_3$(μ$_3$-DMSO)	114.5(1)	31.3(1)	−46.5
CeCu$_3$(μ$_3$-DMSO)	114.6(2)	30.8(1)	−41.1
PrCu$_3$(μ$_3$-DMSO)	116.0(5)	31.3(3)	−59.8
NdCu$_3$(μ$_3$-DMSO)	114.6(2)	31.3(1)	−40.3

Table 2 shows the theoretical magnetic coupling constant correlated with the Cu-O-Cu bridging angles (θ) and with the deviation of the copper(II) basal plane from the plane of the three bridging mesoxalate alkoxo oxygens (hinge distortion γ). We have calculated also the energies and the magnetic coupling constant of the [Cu$_3$(Hmesox)$_3$μ$_3$-H$_2$O]$^{3-}$ to see the effect of the substitution of a DMSO molecule by water in the apical position.

All the compounds which crystallize in the cubic space group (**LaCu$_3$**, **CeCu$_3$**, **PrCu$_3$** and **NdCu$_3$**) show very similar Cu-O-Cu bridging angles and hinge distortions, in the range 114.5º-116.0º and 30.8º-31.3º, respectively. The magnetic coupling constant in the range from −40.3 to −59.8 indicate moderate antiferromagnetic couplings among the copper(II) ions and the trend shows larger antiferromagnetic couplings for larger Cu-O-Cu bridging angles, in agreement with numerous experimental and theoretical studies.[55-57, 60]
However, the values found are much lower than those expected for the occurring Cu-O-Cu bridging angles. The hinge distortion is responsible for the rather low antiferromagnetic coupling observed at angles for which strong antiferromagnetic coupling should be observed.[55, 56] The deviation from the planarity decreases the overlap among the magnetic orbitals centred in the copper(II) ions which are directly related to the intensity of the antiferromagnetic coupling.[54] We find very interesting that the theoretical value found for the **LaCu$_3$** triangle is very close to that obtained from the experimental susceptibilities with eq 2 (J = –45 cm^{-1}), which gave a mean value of the magnetic coupling constant in compound **LaCu$_3$**. Nevertheless, the substitution of the apical DMSO molecule by water has little effect, much lower than that predicted by the magnetic susceptibility measurements. This little effect in the theoretical magnetic coupling constants is a consequence of the little contribution of the apical bridging-group in the transmission of the magnetic interaction in copper(II) ions with square pyramidal environment which have the unpaired electron mainly in the $d_{x^2-y^2}$ orbital with little contribution of the d_{z^2}. The calculation has been performed keeping constant the structural parameters of the triangle with the μ$_3$-DMSO apical molecule. However, the apical water molecules, that we proposed in the magnetic susceptibility studies, if the structure were optimized, would affect to the Cu-O(mesoxalate)-Cu angles and those changes would have much more effect and probably could clarify why the magnetic properties of the **LaCu$_3$** compound are better explained by a model which considers two triangles and two magnetic coupling constants.

We have also calculated the three magnetic coupling constants of each scalene triangle of the **EuCu$_3$** compound and they are shown in Table 3. The scalene triangles have a somewhat different treatment described in the experimental section. Because of the lower Cu-O-Cu bridging angles, these triangles show lower antiferromagnetic couplings, but with the same trend, displaying larger antiferromagnetic couplings for larger angles. So we can conclude that the DFT study gave a good approximation to the magnetic coupling constants among the copper(II) ions determined experimentally and correlated values for those compounds that could not be investigated by magnetic susceptibility measurements.

Table 3 Hinge distortion, Cu-O-Cu bridging angles and theoretical magnetic

γ/°	Cu-O-Cu/°	coupling constants value/cm^{-1}
γ_1=33.50	110.7(3)	$J_{13} = -20.5$
γ_2=29.53	112.9(3)	$J_{12} = -18.5$
γ_3=31.62	112.8(3)	$J_{23} = -18.5$
γ_4=36.47	110.3(3)	$J_{45} = -4.81$
γ_5=29.95	110.1(3)	$J_{46} = -15.1$
γ_6=31.18	114.6(3)	$J_{56} = -35.8$

coupling constants among the copper(II) ions for the **EuCu$_3$** triangles

Conclusions

A new family of compounds combining the $[Cu_3(Hmesox)_3]^{3-}$ trinuclear unit with several lanthanoid (III) ions, which were not obtained in pure water have been obtained in mixed DMSO/water medium. Gel crystallization has been crucial to obtaining these compounds which didn´t crystallize by slow diffusion.

LaCu$_3$, **CeCu$_3$**, **PrCu$_3$** and **NdCu$_3$** crystallize in neutral (10,3)-a frameworks which host water and DMSO molecules in their pores. These frameworks are chiral and chiral crystals are obtained by spontaneous resolution upon crystallization. In these compounds DMSO molecules acting as μ_3-bridge mainly fill the apical position of the three copper (II) ions in the trinuclear $[Cu_3(Hmesox)_3DMSO]^{3-}$ units. The presence of the DMSO molecules makes the copper (II) triangles to adopt an equilateral triangular structure with all the Cu-O-Cu angles equivalent. This fact results in the crystallization in a three-dimensional (10,3)-a network instead of the two-dimensional (6,3) network observed in the compounds $[La(H_2O)_3Cu_3(Hmesox)_3(H_2O)_5]\cdot 8H_2O$ and $[La(H_2O)_2Cu_3(Hmesox)_3(H_2O)_3]\cdot 7H_2O$ which were obtained in pure water. However, due to the lower coordination number of the Eu(III), the metal ion behaves as two-connecting node yielding chains structure.

The magnetic susceptibility study carried out for the **LaCu$_3$** reveals the occurrence of antiferromagnetically coupled copper(II) equilateral triangles whose apical positions can also be occupied by water molecules. The μ_3-oxygens of both water and DMSO, pull the copper(II) ions out of the plane formed by the three μ_2-O(mesoxalate) oxygens making the antiferromagnetic contribution lower than expected for the observed Cu-O-Cu bridging angles.

DFT calculations performed in the copper(II) triangles of all compounds show a correlation between the antiferromagnetic coupling and the bridging Cu-O-Cu angles with larger antiferromagnetic couplings for larger Cu-O-Cu bridging angles.

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Notes and references

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† CCDC numbers 1402451-1402455 for compounds **LaCu$_3$**, **CeCu$_3$**, **PrCu$_3$**, **NdCu$_3$** and **EuCu$_3$**, respectively. Electronic Supplementary Information (ESI) available: TG plots, IR spectra, X-ray Powder Diffraction Patterns and Tables with main distances and angles. See DOI: 10.1039/b000000x/

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Table of Contents

The combination of $[Cu_3(Hmesox)_3]^{3-}$ with La(III), Ce(III), Pr(III), Nd(III) and Eu(III) in DMSO/H_2O yields 3d-4f heterometallic metal-organic frameworks, the dimensionality of the network being controlled by the coordination number of the Ln(III) ion.