

Structural studies of a dinuclear (Cu, Gd) and two trinuclear (Cu₂, Ln) complexes (Ln = Ce, Er). Magnetic properties of two original (Cu, Gd) complexes†

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With the aim of increasing the number of structurally characterized dimetallic (Cu^{II}, Ln^{III}) complexes, we have obtained a strictly dinuclear (Cu^{II}, Gd^{III}) complex **1** in which, according to structural data, the two metal ions are triply bridged. Then, we have investigated the capability of Cusalen precursors for complexing lanthanide ions. Structural and magnetochemical studies show that dinuclear entities with a CuO₂Ln bridging network can only be isolated with the heavier lanthanide ions such as gadolinium or erbium (complexes **2**, **3** and **4**) while trinuclear (CuO₂LnO₂Cu) complexes are obtained in the case of lighter Ln^{III} ions, such as cerium (complex **5**) for example. Ferromagnetic interactions with *J* values of 4.2 and 3.5 cm⁻¹ characterize complexes **1** and **2**, respectively.

In recent papers,^{1,2} we described the structures and magnetic properties of discrete (Cu, Gd) complexes. We also developed a general route allowing the nature of the 3d and 4f ions to be varied^{3,4} without destroying the strictly dinuclear nature of the resulting complexes. This route relies on stepwise complexation of a compartmental ligand with a 3d ion and then a 4f ion to afford the desired heterodinuclear complex. The lanthanide complexation site is made of neutral or deprotonated oxygen atoms so that the electroneutrality of the resulting complexes necessitates the presence of anions around the 4f centres. As nitrate anions completed the coordination number of the 4f centres in the entire set of our previous examples, we have tried to replace them by other types of anionic ligands such as the deprotonated form of tetramethylheptanedione (abbreviated thd in the following). Furthermore, we have tried to use mononuclear precursors devoid of any free complexation site, following the 'complexes as ligands' synthesis method, to check if it is also possible to obtain other types of heterodinuclear complexes⁵ (Fig. 1).

Results

In this work, our goal was to prepare new strictly dinuclear (Cu^{II}, Ln^{III}) entities with a CuO₂Gd bridging core and different values of the dihedral angle between the O—Cu—O and O—Ln—O planes. In a first attempt, starting with the heterodinuclear Cu—Gd complexes previously synthesized, we tried to replace the nitrate ions around the Gd centres by the more voluminous thd anions. Complex **1** has been isolated following two different experimental procedures. In the first approach, mixing the monometallic copper precursor L¹Cu·2H₂O and Gd₂(thd)₆ in methanol yields **1**. This complex is also obtained in better yield by mixing L¹Cu·2H₂O with a methanolic solution of Hthd and the equivalent amount of CsOH·H₂O and then adding gadolinium chloride. The second method uses L²Cu derivatives [L²

stands for *N,N'*-ethylenebis(salicylideneiminato)] as ligands to isolate other heterodinuclear Cu—Gd complexes, as in **2**. Unfortunately, this approach does not seem as efficient as the synthesis using compartmental ligands.

For the five complexes, the most intense mass spectral signals correspond to the [L¹CuGd(thd)₂]⁺ or [L²CuLn(NO₃)₂]⁺ ions, as expected. They appear at *m/z* = 955 (100%) for **1**, 639 (100) for **2**, 649 (29) for **3** and **4** and 621 (100) for **5**. In the case of **1** a second signal is observed at *m/z* = 772. It corresponds to the loss of a second thd unit, suggesting a change of the oxidation state or the formation of a radical cation [L¹CuGd(thd)]⁺. For complexes **2–5**, the results are more striking for we also observe a second signal at, respectively, 998 (12%), 1008 (3), 1008 (3) and 980 (16), which may be attributed to the [(L²Cu)₂Ln(NO₃)₂]⁺ ions. Finally, these data confirm the existence of a heterodinuclear complex for **1** but they do not give any firm information about the nuclearity of complexes **2–5**. On the contrary, microanalytical data, and particularly the copper content, support the view that **2** and **3** may be considered as dinuclear complexes and **4** and **5** as trinuclear complexes.

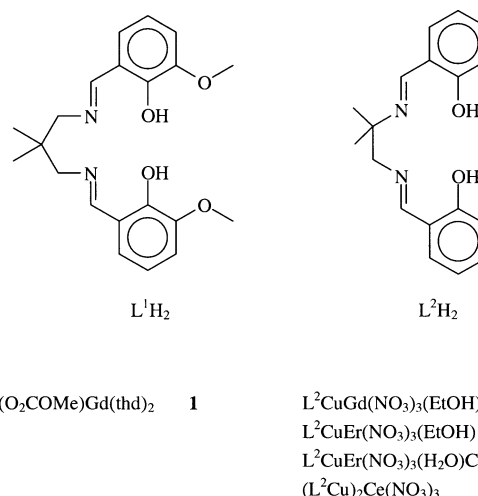


Fig. 1 Schematic representation of the L¹H₂ and L²H₂ ligands and numbering of the different complexes

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‡ Taken from the Ph.D. Dissertation of A. Dupuis, Université Paul Sabatier, Toulouse, France, 1998 (n° 3004).

Description of the structures of 1, 4 and 5

Complex 1. In $[\text{L}^1\text{Cu}(\text{O}_2\text{COMe})\text{Gd}(\text{thd})_2]$ (Fig. 2) the central region is occupied by Cu^{II} and Gd^{III} ions that are triply bridged one to the other by two phenolato oxygen atoms from the ligand L^1 and the oxygen atoms from the monomethyl carbonate anion. The copper gadolinium separation is 3.4727(4) Å. The copper ion adopts a square-based 4 + 1 coordination mode; the equatorial N_2O_2 donors are provided by L^1 while the axial position is occupied by a CO_2 group from the monomethyl carbonate anion. The copper centre is displaced from the mean equatorial N_2O_2 coordination plane by 0.2185(4) Å. The gadolinium ion is nona-coordinated. In addition to the two phenolate oxygens, the rare earth ion completes its environment with two oxygen atoms from the OMe side arms, four oxygens coming from the two bidentate tetramethylheptanedionato units and one oxygen from the monomethyl carbonate anion. The two longest Gd—O bonds involve the OMe side arms [2.639(3) and 2.650(3) Å]; the other Gd—O bonds vary from 2.343(3) to 2.434(2) Å (Table 1). The separations between metal ions belonging to neighbouring molecules are large: the $\text{Cu}\cdots\text{Cu}$ separation is equal to 6.6550(9) Å while values of 10.1799(3) and 8.4128(5) Å are respectively observed for $\text{Gd}\cdots\text{Gd}$ and for $\text{Cu}\cdots\text{Gd}$. They preclude any significant intermolecular interaction of a magnetic nature. The four atoms of the bridging entity are not exactly coplanar, leading to a roof-shaped CuO_2Gd core. The dihedral angle between the planes $\text{O}(1)\text{—Cu—O}(2)$ and $\text{O}(1)\text{—Gd—O}(2)$ is equal to 19.1(2) Å.

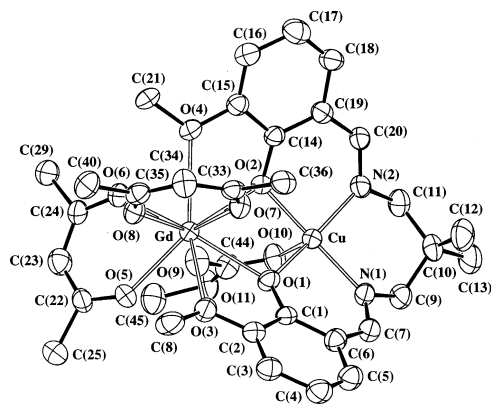


Fig. 2 Molecular plot for $[\text{L}^1\text{Cu}(\text{O}_2\text{COMe})\text{Gd}(\text{thd})_2]$ **1** with ellipsoids drawn at the 40% probability level (methyl substituents of Bu^t groups are omitted for clarity)

Complex 4. The structure of $[\text{L}^2\text{CuEr}(\text{NO}_3)_3(\text{H}_2\text{O})\text{L}^2\text{Cu}]$ is represented in Fig. 3. This structure is unexpected although consistent with the microanalysis data. It comprises a dinuclear (Cu, Er) complex and a mononuclear (Cu) entity. The two fragments are linked *via* a water molecule bonded to Er^{3+} and hydrogen-bonded to the phenoxo oxygen atoms of the mononuclear complex.

The central part of the dinuclear entity is occupied by the expected CuO_2Er bridging core. With a dihedral angle of 30.6(1) between the $\text{O}(1)\text{—Cu—O}(2)$ and $\text{O}(1)\text{—Er—O}(2)$ planes, it is more twisted than in the previous cases. The $\text{Cu}(1)\cdots\text{Er}$ separation [3.2082(5) Å] is rather short but the $\text{Cu}(2)\cdots\text{Er}$ separation [5.9082(5) Å] is longer. The separations between metal ions belonging to neighbouring molecules are again large [$\text{Er}\cdots\text{Cu}(1) = 7.1582(4)$ and $\text{Er}\cdots\text{Cu}(2) = 7.5539(5)$ Å, $\text{Cu}(1)\cdots\text{Cu}(1) = 5.9397(7)$ and $\text{Cu}(2)\cdots\text{Cu}(2) = 5.832(1)$ Å]. Erbium is nona-coordinated to only two oxygen phenolato atoms of the L^2 ligand and to six oxygen atoms of the three coordinated nitrate anions, the ninth position being occupied by a water molecule. The two copper atoms are fourfold coordinated to the equatorial L^2 ligand, without any solvent molecule in an axial position. The copper environment can be considered as square planar, with the copper atoms being situated not far from the mean N_2O_2 coordination plane [0.0591(5) Å for $\text{Cu}(1)$ and 0.0250(5) Å for $\text{Cu}(2)$]. Finally, **4** is made up of two quasi-independent entities, dinuclear (Cu,Gd) and mononuclear (Cu) fragments and cannot be considered as a genuine trinuclear compound. Selected bond distances and angles appear in Table 1.

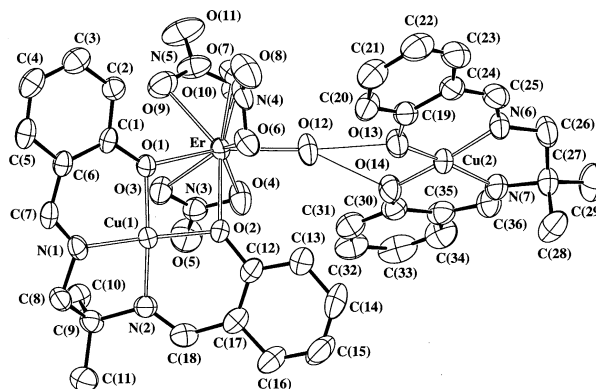


Fig. 3 Molecular plot for $[\text{L}^2\text{CuEr}(\text{NO}_3)_3(\text{H}_2\text{O})\text{L}^2\text{Cu}]$ **4** with ellipsoids drawn at the 50% probability level

Table 1 Selected bond lengths (Å) and angles (deg) for $[\text{L}^1\text{Cu}(\text{O}_2\text{COMe})\text{Gd}(\text{thd})_2]$ **1**, $[\text{L}^2\text{CuEr}(\text{NO}_3)_3(\text{H}_2\text{O})\text{L}^2\text{Cu}]$ **4** and $[(\text{L}^2\text{Cu})_2\text{Ce}(\text{NO}_3)_3]$ **5**

	1	4	5
Cu—O(1)	1.973(3)	1.932(2)	1.901(3)
Cu—O(2)	1.965(3)	1.919(2)	1.921(3)
Cu—O(10)	2.157(3)	—	—
Cu—N(1)	1.976(3)	1.920(3)	1.923(3)
Cu—N(2)	2.002(3)	1.924(3)	1.908(4)
Ln—O(1)	2.420(3)	2.360(2)	2.552(3)
Ln—O(2)	2.434(2)	2.315(2)	2.557(3)
Ln—O(OMe)	2.639(3)–2.650(3)	—	—
Ln—O(thd)	2.343(3)–2.361(3)	—	—
Ln—O(9)(carbonato)	2.396(3)	—	—
Ln—O(nitrato) ^a	—	2.397(3)–2.447(3)	2.536(3)–2.629(3)
Ln—O(12)(water)	—	2.313(3)	—
Ln—O(1)—Cu	103.98(10)	96.24(10)	98.62(11)
Ln—O(2)—Cu	103.77(10)	98.10(10)	97.92(10)
O(1)—Cu—O(2)	83.04(10)	86.94(10)	85.88(11)
O(1)—Ln—O(2)	65.07(8)	69.06(9)	61.29(9)
<i>a</i> ^b	19.1(2)	30.6(1)	141.21(8)

^a Minimum and maximum values. ^b Dihedral angle between the $\text{O}(1)\text{—Cu—O}(2)$ and $\text{O}(1)\text{—Ln—O}(2)$ planes.

Complex 5. The structural determination of $[(L^2Cu)_2Ce(NO_3)_3]$ (Fig. 4 and Table 1) confirms the existence of a 'true' trinuclear species. Indeed, the cerium centre is surrounded by two L^2Cu entities and three nitrate anions. It is linked to ten oxygen atoms, four coming from the phenolato atoms and six from the NO_3 anions. The copper environment can be considered as square planar for it is situated in the mean N_2O_2 coordination plane. The presence of an oxygen atom of a nitrate anion at 2.688(4) Å is surely responsible for the absence of any solvent molecule in an axial position. The $Cu \cdots Ce$ and $Cu' \cdots Ce$ separations are equal to 3.4031(5) Å. The separations between metal ions belonging to neighbouring molecules are again large [$Ce \cdots Cu = 6.9602(4)$ and $Ce \cdots Ce = 10.1253(2)$ Å] except for the $Cu \cdots Cu$ separations, which are shorter [4.1867(8) Å].

Magnetic properties of 1 and 2

Owing to the difficulties in analysing the magnetic properties of (Cu, Ln) pairs involving a Ln^{3+} ion, which possesses a first-order orbital moment,⁶ we restricted ourselves to consider only the (Cu, Gd) complexes **1** and **2**. The temperature dependence of the magnetic susceptibility of complex **2** in the range 2–200 K is shown in Fig. 5 in the form of $\chi_M T$ vs. T . At 180 K, $\chi_M T$ is equal to 8.4 cm³ K mol⁻¹, which roughly corresponds to the value expected for the two uncoupled metal ions. Lowering the temperature causes $\chi_M T$ to increase to 10.1 cm³ K mol⁻¹ at 2 K. This value compares well with that (10.0 cm³ K mol⁻¹) expected for the $S = 4$ spin state resulting from ferromagnetic coupling between Gd^{III} ($S = 7/2$) and Cu^{II} ($S = 1/2$) and assuming that $g_{Gd} = g_{Cu} = 2.0$. Very similar data have been obtained for **1**.

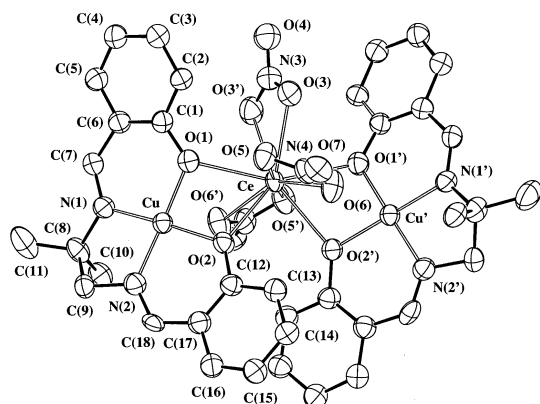


Fig. 4 Molecular plot for $[(L^2Cu)_2Ce(NO_3)_3]$ **5** with ellipsoids drawn at the 40% probability level

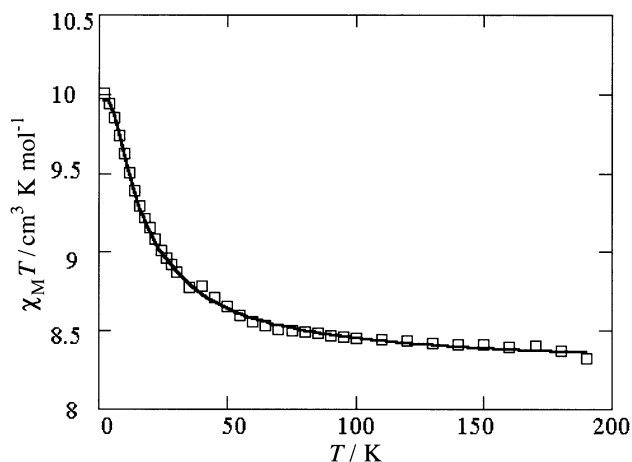


Fig. 5 Thermal dependence of $\chi_M T$ for $[L^2CuGd(NO_3)_3(EtOH)]$ **2** at 0.1 T. The full line corresponds to the best data fit

A quantitative analysis can be performed on the basis of a spin-only expression derived from a spin Hamiltonian $H = -JS_{Cu}S_{Gd}$. Taking into consideration that the two low-lying levels $E(4) = 0$ and $E(3) = 4J$ may have different g values,⁷ [$g_4 = (7g_{Gd} + g_{Cu})/8$ and $g_3 = (9g_{Gd} - g_{Cu})/8$], the experimental data are fitted using the expression:

$$\chi_M T = \frac{4N\beta^2}{k} \cdot \left[\frac{15g_4^2 + 7g_3^2 \cdot e^{-4J/kT}}{9 + 7 \cdot e^{-4J/kT}} \right]$$

The resulting values of the parameters are $J = 4.2$ cm⁻¹, $g_{Cu} = 2.05$, $g_{Gd} = 2.0$ and $R = [(\chi_{obs} T - \chi_{cal} T)^2 / (\chi_{obs} T)^2] = 3.7 \times 10^{-5}$ for **1** and $J = 3.5$ cm⁻¹, $g_{Cu} = 2.05$, $g_{Gd} = 2.0$ and $R = 1 \times 10^{-5}$ for **2**. For the two complexes, there is no doubt that the observed ferromagnetic behaviour is an intrinsic property of the CuO_2Gd core. The J values are slightly lower than those previously published^{1,2} for four structurally characterized heterodinuclear (Cu, Gd) complexes. The structural study of **1** shows that a third bridge joins an axial site of Gd to an axial site of Cu which has, at best, a very feeble spin density. This is the reason why this bridge has no effect on the magnetic properties of **1**. The observed J value (4.2 cm⁻¹) is quite similar to those found^{1,2} for complexes in which the magnetic interaction is mediated by a double CuO_2Gd bridge, as in previous examples.^{1,2} Furthermore, the very nice fit obtained for **2** (Fig. 5) with the help of the above expression corresponding to a dinuclear Cu–Gd complex confirms the dinuclear character of the powdered sample **2**.

Discussion and Conclusions

It has been previously demonstrated⁸ that bases favour the formation of monomethyl carbonate. In fact, the yield of **1** is increased in the second preparation method, which is performed in presence of CsOH. As we work in an open flask, CO_2 is taken up spontaneously from air at room temperature, under very mild conditions. The literature furnishes examples of monomethyl carbonate ions bridging two identical metal atoms, such as Cu,⁸ Zn⁹ and W,¹⁰ or coordinated to a metal centre (Zn,⁹ and W¹¹, Mo,¹² Mn,¹³ Ni⁸) as a unidentate ligand. The two C–O bond lengths involving the two bridging oxygen atoms in **1** are equal [1.245(5) Å] and quite similar to the values previously published, as is the other C–O bond not involved in metal coordination. The Cu–O(10) bond length [2.157(3) Å] is comparable to the Zn–O [2.143(3) Å]⁹ and shorter than the Cu–O [2.352(5) Å]⁸ bond lengths of bridging μ -monomethyl carbonate ligands, while Gd–O(9) equals 2.396(3) Å. In our opinion, **1** is the first example of a monomethyl carbonate ligand bridging two different metal centres.

In a previous paper, we studied the $[L^1CuGd(NO_3)_3]$ complex derived from the same mononuclear precursor. The main difference between this complex and **1** comes from the replacement of nitrate anions by two thd ligands and a deprotonated monomethyl carbonate. As we reacted the copper complex with $Gd_2(thd)_6$, we can remark that one thd ligand has disappeared. It has been replaced by the deprotonated monomethyl carbonate synthesized during the reaction. This ligand makes a supplementary bridge between the Cu and Gd centres. Depending on its coordination mode, the Gd coordination number decreases from 10 to 9. Conversely, the Gd–O (thd) bonds are shorter than the Gd–O (nitrate) bonds. If the Cu centre is always fivefold coordinate, the axial Cu–O bond length is shorter [2.157(3) Å instead of 2.522(3) Å], inducing a displacement of the Cu centre from the mean equatorial N_2O_2 coordination plane by 0.2185(4) Å. In spite of these changes, there is only a slight increase of the dihedral angle between the O(1)–Gd–O(2) and O(1)–Cu–O(2) planes {19.1(2)° for **1** instead of 16.6(2)° for $[L^1CuGd(NO_3)_3]$ }.

The other way to make (3d, 4f) complexes is to start with salen-type copper precursors (L^2Cu), which do not possess a

second vacant coordination site. Until recently, structural determinations of 3d–4f complexes deriving from salen-type Schiff base ligands pointed out their tri- or tetranuclearity,^{14–17} although analytical data suggest the occurrence of dinuclear complexes in some instances.¹⁶ Recently,¹⁸ it was reported that a dimetallic complex derived from Cusalen and $[\text{Gd}(\text{hfa})_3 \cdot 2\text{H}_2\text{O}]$ (hfa = hexafluoroacetylacetonato) actually is a tetranuclear entity, which can be converted to a dinuclear complex by addition of imidazole. In order to prevent such a dimerization through the Cusalen part of our complexes, we added a dimethyl substituent on the diamine arm of the L^2 ligand. With the help of the copper precursors L^2Cu resulting from the reaction of salicylaldehyde and 1,2-diamino-2-methylpropane, we succeeded, at least in part, in synthesizing and crystallizing such compounds. In the presence of EtOH solutions of Ln salts, these precursors give powders that correspond to $[\text{L}^2\text{CuLn}(\text{NO}_3)_3]$ for Ln = Gd, Er, Yb. Crystallization of the Cu–Er powder in acetone furnished crystals with different microanalytical results. This was confirmed by a structural determination, as shown in Fig. 3. Indeed, we are in the presence of a dinuclear Cu–Er pair, but the erbium-coordinated water is involved in hydrogen bonds with the phenolic oxygen atoms of a L^2Cu entity. This is confirmed by the presence of a short $\text{Cu}(1) \cdots \text{Er}$ separation [3.2082(5) Å] and a longer $\text{Cu}(2) \cdots \text{Er}$ separation [5.9082(5) Å]. In compound 4, we find a non-planar CuO_2Er core. The separations between metal ions belonging to neighbouring molecules are again large (greater than 5.8 Å).

It is well-known that crystal structures of the rare earth complexes change along the lanthanide series.¹⁹ With lanthanides having the largest ionic radii, the previous reaction yielded products that analysed as trinuclear complexes, as shown in the literature and confirmed by the structural determination of the (Cu, Ce) complex (Fig. 4). In this example, the cerium is wrapped up by two L^2Cu entities and three NO_3 anions.

Interestingly the variation of J still parallels that of the dihedral angle α between the two halves (OCuO and OGdO) of the bridging core. From previous work,^{1,2} it appears that the highest exchange parameters ($J = 7 \text{ cm}^{-1}$) correspond to α angles of 12.5(2)–12.9(2)°. Increasing the α angle to 16.6(2)° and ca. 40°¹⁸ causes J to decrease to 4.8 and 1.4 cm^{-1} , respectively. In the present work, a 4.2 cm^{-1} J value is associated with a 19.1(2)° α angle and the 3.5 cm^{-1} J value with an α angle of ca. 30°, if we suppose that $[\text{L}^2\text{CuEr}(\text{NO}_3)_3]$ and $[\text{L}^2\text{CuGd}(\text{NO}_3)_3]$ are isostructural. Furthermore, a more important bending of the CuO_2Gd core¹⁸ results in a more depressed J value (1.42 cm^{-1}).

In conclusion, the main interest of this paper is the description of supplementary simple synthetic pathways to strictly dinuclear Cu–Gd complexes. One process makes use of compartmental ligands as in our previous work.^{1,2} The resulting complex differs from the preceding ones by replacement of the three nitrate anions coordinated to the Ln centre by two thd and an unexpected monomethyl carbonate ligand. The other process concerns ‘metal complexes used as ligands’. If it is not a new process in itself, for it has been previously used to give heterotrinuclear (Cu_2 , Ln) complexes, we demonstrate with the help of a structural determination and of a magnetic study that it can also yield strict heterodinuclear (Cu, Gd) complexes. Unfortunately, this process seemingly works with the heavier lanthanides (from Gd to Lu) but not with those having larger ionic radii, such as lanthanum or cerium.

Experimental

All starting materials were purchased from Aldrich and were used without further purification. Elemental analyses (C, H, N) were carried out by the Service de Microanalyse du Labor-

atoire de Chimie de Coordination, Toulouse. Fourier transform infrared spectroscopy on KBr pellets was performed on a Perkin Elmer 1725 X FT-IR instrument. Mass spectra (FAB^+) were recorded in DMF or DMSO as solvents and 3-nitrobenzyl alcohol matrix with a Nermag R10-10 spectrometer. Magnetic susceptibility data were collected on powdered samples of the different compounds with use of a SQUID-based sample magnetometer on a Quantum Design model MPMS instrument. All data were corrected for diamagnetism of the ligands estimated from Pascal's constants.²⁰

Synthesis of the ligands and complexes

The mononuclear precursors $\text{L}^1\text{Cu} \cdot 2\text{H}_2\text{O}$,²¹ L^2Cu ²¹ and $\text{Gd}_2(\text{thd})_6$ ²² were obtained according to published procedures.

$[\text{L}^1\text{Cu}(\text{O}_2\text{COMe})\text{Gd}(\text{thd})_2]$ 1. $\text{L}^1\text{Cu} \cdot 2\text{H}_2\text{O}$ (0.2 g, 0.43 mmol) and $\text{Gd}_2(\text{thd})_6$ (0.3 g, 0.43 mmol) in methanol (15 mL) were mixed together and set aside until crystals appeared. They were filtered off, washed with acetone and diethyl ether. Yield: 0.1 g, 23%. Anal. calcd for $\text{C}_{45}\text{H}_{65}\text{CuGdN}_2\text{O}_{11}$: C, 52.5; H, 6.3; N, 2.7. Found: C, 52.4; H, 6.1; N, 2.6. This product was also prepared in better yield with the following experimental procedure. $\text{CsOH} \cdot \text{H}_2\text{O}$ (0.5 g, 3 mmol) and tetramethylheptanedione (Hthd) (0.55 g, 3 mmol) were mixed and stirred in methanol (15 mL). Then $\text{L}^1\text{Cu} \cdot 2\text{H}_2\text{O}$ (0.47 g, 1 mmol) and $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ (0.37 g, 1 mmol) were added and stirred at ambient temperature for 30 min. The solution was set aside and crystals appeared several hours later. They were isolated by filtration and gave identical analytical results. Yield: 0.6 g, 60%.

$[\text{L}^2\text{CuGd}(\text{NO}_3)_3 \cdot \text{EtOH}]$ 2. Complexes 2, 3 and 5 were prepared using the same experimental procedure, which will be described only for 2. L^2Cu (0.3 g, 0.84 mmol) and $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.38 g, 0.84 mmol) were mixed in EtOH (20 mL) until a precipitate appeared. It was filtered, washed with a small amount of ethanol and diethyl ether, then dried. Yield: 0.5 g, 78%. Anal. calcd for $\text{C}_{18}\text{H}_{18}\text{CuGdN}_5\text{O}_{11} \cdot \text{EtOH}$: C, 32.1; H, 3.2; Cu, 8.5; N, 9.4. Found: C, 32.0; H, 3.2; Cu, 8.4; N, 9.2.

$[\text{L}^2\text{CuEr}(\text{NO}_3)_3 \cdot \text{EtOH}]$ 3. Yield: 75%. Anal. calcd for $\text{C}_{18}\text{H}_{18}\text{CuErN}_5\text{O}_{11} \cdot \text{EtOH}$: C, 31.7; H, 3.2; Cu, 8.4; N, 9.2. Found: C, 31.8; H, 3.0; Cu, 8.5; N, 9.2. Crystals of 4 were obtained by slow evaporation of an acetone solution of L^2Cu and $\text{Er}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. They gave a quite different analytical result. Anal. calcd for $\text{C}_{36}\text{H}_{38}\text{Cu}_2\text{ErN}_7\text{O}_{14}$: C, 39.8; H, 3.5; Cu, 11.7; N, 9.0. Found: C, 39.5; H, 3.4; Cu, 11.5; N, 9.1.

$[(\text{L}^2\text{Cu})_2\text{Ce}(\text{NO}_3)_3]$ 5. Yield: 70%. Anal. calcd for $\text{C}_{36}\text{H}_{36}\text{CeCu}_2\text{N}_7\text{O}_{13}$: C, 41.5; H, 3.5; Cu, 12.2; N, 9.4. Found: C, 41.6; H, 3.3; Cu, 12.0; N, 9.5. Crystals were obtained by slow evaporation of a methanolic solution of L^2Cu and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$.

Crystal structure determinations of 1, 4 and 5

Crystal data for all structures are presented in Table 2. For complexes 1 and 5, data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromatized $\text{MoK}\alpha$ ($\lambda = 0.71073 \text{ Å}$) radiation using $\omega - 2\theta$ scans. Data reduction²³ was performed and absorption corrections²⁴ from Ψ scans were applied. For complex 4 data were collected on a STOE-IPDS diffractometer with graphite-monochromatized $\text{MoK}\alpha$ radiation using ϕ rotation movement mode. Data reduction was performed²⁵ and numerical absorption corrections²⁶ were applied.

All structures were solved using a Patterson procedure with the SHELXS-97²⁷ program and refined against F_o^2 (SHELXL-97).²⁸ All non-hydrogen atoms were refined anisotropically.

Table 2 Crystallographic data for [L¹Cu(O₂COMe)Gd(thd)₂] **1**, [L²CuEr(NO₃)₃(H₂O)L²Cu] **4** and [(L²Cu)₂Ce(NO₃)₃] **5**

	1	4	5
Formula	C ₄₅ H ₆₅ CuGdN ₂ O ₁₁	C ₃₆ H ₃₈ Cu ₂ ErN ₇ O ₁₄	C ₃₆ H ₃₆ CeCu ₂ N ₇ O ₁₃
FW	1030.78	1087.09	1041.92
Crystal habit	Green block	Dark red plate	Red plate
Crystal dimensions/mm	0.45 × 0.40 × 0.30	0.50 × 0.20 × 0.10	0.40 × 0.25 × 0.10
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> $\bar{1}$ (No. 2)	<i>C</i> 2/ <i>c</i> (No. 15)
<i>a</i> /Å	13.4151(18)	13.183(3)	13.5350(13)
<i>b</i> /Å	14.810(2)	16.509(3)	17.113(3)
<i>c</i> /Å	12.4155(14)	9.5773(18)	17.216(3)
α /°	95.318(15)	94.451(17)	
β /°	95.268(18)	98.843(17)	102.690(13)
γ /°	92.10(2)	80.008(17)	
<i>U</i> /Å ³	2443.2(6)	2025.5(7)	3890.2(11)
<i>Z</i>	2	2	4
<i>F</i> (000)	1060	1082	2084
λ /Å	0.71073	0.71073	0.71073
<i>T</i> /K	293	293	293
<i>D</i> _{calc} /cm ⁻¹	1.401	1.782	1.779
μ (MoK α)/mm ⁻¹	1.836	3.083	2.309
<i>T</i> _{min} – <i>T</i> _{max}	0.8582–0.9994	0.4531–0.6999	0.8621–0.9995
2 θ range/°	3–54	4.4–48.4	3–50
No. of data collected	10641	16199	3565
No. of unique data	10641	5983	3419
		[<i>R</i> (int) = 0.0315]	[<i>R</i> (int) = 0.0213]
No. of variable params	541	549	268
No. of obs. refl. ^a	8703	5248	2639
<i>R</i> ^b obs. all	0.0367, 0.0472	0.0281, 0.0332	0.0359, 0.0472
<i>wR</i> ^c obs. all	0.0598, 0.0736	0.0534, 0.0587	0.0523, 0.0638
<i>w</i> ^d <i>a</i> , <i>b</i>	0.0564, 1.0405	0.0473, 0	0.0689, 0
<i>S</i>	1.069	0.983	0.978
(Δ /σ) _{max}	0.002	0.008	0.003
(Δ /ρ) _{max, min} /e Å ⁻³	0.778, –0.666	1.015, –1.236	0.421, –0.448

^a Data with $F_o > 4\sigma(F_o)$. ^b $R = \Sigma \|F_o\| - |F_c| / \Sigma |F_o|$. ^c $wR = [\Sigma w(|F_o|^2 - |F_c|^2)^2 / \Sigma w |F_o|^2]^2$. ^d $w = [\sigma(F_o^2) + (aP)^2 + bP]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$ and *a* and *b* are coefficients adjusted by the program.

Hydrogen atoms were included using a riding model with *U* equal to 1.1 times *U*_{eq} of the attachment atom, except those bonded to the water molecule O(12) in **4**, which were allowed to vary. Atomic scattering factors were taken from a standard source.²⁹

CCDC reference number 440/060.

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Received in Montpellier, France, 23rd April 1998;
Paper 8/03125H