

Article



# Key Role of Size and Electronic Configuration on the Sign and Strength of the Magnetic Coupling in a Series of $Cu_2Ln$ Trimers (Ln = Ce, Gd, Tb, Dy and Er)

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Five new trinuclear complexes with formula  $[(CuL^{\alpha-Me})_2Ce(NO_3)_3]$  (1) and Abstract:  $[(CuL^{\alpha-Me})_2Ln(H_2O)(NO_3)_2](NO_3) \cdot 2(CH_3OH)$  (Ln = Gd(2), Tb(3), Dy(4) and Er(5)) have been synthesized using the bidentate  $N_2O_2$  donor metalloligand  $[CuL^{\alpha-Me}]$   $(H_2L^{\alpha-Me} =$  $N_{\rm A}N'$ -bis( $\alpha$ -methylsalicylidene)-1,3-propanediamine) and structurally characterized. In the case of compound 1, the larger ionic radius of Ce(III) leads to a neutral trinuclear complex with an asymmetric CeO<sub>10</sub> tetradecahedron coordination geometry formed by four oxygen atoms from two  $(CuL^{\alpha-Me})$  units and three bidentate NO<sub>3</sub><sup>-</sup> ligands. In contrast, the isomorphic complexes 2–5, with smaller Ln(III) ions, give rise to monocationic trinuclear complexes with a non-coordinated nitrate as a counter ion. In these complexes, the Ln(III) ions show a LnO<sub>9</sub> tricapped trigonal prismatic coordination geometry with C<sub>2</sub> symmetry formed by four oxygen atoms from two (CuL<sup> $\alpha$ -Me</sup>) units, two bidentate  $NO_3^{-1}$  ligands and a water molecule. The magnetic properties show the presence of weak antiferromagnetic interactions in 1 and weak ferromagnetic interactions in 2–5. The fit of the magnetic properties of compounds 2-5 to a simple isotropic-exchange symmetric trimer model, including the anisotropy of the Ln(III) ions, shows that in all cases the Cu-Ln magnetic coupling is weak ( $J_{Cu-Ln} = 1.81$ , 1.27, 0.88 and 0.31 cm<sup>-1</sup> for 2–5, respectively) and linearly decreases as the number of unpaired f electrons of the Ln(III) decreases. The value found in compound 2 nicely fits with the previously established correlation between the dihedral Cu–O–O–Gd angle and the J value.

**Keywords:** 3d-4f complexes; crystal structure; magnetic properties; coupling constants; magnetostructural correlations; lanthanide series

# 1. Introduction

Lanthanide ions have attracted enormous interest in molecular magnetism during the last few years [1–4]. They are often combined with 3d metal ions or other magnetic centers [5–7] to create a large ground spin state (*S*) and uniaxial anisotropy (*D*) that play an essential role in creating magnetic bi-stability and related memory effects in single-molecule magnets (SMMs) and single-chain magnets (SCMs) [8–11]. An advantage of 3d-4f coordination clusters is the possibility of obtaining high coercitivity in SMMs, since the exchange interaction serves as an internal bias field that suppresses quantum tunnelling of the magnetization [12–17]. Thus, notable SMM behaviours have been recently observed without any applied bias field for 3d-4f complexes with relatively high energy barriers for the reversal of the magnetization (U<sub>eff</sub>) [15–17]. Therefore, the exchange coupling between 3d and 4f centres has become a matter of potential relevance in the design of lanthanide-based SMMs or

SCMs. The determination of the coupling constant of 3d-4f magnetic exchange from the theoretical fitting of susceptibility measurements is usually done with Gd(III) due to its isotropic nature [18–22]. On the other hand, the presence of large first order spin-orbit coupling of the f-shell electrons in other lanthanides makes it very hard to explain their susceptibility data theoretically [23–25]. Hence, the determination of magnetic coupling constants of 3d-4f (other than Gd(III)) from susceptibility data is rather challenging unless other techniques are used [16,26–29].

The coupling constants between 3d and 4f metal ions were determined first for a bis(diphenoxido) bridged Cu<sub>2</sub>Gd trinuclear family of complexes about three decades ago [18]. The complexes were obtained by reacting a bidantate [CuL] metalloligand derived from a salen type N<sub>2</sub>O<sub>2</sub> Schiff base ligand (H<sub>2</sub>L) with various Gd(III)-salts [30–34]. This study raised an enormous interest in the field of 3d-4f coordination complexes and subsequently various types of 3d-4f complexes were prepared and studied [2,35–37]. However, since then, only a few reports on this particular trinuclear family of complexes have been published [30–34]. Literature shows that only four [CuL] metalloligands ([CuL<sup>1</sup>], [CuL<sup>2</sup>], [CuL<sup>3</sup>] and [CuL<sup>4</sup>] of Scheme 1) along with the lanthanides Ce(III), Eu(III), Gd(III) and Dy(III) were used for the synthesis of such trinuclear species. Very recently, we determined the structure and evaluated the SMM properties of the Tb<sup>III</sup> complexes of this long known but less investigated family of complexes [(CuL)<sub>2</sub>Ln(X)<sub>n</sub>] (X = uninegative anion) [38]. Also, these complexes have been proven to be very flexible and can take on either *cisoid* or *transoid* orientations, controlled by reaction conditions [38,39].



Scheme 1. The metalloligands used earlier and the one used in this study to prepare Cu<sub>2</sub>Ln compounds.

In this present endeavour, the  $\alpha$ -methylated N<sub>2</sub>O<sub>2</sub> metalloligand [CuL<sup> $\alpha$ -Me</sup>] (H<sub>2</sub>L<sup> $\alpha$ -Me</sup> = N,N'-bis( $\alpha$ -methylsalicylidene)-1,3-propanediamine, Scheme 1) has been used for the first time to synthesize a series of [(CuL<sup> $\alpha$ -Me</sup>)<sub>2</sub>Ln(X)<sub>n</sub>] complexes (Ln = Ce(III), Gd(III), Tb(III), Dy(III) and Er(III)). Structural characterization reveals that unlike their non- $\alpha$ -methylated analogous metalloligands (which form both *cisoid* and *transoid* complexes) they only form *transoid* coordination complexes under similar crystallization conditions [38,39]. The nature and magnitude of the coupling constants of the magnetic exchange between the Cu(II) and Ln(III) centers of these complexes are determined from the fits of variable temperature magnetic susceptibility and isothermal magnetisation measurements, and a magneto-structural correlation is drawn. This is only the second instance where the fitting of the magnetic susceptibility of trimeric Cu<sub>2</sub>Ln complexes (Ln = Tb, Dy and Er) has been performed.

# 2. Results and Discussion

# 2.1. Syntheses and Spectroscopic Characterizations of the Complexes

In previous studies, we have synthesized some trinuclear [{ $(CuL)_2M'$ } $X_n$ ] complexes using [CuL] and [CuL<sup> $\alpha$ -Me</sup>] as metalloligands (where, M' are different s-, p- and d-block elements). These studies established that the  $\alpha$ -methylation on the N<sub>2</sub>O<sub>2</sub> donor Schiff base ligand has a key role in determining the structures of the resulting compounds [40–46]. However, such studies have not been performed with lanthanide-containing trinuclear coordination clusters for these complexes. Recently, we reported some trinuclear [{ $(CuL^3)_2Ln$ } $X_n$ ] complexes (H<sub>2</sub>L<sup>3</sup> =  $N_iN'$ -bis(salicylidene)-1,3-propanediamine,

Scheme 1, Ln = Tb, Dy) [38,39]. In the present endeavour, we have used [CuL<sup> $\alpha$ -Me</sup>] as a metalloligand and we have reacted it with a series of lanthanides nitrates (Ce, Gd, Tb, Dy and Er) in a 2:1 ratio following the same procedures already used by us for the [CuL<sup>3</sup>] metalloligand [38,39]. This study will allow us to evaluate any structural change that might occur due to  $\alpha$ -methylation. As expected, we have isolated the trinuclear Cu<sub>2</sub>Ln complexes for all the used lanthanides, indicating that these lanthanides can accommodate two [CuL<sup> $\alpha$ -Me</sup>] metalloligands around themselves irrespective of their size. Moreover, unlike the previously reported [{(CuL<sup>3</sup>)<sub>2</sub>Tb}X<sub>n</sub>] complex, which is *cisoid*, in these complexes the relative orientation of the two [CuL<sup> $\alpha$ -Me</sup>] around the central Ln(III) ions is always *transoid*.

Besides elemental analyses, all the complexes were primarily characterized by IR spectra. The metalloligand [CuL<sup> $\alpha$ -Me</sup>] is neutral and does not possess any counter anion, whereas all the complexes contain nitrato coligands. The presence of the nitrato anion and its bidentate chelation ( $\kappa^2 O, O'$ ) in each compound is illustrated by characteristic IR bands [47,48]. The broad strong bands of the chelated nitrates are observed at 1485, 1445 cm<sup>-1</sup> (B<sub>1</sub>), and 1384, 1290 cm<sup>-1</sup> (A<sub>1</sub>) for **1**; 1481, 1439 cm<sup>-1</sup> (B<sub>1</sub>) and 1384, 1300 cm<sup>-1</sup> (A<sub>1</sub>) for **2**; 1482, 1438 cm<sup>-1</sup> (B<sub>1</sub>) and 1384, 1299 cm<sup>-1</sup> (A<sub>1</sub>) for **3**; 1482, 1439 cm<sup>-1</sup> (B<sub>1</sub>) and 1383, 1299 cm<sup>-1</sup> (A<sub>1</sub>) for **4** and finally 1482, 1440 cm<sup>-1</sup> (B<sub>1</sub>) and 1384, 1300 cm<sup>-1</sup> (A<sub>1</sub>) for **5**. A strong and sharp band due to the azomethine [ $\nu$ (C=N)] group of the Schiff base appears around 1600–1602 cm<sup>-1</sup> for complexes **1**–5.

# 2.2. Description of the Structures

The molecular structure of complexes **1** and **2** along with the partial atomic numbering scheme is shown in Figures **1** and **2** respectively. The detailed crystallographic and structural parameters are given in Table **1** and Table S1. Complexes **2–5** are isomorphs, differing only in the central Ln atom. Therefore, here we describe only the structure of compound **2**. The structures of compounds **3–5** are shown in Figures S1–S3, Supplementary Information respectively.

Compound	1	2	3	4	5
Formula	C <sub>38</sub> H <sub>40</sub> N <sub>7</sub> O <sub>13</sub> Cu <sub>2</sub> Ce	$C_{40}H_{50}N_7O_{16}Cu_2Gd$	$C_{40}H_{50}N_7O_{16}Cu_2Tb$	C40H50N7O16Cu2Dy	C40H50N7O16Cu2Er
Formula Weight	1069.99	1169.22	1170.90	1174.47	1179.23
Space group	Pbca	C2/c	C2/c	C2/c	C2/c
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
a/Å	18.380(4)	16.112(5)	16.259(5)	16.192(5)	16.257(5)
b/Å	21.084(5)	19.288(5)	19.449(5)	19.380(5)	19.458(5)
c/Å	21.284(5)	14.740(5)	14.826(5)	14.884(5)	14.815(5)
β/°	90	97.875(5)	97.882(5)	97.948(5)	97.996(5)
$V/Å^3$	8248(3)	4538(2)	4644(2)	4626(2)	4641(2)
Ζ	8	4	4	4	4
$D_{\rm calc}/g \cdot {\rm cm}^{-3}$	1.723	1.711	1.675	1.686	1.688
$\mu/mm^{-1}$	2.181	2.451	2.490	2.586	2.776
F(000)	4296	2356	2360	2364	2372
R(int)	0.0538	0.0723	0.0701	0.0490	0.0370
θ range (deg)	1.75-25.14	1.66-25.01	1.64-25.14	1.65-25.02	1.64-25.21
Total reflections	55203	9971	25546	24215	9997
Unique reflections	7349	3829	4123	4058	3967
Data with $I > 2\sigma(I)$	5396	2689	3370	3381	3271
$R_1^a \text{ on } I > 2\sigma(I)$	0.0313	0.0669	0.0464	0.0475	0.0361
wR <sub>2</sub> <sup>b</sup> (all)	0.0751	0.1819	0.1312	0.1302	0.1079
GOF <sup>c</sup> on F <sup>2</sup>	1.010	0.996	1.082	1.079	1.055
Temp (K)	293	293	293	293	293
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Table 1. Crystal data and structure refinement parameters of complexes 1-5.

<sup>a</sup>  $R_1 = \Sigma ||F_0| - |F_c|| /\Sigma |F_0|$ . <sup>b</sup>  $wR_2 = [\Sigma w (F_0^2 - F_c^2)^2 / \Sigma w (F_0^2)^2]^{1/2}$ . <sup>c</sup> GOF =  $[\Sigma [w (F_0^2 - F_c^2)^2 / (N_{obs} - N_{params})]^{1/2}$ .



**Figure 1.** ORTEP diagram of complex **1** with thermal ellipsoids at 30% probability (**Left**) and Cerium coordination polyhedron (**Right**). Colour code: C = brown, N = blue, O = red, Cu = cyan and Ce = pink.



**Figure 2.** ORTEP diagram of complex **2** with thermal ellipsoids at 30% probability (**left**) and Ln(III) coordination polyhedron (Ln = Gd, Dy, Tb and Er) with the C<sub>2</sub> axis (dotted line) passing through the Ln ion (**right**). Colour code Gd = bronze, Ln = magenta, C = brown, O = red, N = blue, H = grey and Cg = green.

Complex  $[(CuL^{\alpha-Me})_2Ce(NO_3)_3]$  (1) crystallizes in the orthorhombic crystal system with *Pbca* space group. The molecule is asymmetric and possesses a trinuclear  $Cu^{II}_2Ce^{III}$  cluster formed by the coordination of two terminal bidentate metalloligands  $[CuL^{\alpha-Me}]$  to the central Ce(III) atom in a *transoid* orientation. Three chelating nitrato ( $\kappa^2O,O'$ ) co-ligands complete the deca-coordination of the Ce<sup>III</sup> ion that appears to be surrounded by ten oxygen atoms with average Ce–O bond distances of 2.58(1) Å. Four of these oxygen atoms, namely O(1), O(2) and O(3), O(4), correspond to the two  $[CuL^{\alpha-Me}]$  metalloligands presenting Ce–O bond distances in the range 2.431(2)–2.612(3) Å. The other six oxygen atoms, O(5), O(7), O(8), O(10), O(11) and O(13), belong to three nitrato co-ligands and are located at distances of 2.561(3)–2.649(4) Å. The coordination polyhedron of the Ce<sup>III</sup> atom can be described as a distorted tetradecahedron geometry [49].

Six oxygen atoms, *i.e.*, O(1), O(5), O(7), O(4), O(11) and O(13), form a nearly equatorial plane, whereas O(2), O(3), O(8) and O(10) are at the opposite sides of this plane in such a way that the O(2)-Ce(1)-O(3) and O(8)-Ce(1)-O(10) planes are nearly orthogonal to the equatorial plane (89.1(1)° and 88.4(1)° respectively) as well as to each other (75.1(1)°). The r. m. s. deviation of the six equatorially coordinated O-atoms from the mean plane passing through them is 0.238(8) Å with the 0.023(1) Å

deviation of Ce(1) from this plane. Two of these three chelating nitrate also bridge  $(1 \kappa O: 2\kappa^2 O, O')$  the Cu atoms with the Ce centres, although with long Cu–O bond distances (see below).

The terminal Cu(1) and Cu(2) atoms are penta-coordinated in a square-pyramidal coordination geometry. Their basal planes include four donor atoms of the Schiff base, namely two imine N atoms (N(1), N(2) for Cu(1) and N(3), N(4) for Cu(2)) with Cu–N bond lengths in the range 1.949(3)–1.959(3) Å and two phenoxido O atoms (O(1), O(2) for Cu(1) and O(5), O(6) for Cu(2)) with Cu–O bond lengths in the range 1.901(3)–1.940(3) Å. The bridging nitrato groups occupy the axial positions of the square pyramids with Cu(1)–O(13) and Cu(2)–O(7) distances of 2.709(4) and 2.489(3) Å, respectively. The Addison parameter ( $\tau_5$ ) amounts to 0.177 and 0.058 for Cu(1) and Cu(2), respectively, confirming the slightly distorted square-pyramidal geometry for the copper(II) ions ( $\tau_5$  is 0 for a perfect square pyramid, whereas it has a value of 1 for a trigonalbipyramid) [50]. The r.m.s. deviations of the four basal donor atoms from the mean planes are 0.217(7) and 0.140(5) Å for Cu(1) and Cu(2), respectively, with the metal atoms located at 0.077(1) and 0.024(1) Å away from the plane, towards the axial O(13) and O(7) atoms, respectively.

Complexes 2-5 also present a trinuclear Cu<sup>II</sup><sub>2</sub>Ln<sup>III</sup> coordination cluster formed by the coordination of two terminal bidentate metalloligands [CuL] to the central Ln(III) atom in a transoid orientation with general formula  $[(CuL^{\alpha-Me})_2Ln(H_2O)(NO_3)_2] \cdot (NO_3) \cdot 2(CH_3OH); Ln = Gd (2), Tb (3), Dy (4) and Cull (1) + Cull (2) +$ Er (5). Unlike 1, these complexes crystallize in the monoclinic crystal system with C2/c space group where the overall molecule has a  $C_2$  axis parallel to the crystallographic *b*-axis passing through the N(40)-O(3)-Ln<sup>III</sup> atoms (Figure 2). The coordination polyhedron of the central Ln<sup>III</sup> ion in complexes 2, 3, 4 and 5 can be defined as a tricapped-trigonal prism [31] formed by nine oxygen atoms with average Ln–O bond distances of 2.43(2), 2.43(1), 2.42(2) and 2.40(1) Å for **2–5**, respectively. Four of the nine oxygen atoms, namely O(1), O(2) and their symmetry-related ones (symmetry operation "b" =  $1-x_y^3/2-z$ ), are  $\mu_2$ -phenoxido oxygen atoms of the two metalloligands connecting the Cu(II) ions to the central Ln(III) ion with Ln–O bond distances of 2.360(5) and 2.409(5) Å for 2, 2.347(4) and 2.418(4) Å for 3, 2.336(4) and 2.410(5) Å for 4 and 2.309(3) and 2.401(3) Å for 5. The coordination polyhedron of the Ln(III) ions also contains four oxygen atoms from two chelating nitrato coligands: O(4) and O(5), and their symmetry related O(4b) and O(5b), (symmetry operation "b" =  $1-x_yy_3/2-z$ ) that also bridge the central Ln(III) with the Cu(II) ions  $(1 \ltimes O : 2 \ltimes^2 O, O')$ . The Ln–O(4) and Ln–O(5) bond distances are, respectively, 2.499(6) and 2.477(6) Å for 2, 2.519(5) and 2.478(4) Å for 3, 2.505(5) and 2.474(5) Å for 4 and 2.488(4) and 2.458(3) Å for 5. The ninth oxygen atom coordinated to the Ln(III) ion, O(3), is a water molecule with Ln–O(3) bond distances of 2.351(10), 2.336(6), 2.357(8) and 2.312(6) Å for 2-5, respectively. The angle between the planes of the two triangular faces of the trigonal prism (O(1), O(2), O(4) and O(1b), O(2b), O(4b)) is 17.6(2)° for **2**, 18.1(1)° for **3**, 18.1(2)° for **4** and 18.6(1)° for **5**. The plane of the three capping atoms (O(3), O(5), and O(5b)) is inclined with respect to the two triangular faces  $14.2(2)^{\circ}$  for 2,  $14.1(1)^{\circ}$  for 3,  $14.0(1)^{\circ}$  for 4 and  $14.0(1)^{\circ}$  for 5. The distances between the centroids of the two triangular faces (Cg(1) and Cg(2)) are nearly equal (3.640(1), 3.644(1), 3.625(1) and 3.591(1) Å for 2–5, respectively). The Cg(1)–Ln(1)–Cg(2) angles (168.5(1)° in 2, 168.7(1)° in 3, 169.1(1)° in 4 and  $169.6(1)^{\circ}$  in 5) deviate from the ideal one (180°), indicating that the Ln(III) ion is not located at the centre of the trigonal prism. Besides the chelating/bridging nitrate ligands  $(1 \kappa O: 2\kappa^2 O, O')$ , there is also a non-coordinated disordered nitrate anion, N(40), located in the interstitial space of the crystal.

The Cu(II) ions of the symmetrical Cu<sub>2</sub>Ln core in complexes **2–5** present a square pyramidal coordination geometry with the four donor atoms of the ligand (O(1), O(2), N(1) and N(2)) occupying the basal positions. An oxygen atom from a bridging nitrate ligand, O(4), occupies the axial position. As usually observed in this coordination geometry, the basal Cu–O and Cu–N bond distances (in the ranges 1.881(6)-1.979(3) Å and 1.936(7)-1.967(6) Å, respectively) are much shorter than the axial one (in the range 2.587(4)-2.614(5) Å). The basal plane around the Cu(1) atom presents r.m.s. deviations of 0.092(13), 0.088(9), 0.084(10) and 0.089(7) Å in **2–5**, respectively, whereas the Cu(1) ion is displaced from the basal plane towards the axial O(4) atom 0.012(1), 0.013(1), 0.012(1) and 0.014(1) Å in **2–5**, respectively. The Addison parameters for Cu(1) (0.065, 0.067, 0.060 and 0.056 in complexes **2–5**, respectively) indicate

that the square pyramidal geometry is only slightly distorted towards the trigonal-bipyramidal geometry. In contrast to 1, complexes 2–5 contain two methanol solvent crystallization molecules that are hydrogen-bonded to the water molecule coordinated to the central Ln(III) ion.

The structures of compounds 1–5 show that  $\alpha$ -methylation of the N<sub>2</sub>O<sub>2</sub> Schif base ligand [H<sub>2</sub>L<sup> $\alpha$ -Me</sup>] leads in all cases to *transoid* trinuclear Cu<sub>2</sub>Ln complexes (Figure S1, Supplementary Information) where the [CuL<sup> $\alpha$ -Me</sup>] metalloligands are located in *trans*, resulting in long intra-molecular Cu–Cu distances (6.313(1), 6.423(3), 6.435(3), 6.418(3) and 6.388(3) Å in 1–5, respectively). This result contrasts with the observed behaviour in other similar non  $\alpha$ -methylated N<sub>2</sub>O<sub>2</sub> Schiff base ligands as H<sub>2</sub>L<sup>3</sup> (Scheme 1) where a *cisoid* Cu<sub>2</sub>Tb complex is obtained when [CuL<sup>3</sup>] is reacted with Tb(III) in methanol [38,39]. Interestingly, this different behaviour has also been observed in the series of trinuclear Cu<sub>2</sub>Ce complexes *cisoid*-[(CuL<sup>1</sup>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>3</sub>], *transoid*-[(CuL<sup>2</sup>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>3</sub>] and *transoid*-[(CuL<sup>3</sup>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>3</sub>], although in this case the complexes were prepared in different solvents [30,32,33]. It is worth mentioning that although there are several Cu<sub>2</sub>Ln systems reported in the literature with different ligands other than N<sub>2</sub>O<sub>2</sub> Schiff bases, none of them show such significant structural modifications as a result of minor changes in the ligand, possibly due to the lack of flexibility of those complexes [51–55]. On the other hand,  $\alpha$ -methylation of the N<sub>2</sub>O<sub>2</sub> Schiff base ligand does not cause any change in the geometry of the *cisoid* trimers [(CuL<sup>1</sup>)<sub>2</sub>Cd(H<sub>2</sub>O)<sub>3</sub>]<sup>3+</sup> and [(CuL<sup>4</sup>)<sub>2</sub>Cd(H<sub>2</sub>O)<sub>3</sub>]<sup>3+</sup> [18].

It is also to be noted that in presence of the coordinating anion nitrate, the larger lanthanide ions accommodate two [CuL<sup>1</sup>] (or [CuL<sup>2</sup>]) metalloligands, whereas the smaller lanthanide ions coordinate only to one metalloligand, presumably to avoid steric hindrance around the smaller Ln(III) ions [32,33]. However, in the present study, the flexibility of the [CuL<sup> $\alpha$ -Me</sup>] metalloligand allows it to re-orientate around the Ln(III) ion, irrespective of its ionic radius, to form the less sterically hindered trinuclear *transoid* cluster [30,31,34]. On the other hand, in these complexes, the coordination number of the Ln(III) is nine except for the largest Ce(III) ion where it is ten, indicating that from Gd (2) to Er (5) ionic radius of the central lanthanide used in the present study has little influence on the coordination number and the coordination geometry of the trinuclear Cu<sub>2</sub>Ln complexes.

## 2.3. Magnetic Properties

The thermal variation of the molar magnetic susceptibility per Cu<sub>2</sub>Ce trimer times the temperature  $(\chi_m T)$  for compound **1** shows, at room temperature, a value of *ca*. 1.6 cm<sup>3</sup> K·mol<sup>-1</sup>, close to the expected one for two isolated Cu(II) S = 1/2 ions (0.75 cm<sup>3</sup> K·mol<sup>-1</sup> with g = 2) plus one Ce(III) ion (0.80 cm<sup>3</sup> K·mol<sup>-1</sup> with  $g_J = 6/7$ ) (Figure 3). When the sample is cooled the  $\chi_m T$  value initially exhibits a smooth decrease down to *ca*. 10 K and a more abrupt decrease at lower temperatures. Unfortunately, all the attempts to fit the magnetic data with a simple model (in order to reduce the number of adjustable parameters) failed, probably due to the larger anisotropy of the Ce(III) ion resulting from the different coordination number and environment of compound **1** when compared with compounds **2–5** (see below).



**Figure 3.** Thermal variation of the  $\chi_m T$  product per Cu<sub>2</sub>Ce trimer for compound **1**.

Compound **2** shows, at room temperature, a  $\chi_m T$  value of *ca*. 8.7 cm<sup>3</sup> K·mol<sup>-1</sup> per Cu<sub>2</sub>Gd trimer, close to the expected one for two Cu(II) ions (0.75 cm<sup>3</sup> K·mol<sup>-1</sup>) plus one Gd(III) ion (7.88 cm<sup>3</sup> K mol<sup>-1</sup>; S = 7/2) with  $g_J = 2$ . When the sample is cooled the  $\chi_m T$  value remains constant down to *ca*. 50 K and then gradually increases to reach a maximum of *ca*. 11.9 cm<sup>3</sup> K·mol<sup>-1</sup> at *ca*. 3.5 K. Below this temperature,  $\chi_m T$  shows a sharp decrease and reaches a value of 11.7 cm<sup>3</sup> K·mol<sup>-1</sup> at 2 K (Figure 4). This behaviour suggests the presence of a predominant ferromagnetic Cu–Gd interaction and, accordingly, we have fitted the magnetic properties to a symmetrical Cu–Gd–Cu trimer model including two equal isotropic interactions and a zero field splitting term to reproduce the decrease at very low temperatures. In order to reduce the number of adjustable parameters, we have fixed g = 2.0 for the Gd(III) ion. This model reproduces very well the magnetic properties of compound **2** (both  $\chi_m T$ , in the whole temperature range, and the isothermal magnetization at 2 K, (Figure 4) with the following set of parameters:  $g_{Cu} = 2.036$ ,  $J_{Cu-Gd} = 1.81$  cm<sup>-1</sup>, D = 0.00 cm<sup>-1</sup> and a tip of  $1.0 \times 10^{-3}$  cm<sup>3</sup> mol<sup>-1</sup> (Table 2, solid lines in Figure 4).



**Figure 4.** Magnetic properties of compound **2**: (**left**) Thermal variation of the  $\chi_m T$  product per Cu<sub>2</sub>Gd trimer; (**right**) Isothermal magnetization at 2 K. Solid lines are the best fit to the model (see text).

<b>Table 2.</b> M	lagnetic	parameters	for	com	pounds	2–5.
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Compound	S <sub>T</sub>	gCu	gLn	J <sub>Cu-Ln</sub> (cm <sup>-1</sup> )	D (cm <sup>-1</sup> )	Tip (cm <sup>3</sup> mol <sup>-1</sup> )	First Excited Level Energy (cm <sup>-1</sup> )
2 (Cu <sub>2</sub> Gd)	9/2	2.036	2.0	1.81	0	$1 \times 10^{-3}$	12.7
3 (Cu <sub>2</sub> Tb)	7	1.990	3/2	1.27	2.0	$0.7 \times 10^{-3}$	11.8
4 (Cu <sub>2</sub> Dy)	17/2	1.991	4/3	0.88	5.1	0	4.53
5 (Cu <sub>2</sub> Er)	17/2	2.131	6/5	0.31	1.4	0	1.33

Compounds 3–5 exhibit, at room temperature,  $\chi_m T$  values of *ca*. 12.4, 15.0 and 12.3 cm<sup>3</sup> K·mol<sup>-1</sup> per  $Cu_2Ln$  trimer (Ln = Tb, Dy and Er in 3–5, respectively), close to the expected values for two Cu(II) ions (0.75 cm<sup>3</sup> K·mol<sup>-1</sup>) plus one Tb(III), Dy(III) or Er(III) ion (11.82 (J = 6), 14.17 (J = 15/2) and 11.48 (J = 15/2) cm<sup>3</sup> K·mol<sup>-1</sup>, respectively) with  $g_I = 3/2$ , 4/3 or 6/5 for 3–5, respectively. When the temperature is lowered, the  $\chi_m T$  value shows a progressive increase and reaches maxima of *ca.* 13.8, 17.6 and 16.0 cm<sup>3</sup> K·mol<sup>-1</sup> at *ca.* 5, 9 and 3 K for 3–5, respectively. Below these temperatures,  $\chi_m T$ shows a sharp decrease in compounds 3 and 4 reaching values of 12.7 and 14.9 cm<sup>3</sup> K mol<sup>-1</sup> at 2 K, respectively. In compound 5,  $\chi_m T$  remains constant from 3 to 2 K. (Figures 5–7). These behaviours suggest the presence of predominant ferromagnetic Cu-Ln interactions in the three compounds and, accordingly, we have fitted the magnetic properties to a symmetrical Cu–Ln–Cu trimer model (Ln = Tb, Dy or Er), including two equal isotropic interactions and a zero field splitting term to reproduce the decrease at very low temperatures. In order to reduce the number of adjustable parameters, we have fixed g = 3/2, 4/3 or 6/5 for the Tb(III), Dy(III) and Er(III) ions, respectively. This model reproduces very well the magnetic properties of the three compounds in the whole temperature range with the following set of parameters:  $g_{Cu} = 1.990$ ,  $J_{Cu-Tb} = 1.27 \text{ cm}^{-1}$ ,  $|D| = 2.0 \text{ cm}^{-1}$  and a tip of  $0.6 \times 10^{-3}$  cm<sup>3</sup> mol<sup>-1</sup> for 3, (Table 2, solid line in Figure 5),  $g_{Cu} = 1.991$ ,  $J_{Cu-Dy} = 0.88$  cm<sup>-1</sup> and

 $|D| = 5.1 \text{ cm}^{-1}$  (Table 2, solid line in Figure 6) for 4 and  $g_{\text{Cu}} = 2.132$ ,  $J_{\text{Cu-Er}} = 0.31 \text{ cm}^{-1}$  and  $|D| = 1.4 \text{ cm}^{-1}$  (Table 2, solid line in Figure 7) for 5.

A confirmation of the weak magnetic couplings found in compounds 1-5 is provided by the isothermal magnetizations at 2 K that show saturation values of *ca*. 2.0, 9.0, 8.5, 9.0 and 7.0 µB for 1-5, respectively (Figure S4, Supplementary Information).

Since compounds 2–5 present ferromagnetic Cu–Ln interactions we have measured these compounds with AC susceptibility in the low temperature range in order to check for the presence of slow relaxation of the magnetization at low temperatures. These measurements show in all cases the absence of an out-of-phase signal at any frequency, indicating the absence of any slow relaxation process above 2 K in these compounds (Figure S5, Supplementary Information).



**Figure 5.** Thermal variation of the  $\chi_m T$  product per Cu<sub>2</sub>Tb trimer for compound **3**. The solid line is the best fit to the model (see text).



**Figure 6.** Thermal variation of the  $\chi_m T$  product per Cu<sub>2</sub>Dy trimer for compound **4**. The solid line is the best fit to the model (see text).



**Figure 7.** Thermal variation of the  $\chi_m T$  product per Cu<sub>2</sub>Er trimer for compound **5**. The solid line is the best fit to the model (see text).

The different behaviour found between compound **1** and the other four compounds (2–5) can be easily rationalized from the structural data that show that compound **1** presents a slightly different coordination environment for the Ln ion. Thus, the Ce ion presents a coordination number of ten with three bidentante  $NO_3^-$  anions and two double phenoxido bridges with Cu(II), whereas in the other four compounds (2–5) the Ln ions contain a water molecule instead of one bidentate  $NO_3^-$  ligand, resulting in a coordination number of nine (see above). This difference has to be attributed to the larger size of Ce(III) (128.3 pm for 8-coordinate) compared with the other four ions (119.3, 118.0, 116.7 and 114.4 pm for the 8-coordinate Ln(III) in 2–5, respectively). As a result of this different coordination number, there are important differences in the structural parameters of the double phenoxido bridges between compound **1** and the other four compounds (see Table 3), leading to the observed differences in the sign of the magnetic coupling. As can be observed in Table 3, the structural parameters of the double phenoxido bridges are almost identical in the non-coordinated complexes **2–5**.

**Table 3.** Cu–O and Ln–O bond distances (Å), Cu–O–Ln bond angles (°) and dihedral Cu–O–O–Ln angles (°) for the double phenoxido bridges in compounds 1–5.

Compound	Cu–O (Å)	Ln–O (Å)	Cu–O–Ln (°)	Cu-O-O-Ln (°)
	1.901	2.612	97.2	
$1(C_{11}, C_{2})^{a}$	1.932	2.431	102.5	34.5
$I(Cu_2Ce)$	1.940	2.464	99.6	42.7
	1.912	2.581	96.4	
<b>2</b> (Cu <sub>2</sub> Gd)	1.971	2.368	97.1	20.0
	1.889	2.414	97.9	38.0
<b>3</b> (Cu <sub>2</sub> Tb)	1.973	2.346	97.9	27.4
	1.898	2.418	97.7	37.4
4 (Cu <sub>2</sub> Dy)	1.975	2.336	97.9	27.0
	1.900	2.410	97.5	37.9
	1.979	2.309	98.0	27.0
$5 (Cu_2 Er)$	1.900	2.401	97.2	37.8

<sup>a</sup> This compound has two crystallographically independent Cu ions.

The magnetic behaviour of compound **1** suggests the possible presence of a very weak antiferromagnetic Cu-Ce coupling. Nevertheless, the first-order angular momentum of the Ce(III) ion avoids an easy interpretation of the magnetic properties in this compound since the magnetic properties arise from both the thermal population of the Stark components of the Ce(III) ions and the possible antiferromagnetic Cu-Ce coupling. A search in the CCDC database shows that there are only six reported Cu<sub>2</sub>Ce trimers with double phenoxido bridges, as in compound **1**. Among these six examples, only three have been magnetically characterized (although no magnetic fit has been reported to date). In the three cases the magnetic properties are very similar to those displayed by compound **1** [33,53,56].

The weak Cu-Gd ferromagnetic coupling shown by compound **2** ( $J = 1.81 \text{ cm}^{-1}$ ) is within the range (1.22–7.38 cm<sup>-1</sup>) observed in the nine Cu<sub>2</sub>Gd trimers with double phenoxido bridges magnetically and structurally characterized reported to date [18,31,34,53,54,57–59]. Furthermore, the J value fits very well with the previous magneto-structural correlation established between the coupling constant and the dihedral CuOOGd angle for Gd-Cu dimers connected by double phenoxido bridges (Figure 8) [54].



**Figure 8.** Correlation between the *J* value and the dihedral CuOOGd angle in different Cu-Gd dimers connected by double phenoxido bridges (data taken from ref. [54]). The solid line is the fit to an exponential law. The red point corresponds to compound **2**.

The magnetic behaviour of compound **3** is similar to those observed in the eight structurally characterized reported examples of Cu<sub>2</sub>Tb trimers with double phenoxido bridges. Furthermore, the observed weak ferromagnetic coupling found in compound **3** ( $J = 1.27 \text{ cm}^{-1}$ ) is of the same order of magnitude as that of the only Cu<sub>2</sub>Tb trimer whose magnetic properties have been fit ( $J = 2.27 \text{ cm}^{-1}$ ) [59].

The Cu<sub>2</sub>Dy compound (4) shows a weak ferromagnetic coupling, similar to those observed in the five structurally characterized reported compounds with Cu<sub>2</sub>Dy trimers with double phenoxido bridges. Interestingly, the value found in 4 ( $J = 0.88 \text{ cm}^{-1}$ ) is very similar to the one found in the only example of Cu<sub>2</sub>Dy trimer whose magnetic properties have been fit ( $J = 0.902 \text{ cm}^{-1}$ ) [59].

Finally, the weak ferromagnetic coupling observed in compound **5** is similar to those observed in the two only examples structurally characterized of Cu<sub>2</sub>Er trimers with double phenoxido bridges [53,59]. Again, in the only example whose magnetic properties have been fitted, the value found ( $J = 0.136 \text{ cm}^{-1}$ ) [59] is of the same order of magnitude than the one found in compound **5** ( $J = 0.31 \text{ cm}^{-1}$ ). Note that the differences observed between our J values and those found by other authors can be easily explained if we consider that other authors include a weak-to-moderate antiferromagnetic Cu-Cu exchange interaction to reproduce the decrease observed in the  $\chi_m T$  product at very low temperatures. In our model we have included a D term to account for this decrease since the Cu(II) ions are too far apart to show any magnetic coupling. Since the moderate  $J_{Cu-Cu}$  affects the magnetic moment at higher temperatures than the D parameter, its inclusion must affect the final  $J_{Cu-Ln}$  value.

Compounds 2–5 show ferromagnetic couplings with coupling constants decreasing as we move forward along the lanthanoids series, *i.e.*, as the number of unpaired f electrons decreases (Table 2). Interestingly, Ishida *et al.* have recently described a similar trend in a series of isomorphous  $Cu_2Ln$  trimers with similar double oxide bridges [59]. Even if Ishida *et al.* use a different model to fit the magnetic properties, our results confirm the idea that the coupling constants decrease as the number of unpaired f electrons decreases (Figure 9). In our case a linear relation can be inferred, although the number of points is still limited, there are other factors that may change *J* (as the dihedral Cu–O–O–Ln angle) and the relative errors in the *J* values are quite big, precluding any definitive correlation.



**Figure 9.** Variation of the coupling constant in complexes **2**–**5** with the number of unpaired f electrons along the lanthanoids series. The solid line is the linear fit.

# 3. Experimental Section

## 3.1. Starting Materials

Reagent grade 2-hydroxyacetophenone and 1,3-propanediamine were obtained from Spectrochem, Mumbai, India and used as received. Reagent grade  $Ln(NO_3)_3 \cdot nH_2O$  were purchased from Aldrich. Other reagents and solvents used were of commercially available reagent quality, unless otherwise stated.

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Though not encountered throughout the experiment, only a small amount of material should be prepared and it should be handled with care.

# 3.2. Synthesis of the Schiff Base Ligand $H_2L^{\alpha-Me}$ and the Metalloligand [CuL<sup> $\alpha-Me$ </sup>]

The di-Schiff base ligand  $H_2L^{\alpha-Me}$  and the metalloligand  $[CuL^{\alpha-Me}]$  were prepared by the reported method described earlier [60].

# 3.3. Synthesis of Complex [ $(CuL^{\alpha-Me})_2Ce(NO_3)_3$ ] (1)

To a solution (10 mL) of the precursor metalloligand  $[CuL^{\alpha-Me}]$  (0.076 g, 0.2 mmol) in methanol, a solution of Ce(NO<sub>3</sub>)<sub>3</sub>· 6H<sub>2</sub>O (0.043 g, 0.1 mmol in 2 mL mehanol) was added and stirred for 30 min at room temperature. The mixture was filtered and kept for slow evaporation at room temperature. Within 24 h, block-shaped dark green X-ray quality single crystals appeared at the bottom of the vessel. They were collected, washed with methanol and allowed to dry in open atmosphere.

**1Ce** Yield: 73% (78 mg), Anal. Calc. for  $C_{38}H_{40}N_7O_{13}Cu_2Ce$  (1069.99): C 42.66, H 3.77, N 9.16; found: C 42.59, H 3.84, N 9.07; IR:  $\nu$ (C=N) = 1602 cm<sup>-1</sup>,  $\nu$ (NO<sub>3</sub><sup>-</sup>) = 1485, 1445, 1384, 1290 cm<sup>-1</sup>.

# 3.4. Synthesis of Complexes [ $(CuL^{\alpha-Me})_2Ln(H_2O)(NO_3)_2$ ]· ( $NO_3$ )· 2( $CH_3OH$ ) (Ln = Gd for 2, Tb for 3, Dy for 4 and Er for 5)

Complexes 2, 3, 4 and 5 were synthesized from methanol in a manner similar to that of 1Ce, using  $Gd(NO_3)_3 \cdot 6H_2O$ ,  $Dy(NO_3)_3 \cdot 6H_2O$ ,  $Tb(NO_3)_3 \cdot 5H_2O$  and  $Er(NO_3)_3 \cdot 5H_2O$  respectively instead of  $Ce(NO_3)_3 \cdot 6H_2O$ . Within 3 days, prismatic-shaped dark green X-ray quality single crystals appeared at the bottom of the vessel. They were collected washed with methanol and allowed to dry in open atmosphere.

**2Gd** Yield: 58% (68 mg), Anal. Calc. for  $C_{40}H_{50}N_7O_{16}Cu_2Gd$  (1169.22): C 41.09, H 4.31, N 8.39; found: C 41.00, H 4.24, N 8.46; IR:  $\nu$ (C=N) = 1600 cm<sup>-1</sup>,  $\nu$ (NO<sub>3</sub><sup>-</sup>) = 1481, 1439,1384, 1300 cm<sup>-1</sup>.

**3Tb** Yield: 60% (70 mg), Anal. Calc. for  $C_{40}H_{50}N_7O_{16}Cu_2Tb$  (1170.90): C 41.03, H 4.30, N 8.37; found: C 40.94, H 4.22, N 8.44; IR:  $\nu$ (C=N) = 1601 cm<sup>-1</sup>,  $\nu$ (NO<sub>3</sub><sup>-</sup>) = 1482, 1438, 1384, 1299 cm<sup>-1</sup>.

**4Dy** Yield: 55% (65 mg), Anal. Calc. for  $C_{40}H_{50}N_7O_{16}Cu_2Dy$  (1174.47): C 40.91, H 4.29, N 8.35; found: C 40.97, H 4.36, N 8.28; IR:  $\nu$ (C=N) = 1600 cm<sup>-1</sup>,  $\nu$ (NO<sub>3</sub><sup>-</sup>) = 1482, 1439, 1383, 1299 cm<sup>-1</sup>.

**5Er** Yield: 63% (75 mg), Anal. Calc. for  $C_{40}H_{50}N_7O_{16}Cu_2Er$  (1179.23): C 40.74, H 4.27, N 8.31; found: C 40.66, H 4.21, N 8.37; IR:  $\nu$ (C=N) = 1600 cm<sup>-1</sup>,  $\nu$ (NO<sub>3</sub><sup>-</sup>) = 1482, 1440, 1384, 1300 cm<sup>-1</sup>.

# 3.5. Physical Measurements

Elemental analyses (C, H and N) were carried out using a Perkin-Elmer 2400 series II CHN analyzer. IR spectra (4000–500 cm<sup>-1</sup>) were recorded by a Perkin-Elmer RXI FT-IR spectrophotometer in KBr pellets.

The magnetic susceptibility measurements were carried out in the temperature range 2–300 K with an applied magnetic field of 0.1 T on polycrystalline samples of compounds 1–5 (with masses of 53.72, 59.37, 30.24, 28.65 and 53.81 mg, respectively) with a Quantum Design MPMS-XL-5 SQUID susceptometer (XL-7 for samples **3** and **4**). The samples were mixed with eicosane to avoid the alignment of the crystals with the magnetic field. The isothermal magnetization was performed on the same samples at 2 K with magnetic fields up to 5 T (7 T for compounds **3** and **4**). The susceptibility data were corrected for the sample holders previously measured using the same conditions and for the diamagnetic contributions of the salt as deduced by using Pascal's constant tables ( $\chi_{dia} = -495.1 \times 10^{-6}, -495.1 \times 10^{-6}, -494.1 \times 10^{-6}, -494.1 \times 10^{-6}$  and  $-493.1 \times 10^{-6}$  emu.mol<sup>-1</sup> for **1–5**, respectively).

# 3.6. Magnetic Model

The data were fitted considering an exchange-coupled trimer model with a single isotropic exchange interaction between the central lanthanide and each terminal copper(II). Calculations were performed with the magnetism package MAGPACK [61,62]. In order to describe the effect of the crystal field (CF) splitting of the central lanthanide, an axial zero-field splitting has been used. Only this parameter has been considered given the limited information provided by a magnetic susceptibility curve, and despite the crucial importance of correctly determination of the crystal field. In order to evaluate the susceptibility curves, the Zeeman term has been added to the Hamiltonian for the three metals. The Hamiltonian used is as follows:

$$\hat{H} = -2J\left(\hat{S}_{Cu1} + \hat{S}_{Cu2}\right)\hat{S}_{Ln} + D\hat{S}_{zLn}^2 + \beta Hg_{Cu}\left(\hat{S}_{Cu1} + \hat{S}_{Cu2}\right) + \beta Hg_{Ln}\hat{S}_{Ln}$$
(1)

# 3.7. Crystallographic Data Collection and Refinement

Suitable single crystals of compounds 1–5 were mounted on a Bruker-AXS SMART APEX II diffractometer with a graphite monochromator and Mo-K $\alpha$  ( $\lambda$  = 0.71073 Å) radiation. The crystals were placed at 60 mm from the CCD. 360 frames were measured with a counting time of 5 s. The structures were solved using Patterson method by using the SHELXS 97. Subsequent difference Fourier synthesis and least-square refinement revealed the positions of the remaining non-hydrogen atoms that were refined with independent anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and their displacement parameters were fixed to be 1.2 times larger than those of the attached non-hydrogen atom except the solvent molecules in 2 to 5 which were assigned from Fourier map. Successful convergence was indicated by the maximum shift/error of 0.001 for the last cycle of the least squares refinement. Absorption corrections were carried out using the SADABS program [63]. All calculations were carried out using SHELXS 97 [64], SHELXL 97 [65], PLATON 99 [66], ORTEP-32 [67] and WinGX system ver-1.64 [68]. Data collection with selected structure refinement parameters and selected bond parameters for all the complexes are given in Table 1 and Tables S1–S3, Supplementary Information respectively. CCDC-1439522 (1), CCDC-1439523 (2), CCDC-1439524 (3), CCDC-1439525 (4) and CCDC-1439526 (5) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

# 4. Conclusions

We have shown that the flexibility of the Schiff base ligand  $L^{\alpha-Me}$  and the use of the corresponding  $[CuL^{\alpha-Me}]$  metalloligand with five different lanthanoid ions has resulted in the synthesis of a new series of trimeric *transoid* complexes of the type [( $CuL^{\alpha-Me}$ )<sub>2</sub>Ce( $NO_3$ )<sub>3</sub>] (1) and  $[(CuL^{\alpha-Me})_2Ln(H_2O)(NO_3)_2] \cdot (NO_3) \cdot 2(CH_3OH); Ln = Gd (2), Tb (3), Dy (4) and Er (5).$  The larger size of the Ce(III) ion has led to a larger coordination number (ten) and to a different coordination geometry as compared with the other Ln(III) complexes (2–5). These complexes show a different magnetic coupling between the Ln(III) ions and the Cu(II) ions: weak antiferromagnetic for compound 1 (in agreement with all the previously prepared  $Cu_2Ce$  complexes) and weak ferromagnetic for compounds 2-5 (also in agreement with all the previously prepared Cu<sub>2</sub>Ln complexes). Compound 2 fits very well with a previous magneto-structural correlation established in Cu-Gd complexes with double phenoxido bridges between the dihedral Cu–O–O–Gd angle and the J value. Furthermore, complexes 3–5 represent the second example of trimeric  $Cu_2Ln$  complexes (Ln = Tb, Dy and Er) whose magnetic properties have been fitted. Finally, the isomorphism of complexes 2–5, with very similar intra-trimer bond distances and angles, has allowed the establishment of a clear relationship between the number of unpaired f electrons and the strength of the magnetic coupling, in agreement with a previous observation in a related series of Cu<sub>2</sub>Ln trimers.

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**Author Contributions:** S.G. participated in the preparations, characterizations and X-ray structural analysis. C.J.G.G. performed the magnetic measurements. Both C.J.G.G. and J.M.C.-J. analyzed the magnetic data. A.G. and C.J.G.G. designed the study and wrote the manuscript.

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