

Structural determinations and magnetic properties of a “chiral at metal” complex and its resulting [Cu–Ln]₂ compounds†

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A chiral trianionic ligand possessing one amide, one imine, two phenol functions and one asymmetric carbon atom into its diamino chain reacts with Cu^{II} ions to yield anionic [LCu][–] units that crystallize in a non-centrosymmetric space group as infinite 1D zig-zag chains in which a transmission of chirality to the Cu^{II} ion is effective. The distorted square planar environment of the Cu^{II} ion is large enough to induce the presence of a stereogenic Cu^{II} centre. Further reaction with Ln^{III} ions in presence of ancillary ligands does not preserve such an arrangement but yields a tetranuclear complex made of two [LCu–Ln] units in a head-to-tail position. The tetranuclear [LCu–Ln]₂ complexes made with the racemic and chiral LCu units crystallize in different space groups, so that racemization does not occur. The structural determinations confirm that a symmetry centre is present in the two structures, except for the methyl groups linked to the chiral carbon atoms, which appear as disordered in the (S–S) tetranuclear entity. Such an arrangement implies a conformation change of the diamino chain linked to the Cu^{II} ion in one [LCu–Ln] unit of the (S–S) entity, and cancels any chirality contribution of the Cu^{II} ions, as in the meso compound. Ferromagnetic Cu–Ln interactions, resulting from an alternate distribution of the Cu^{II} and Ln^{III} ions, are the only ones to be active. Eventually the micro-Squid studies confirm that the hysteresis loops of the corresponding racemate and chiral tetranuclear [LCu–Dy]₂ entities are slightly different.

Introduction

A family of ligands possessing at least one amide, one imine and two phenol functions has been developed in the last decade by Matsumoto's team¹ and our team² in order to synthesize 3d–4f complexes. These ligands possess three functions that can be deprotonated, with an inner N₂O₂ coordination site able to chelate 3d ions in their II oxidation state to yield anionic ligand–metal complexes prone to react with 4f ions. The oxygen atom of the amide function not involved in the inner coordination site is able to enter into coordination with 4f ions, thus yielding final tetranuclear complexes that are characterized by an alternate arrangement of two 3d and

two 4f ions. More recently it has been shown by Matsumoto's team³ that the introduction of two asymmetric carbon atoms in the diamine chain constituting these ligands could modify the final arrangement and give infinite Cu–Ln chains with an alternate distribution of the Cu and Ln ions. In view of these results we tried to prepare a genuine ligand involving a unique chiral carbon atom, in order to show if it is again possible to change the nuclearity of the expected resulting 3d–4f complex. A comparison of the starting chiral and achiral LCu^{II} and final [LCu^{II}–Ln^{III}] complexes allows a better understanding of the structural data and a comparison of their magnetic and SMM properties.

Experimental section

Materials

Racemic 1,2-diamino-2-methylpropane and (S)-1,2-diaminopropane dihydrochloride, salicylaldehyde, *ortho*-vanillin, Cu(OAc)₂·4H₂O, GdCl₃·6H₂O (Aldrich) were used as purchased. Gd(hfa)₃·2H₂O, (hfa = hexafluoroacetylacetonate), Tb(hfa)₃·2H₂O and Dy(hfa)₃·2H₂O were prepared as previously described.⁴ High-grade solvents (2-propanol, diethyl ether, di-

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methylformamide, acetone and methanol) were used for the syntheses of ligands and complexes.

Ligands

The method used to synthesize the racemic 2-hydroxy-*N*-(2-[(2-hydroxyphenyl)methylidene]amino)propyl)benzamide ligand LH₂ was described earlier.^{2f} The pure enantiomer (*S*)-2-hydroxy-*N*-(2-[(2-hydroxyphenyl)methylidene]amino)propyl)benzamide ligand was not isolated and directly reacted with copper acetate in order to increase the yield.

[LCu]pipH. 1. A methanol solution (30 mL) containing L¹H₂, *N*-(2-aminopropyl)-2-hydroxybenzamide (0.97 g, 5 × 10⁻³ mol), and salicylaldehyde (0.65 g, 5.3 × 10⁻³ mol) was heated and stirred for 20 min. Copper acetate (1 g, 5 × 10⁻³ mol) and piperidine (1.6 g, 1.9 × 10⁻³ mol) were then added while heating was pursued for 30 min. The resulting solution was cooled and the violet precipitate that appeared was filtered off by suction, washed by methanol, diethyl ether and dried. Yield: 1.6 g (70%). Anal. Calcd for C₂₂H₂₇CuN₃O₃ (445.0): C, 59.4; H, 6.1; N, 9.4. Found: C, 59.0; H, 5.9; N, 9.2. IR (ATR): 3051w, 3020w, 2957w, 2921w, 2890w, 2863w, 2584w, 2482w, 2406w, 1632m, 1622m, 1593s, 1562s, 1526s, 1466m, 1441s, 1387s, 1341m, 1309s, 1260s, 1133m, 1039w, 894w, 755s, 704w, 653w cm⁻¹.

Replacement of salicylaldehyde by *ortho*-vanillin yielded the L²CupipH 2 complex as crystals that appeared from the mother solution. Yield: (75%). Anal. Calcd for C₂₃H₂₉CuN₃O₄ (475.0): C, 58.1; H, 6.1; N, 8.8. Found: C, 57.8; H, 5.9; N, 8.6. IR (ATR): 3057w, 2963m, 2943m, 2875m, 2852m, 2747m, 2626w, 2518w, 1638s, 1591s, 1561s, 1526s, 1436s, 1392m, 1381m, 1328m, 1311s, 1262m, 1246m, 1213m, 1080m, 1037m, 967w, 898w, 752w, 734m, 704w, 651w cm⁻¹.

(S)-[LCu]pipH. 3. Potassium hydroxide (0.76 g, 1.4 × 10⁻² mol) was added to a methanol solution (30 mL) of (*S*)-1,2-diaminopropane dihydrochloride (1 g, 6.8 × 10⁻³ mol). The mixture was stirred for 2 h and the resulting potassium chloride was eliminated by filtration. Phenyl salicylate (1.5 g, 7 × 10⁻³ mol) was then added to the filtered solution and the mixture was heated to reflux for 30 min under stirring. Addition of picric acid (1.6 g, 7 × 10⁻³ mol) to the cooled solution yielded a yellow precipitate that was filtered off 1 h later and dried (1.5 g). 0.6 g of the precipitate and salicylaldehyde (0.17 g, 1.4 × 10⁻³ mol) were dissolved in methanol (20 mL). After a 20 min heating under stirring, copper acetate (0.28 g, 1.4 × 10⁻³ mol) and piperidine (0.5 g, 5.9 × 10⁻³ mol) were added, followed by a 30 min heating under stirring. The solution was reduced to a few mL. Addition of acetone (40 mL) and stirring at room temperature yielded a violet precipitate that was filtered off and washed with acetone and diethyl ether. Yield: 0.5 g (78%). Anal. Calcd for C₂₂H₂₇CuN₃O₃ (445.0): C, 59.4; H, 6.1; N, 9.4. Found: C, 59.1; H, 6.0; N, 9.2. IR (ATR): 3051w, 3020w, 2957w, 2921w, 2890w, 2863w, 2584w, 2482w, 2406w, 1632m, 1622m, 1593s, 1562s, 1526s, 1466m, 1441s, 1387s, 1341m, 1309s, 1260s, 1133m, 1039w, 894w, 755s, 704w, 653w cm⁻¹. [α]_D²⁰_{Hg436}, (-360.7), *c* 0.05, MeOH. Crystals were obtained by slow diffusion of diethyl ether in a methanol solu-

tion of the complex. Anal. Calcd for C₂₃H₃₁CuN₃O₄ (477.0): C, 57.9; H, 6.5; N, 8.8. Found: C, 57.5; H, 6.2; N, 8.6.

Heteronuclear Cu^{II}Ln^{III} complexes

The complexes involving hfa ligands were prepared according to the general process described hereunder, starting with the racemic [LCu]pipH·MeOH or the pure enantiomeric (*S*)-[LCu]pipH·MeOH complex.

(S-S)-[LCu(dmf)Gd(hfa)₂(dmf)]₂. 4. (*S*)-[LCu]pipH·MeOH (37 mg, 7.8 × 10⁻⁵ mol) and Gd(hfa)₃·2H₂O (63 mg, 7.8 × 10⁻⁵ mol) were poured in a test tube with 2 mL of dimethylformamide, giving a few days later blue crystals suitable for XRD. Yield: 70 mg (83%). Anal. Calcd for C₆₆H₆₂Cu₂F₂₄Gd₂N₈O₁₈ (2152.8): C, 36.8; H, 2.9; N, 5.2. Found: C, 36.6; H, 2.8; N, 5.0. IR (ATR): 2933w, 1683w, 1651s, 1600m, 1579m, 1546m, 1529m, 1513m, 1475m, 1451w, 1408w, 1380m, 1249s, 1195s, 1135s, 1098s, 896w, 793w, 761m, 659m cm⁻¹.

(S-S)-[LCu(dmf)Tb(hfa)₂(dmf)]₂. 5. Yield: (75%). Anal. Calcd for C₆₆H₆₂Cu₂F₂₄N₈O₁₈Tb₂ (2156.1): C, 36.8; H, 2.9; N, 5.2. Found: C, 36.7; H, 2.9; N, 5.1. IR (ATR): 2933w, 1651s, 1600m, 1578m, 1545m, 1529m, 1513m, 1475m, 1450w, 1407w, 1380m, 1248s, 1196s, 1134s, 1098s, 896w, 793w, 761m, 659m cm⁻¹.

(S-S)-[LCu(dmf)Dy(hfa)₂(dmf)]₂. 6. Yield: (80%). Anal. Calcd for C₆₆H₆₂Cu₂Dy₂F₂₄N₈O₁₈ (2163.3): C, 36.6; H, 2.9; N, 5.2. Found: C, 36.5; H, 2.8; N, 5.0. IR (ATR): 2933w, 1651s, 1600m, 1579m, 1547m, 1530m, 1513m, 1475m, 1449w, 1407w, 1381m, 1249s, 1195s, 1135s, 1099s, 896w, 792w, 761m, 659m cm⁻¹.

(R-S)-[LCu(dmf)Gd(hfa)₂(dmf)]₂. 7. Yield: (81%). Anal. Calcd for C₆₆H₆₂Cu₂F₂₄Gd₂N₈O₁₈ (2152.8): C, 36.8; H, 2.9; N, 5.2. Found: C, 36.7; H, 2.7; N, 5.0. IR (ATR): 2933w, 1650s, 1601m, 1577m, 1542m, 1529m, 1509m, 1475m, 1451w, 1407w, 1379m, 1248s, 1195s, 1135s, 1096s, 899w, 793w, 762m, 660m cm⁻¹.

(R-S)-[LCu(dmf)Dy(hfa)₂(dmf)]₂. 8. Yield: (80%). Anal. Calcd for C₆₆H₆₂Cu₂Dy₂F₂₄N₈O₁₈ (2163.3): C, 36.6; H, 2.9; N, 5.2. Found: C, 36.4; H, 2.8; N, 5.1. IR (ATR): 2935w, 1652s, 1601m, 1577m, 1542m, 1528m, 1508m, 1476m, 1449w, 1407w, 1379m, 1250s, 1196s, 1133s, 1096s, 899w, 792w, 762m, 659m cm⁻¹.

(R-S)-[LCuGd(thd)₂(H₂O)]₂. 9. A mixture of LCupipH (0.22 g, 4.9 × 10⁻⁴ mol), GdCl₃·6H₂O (0.18 g, 4.9 × 10⁻⁴ mol), tetramethylheptanedione (0.20 g, 1.1 × 10⁻³ mol) and piperidine (0.1 g, 1.2 × 10⁻³ mol) in methanol (10 mL) was stirred and heated for twenty minutes, giving a glycin-colored precipitate. After cooling at room temperature, the solution was filtered off, yielding a solid that was washed with water, methanol, diethyl ether and then dried. Yield: 0.25 g (56%). Anal. Calcd for C₇₈H₁₁₀Cu₂Gd₂N₄O₁₆: (1801.3) C, 52.0; H, 6.2; N, 3.1. Found: C, 52.1; H, 6.0; N, 3.0. IR (ATR): 2956m, 2903w, 2864w, 1642w, 1615w, 1600m, 1574s, 1537s, 1504s, 1443m, 1403s, 1387m, 1356m, 1296m, 1248w, 1225w, 1182w, 1139w, 1024w, 869w, 792w, 761m, 709w, 657w cm⁻¹.

Physical measurements

C, H, and N elemental analyses were carried out at the Laboratoire de Chimie de Coordination Microanalytical Laboratory in Toulouse, France. IR spectra were recorded with a PerkinElmer Spectrum 100FTIR using the ATR mode.

Magnetic data were obtained with a Quantum Design MPMS SQUID susceptometer. Magnetic susceptibility measurements were performed in the 2–300 K temperature range under a 0.1 T applied magnetic field, and diamagnetic corrections were applied by using Pascal's constants.⁵ Isothermal magnetization measurements were performed up to 5 T at 2 K. The magnetic susceptibilities have been computed by exact calculations of the energy levels associated to the spin Hamiltonian through diagonalization of the full matrix with a general program for axial symmetry,⁶ and with the MAGPACK program package⁷ in the case of magnetization. Least-squares fittings were accomplished with an adapted version of the function-minimization program MINUIT.⁸

Crystallographic data collection and structure determination for the complexes 2, 3, 5, 7

Crystals of 2, 3, 5, and 7 were kept in the mother liquor until they were dipped into oil. The chosen crystals were mounted on a Mitegen micromount and quickly cooled down to 180 K (2, 3, 5) or 100 K (7). The selected crystals of 2 (brown, 0.40 × 0.20 × 0.15 mm³), 3 (pale green, 0.18 × 0.10 × 0.02 mm³), 5 (violet, 0.375 × 0.25 × 0.125 mm³), 7 (violet, 0.20 × 0.20 × 0.05 mm³) were mounted on a Bruker Kappa Apex II (3, 7) or a Stoe Imaging Plate Diffractometer System (IPDS) (2, 5) using molybdenum ($\lambda = 0.71073 \text{ \AA}$) and equipped with an Oxford Cryosystems cooler device. The unit cell determination and data integration were carried out using XRED,⁹ CrySAlis RED or SAINT packages.^{10–12} The structures have been solved using SIR92,¹³ SUPERFLIP¹⁴ or SHELXS-97¹⁵ and refined by least-squares procedures using the software packages CRYSTALS¹⁶ or WinGX version 1.63.¹⁷ Atomic Scattering Factors were taken from the International tables for X-Ray Crystallography.¹⁸ All hydrogen atoms were refined by using a riding model. When it was possible, all non-hydrogen atoms were anisotropically refined. Drawings of molecules have been performed with the program CAMERON.¹⁹ Cif data for 2, 3, 5 and 7 have been deposited at CCDC with CCDC references 2125504, 2125506, 2125505, 2094994 respectively.†

Crystal data for 2. C₂₃H₂₉CuN₃O₄, $M = 475.03$, triclinic, $P\bar{1}$, $Z = 4$, $a = 10.8680(14)$, $b = 13.7058(15)$, $c = 15.7502(19) \text{ \AA}$, $\alpha = 90.405(14)$, $\beta = 100.814(15)$, $\gamma = 109.515(14)^\circ$, $V = 2165.9(5) \text{ \AA}^3$, 21546 collected reflections, 7993 unique reflections ($R_{\text{int}} = 0.0855$), R -factor = 0.0725, weighted R -factor = 0.1887 for 5209 contributing reflections [$I > 2\sigma(I)$].

Crystal data for 3. C₂₃H₃₁CuN₃O₄, $M = 477.05$, monoclinic, $P2_1$, $Z = 2$, $a = 11.1322(3)$, $b = 7.6035(2)$, $c = 13.5075(4) \text{ \AA}$, $\alpha = \gamma = 90^\circ$, $\beta = 104.642(2)^\circ$, $V = 1106.19(5) \text{ \AA}^3$, 10 706 collected reflections, 4259 unique reflections ($R_{\text{int}} = 0.044$), R -factor = 0.0363, weighted R -factor = 0.0644 for 3740 contributing reflections [$I > 2\sigma(I)$], Flack parameter = 0.016(12).

Crystal data for 5. C₆₆H₅₈Cu₂F₂₄N₈O₁₈Tb₂, $M = 2152.17$, triclinic, $P\bar{1}$, $Z = 1$, $a = 11.762(5)$, $b = 13.282(5)$, $c = 14.143(5) \text{ \AA}$, $\alpha = 110.869(5)$, $\beta = 92.722(5)$, $\gamma = 93.723(5)^\circ$, $V = 2046.9(14) \text{ \AA}^3$, 19 355 collected reflections, 7025 unique reflections ($R_{\text{int}} = 0.0391$), R -factor = 0.0827, weighted R -factor = 0.2421 for 6104 contributing reflections [$I > 2\sigma(I)$].

Relevant parameters for complexes (S-S)-[LCu(dmf)Gd(hfa)₂(dmf)₂] 4 and (S-S)-[LCu(dmf)Dy(hfa)₂(dmf)₂] 6. 4: Space group: $P\bar{1}$ (293 K), lattice parameters: $a = 11.6886(6)$, $b = 13.2647(6)$, $c = 14.0710(6) \text{ \AA}$, $\alpha = 110.738(2)$, $\beta = 94.448(2)$, $\gamma = 93.844(2)^\circ$, $V = 2023.7(1) \text{ \AA}^3$. 6: Space group: $P\bar{1}$ (180 K), lattice parameters: $a = 11.774(1)$, $b = 13.287(1)$, $c = 14.138(1) \text{ \AA}$, $\alpha = 110.836(4)$, $\beta = 94.932(4)$, $\gamma = 93.596(3)^\circ$, $V = 2049.0(3) \text{ \AA}^3$.

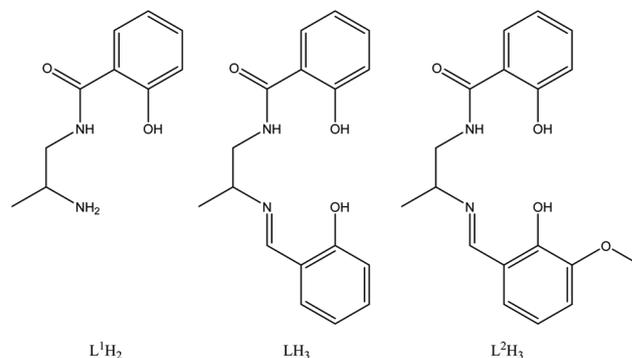
Crystal data for 7. C₆₆H₆₂Cu₂F₂₄Gd₂N₈O₁₈, $M = 2152.80$, monoclinic, $C2/c$, $Z = 4$, $a = 32.1119(8)$, $b = 13.6748(3)$, $c = 17.8270(4) \text{ \AA}$, $\alpha = \gamma = 90$, $\beta = 91.4280(10)^\circ$, $V = 7825.8(3) \text{ \AA}^3$, 98609 collected reflections, 13378 unique reflections ($R_{\text{int}} = 0.0356$), R -factor = 0.027, weighted R -factor = 0.0285 for 10508 contributing reflections [$I > 2\sigma(I)$].

Results and discussion

If the racemates L¹H₂ and LH₃ ligands (Scheme 1) were previously described,^{2f} the pure enantiomer (S)-LH₃ ligand has been isolated and characterized under its coordinated (S)-[LCu] pipH form, in which the starting copper complex possesses a chiral carbon atom in the diamino chain of the ligand. The synthetic route to tetranuclear [LCu–Ln]₂ complexes 4–9 makes use of a stepwise process that consists in reacting the corresponding anionic LCu racemate or pure enantiomeric copper complex with Gd(hfa)₃·2H₂O or with the lanthanide chloride salt, in presence of tetramethylheptanedione (Hthd) and piperidine as deprotonating agent. The isolated complexes can be formulated LCuLn(hfa)₂(dmf)₂ or L²CuGd(thd)₂ on the basis of chemical analysis. Strong stretching CF, CO and CH bands in the 1250–1100, 1650–1600 and 3000–2950 cm⁻¹ areas do confirm the presence of hfa and thd ligands in the infrared spectra of these complexes. The ligands furnish multiple bands, from which the strong antisymmetrical amide stretching bands at 1600–1550 cm⁻¹ can be easily assigned.

Structural studies

The crystallographic data of complex 2 are summarized in the Experimental section while a view of the asymmetric unit is reported in Fig. 1. Relevant bond distances and angles are colated in the figure caption. The structure crystallizes in the tri-



Scheme 1 Schematic representation of the ligands.

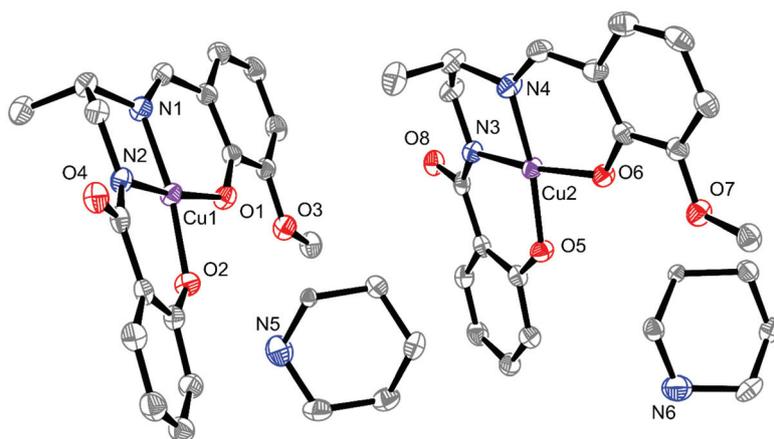


Fig. 1 View of the mononuclear $[L^2Cu](C_5H_{12}N)$ complex **2**. Selected bond lengths (Å): Cu1 N2 1.918(4), Cu1 N1 1.952(4), Cu1 O1 1.958(4), Cu1 O2 1.893(4), O4 C12 1.257(6), Cu2 N3 1.919(4), Cu2 N4 1.955(5), Cu2 O5 1.883(4), Cu2 O6 1.958(3), O8 C30 1.255(6) Å.

clinic $P\bar{1}$ space group, with two different mononuclear molecules. Each molecule consists of a mononuclear anionic L^2Cu^{II} unit with the Cu^{II} ion located in the N_2O_2 site of the triply deprotonated ligand, along with a piperidinium entity (Fig. 1).

The presence of two different molecules is due to the asymmetric carbon atom located in the diamino chain that yields two enantiomers crystallizing as a true racemate. The five-membered rings formed by the diamine chain chelating the copper ion are non planar, as usual, with δ *gauche* conformation for the $C^*(R)$ enantiomer and λ *gauche* conformation for the $C^*(S)$ enantiomer, respectively. In each molecule, the methyl substituent is in an axial position. The copper ion in the N_2O_2 site slightly deviates from a square planar coordination, with angles of 11.52(8) and 13.41(9)° between the mean planes of the two six-membered cycles chelating the Cu ion. The resulting Δ and Λ enantiomers are respectively associated to the $C^*(S)$ and $C^*(R)$ centres. Surprisingly, there are no hydrogen bonds between the piperidinium nitrogen cation and the phenoxo or amidato oxygen atoms. The molecules are associated by pairs of different enantiomers separated by a large $Cu \cdots O(\text{amidato})$ distance of 4.270(1) Å.

Complex **3** is a pure enantiomer that crystallizes in a non-centrosymmetric space group, $P2_1$ (Fig. 2). The $C^*(S)$ carbon atom is associated to a δ *gauche* conformation of the five-membered ring, with the methyl substituent in an equatorial position. The deviation from the square planar coordination of the central Cu ion is more pronounced, the angle between the two six-membered chelating cycles being equal to 21.21(6)°. The present enantiomer has a S_{Cu} configuration. The oxygen atom of the amide function that is not involved in the coordination site establishes an apical contact with the neighboring copper ion, with a large $Cu \cdots O4$ distance (2.610(2) Å), and creates a zig-zag 1D chain. This contact gives an umbrella form to each (*S*)-LCu unit. The nitrogen of the cationic piperidinium entity is directly bonded to these two LCu units by hydrogen bonds while indirect hydrogen bonds through the non coordinated methanol molecule are also present (Fig. 3). Along the *b* axis,

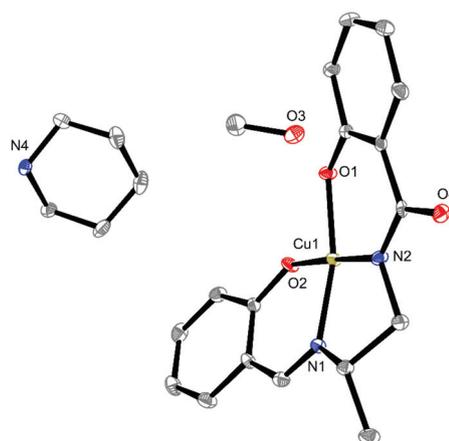


Fig. 2 View of the mononuclear (*S*)-[LCu]($C_5H_{12}N$) complex **3**. Selected bond lengths and distances (Å): Cu1 N2 1.915(3), Cu1 N1 1.967(2), Cu1 O1 1.918(2), Cu1 O2 1.932(2), O4 C11 1.276(3), Cu1 O4 2.610(2) Å.

the (*S*)-LCu units are arranged in two head-to-head stacking columns with an intracolumn $Cu \cdots Cu$ distance of 7.604(7) Å and a 180° rotation of these (*S*)-LCu units. The intercolumn $Cu \cdots Cu$ distance is equal to 6.053(6) Å.

The main difference between complexes **2** and **3** comes from the $Cu-O(\text{amide})$ link that is observed in complex **3** and absent in complex **2**. Such a contact must play a role in the position of the methyl group, which is axial in **2** and equatorial in **3**, while the mean $Cu-O$ and $Cu-N$ bond lengths of the two complexes are quite similar. In our mononuclear complex **3** the four oxygen and nitrogen atoms are different, with a significant deviation from the mean coordination copper plane. And the transmission of chiral information from the enantiopure diamine ligand to the copper centre is evidenced by the large optical rotation $[\alpha]_{Hg436}^{20}$ of complex **3** (−360.7) compared to the $[\alpha]_D^{20}$ of (*S*)-diaminopropane (−4), which does confirm the presence of two chirality centres, the $C^*(S)$ carbon atom and the copper metal ion.²⁰

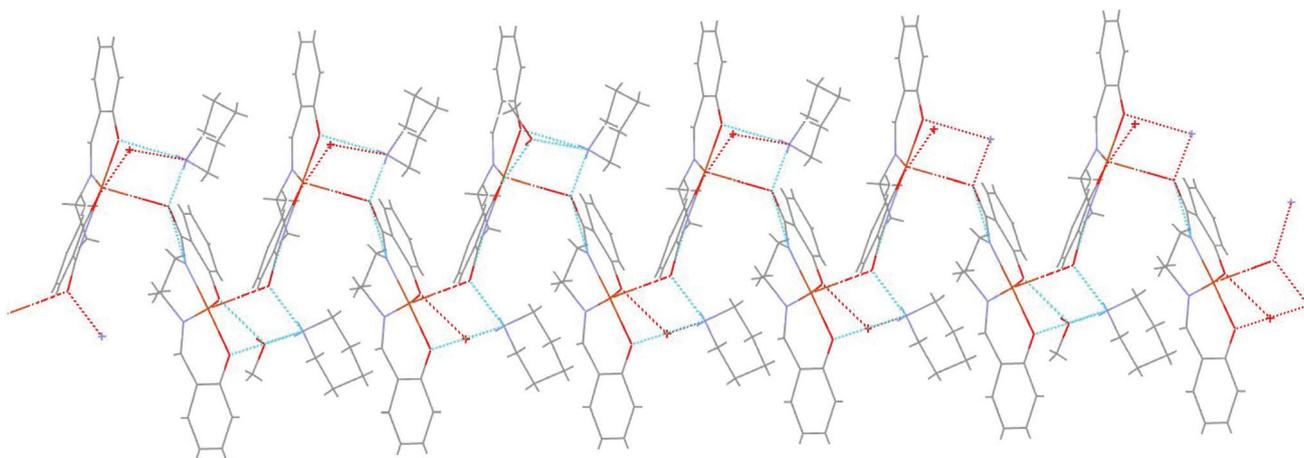
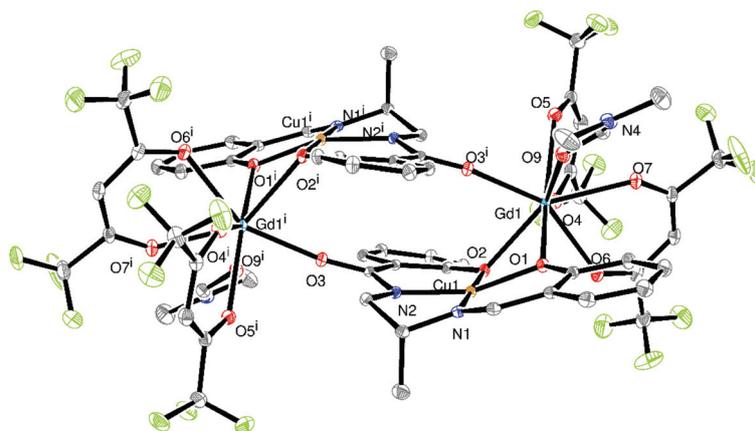


Fig. 3 The zig-zag 1D chain resulting from axial coordination of the amide oxygen atom in the [(S)-LCu]pipH complex 3.

The tetranuclear molecules 4–9 are made of two [LCu(dmf) Ln(hfa)₂(dmf)] (4–8) or [L²CuLn(thd)₂] (9) entities arranged in a head to tail position and linked through the oxygen atoms of the amido functions to form a double (Cu–N–C–O–Gd) bridge. The complex 7 prepared with the racemate ligand (Fig. 4) crystallizes in the monoclinic *C2/c* space group. A ligand possessing the *C*^{*}(*S*) carbon atom along with the λ *gauche* conformation of the diamine chain is associated to a ligand possessing the *C*^{*}(*R*) carbon atom and the δ *gauche* conformation of the diamine chain, so that the resulting molecule is a true racemate. This arrangement resulting from the presence of a symmetry centre induces an axial position for the methyl groups linked to the asymmetric carbon atoms. The copper coordination is increased to five by an axial coordination of the oxygen atom coming from a dmf molecule (Fig. S1†). The Gd ion is eight-coordinate to eight oxygen atoms coming from the main ligand (two deprotonated phenoxo atoms), the ancillary hfa and dmf ligands (respectively four and one oxygen atoms) and the amidato brid-

ging oxygen atom. The axial Cu–O bond length is much larger (2.515(2) Å) than the equatorial ones (1.922(1)–1.959(1) Å). If the Gd–O amidato bond is the shortest one (2.242(1) Å), the other Gd–O bonds vary from 2.378(1) to 2.473(2) Å. The hinge angle between the (OCuO) and (OGdO) planes involving the bridging phenoxo oxygen atoms and each metal ion is equal to 33.2(1)°, which induces a Cu...Gd separation of 3.318(1) Å, while the angle of the single amidato C–O–Gd bridge is equal to 170.0(1)°. Within the tetranuclear complex the Cu...Cu and Gd...Gd distances are respectively equal to 5.940(1) and 7.878(1) Å. There are no intra or inter hydrogen bonds and the shortest interunit Cu...Cu and Gd...Gd contacts are equal to 7.678(1) and 10.869(1) Å, so that these tetranuclear units are well isolated from each other. Note that such a large interunit separation is favored by the coordination of dmf molecules on each Cu and Ln metal centre.

The structural determination of the tetranuclear complex 5 obtained with the enantiomeric pure copper complex has been



made difficult by the head-to-tail arrangement of the two (*S*)-[LCu(dmf)Tb(hfa)₂(dmf)] units. This complex crystallizes in a triclinic space group, different from the monoclinic space group found in the case of the racemate unit (Fig. 5 and S2†). This change does confirm that we are dealing with a pure enantiomeric species. In the previous racemate complex 7, we have seen that the *gauche* conformation change from λ to δ of the diamine chain allows conservation of a symmetry centre in presence of the (*R*) and (*S*) enantiomers, with the Methyl groups linked to the asymmetric carbon atoms in axial position. As we also observe the conformation change of the diamine chain in complex 5, the centre of symmetry is preserved for the entire set of atoms involved in the (*S*)-[LCu(dmf)Tb(hfa)₂(dmf)] unit, except for the carbon atoms of the Methyl group linked to the chiral carbon atom. This is the reason why these Methyl carbon atoms appear as disordered. If the structural determination was correctly solved, the asymmetric unit should be the tetranuclear (*S-S*)-[LCu(dmf)Tb(hfa)₂(dmf)]₂ entity and not the dinuclear [LCu(dmf)Tb(hfa)₂(dmf)] unit, as observed here and in the case of the racemate complex 7. Each dinuclear [LCu(dmf)Tb(hfa)₂(dmf)] unit is made of 60 CNOCuTb heavy atoms among them 59 are symmetry-related against one which is not symmetry-related and appears as disordered. This observation explains the difficulty to solve the structural determination of the tetranuclear complex 5 in a non centrosymmetric space group. We can also highlight that the interunit separation in this enantiomeric pure complex is increased, in comparison to the one observed in the racemic tetranuclear complex 7. The torsion angle Cu–O–C–N involving the dmf molecule linked to the Cu ion varies from 110.7(2)° (racemate) to 172.0(9)° (*S-S* enantiomer), thanks to the

different orientation of the dmf molecules linked to the Cu atoms, the Cu...Cu and Tb...Tb contacts becoming now equal to 8.896(1) and 11.939(1) Å instead of 5.940(1) and 7.878(1) Å for the racemate complex. Eventually note that the three tetranuclear complexes 4, 5, 6, prepared from the pure enantiomer (*S*)-[LCu]pipH complex 3 crystallize in the same space group with similar lattice parameters, which are different from the ones of the racemate complex 7.

Magnetic properties

The magnetic susceptibilities of the copper complexes 1–3 have been measured in the 2–300 K temperature range under an applied magnetic field of 0.1 T. The thermal variation of the $\chi_M T$ product for complex 3 is displayed in Fig. 6, χ_M being the molar magnetic susceptibility of the dinuclear species corrected for the diamagnetism of the ligands. At 300 K, $\chi_M T$ is equal to 0.44 cm³ mol⁻¹ K which is larger than expected for a copper ion with $g = 2$. This value remains constant till 10 K and increases below 10 K up to a value of 0.53 cm³ mol⁻¹ K at 2 K. This behavior indicates that a ferromagnetic interaction between the Cu^{II} ions operates at low temperature, in agreement with the structural determination. These experimental data have been fitted with the Fisher's model for an infinite chain of $\frac{1}{2}$ local spins.²¹ The best result yields a J value of 0.44 cm³ mol⁻¹ K and a g factor of 2.17 with an agreement factor R ($R = \Sigma[(\chi T)_{\text{obs}} - (\chi T)_{\text{calc}}]^2 / \Sigma[(\chi T)_{\text{obs}}]^2$) of 1.0×10^{-5} . The experimental magnetization curve at low temperature has been fitted with the Magpack program and an approximate model using a set of eight Cu ions. A correct agreement validates the data (Fig. S3†). A similar behavior is observed for the racemic complex 1, (Fig. S4†) the best parameters being equal to

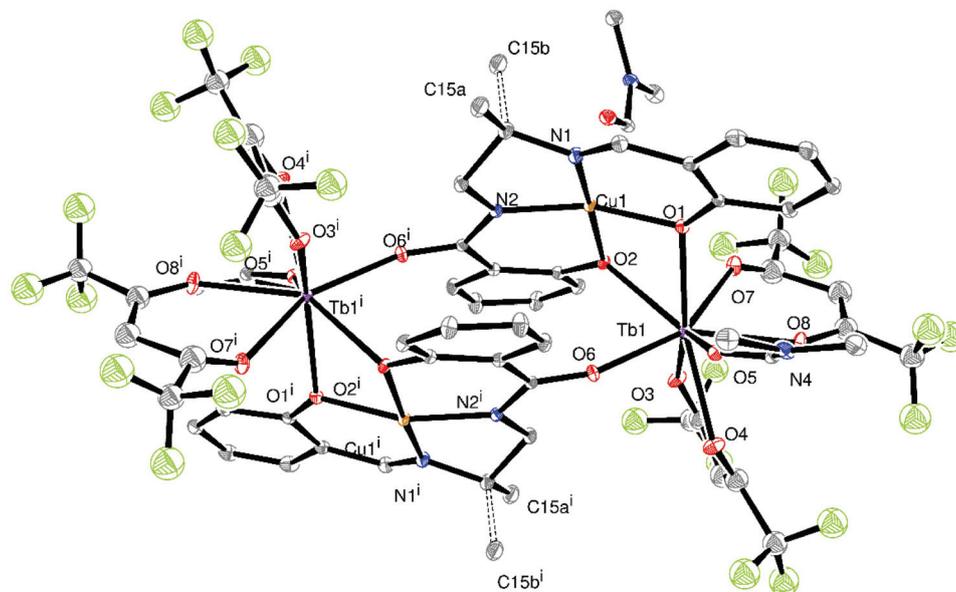


Fig. 5 View of the tetranuclear complex 5. Selected bond lengths (Å) and angles (°): Cu1 N2 1.933(8), Cu1 N1 1.950(8), Cu1 O1 1.972(7), Cu1 O2 1.917(6), Cu1 O9 2.330(8), O6 C36 1.290(7), Tb1 O2 2.382(7), Tb1 O1 2.385(6), Tb1 O3 2.325(7), Tb1 O4 2.469(9), Tb1 O5 2.402(7), Tb1 O6 2.211(6), Tb1 O7 2.467(8), Tb1 O8 2.363(7) Å, Tb1 O1 Cu1 98.6(3), Tb1 O2 Cu1 100.4(3)°.

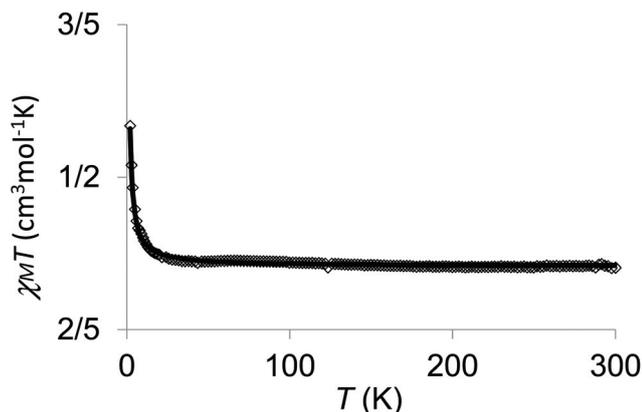


Fig. 6 Temperature dependence of the $\chi_M T$ product for complex **3** at 0.1 T applied magnetic field. The solid line corresponds to the best data fit (see text).

0.31 cm³ mol⁻¹ K for J and 2.19 for g . Observation of a similar behavior for the racemate complex **1** is in agreement with the formation of 1D chains of each enantiomer. On the contrary the $\chi_M T$ product for complex **2** (Fig. S5[†]) is constant and equal to 0.42 cm³ mol⁻¹ K from 300 to 2 K, which corresponds to an absence of interaction between the Cu ions, as expected from the structural determination.

The magnetic susceptibility of the tetranuclear complex **7**, which is reported in Fig. 7 as the $\chi_M T$ vs. T plot, has been measured in the 2–300 K temperature range in a 0.1 T applied magnetic field. At 300 K, $\chi_M T$ is equal to 16.47 cm³ mol⁻¹ K, in agreement with the expected value for two Cu^{II} and two Gd^{III} uncoupled ions (16.50 cm³ mol⁻¹ K with $g = 2$). Lowering the temperature causes $\chi_M T$ to increase and reach a value of 30.25 cm³ mol⁻¹ K at 2 K, which is larger than expected (2×10 cm³ mol⁻¹ K) for two uncorrelated pairs of ferromagnetically coupled Cu^{II} and Gd^{III} ions but smaller than the maximum value attributable (36 cm³ mol⁻¹ K) to a $S = 8$ spin state resulting from the ferromagnetic coupling of two Cu–Gd

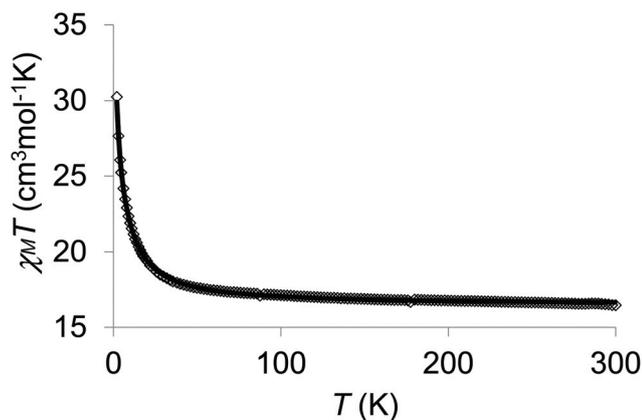


Fig. 7 Temperature dependence of the $\chi_M T$ product for complex **7** at 0.1 T applied magnetic field. The solid line corresponds to the best data fit (see text).

pairs. Such a behavior is consistent with the simultaneous occurrence of two ferromagnetic Cu–Gd interactions which operate within each Cu–Gd pair and between two pairs respectively. A quantitative analysis based on a “dimer of dimer” model directly derived from the structural data and using the Hamiltonian $H = -J(S_{Cu} \cdot S_{Gd} + S_{Cu'} \cdot S_{Gd'}) - J'(S_{Cu} \cdot S_{Gd'} + S_{Cu'} \cdot S_{Gd}) + \sum_{ij} g_i \beta H_j S_{ij}$ with the terms gauged by the J and J' parameters accounting for the spin exchange and the last term accounting for the Zeeman contributions where $i = Cu, Gd$ and $j = x, y, z$, leads to $J = 4.28(5)$ cm³ mol⁻¹ K, $J' = 0.66(5)$ cm³ mol⁻¹ K, $g = 2.00$ with an agreement factor R equal to 1.4×10^{-5} . The two coupling constants characterizing complex **7** differ by an order of magnitude so that their respective pathways are easily recognized, the larger value corresponding to the double phenoxo Cu–(O₂)–Gd bridging and the lower value to the single amidato bridge (Cu–N–C–O–Gd'), in agreement with previous results.^{1,2} A comparison of the racemic tetranuclear complex **7** with the pure enantiomeric complex **4** confirms the similar behaviour of the two complexes. $\chi_M T$ varies from 16.60 cm³ mol⁻¹ K at 300 K to 30.10 cm³ mol⁻¹ K at 2 K for complex **4** (Fig. S6[†]) and the quantitative analysis gives to $J = 3.75(5)$ cm³ mol⁻¹ K, $J' = 0.64(5)$ cm³ mol⁻¹ K, $g = 2.01$ with R equal to 3.4×10^{-5} . On the contrary, replacement of hfa ligands by the more crowded thd ligands (thd = deprotonated form of 2,2,6,6-tetramethylheptanedione) chelated to the Gd ions induces a decrease of the J parameters for complex **9**, $J = 1.54(5)$ cm³ mol⁻¹ K, $J' = 0.47(5)$ cm³ mol⁻¹ K, $g = 2.00$ with R equal to 1.1×10^{-5} (Fig. S7[†]). These J values do agree with data reported for previously published tetranuclear complexes obtained with non symmetric amide–imine ligands.^{1,2}

The $\chi_M T$ variations for the tetranuclear (*S-S*)-[LCu(dmf)Tb(hfa)₂(dmf)]₂ **5** and (*S-S*)-[LCu(dmf)Dy(hfa)₂(dmf)]₂ **6** complexes are very similar, and the thermal variation of the $\chi_M T$ vs. T plot for complex **5** is given on Fig. S8.[†] At 300 K, $\chi_M T$ is equal to 24.0 cm³ mol⁻¹ K, in agreement with the expected value for two Cu^{II} and two Tb^{III} uncoupled ions (24.44 cm³ mol⁻¹ K with $g = 2$). It remains constant till 100 K, then decreases to 22.6 cm³ mol⁻¹ K at 26 K and eventually increases to 35.5 cm³ mol⁻¹ K at 2 K. Such a behaviour indicates presence of ferromagnetic Cu–Tb and Cu–Dy interactions in complexes **5** and **6**, respectively.

Preliminary results of alternating current susceptibility measurements gave similar information for the two tetranuclear complexes **4** and **7**. The plots of the in-phase (χ'_M) and out-of-phase (χ''_M) susceptibilities versus T for different frequencies of the external field are characteristic for slow relaxation of the magnetization. We also performed magnetization hysteresis loop and magnetization relaxation measurements performed on single micro-crystals of our two (*R-S*) and (*S-S*)-[LCu(dmf)Dy(hfa)₂(dmf)]₂ complexes, which were thermalized using Apiezon grease, with use of a micro-SQUID apparatus.²² The field was aligned with the easy axes of magnetization using the transverse field method.²³ Fig. 8 shows magnetization versus magnetic field hysteresis loops for single crystals of **8** and **6** at different temperatures and field sweep rates. The strong temperature and field sweep dependent hysteresis loops establish SMM behaviour. A slow relaxation of magnetization

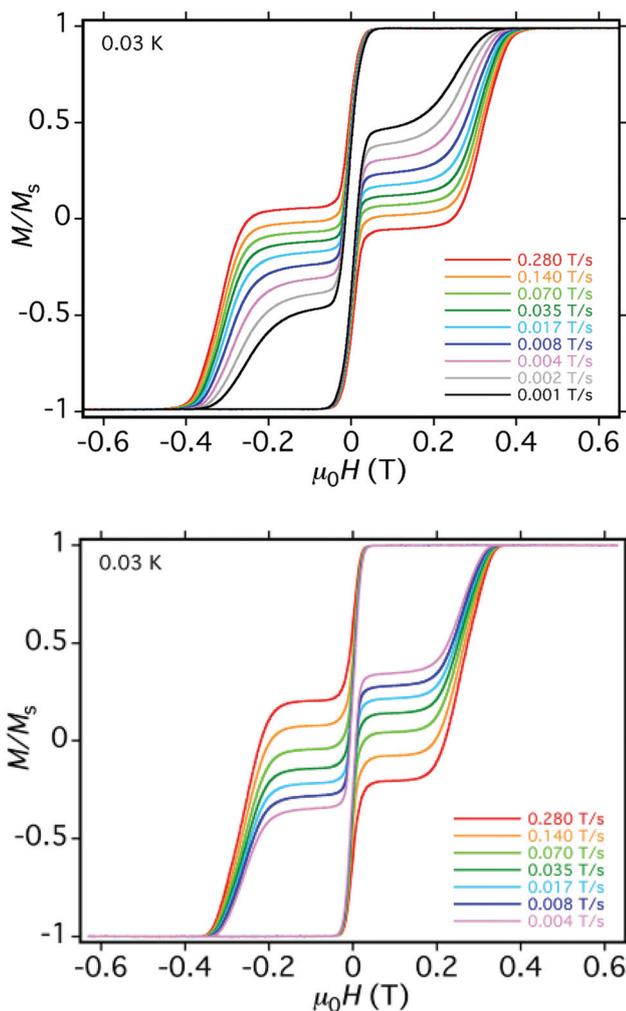


Fig. 8 Single-crystal magnetization (M) vs. applied field measurements (μ_0H) for complexes **8** (up) and **6** (down) at 0.03 K for several field sweep rates (bottom). M is normalized to its saturation value at 1.4 T.

is observed in both samples, which is evidenced by large hysteresis loops whose coercivity is temperature and sweep-rate dependent (Fig. 8 and S9[†]), increasing with decreasing temperature and increasing field sweep rate, as expected for the superparamagnetic-like behaviour of an SMM. There is no large difference in the two complexes, except that a slightly larger coercive field is present in the racemic complex **8**.

Discussion

The LH_3 and L^2H_3 ligands used in this work present several similarities. First of all they are non-symmetric, with a main N_2O_2 coordination site able to link 3d ions. The nitrogen atoms come from imine and amide functions while the oxygen atoms involve phenol functions, so that these ligands behave as trianionic ligands. They only differ by the presence (L^2H_3) or the absence (LH_3) of a methoxy substituent in the vicinity of the coordination site. But their complexation by Cu^{II} ions gives

very different complexes. The structural determination of the Cu^{II} complex resulting from the L^2H_3 ligand possessing a methoxy group on a phenyl ring (complex **2**) shows that we are dealing with well isolated $[L^2Cu]pipH$ units, with the Cu^{II} ions in a slightly distorted square planar environment. Complexation of LH_3 yields a 1D chain made of anionic $[LCu]$ metal–ligand entities linked by apical coordination of the oxygen atom of the amide function, located out of the N_2O_2 site, to the Cu^{II} ion of the neighboring entity. This supplementary coordination induces a deformation of the square-based pyramidal environment of the Cu^{II} ion. As expected the $[(S)-LCu]pipH$ complex **3** crystallizes as an infinite 1D chain in a non centrosymmetric $P2_1$ space group. A slight ferromagnetic $Cu-Cu$ interaction through the amido function is evidenced by the magnetic study. Such a ferromagnetic interaction is also observed in the racemic complex $[LCu]pipH$ **1**, which means that the chain arrangement is conserved in the racemic sample. Further information [†] is given by the optical activity measurement of complex **3**, for which the α parameter (-360.7) is much larger than the one due to the chiral carbon atom. The optical activity coming from the $C^*(S)$ of the diamine is very weak (-4) for it comes from a $n - \sigma^*$ transition. Observation of this large α value confirms that a chirality transfer is active,²⁰ the optical activity coming from the intense charge-transfer band of the Cu^{II} centre. A comparison of the structural determinations of complexes **2** and **3** confirms that a larger distortion of the Cu^{II} basal N_2O_2 environment is observed in complex **3**. The large apical $Cu \cdots O4$ distance and the large solubility of **3** in methanol do agree with a distorted square planar environment of the Cu^{II} ions in solution. This large deformation is responsible for the presence of a stereogenic Cu^{II} centre.

Addition of $Ln(hfa)_3 \cdot 2H_2O$ to the racemic or pure S -enantiomer $[LCu]$ anionic metal–ligand units furnishes neutral $[LCuLn(hfa)_2]$ complexes in which the Ln^{III} ions are linked to the two phenoxo oxygen atoms of the main ligand. Furthermore the oxygen atom of the amido function enters into coordination with the Ln^{III} ion of a neighboring complex to yield a final tetranuclear complex made of two $[LCuLn(hfa)_2]$ units arranged in a head to tail fashion. As the addition is realized in dmf solvent the Cu^{II} and Ln^{III} ions complete their environments by picking dmf molecules, the final product corresponding to the $[LCu(dmf)Ln(hfa)_2(dmf)]_2$ formulation. With use of the starting racemic $[LCu]$ metal–ligand, the tetranuclear complex **7** crystallizes in a monoclinic centrosymmetric $P2/c$ group. A metal–ligand possessing the $C^*(S)$ carbon atom along with a λ *gauche* conformation of the diamine chain is associated to a metal–ligand possessing the $C^*(R)$ carbon atom and a δ *gauche* conformation of the diamine chain, so that the resulting molecule is a true racemate, a meso compound devoid of any optical activity. This arrangement resulting from the presence of a symmetry centre induces an axial position for the methyl groups linked to the asymmetric carbon atoms. A very similar observation can be made for the tetranuclear complex derived from the pure (S) - LCu enantiomer. Such an arrangement necessitates a conformation change of the diamino chain for one (S) - $[LCu-Gd]$

unit, which preserves the symmetry relation for the entire set of atoms, except for the methyl group linked to the asymmetric carbon atom. In the complex **5**, the optical activity is limited to the C^* atoms and of course very weak, the one coming from the Cu^{II} centres being suppressed by symmetry, as in the meso tetranuclear compound **7**. Furthermore, the results reported above clearly demonstrate that the introduction of a chiral carbon atom in the diamino chain of the main ligand yielding (S) -[LCu(dmf)Ln(hfa)₂(dmf)] units is not sufficient to avoid formation of tetranuclear complexes resulting from a head to tail arrangement of two (S) -[LCu-Ln] units. Isolation of an infinite 1D chain made of [LCu-Ln] units in an alternate arrangement of the Cu and Ln ions would only be possible in absence of a conformation change in the diamino chain of the main chiral ligand. This could be realized if we were able to build an infinite [LCu-Ln]_n chain keeping the reported 1D structure of the starting (S) -LCu material. In such a case the stereogenic Cu^{II} centres would be preserved. Till now a few examples of achiral tetranuclear complexes and chiral chains involving Cu-Ln,^{3a} Ni-Fe²⁴ compounds or achiral dinuclear Dy-Dy and chiral [Dy]_n chains²⁵ have been reported in literature. In these examples chirality is introduced by the main or helicene ligands but the metal ions are not stereogenic centres.

We have previously shown that tetranuclear [Cu-Dy]₂ complexes prepared with similar ligands behave as SMMs and that the rate of ground-state quantum tunnelling of magnetization can be modulated by the presence of auxiliary or solvent molecule ligands. The complexation of a dmf molecule in the apical position of the square pyramidal copper coordination sphere increases the Cu...Cu intermolecular distances between the [LCu-Dy]₂ tetranuclear units,^{2e} thus reducing the intermolecular magnetic dipolar interactions and also impeding any magnetic exchange interaction between the copper centres of neighbouring units. So larger hysteresis loops are observed, as a consequence of a much slower relaxation. In order to compare our two $(R-S)$ and $(S-S)$ -[LCu(dmf)-Dy(hfa)₂(dmf)]₂ tetranuclear units (respectively complexes **8** and **6**) a study of their magnetization dynamics down to 0.04 K was performed on single micro-crystals with use of a micro-SQUID apparatus.²¹ As expected a slow relaxation of magnetization is observed in both samples (Fig. 8 and S9[†]), which is evidenced by hysteresis loops whose coercivity is temperature and sweep-rate dependent, increasing with decreasing temperature and increasing field sweep rate, as expected for the superparamagnetic-like behaviour of a SMM. Although the Cu...Cu intermolecular distances between the [LCu(dmf)-Dy(hfa)₂(dmf)]₂ tetranuclear units increase in going from the racemate **8** to the $(S-S)$ enantiomer **6** complexes, the observed hysteresis loops are slightly larger for the racemate sample. This result evidences the main role played by the dmf coordinated to the Cu ions, thus avoiding any magnetic exchange interaction between the copper centres of neighbouring units in each sample. So the change in the hysteresis loops must be an intrinsic property of the tetranuclear complexes, the molecule $((R-S)$ -[LCu(dmf)-Dy(hfa)₂(dmf)]₂) **8** with the higher symmetry presenting slightly larger hysteresis loops than the $(S-S)$ -[LCu

(dmf)-Dy(hfa)₂(dmf)]₂ **6** complex. This difference, along with the change of the crystallization space group, does confirm that racemization does not occur in complex **6**.

Conclusion

This work demonstrates that the introduction of a chiral carbon atom in the diamino chain of the non symmetric ligand L coordinated to a Cu^{II} metal ion induces a chirality transfer to the Cu^{II} metal ion, so that two centres of optical activity, the asymmetric carbon atom and the copper ion, are present in each (S) -[LCu] synthon of the resulting infinite 1D-chain. Unfortunately the complexation of Ln ions to this starting synthon destroys the chain arrangement to yield again a final $(S-S)$ -[LCu-Ln]₂ tetranuclear complex. The loss of the chain arrangement for a head to tail arrangement of the dinuclear (S) -[LCu-Ln] entities is made possible by the conformation change of the Cu^{II} coordination sphere belonging to one of these (S) -[LCu-Ln] entities. So the two (S) -[LCu-Ln] entities involved in the tetranuclear complex are related by a symmetry centre, except for the two methyl groups linked to the asymmetric carbon atom, which appear disordered as they are not symmetry-related. Such an arrangement is responsible for the observation of a centrosymmetric space group in the structural determination. It results in a loss of the optical activity coming from the Cu^{II} metal ions, which becomes reduced to the two asymmetric carbon atoms. It is clear that introduction of a dmf molecule into the Cu^{II} coordination sphere has a positive effect on the SMM properties of the [LCu(dmf)Dy(hfa)₂(dmf)]₂ units. The large separation of the neighbouring units impedes any magnetic exchange interaction between the copper centres and allows appearance of hysteresis loops. Although the $(S-S)$ -[LCu(dmf)-Ln(hfa)₂(dmf)]₂ complexes **4–6** do not crystallize in a non-centrosymmetric space group, the differences observed in the structural determinations and the hysteresis loops of the racemic $(R-S)$ -[LCu(dmf)-Dy(hfa)₂(dmf)]₂ and the $(S-S)$ -[LCu(dmf)-Dy(hfa)₂(dmf)]₂ tetranuclear complexes confirm that we are dealing with two different tetranuclear units. Eventually, it becomes evident that the preparation of an infinite 1D chain made of [LCu-Ln] units possessing a chiral ligand and a chiral Cu^{II} metal ion will be successful only if we are able to avoid the conformation change observed in the $(S-S)$ -[LCu(dmf)-Ln(hfa)₂(dmf)]₂ complex characterized in this work. In other words, the only way to keep active the chirality transfer to the Cu^{II} ions implies that the 1D infinite chain arrangement observed for the starting (S) -[LCu] synthons must be conserved after complexation of Ln^{III} ions to these synthons. This could be a way toward the preparation of chiral 3d–4f single-chain magnets As with stereogenic Cu centres.

Conflicts of interest

There are no conflicts to declare.

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