Hydrothermal Syntheses, Crystal Structures, Magnetism and Fluorescence Quenching of Oxamidato-Bridged Pentanuclear $Cu^{II}_4Ln^{III}$ Complexes Containing Macrocyclic Ligands (Ln = Eu, Tb) and the Crystal Structure of a Hexanuclear $Ni^{II}_5Sm^{III}$ Complex

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Three novel oxamidato-bridged complexes incorporating a macrocyclic oxamide of formula $[(CuL)_3\{CuL(C_2H_5OH)\}Eu(H_2O)](ClO_4)_3\cdot 1.5H_2O$ (**1**), $[(CuL)_3\{CuL(C_2H_5OH)\}Tb(H_2O)](ClO_4)_3\cdot 2H_2O$ (**2**) and $[(NiL)_5Sm](ClO_4)_3\cdot 2H_2O$ (**3**) (CuL and NiL, H_2L = 2,3-dioxo-5,6,14,15-dibenzo-1,4,8,12-tetraazacyclopentadeca-7,13-dien), have been hydrothermally synthesized and structurally characterized. In these complexes, the central Ln^{III} and external copper (or nickel) ions are bridged by macrocyclic oxamide groups. The Eu^{III} (or Tb^{III}) ion of **1** (or **2**) resides in a distorted tricapped trigonal prismatic environment surrounded by eight oxygen atoms from four oxamide groups and one oxygen atom from a water molecule, whereas the Sm^{III} ion of **3** resides in a distorted bicapped square antiprismatic environment surrounded by ten oxygen atoms from five oxamide groups. Furthermore, there are hydrogen bonding interactions in **1** and **2** between perchlorate, ethanol and water moieties. Especially for **1** and **2**, O–H···O and weak coordination of ClO_4^- groups link the pentanuclear fragments and perchlorate ions to form a 1-D supramolecular architecture. The fluorescence of Eu^{III} and Tb^{III} are almost completely quenched in **1** and **2**. The magnetic properties of **1** and **2** have been characterized.
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Introduction

Molecular magnetism and macrocyclic compounds are two active fields of research encompassing chemistry, physics, biology, and material science.[1,2] The field of molecular-based magnetic materials has shown spectacular advances in the last two decades, especially for metal complex-based magnetic compounds.[2] Assembly of metal complexes which may act as light switchable magnets and single molecule magnets has attracted special attention in the latest decade.[3−5] The mechanisms responsible for the magnetic interactions between d ions are reasonably well understood, and efficient models have been proposed to rationalize the various types of magnetic behavior.[2,6] As far as magnetic coupling between f ions and d ions is concerned, the situation is much less advanced because the behavior of the Ln^{III} ion with a first-order orbital momentum is much more complicated. Indeed, the 4f configuration of a Ln^{III} ion is split into $^{2S+1}L_J$ states by the inter-electronic repulsion and the spin-orbit coupling. Each of these states is further split into Stark components due to the crystal field perturbation. It follows that it is in principle very difficult to determine not only the magnitude of the $Ln^{III}-Cu^{III}$ interactions but even their nature. It is therefore essential for further development of 3d-4f magnetochemistry in order to obtain accurate information on the 3d-4f magnetic interactions and a synthetic design without 3d-3d and 4f-4f magnetic interactions.[7,8] Since Gatteschi and co-workers discovered a ferromagnetic coupling between Cu^{II} and Gd^{III} ions in 1985,[9] the design and properties of molecular complexes simultaneously comprising lanthanide and transition metal ions[9−15] have been of considerable interest. However, most of the studies have been focused on the $Gd^{III}-Cu^{II}$ couple[9−15] which has been found to be directly ferromagnetic in most cases. In comparison, polynuclear complexes containing other $Ln^{III}-Cu^{II}$ couples have been poorly investigated.[12,16−18] In addition, the majority of the mixed metal complexes are bridged by polydentate Schiff bases, pyridonates, carboxylate or oxamide ligands.[12,13,19−21] In particular, the oxamide group has been noted as an efficient

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mediator of magnetic exchange between 3d-3d centers. However, heterometallic complexes of the macrocyclic oxamide, especially of those containing 3d-4f metals, have been rarely prepared,[22] although metal complexes of macrocyclic ligands have been of great interest to coordination chemists for their special structures, properties, and/or functionalities.[1][8a,23]

On the other hand, investigations of the effect of metal complexes upon the fluorescence of rare earth ions will give basic and useful information for the development of fluorescent materials, since the metal complexes reported so far are beyond enumeration and show a great variety of characteristic colors. Recently, many complexes containing rare earth ions have been prepared, and their fluorescent proprieties have been studied,[24−27] but heterometallic complexes of this kind, especially those containing 3d-4f metals have been rarely investigated.[12,27]

With these facts in mind and in continuation of our work on polynuclear macrocyclic complexes,[20−22] the macrocyclic oxamido-copper (II) and oxamido-nickel(II) complexes were used as ligands to synthesize new complexes. The result is that two novel pentanuclear $Cu^{II}_4Ln^{III}$ complexes (Ln = Eu, Tb) and one hexanuclear $Ni^{II}_5Sm^{III}$ complex have been isolated and structurally characterized, the magnetic and fluorescent properties of **1** and **2** have also been subjected to a preliminarily investigation.

Results and Discussion

Synthesis

The hydrothermal technique not only provides a pathway to stable structures utilizing inorganic molecular units of a desired geometry or composition but also allows the introduction of a variety of inorganic cations to act as templates in directing the organization of the complexes. In those reactions the Ln(III) ions were used as templating reagents. Under appropriate conditions, large single crystals were obtained in high yield.

Structures

Description of the Structure of 1

Complex **1** consists of pentanuclear $[(CuL)_3\{CuL(C_2H_5OH)\}Eu(H_2O)]^{3+}$ cations, monovalent ClO_4^- anions, and water. A perspective view of the pentanuclear cation is depicted in Figure 1, and selected bond lengths and angles are listed in Table 1. The central europium and external copper ions are bridged by macrocyclic oxamide groups. The external Cu1 ion is coordinated by four nitrogen atoms from the macrocyclic organic ligand, with the $[Cu1N_4]$ chromophore exhibiting near planarity. The Cu1 ion is displaced from the least-square plane by +0.1130Å. The coordination environment of Cu2 is similar to that of Cu1. Cu3 is located in a slightly distorted square-based pyramidal environment with the basal plane composed of atoms N9, N10, N11 and N12 from the macrocyclic oxamide groups, the axial position is occupied by an ethanol molecule. The deviations of the four donor atoms (N9, N10, N11 and N12) from their mean plane are −0.1756, +0.1023, −0.1645 and +0.1607 Å, respectively, and Cu3 is located +0.1521Å out of the plane. Cu4 is also located in a slightly distorted square pyramidal environment with the basal plane composed of atoms N13, N14, N15 and N16 from the macrocyclic oxamide groups, the axial position is occupied by perchlorate weakly coordinated with Cu4, and the Cu4···O14 distance is 2.460 Å. The central europium atom resides in a distorted tricapped trigonal prismatic environment surrounded by eight oxygen atoms from four oxamide groups and the O1w atom of the water molecule. The O1w, O3 and O8 atoms are located on the respective caps. The trigonal prism is composed of O1, O2, O4, O5, O6 and O7, with one basal plane constructed from O4, O5, O6 and the other basal plane constructed from O7, O1 and O2. The flank of the trigonal prism is slightly distorted square-planar because the deviations of the four oxygen atoms (O6, O2, O4, O7 of one flank) are −0.0980, −0.1101, +0.1046 and +0.1035 Å, respectively, and the deviations of atoms from another flank (O1, O2, O4, O5) are −0.1284, +0.1397, −0.1228 and +0.1115 Å, respectively. Thus, the coordination geometry around the europium ion can be described as distorted tricapped trigonal prismatic. As depicted in Figure 2, the cations are alternately bridged by perchlorates to give infinite chains in which O−H···O interactions between coordinated ethanol and perchlorate ($d_{O\cdots O}$ = 2.855 Å), and ClO_4^-→Cu weak coordination pull the cations together ($d_{O\cdots Cu}$ = 2.558 Å). Furthermore, there are other O−H···O interactions between coordinated water and free water and free perchlorate, the O···O distances are 2.850 and 2.972 Å, respectively. In addition, there are π-π interactions between benzene rings of the CuL units of different cations in the cell which are parallel to each other

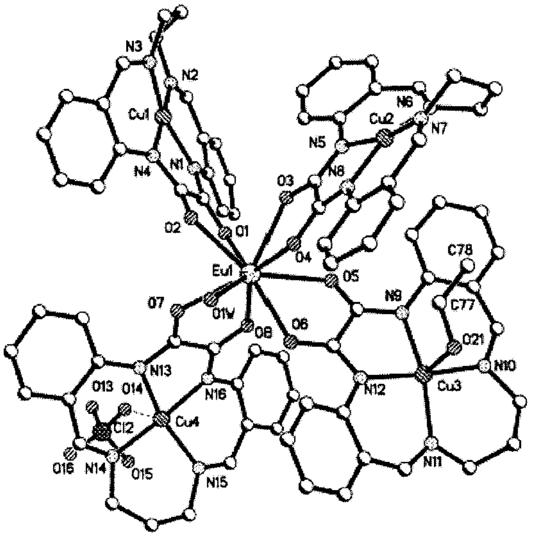

Figure 1. Perspective view of the pentanuclear complex cation of **1**

Table 1. Selected Bond lengths (Å) and Angles (deg) for **1**

Eu(1)−O(6)	2.433(5)	Cu(1)−N(4)	1.944(6)
Eu(1)−O(2)	2.448(5)	Cu(1)−N(2)	1.947(7)
Eu(1)−O(1)	2.459(5)	Cu(1)−N(1)	2.012(5)
Eu(1)−O(7)	2.468(5)	Cu(1)−N(3)	2.047(7)
Eu(1)−O(4)	2.478(5)	Cu(3)−N(12)	1.993(6)
Eu(1)−O(5)	2.487(5)	Cu(3)−N(10)	2.002(7)
Eu(1)−O(1 W)	2.494(6)	Cu(3)−N(9)	2.016(6)
Eu(1)−O(3)	2.497(5)	Cu(3)−N(11)	2.031(6)
Eu(1)−O(8)	2.498(5)	Cu(3)−O(21)	2.423(6)
O(6)−Eu(1)−O(2)	144.32(17)	O(2)−Eu(1)−O(1 W)	72.87(18)
O(6)−Eu(1)−O(1)	146.84(16)	O(1)−Eu(1)−O(1 W)	132.74(17)
O(6)−Eu(1)−O(7)	95.64(18)	O(7)−Eu(1)−O(1 W)	65.40(19)
O(6)−Eu(1)−O(4)	77.06(18)	O(4)−Eu(1)−O(1 W)	69.29(18)
O(6)−Eu(1)−O(5)	64.42(16)	O(5)−Eu(1)−O(1 W)	128.73(17)
O(6)−Eu(1)−O(1 W)	71.60(18)	O(1 W)−Eu(1)−O(3)	121.80(18)
O(6)−Eu(1)−O(3)	124.78(17)	O(1 W)−Eu(1)−O(8)	117.01(17)
O(6)−Eu(1)−O(8)	76.95(17)	N(4)−Cu(1)−N(2)	176.1(3)
N(10)−Cu(3)−N(9)	92.3(3)	N(4)−Cu(1)−N(1)	84.3(2)
N(12)−Cu(3)−N(11)	90.5(3)	N(2)−Cu(1)−N(1)	93.6(3)
N(10)−Cu(3)−N(11)	94.1(3)	N(4)−Cu(1)−N(3)	89.6(3)
N(9)−Cu(3)−N(11)	162.5(3)	N(2)−Cu(1)−N(3)	93.5(3)
N(12)−Cu(3)−O(21)	89.4(2)	N(1)−Cu(1)−N(3)	160.1(3)
N(10)−Cu(3)−O(21)	90.6(3)	N(9)−Cu(3)−O(21)	95.2(2)

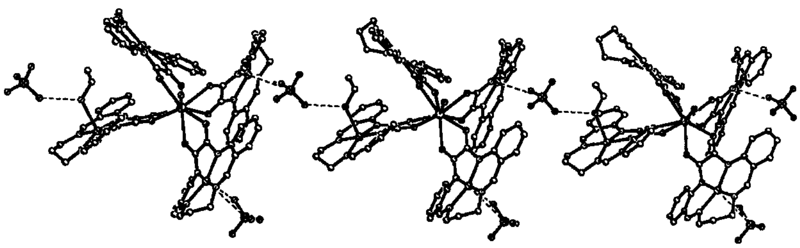

Figure 2. View of the self-assembled 1-D supramolecular architecture through O−H···O and weak coordination interactions of ClO_4^- for **1** and **2**

and the distance between carbon atoms is approximately 3.416 Å.

Description of the Structure of 2

X-ray structural analysis shows that the structure of the pentanuclear $[(CuL)_3\{CuL(C_2H_5OH)\}Tb(H_2O)]^{3+}$ cation is similar to that in **1** (Figure 3). There is an oxamide bridge between the Tb(III) and each Cu(II) ion. The coordination environments of the Cu1 and Cu2 ions are similar and slightly distorted square-planar with the basal planes composed of four nitrogen atoms from the macrocyclic oxamide groups with the axial positions occupied by perchlorates weakly coordinated to Cu1 and Cu2. The Cu3 ion is coordinated by four nitrogen atoms of the macrocyclic organic ligand with the $[Cu1N_4]$ chromophore exhibiting near planarity. Cu4 is located in a slightly distorted square pyramidal environment with the basal plane composed of atoms N13, N14, N15 and N16 from the macrocyclic oxamide groups, with the axial position being occupied by an ethanol molecule. The central terbium ion resides in a distorted tricapped trigonal prismatic environment surrounded by eight oxygen atoms from four oxamide groups and the O9 atom of a water molecule. The O9, O5 and O8 atoms are located on the respective caps, while the trigonal prism is composed of O1, O2, O3, O4, O6 and O7 with one basal plane constructed from O4, O2, O6 and the other basal plane constructed from O7, O1 and O3. As depicted in Figure 2, the cations are alternately bridged by perchlorates giving infinite chains in which the O−H···O interactions between coordinated ethanol and perchlorate groups ($d_{O\cdots O}$ = 2.825 Å), and ClO_4^-→Cu weak coordination ($d_{O\cdots Cu}$ = 2.528 Å) pull the cations together. Furthermore, there are other O−H···O interactions between coordinated water and free water and free perchlorate and the O···O distances are 2.821 and 2.943 Å, respectively. In addition, there are π-π interactions between benzene rings of the CuL moieties of different cations in the cell which are parallel to each other and the distance between carbon atoms is approximately 3.400 Å (Table 2).

Description of the Structure of 3

Complex **3** consists of hexanuclear $[(NiL)_5Sm]^{3+}$ cations, monovalent ClO_4^- anions, and water. A perspective view of the hexanuclear cation is depicted in Figure 4, and selected bond lengths and angles are listed in Table 3. The central samarium and external nickel ions are bridged by

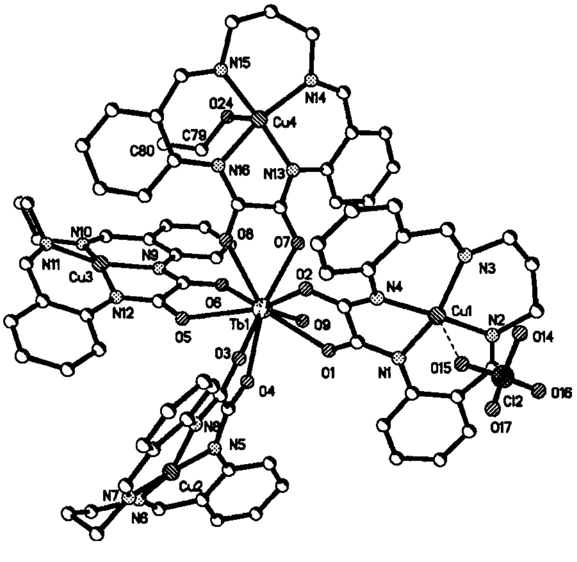

Figure 3. Perspective view of the pentanuclear complex cation of **2**

Table 2. Selected bond lengths (Å) and angles (deg) for **2**

Tb(1)−O(7)	2.377(5)	Cu(1)−N(4)	1.962(6)
Tb(1)−O(4)	2.401(5)	Cu(1)−N(2)	1.966(8)
Tb(1)−O(1)	2.405(5)	Cu(1)−N(1)	1.979(6)
Tb(1)−O(3)	2.424(5)	Cu(1)−N(3)	2.029(8)
Tb(1)−O(6)	2.434(5)	Cu(4)−N(13)	1.973(6)
Tb(1)−O(8)	2.447(5)	Cu(4)−N(15)	1.975(7)
Tb(1)−O(2)	2.452(5)	Cu(4)−N(16)	2.003(6)
Tb(1)−O(5)	2.454(5)	Cu(4)−N(14)	2.021(7)
Tb(1)−O(9)	2.491(6)	Cu(4)−O(24)	2.394(6)
O(7)−Tb(1)−O(4)	143.60(17)	O(4)−Tb(1)−O(9)	72.94(18)
O(7)−Tb(1)−O(1)	94.55(17)	O(1)−Tb(1)−O(9)	64.99(18)
O(7)−Tb(1)−O(3)	146.67(16)	O(3)−Tb(1)−O(9)	132.88(17)
O(7)−Tb(1)−O(6)	77.18(18)	O(6)−Tb(1)−O(9)	69.15(18)
O(7)−Tb(1)−O(8)	65.29(16)	O(8)−Tb(1)−O(9)	128.78(18)
O(7)−Tb(1)−O(2)	76.82(17)	O(2)−Tb(1)−O(9)	117.14(17)
O(7)−Tb(1)−O(5)	125.40(17)	O(5)−Tb(1)−O(9)	22.02(18)
O(7)−Tb(1)−O(9)	70.80(18)	N(4)−Cu(1)−N(2)	174.3(3)
N(13)−Cu(4)−O(24)	89.6(2)	N(4)−Cu(1)−N(1)	82.5(2)
N(15)−Cu(4)−O(24)	90.9(3)	N(2)−Cu(1)−N(1)	92.1(3)
N(16)−Cu(4)−O(24)	95.3(2)	N(4)−Cu(1)−N(3)	89.4(3)
N(14)−Cu(4)−O(24)	100.5(3)	N(2)−Cu(1)−N(3)	95.1(3)

macrocyclic oxamide groups. The external nickel ions are coordinated by four nitrogen atoms from the macrocyclic organic ligand, with the [NiN_4] chromophore exhibiting a distorted planar arrangement. The deviations of the four donor atoms (N1, N2, N3 and N4) from their mean plane are −0.2695, +0.2713, −0.2627 and +0.2699 Å, respectively, and Ni1 is located −0.0089 Å out of the plane. The central samarium ion resides in a distorted bicapped square antiprismatic environment surrounded by ten oxygen atoms from five oxamide groups. O6 and O9 are located on the respective caps. The square antiprism is composed of O1, O2, O3, O4, O5, O7, O8 and O10, with one basal plane constructed from O1, O3, O7 and O10 and the other basal plane constructed from O2, O4, O5 and O8. The deviations of the atoms of one basal plane (O1, O3, O7, O10) are −0.1697, +0.1269, −0.1097 and +0.1525 Å, respectively. Thus, the coordination geometry around the samarium ion can be described as distorted bicapped square antiprismatic. In addition, there are π-π interactions between benzene rings of the NiL units of different cations in the cell which are parallel to each other and the distance between carbon atoms is approximately 3.301 Å.

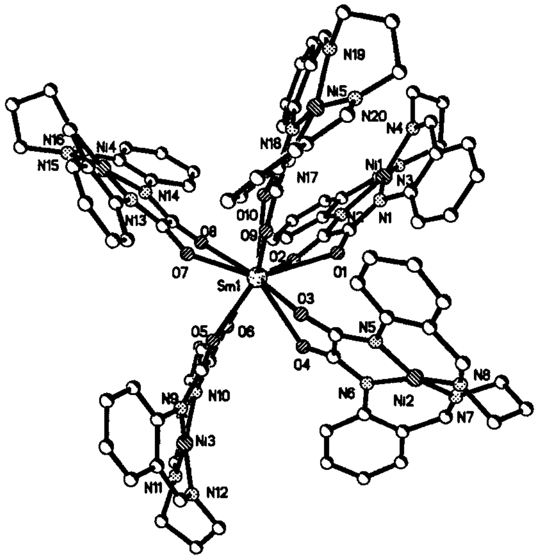

Figure 4. Perspective view of the hexanuclear complex cation of **3**

Table 3. Selected bond lengths (Å) and angles (deg) for **3**

Sm(1)−O(7)	2.428(6)	Sm(1)−O(9)	2.562(6)
Sm(1)−O(5)	2.461(6)	Sm(1)−O(8)	2.576(6)
Sm(1)−O(2)	2.482(5)	Sm(1)−O(4)	2.620(6)
Sm(1)−O(3)	2.505(5)	Ni(1)−N(4)	1.862(9)
Sm(1)−O(6)	2.530(6)	Ni(1)−N(3)	1.875(7)
Sm(1)−O(10)	2.530(6)	Ni(1)−N(2)	1.899(7)
Sm(1)−O(1)	2.552(6)	Ni(1)−N(1)	1.903(7)
O(7)−Sm(1)−O(5)	67.5(2)	O(10)−Sm(1)−O(9)	62.3(2)
O(7)−Sm(1)−O(2)	134.28(19)	O(1)−Sm(1)−O(9)	72.6(2)
O(5)−Sm(1)−O(2)	135.4(2)	O(7)−Sm(1)−O(8)	63.0(7)
O(7)−Sm(1)−O(3)	104.63(19)	O(5)−Sm(1)−O(8)	99.57(19)
O(5)−Sm(1)−O(3)	71.97(18)	O(2)−Sm(1)−O(8)	73.16(19)
O(2)−Sm(1)−O(3)	119.47(18)	O(3)−Sm(1)−O(8)	167.36(18)
O(7)−Sm(1)−O(6)	98.7(2)	O(6)−Sm(1)−O(8)	65.39(19)
O(5)−Sm(1)−O(6)	64.71(19)	O(10)−Sm(1)−O(8)	65.6(2)
O(2)−Sm(1)−O(6)	72.8(2)	O(1)−Sm(1)−O(8)	124.03(19)
O(3)−Sm(1)−O(6)	116.89(19)	O(9)−Sm(1)−O(8)	110.4(2)
O(7)−Sm(1)−O(10)	79.6(2)	O(7)−Sm(1)−O(4)	142.4(2)
O(5)−Sm(1)−O(10)	146.99(19)	O(5)−Sm(1)−O(4)	74.88(18)
O(2)−Sm(1)−O(10)	70.9(2)	O(2)−Sm(1)−O(4)	74.83(18)
O(3)−Sm(1)−O(10)	116.36(19)	O(3)−Sm(1)−O(4)	62.39(18)
O(6)−Sm(1)−O(10)	125.21(19)	O(6)−Sm(1)−O(4)	63.53(19)
O(7)−Sm(1)−O(1)	135.3(2)	O(10)−Sm(1)−O(4)	138.04(19)
O(5)−Sm(1)−O(1)	135.94(18)	O(1)−Sm(1)−O(4)	74.7(2)
O(2)−Sm(1)−O(1)	62.73(19)	O(9)−Sm(1)−O(4)	124.12(19)
O(3)−Sm(1)−O(1)	65.94(18)	O(8)−Sm(1)−O(4)	125.46(19)
O(6)−Sm(1)−O(1)	125.06(18)	N(4)−Ni(1)−N(3)	90.7(4)
O(10)−Sm(1)−O(1)	68.5(2)	N(4)−Ni(1)−N(2)	162.8(3)
O(7)−Sm(1)−O(9)	65.0(2)	N(3)−Ni(1)−N(2)	93.8(4)
O(5)−Sm(1)−O(9)	99.9(2)	N(4)−Ni(1)−N(1)	93.0(4)
O(2)−Sm(1)−O(9)	124.1(2)	N(3)−Ni(1)−N(1)	164.3(3)
O(3)−Sm(1)−O(9)	63.26(19)	N(2)−Ni(1)−N(1)	87.1(3)
O(6)−Sm(1)−O(9)	161.73(19)		

IR and Electronic Spectra

The IR spectra of **1, 2** and **3** show three strong bands at around 1639, 1610 and 1448 cm^{-1} which can be attributed to the υ(N−C−O) stretching bands and are characteristic of the bridging oxamide group.[28] The broad bands of **1, 2** and **3** around 1090 cm^{-1} in each case can be attributed to the ClO_4^- group.[29]

The electronic absorption spectra of the **1** and **2** were measured in DMF solution. In complexes **1** and **2**, a broad strong band centered at 613 nm can be attributed to the d-d transitions of five or six coordinate copper atoms,[30] the latter geometry being due to the fact that DMF is axially bound to the distorted square planar Cu(II) sites. All complexes exhibit intense bands below 550 nm, assignable to charge-transfer transitions in the [CuL] chromophores and/or intraligand π-π* interactions.[28] The hypersensitive transition bands of the rare earth metal ions were not observed.[31]

Fluorescence Properties

The fluorescence spectra of the $Cu^{II}_4Ln^{III}$ complexes (Ln = Eu, Tb) are given in Figure 5. The fluorescence spectra of $Ln(ClO_4)_3 \cdot 6H_2O$, which are included in Figure 5 were also measured for comparison. $Eu(ClO_4)_3 \cdot 6H_2O$ and $Tb(ClO_4)_3 \cdot 6H_2O$ exhibit fluorescence bands attributable to $^5D_0 \rightarrow {^7F_1}$ transitions in the 580−700 nm region and $^5D_4 \rightarrow {^7F_1}$ transitions in the 440−600 nm region, respectively. These fluorescence bands disappear almost completely in both complexes. According to the most probable quenching mechanism, we presume that the energy transfer occurs from the excited Ln(III) to the Cu(II) center through the oxamidic oxygen bridges.[24−27]

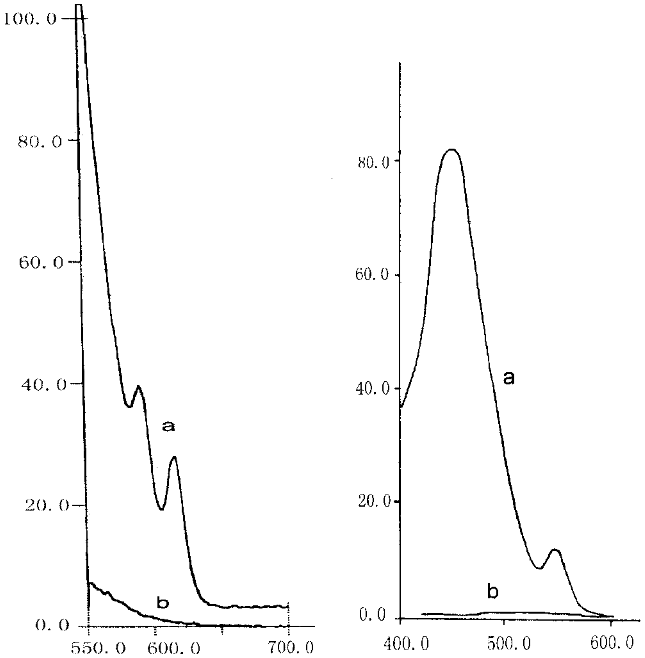

Figure 5. left: The fluorescence spectra of $Eu(ClO_4)_3 \cdot 6H_2O$ (a) and **1** (b), in DMF solution; the exciting wavelength is 394 nm; slim widths (excitation and emission sides) are 3 and 3 nm; ordinate scales are × 7 for (a) and for (b). right: The fluorescence spectra of $Tb(ClO_4)_3 \cdot 6H_2O$ (a) and **2** (b), in DMF solution; the exciting wavelength is 355 nm; slim widths (excitation and emission sides) are 2 and 2 nm; ordinate scales are × 8 for (a) and for (b)

Magnetic Properties

The magnetic susceptibilities (χ_M) of **1** was measured in the temperature range 2−300 K (Figure 6). The μ_{eff} value of 4.95 B.M. at room temperature continuously decreased with temperature to a value of 3.59 B.M. at 2 K. The μ_{eff} value is 3.59 B.M. at 2 K which is very close to the four copper(II)-only value(3.46 B.M.). This may be due to the thermal depopulation of excited levels (J = 1−6) of Eu(III), leading to the four copper(II)-only value since the $^7F_0$ ground state of Eu(III) is diamagnetic. As a first approach to simulating experimental magnetic behavior, the magnetic susceptibility of **1** was treated as sum of the contributions of one Eu(III) and four Cu(II) ions [Equation (1)].

$$\chi = 4\chi_{Cu} + \chi_{Eu} \tag{1}$$

where the first term $4\chi_{Cu}$ is the magnetic susceptibility for four Cu(II) ions [Equation (2)].

$$\chi_{Cu} = \frac{Ng^2\beta^2}{3KT}\frac{1}{2}\left(\frac{1}{2}+1\right) \tag{2}$$

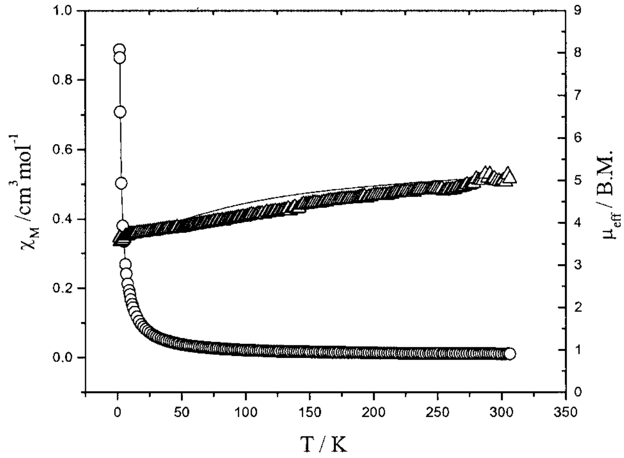

Figure 6. χ_M (circles) versus T and μ*(T)* (triangles) versus plots for the pentanuclear species **1**

The second term χ_{Eu} is the magnetic susceptibility for the Eu(III) ion. For the latter, the ^7F ground term is split by spin-orbit coupling into seven states, ^7F_J, with J taking integral values from 0 to 6. If the energy of the $^7F_0$ ground state is taken as the origin, the magnetic susceptibility may be expressed as in [Equation (3)].[32]

$$\chi_{Eu} = \frac{N\beta^2}{3KT}\frac{\left\{\begin{array}{l}144/x+(27/2-9/x)\exp(-x/6)+(135/2-15/x)\exp(-x/2)+\\(189-21/x)\exp(-2x)+(405-27/x)\exp(-10x/3)+(1485/2-\\33/x)\exp(-5x)+(2457/2-39/x)\exp(-7x)\end{array}\right\}}{\begin{array}{c}1+3\exp(-x/6)+5\exp(-x/2)+7\exp(-2x)+\\9\exp(-10x/3)+11\exp(-5x)+13\exp(-7x)\end{array}} \tag{3}$$

Where $x = \zeta/KT$, ζ is the spin-orbit coupling constant for Eu(III). Taking into account the interaction between Cu(II) and Eu(III) ions, a correction for a molecular field can be made [Equation (4)].

$$\chi_M = \frac{\chi}{1-(2ZJ'/Ng^2\beta^2)\chi} \tag{4}$$

The least-squares fit of Equation (4) to the data yielded the parameters $g = 2.13$, $\zeta = 1358$, $ZJ' = -0.12$, where the agreement factor defined as:

$$R = \Sigma[(\chi_M)^{Cal} - (\chi_M)^{obsd}]^2 / \Sigma[(\chi_M)^{obsd}]^2$$

is 8.40×10^{-3}.

The value of ZJ' reveals weak antiferromagnetic interaction between the Cu(II) ions and the Eu(III) ion.

The magnetic susceptibilities (χ_M) of **2** were measured in the temperature range 4−300 K (Figure 7). The observed μ_{eff} value for **2** was 10.54 B.M. at room temperature. This value is slightly higher than that expected if the metal centers are not interacting (for, **2**, 10.32 B.M., assuming $g_{Cu} = 2.0$, $g_{Tb} = 3/2$). For **2**, this values declines gradually between 300 and 8 K, where at the latter temperature the μ_{eff} value is 9.41 B.M. Below 8 K, it falls sharply reaching 8.84 B.M. at 4 K. In contrast to the Cu_4Eu case, a similar treatment of **2** does not give reasonable results. To gain some information concerning the interaction between Tb and Cu, Kahn and Costes et al. have developed an experimental approach. For this, it appeared necessary to synthesize an isostructural Ln^{III} complex with a diamagnetic surrounding.[7d,33] Unfortunately, for **2**, we have been unable to crystallized an isostructural series. However, we synthesized a hexanuclear Ni_5Ln (Ln = Sm) complex using $Ni^{II}L$ as a ligand. Thus, to get insight into the strength of these interactions, accurate models involving both the orbital contribution and the ligand field effect have to be developed.

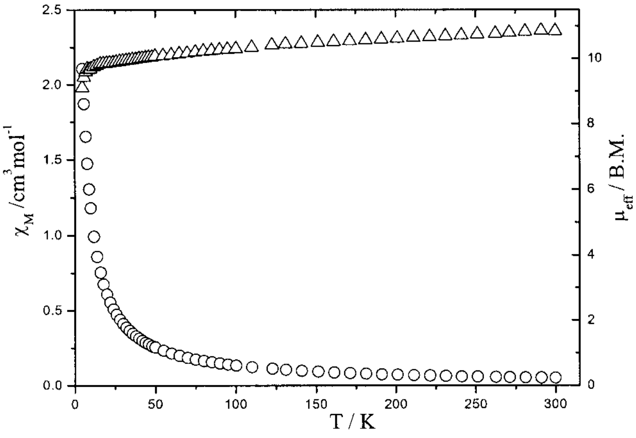

Figure 7. χ_M (circles) versus T and $\mu(T)$ (triangles) versus plots for the pentanuclear species **2**

Conclusion

Two novel oxamidato-bridged $Cu^{II}_4Ln^{III}$ pentanuclear complexes of formula $[(CuL)_3\{CuL(C_2H_5OH)\}Eu(H_2O)](ClO_4)_3\cdot1.5H_2O$, $[(CuL)_3\{CuL(C_2H_5OH)\}Tb(H_2O)](ClO_4)_3\cdot2H_2O$ and $[(NiL)_5Sm](ClO_4)_3\cdot2H_2O$ incorporating a macrocyclic oxamide have been hydrothermally synthesized and structurally characterized. The hydrogen bonds play an important role in the 1-D supramolecular architectures of **1** and **2**. The magnetic and fluorescent properties of **1** and **2** have also been characterized.

Experimental Section

***Caution !** Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled very carefully and in small quantities.*

General Remarks: All the starting reagents were of A. R. grade and were used as purchased. The complex ligand CuL was prepared as described according to the literature.[34] The complex ligand NiL was prepared in the same way as CuL.

$[(CuL)_3\{CuL(C_2H_5OH)\}Eu(H_2O)](ClO_4)_3\cdot1.5H_2O$ (1): The complex was prepared by a hydrothermal reaction. A mixture of CuL, $Eu(ClO_4)_3\cdot6H_2O$, CH_3CH_2OH and H_2O in a molar ratio of 4.0:1.0:40:300 was sealed in an 18 cm^3 capacity Teflon-lined reactor which was kept at 160 °C for 72 h. Deep brown-green crystals of the compound were isolated (yield 89.5 % base on Eu) by filtering and washing with water. $C_{78}H_{75}Cl_3Cu_4EuN_{16}O_{23.5}$ (2125.0): calcd. C 44.09, H 3.56, N 10.55; found C 44.10, H 3.45, N 10.48. Main IR bands (KBr, cm^{-1}): $\tilde{\nu}$ = 3414 s (br), 1640 vs, 1610 vs, 1445 m, 1088 vs (br), 776 w, 620 w.

$[(CuL)_3\{CuL(C_2H_5OH)\}Tb(H_2O)](ClO_4)_3\cdot2.0H_2O$ (2): The complex was prepared in the same way as **1**, using terbium perchlorate instead of europium perchlorate. Deep brown-green crystals were obtained (yield 87 % based on Tb). $C_{78}H_{76}Cl_3Cu_4N_{16}O_{24}Tb$ (2141.0): calcd. C 43.76, H 3.58, N 10.47; found C 46.18, H 3.51, N 11.35. Main IR bands (KBr, cm^{-1}): $\tilde{\nu}$ = 3417 s (br), 1639 vs, 1615 vs, 1448 m, 1090 vs (br), 777 w, 623 w.

$[(NiL)_5Sm](ClO_4)_3\cdot2H_2O$ (3): The complex was prepared by a hydrothermal reaction. A mixture of NiL, $Sm(ClO_4)_3\cdot6H_2O$, CH_3CH_2OH and H_2O in a molar ratio of 4.0:1.0:40:300 was sealed in an 18 cm^3 capacity Teflon-lined reactor which was kept at 165 °C for 72 h. Deep brown-red crystals of the compound were isolated (yield 80.5 % base on Sm) by filtering and washing with water. $C_{95}H_{84}Cl_3N_{20}Ni_5O_{24}Sm$ (2440.1): calcd. C 46.76, H 3.47, N 11.48; found C 46.78, H 3.41, N 11.45. Main IR bands (KBr, cm^{-1}): $\tilde{\nu}$ = 3415 s(br), 1636 vs, 1611 vs, 1445 m, 1090 vs (br), 778 w, 621 w.

Physical Measurements: C, H and N analyses were determined on a Perkin−Elmer 240 Elemental analyzer. IR spectra were recorded in KBr discs on a Shimadzu IR-408 infrared spectrophotometer in the 4000−600cm^{-1} range. Electronic spectra in DMF were recorded on a Shimadzu UV-2101 PC scanning spectrophotometer. Variable-temperature magnetic susceptibilities were measured on an MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms.[35]

X-ray Diffraction Data Collection and Structure Refinement − Crystallographic Studies: All data were collected on a Bruker Smart-1000-CCD area detector using graphite monochromated

Table 4. Summary of crystallographic data for complexes **1, 2** and **3**

	1	**2**	**3**
Empirical formula	$C_{78}H_{75}O_{23.5}N_{16}Cl_3Cu_4Eu$	$C_{78}H_{76}O_{24}N_{16}Cl_3Cu_4Tb$	$C_{95}H_{84}O_{24}N_{20}Cl_3Ni_5Sm$
M	2125.01	2140.96	2440.07
System	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a (Å)	15.024(8)	14.901(4)	17.810(5)
b (Å)	16.994(8)	16.833(5)	24.023(7)
c (Å)	17.991(9)	17.778(5)	23.569(7)
α/°	74.806(8)	74.953(5)	90
β/°	82.516(8)	82.697(6)	102.984(6)
γ/°	70.220(7)	70.099(5)	90
V/Å^3	4167(3)	4045(2)	9826(5)
Z	2	2	4
ρ_{caled} g.cm^{-3}	1.694	1.758	1.649
μ(Mo-K_α) mm^{-1}	0.71073	0.71073	0.71073
Crystalsize mm	0.50 × 0.40 × 0.20	0.30 × 0.25 × 0.20	0.30 × 0.25 × 0.20
θ range/°	1.17−24.69	1.19−25.03	1.83 to 25.03
F(000)	2146	2040	4956
R1[a] [$I > 2\sigma(I)$]	0.0587	0.0520	0.0708
$wR2$[b] [$I > 2\sigma(I)$]	0.1291	0.1139	0.0919
GOF	0.992	1.029	0.912

Mo-K_α radiation (= 0.71073 Å). The structures were solved by direct method and subsequent Fourier difference techniques and refined using a full-matrix least-squares procedure on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXS-97 and SHELXL-97).[36] Hydrogen atoms were added geometrically and refined with riding model positional parameters and fixed isotropic thermal parameters. Crystal data collection and refinement parameters are given in Table 4. CCDC 208850 (for **1**), 214752 (for **2**) and -218203 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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