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Synthesis, Crystal Structure, and Magnetic Properties of the First Nonanuclear Lanthanide(III)–Copper(II) Complexes of Macrocyclic Oxamide [$NaLn_2Cu_6$] (Macrocyclic Oxamide = 1,4,8,11-Tetraazacyclotradecanne-2,3-dione, Ln = Pr, Nd)

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Two new nonanuclear lanthanide(III)–copper(II) complexes of macrocyclic oxamide $[NaPr_2(CuL)_6(H_2O)_6](ClO_4)_6Cl\cdot 6H_2O$ (**1**) and $[NaNd_2(CuL)_6(H_2O)_6](ClO_4)_6Cl\cdot 8H_2O$ (**2**) have been synthesized and characterized by means of elemental analysis, IR, and electronic spectra, where L = 1,4,8,11-tetraazacyclotradecanne-2,3-dione. The crystal structures of the two complexes have been determined. The structures of **1** and **2** consist of nonanuclear cations, perchlorate and chloride anions, and water molecules. In the two complexes, each copper(II) ion is connected to lanthanide(III) ion via the *exo-cis* oxygen atoms of the oxamido macrocyclic ligands, resulting in a tetranuclear subunit. The sodium ion links two tetranuclear subunits via the *exo* oxygen atoms of the oxamido macrocyclic ligands which results in a novel nonanuclear complex. The magnetic properties of the two complexes have been investigated. Preliminary treatment of the magnetic data by considering Ln(III) as free ion cannot give reasonable results, and accurate models involving both the orbital contribution and ligand field effect have to be developed.

Introduction

Molecular magnetism and macrocyclic compounds are two active fields of research, encompassing chemistry, physics, biology, and material science.[1,2] At the meeting point of these two fields, polynuclear macrocyclic complexes have received considerable attention.[3−7] Polynuclear complexes are of considerable interest for designing new magnetic materials and for investigating the structure and the role of the polymetallic active sites in biological systems.[2,8−10] For two decades or so, an increasing interest has been given to the design and properties of molecular complexes comprising

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simultaneously lanthanide and transition metal ions.[11−16] However, most of the studies were focused on the Gd(III)−Cu(II) couple[11−15] which has been found to be directly ferromagnetic in most cases. By comparison, the polynuclear complexes containing other lanthanide(III)−copper(II) mixtures have been poorly investigated.[12,16−18] In addition, the majority of the mixed-metal complexes are bridged by polydentate Schiff-base, pyridonates, carboxylate, and oxamido ligands.[11] Especially, the oxamido group has been noted as an efficient mediator of magnetic exchange between paramagnetic centers.[2] However, little work has been devoted to designing mixed-metal complexes containing oxamido-based macrocyclic ligands, although metal complexes of macrocyclic ligands have been of great interest to coordination chemists for their special structures, properties, and/or functionalities.[1,19−20]

With these facts in mind and in continuation of our work on polynuclear macrocyclic complexes,[6] macrocyclic oxamido−copper(II) complexes were used as complex ligands, and two types of inorganic anions were introduced, which lead to novel complexes incorporating 3d, 4f metals with an alkali metal center. To our knowledge, these complexes represent the first examples of a nonanuclear Na−Ln−Cu system with this kind of bridging.

Experimental Section

Material and Synthesis. All the starting chemicals were of A. R. grade and used as received. The mononuclear precursor CuL[21] was prepared as described in the literature.

$[NaPr_2(CuL)_6(H_2O)_6](ClO_4)_6Cl{\cdot}6H_2O$, 1. An aqueous solution of CuL precursor (0.9 mmol) was added to an ethanol solution of praseodymium chloride (0.3 mmol). The red crystals were obtained upon slow evaporation of the solvent in the presence of an excessive amount of $NaClO_4$ at room temperature over a period of several days. Yields 70%. Anal. Calcd for $C_{60}H_{132}Cl_7Cu_6N_{24}NaO_{48}Pr_2$: C, 24.9; H, 4.6; N, 11.6. Found: C, 24.7; H, 4.6; N, 11.7. Main IR bands (KBr, cm^{-1}): 3350s(br), 2850m, 1610vs, 1430m, 1340m, 1310w, 1090vs(br), 930w, 880w, 810w.

$[NaNd_2(CuL)_6(H_2O)_6](ClO_4)_6Cl{\cdot}8H_2O$, 2. The complex was prepared in the same way as **1**, using neodymium chloride instead of praseodymium chloride. Red crystals were obtained by slow evaporation of the resulting solution at room temperature. Yields 68%. Anal. Calcd for $C_{60}H_{136}Cl_7Cu_6N_{24}NaNd_2O_{50}$: C, 24.6; H, 4.7; N, 11.5. Found: C, 24.7; H, 4.6; N, 11.2. Main IR bands (KBr, cm^{-1}): 3300s(br), 2900m, 1600vs, 1430m, 1340m, 1300w, 1080vs(br), 930w, 870w, 800w.

Physical Measurements. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240 analyzer. IR spectra were recorded on a Shimadzu IR-408 spectrometer as KBr pellets, and electronic spectra on a Shimadzu UV-2401 PC spectrophotometer in acetronitrile. Variable-temperature magnetic susceptibilities were measured on a Quantum Design MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms.[22]

Crystallographic Studies. Determination of the unit cell and data collection were performed at room temperature on a BRUKER SMART 1000 area detector, all using graphite-monochromated Mo Kα radiation (=0.71073 Å). The structures were solved by direct methods using SHELXS-97 and refined by least-squares procedures on F_o^2 with SHELXL-97 by minimizing the function $\sum w(F_o^2-F_c^2)^2$, where F_o and F_c are, respectively, the observed and calculated structure factors.[23] The hydrogen atoms were located geometrically and refined isotropically. Crystal data collection and refinement parameters are given in Table 1.

Results and Discussion

Description of the Structures of 1. The structure of complex **1** consists of nonanuclear $[NaPr_2(CuL)_6(H_2O)_6]^{7+}$ cations, perchlorate, chloride anions, and water molecules. A perspective view of the nonanuclear cation is depicted in Figure 1, and selected bond lengths and angles are listed in Table 2. Each Cu(II) ion is coordinated by four amino

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Table 1. Summary of Crystallographic Data for Complexes **1** and **2**

	1	**2**
formula	$C_{60}H_{132}Cl_7Cu_6N_{24}NaO_{48}Pr_2$	$C_{60}H_{136}Cl_7Cu_6N_{24}NaNd_2O_{50}$
fw	2892.10	2934.79
space group	$\bar{P}1$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	13.8802(11)	13.892(3)
b, Å	14.41442(11)	14.477(3)
c, Å	16.1663(13)	16.213(4)
α, deg	98.064(2)	98.195(4)
β, deg	96.378(2)	96.602(4)
γ, deg	114.27000(10)	114.109(4)
V, Å^3	2867.6(4)	2891.2 (11)
Z	1	1
ρ_{calcd}, g/cm^3	1.675	1.686
μ(Mo Kα), mm^{-1}	2.181	2.221
T, K	293(2)	293(2)
R1[a] [$I > 2\sigma(I)$]	0.0104	0.0130
wR2[b] [$I > 2\sigma(I)$]	0.0223	0.0445

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

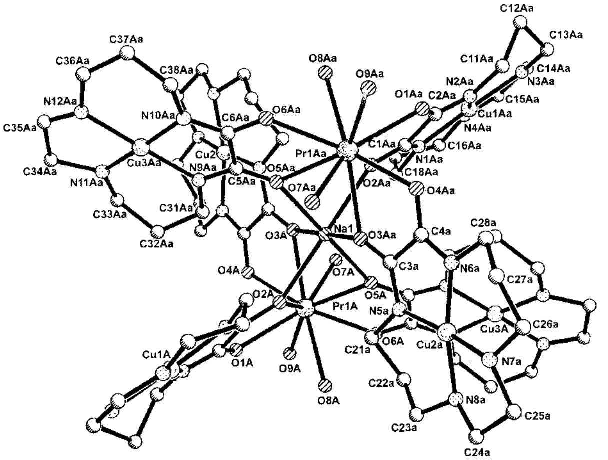

Figure 1. ORTEP view of the nonanuclear complex cation in **1** with the atom numbering scheme.

nitrogen atoms of the macrocyclic organic ligand with the CuN_4 chromophore exhibiting planarity. Each copper(II) atom is connected to the Pr(III) via the *exo-cis* oxygen atoms of the oxamido macrocyclic ligands (average Pr−O distance 2.496 Å) with Pr−Cu separations of 5.857, 5.823, and 5.842 Å for Cu(1), Cu(2), and Cu(3), respectively, resulting in a tetranuclear subunit. The coordination sphere of the Pr(III) ion is completed by three aqua ligands (Pr−O bond length range 2.5180−2.6168 Å). The oxygen atoms of the oxamido macrocyclic ligands adopt two coordination modes. One binds the lanthanide ion directly; the other acts as a monatomic bridge linking the lanthanide ion and a sodium ion. Thus, the sodium ion links two tetranuclear subunits (Pr−Na separation of 3.5826 Å) via the *exo* oxygen atoms of the oxamido macrocyclic ligands and results in a novel nonanuclear complex. The sodium is six-coordinated with Na−O distances from 2.3719 to 2.4632 Å. It is unlikely that an empty center is preformed for the encapsulation of the sodium ion; instead, the formation of the nonanuclear complex may be best described as a sodium-induced self-assembly of the lanthanide ions with help of the macrocyclic oxamido−copper(II) complex ligands. In other words, the sodium ion serves as a template in the formation of this novel complex. Experiments without $NaClO_4$ did not give rise to the $NaLn_2Cu_6$ nonanuclear complex, supporting this supposition, and hence, this may furnish an exciting addition to the examples of cation-templated synthesis. As counteranions, both Cl^- and ClO_4^- may play a crucial role in the formation of the complexes.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1**

Pr1−O1	2.4982(8)	Cu1−N3	1.9392(17)
Pr1−O2	2.5203(8)	Cu1−N4	1.9803(10)
Pr1−O3	2.5048(7)	Cu2−N5	1.9424(9)
Pr1−O4	2.4741(7)	Cu2−N6	1.9453(8)
Pr1−O5	2.4913(7)	Cu2−N7	1.9754(9)
Pr1−O6	2.4829(7)	Cu2−N8	1.9986(8)
Pr1−O7	2.6168(11)	Cu2−O32-d	2.717(3)
Pr1−O8	2.5542(9)	Cu3−N9	1.9552(10)
Pr1−O9	2.5180(12)	Cu3−N10	1.9563(8)
Na1−O2	2.4252(7)	Cu3−N11	1.9654(9)
Na1−O6	2.4632(7)	Cu3−N12	1.9679(9)
Na1−O3	2.3719(7)	Cu3−O1W-a	2.6606(16)
Cu1−N1	1.9662(11)	Cu3−O12-c	2.856(2)
Cu1−N2	1.9349(9)		

O1−Pr1−O2	64.83(2)	O4−Pr1−O9	74.14(3)
O1−Pr1−O3	105.91(2)	O5−Pr1−O6	65.83(2)
O1−Pr1−O4	73.51(3)	O5−Pr1−O7	67.19(3)
O1−Pr1−O5	131.25(2)	O5−Pr1−O8	68.97(3)
O1−Pr1−O6	134.59(2)	O5−Pr1−O9	72.63(3)
O1−Pr1−O7	139.37(3)	O6−Pr1−O7	84.59(3)
O1−Pr1−O8	70.53(3)	O6−Pr1−O8	84.42(2)
O1−Pr1−O9	74.64(3)	O6−Pr1−O9	138.45(3)
O2−Pr1−O3	69.38(2)	O7−Pr1−O8	135.51(3)
O2−Pr1−O4	103.46(2)	O7−Pr1−O9	80.35(4)
O2−Pr1−O5	127.68(2)	O8−Pr1−O9	79.92(3)
O2−Pr1−O6	72.95(2)	N1−Cu1−N2	84.09(4)
O2−Pr1−O7	139.29(3)	N1−Cu1−N3	177.31(5)
O2−Pr1−O8	76.48(3)	N1−Cu1−N4	96.00(4)
O2−Pr1−O9	137.90(3)	N2−Cu1−N3	96.65(5)
O3−Pr1−O4	64.56(2)	N2−Cu1−N4	179.59(4)
O3−Pr1−O5	122.75(2)	N3−Cu1−N4	83.28(5)
O3−Pr1−O6	72.41(2)	N5−Cu2−N6	84.32(3)
O3−Pr1−O7	71.66(3)	N5−Cu2−N7	173.71(4)
O3−Pr1−O8	142.96(3)	N5−Cu2−N8	96.39(3)
O3−Pr1−O9	136.03(3)	O32-d−Cu2−N5	91.15(6)
O4−Pr1−O5	128.30(3)	N6−Cu2−N7	95.57(3)
O4−Pr1−O6	134.58(2)	N6−Cu2−N8	168.93(4)
O4−Pr1−O7	69.09(3)	O32-d−Cu2−N6	110.58(6)
O4−Pr1−O8	139.99(2)	N7−Cu2−N8	84.94(3)

Description of the Structures of 2. The structure of **2** is similar to that of **1** and consists of nonanuclear $[NaNd_2(CuL)_6(H_2O)_6]^{7+}$ cations, perchlorate and chloride anions, and water molecules. Selected bond lengths and angles are listed in Table 3. Each copper(II) atom is connected to the Nd(III) via the *exo-cis* oxygen atoms of the oxamido macrocyclic ligands (average Nd−O distance 2.493 Å) with the Nd−Cu separations of 5.860, 5.824, and 5.847 Å for Cu(1), Cu(2), and Cu(3), respectively, resulting in a tetranuclear subunit. The coordination sphere of the Nd(III) ion is completed by three aqua ligands (Nd−O bond length range 2.5099−2.5971 Å). The average Nd−O distance is slightly shorter than the Pr−O distances in complex **1**. The sodium ion links two tetranuclear subunits (Nd−Na separation of 3.578 Å) via the *exo-cis* oxygen atoms of the oxamido macrocyclic ligands and results in nonanuclear complex.

IR and Electronic Spectra. The IR spectra of nonanuclear species **1** and **2** showing two strong bands at ∼1600 and ∼1430 cm^{-1}, attributed to the ν(N−C−O) stretching bands,

Table 3. Selected Bond Distances (Å) and Angles (deg) for **2**

Nd1−O1	2.5025(11)	Cu1−N3	1.977(3)
Nd1−O2	2.5138(11)	Cu1−N4	1.964(3)
Nd1−O3	2.5029(9)	Cu2−N5	1.9509(10)
Nd1−O4	2.4697(10)	Cu2−N6	1.9480(11)
Nd1−O5	2.4657(9)	Cu2−N7	1.9808(16)
Nd1−O6	2.5014(11)	Cu2−N8	2.0289(14)
Nd1−O7	2.5971(14)	Cu2−O23-a	2.738(3)
Nd1−O8	2.5577(14)	Cu3−O3W	2.656(7)
Nd1−O9	2.5099(15)	Cu3−N9	1.9331(10)
Na1−O2	2.4289(9)	Cu3−N10	1.9500(12)
Na1−O5	2.4527(10)	Cu3−N11	1.927(3)
Na1−O3	2.3768(9)	Cu3−N12	1.960(3)
Cu1−N1	1.9392(11)	Cu3−O13-c	2.831(4)
Cu1−N2	1.9523(13)		
O1−Nd1−O2	65.40(3)	O4−Nd1−O9	73.61(3)
O1−Nd1−O3	106.45(3)	O5−Nd1−O6	65.95(3)
O1−Nd1−O4	72.39(3)	O5−Nd1−O7	83.86(3)
O1−Nd1−O5	135.03(3)	O5−Nd1−O8	84.64(3)
O1−Nd1−O6	131.31(3)	O5−Nd1−O9	138.17(3)
O1−Nd1−O7	139.79(3)	O6−Nd1−O7	66.13(4)
O1−Nd1−O8	70.27(3)	O6−Nd1−O8	69.73(4)
O1−Nd1−O9	74.74(4)	O6−Nd1−O9	72.23(3)
O2−Nd1−O3	69.53(2)	O7−Nd1−O8	135.31(4)
O2−Nd1−O4	103.50(3)	O7−Nd1−O9	80.08(5)
O2−Nd1−O5	72.77(3)	O8−Nd1−O9	80.36(4)
O2−Nd1−O6	127.74(3)	N1−Cu1−N2	84.37(5)
O2−Nd1−O7	139.30(3)	N1−Cu1−N3	178.57(8)
O2−Nd1−O8	76.01(4)	N1−Cu1−N4	95.23(9)
O2−Nd1−O9	138.52(4)	N2−Cu1−N3	96.72(8)
O3−Nd1−O4	65.59(2)	N2−Cu1−N4	177.94(8)
O3−Nd1−O5	71.98(2)	N3−Cu1−N4	83.72(11)
O3−Nd1−O6	122.18(2)	N5−Cu2−N6	84.31(4)
O3−Nd1−O7	71.76(3)	N5−Cu2−N7	171.89(5)
O3−Nd1−O8	142.65(4)	N5−Cu2−N8	96.61(5)
O3−Nd1−O9	136.02(4)	O23-a−Cu2−N5	86.66(7)
O4−Nd1−O5	135.40(3)	N6−Cu2−N7	96.43(5)
O4−Nd1−O6	128.29(3)	N6−Cu2−N8	165.81(5)
O4−Nd1−O7	70.68(3)	O23-a−Cu2−N6	111.94(7)
O4−Nd1−O8	138.82(3)	N7−Cu2−N8	84.66(6)

are characteristic of the bridging oxamido group,[24] and a broad strong band at ~1080 cm^{-1} is characteristic of perchlorate ions.[25]

The electronic absorption spectra of the two complexes were measured in acetronitrile solution. All complexes exhibit very intense bands below 400 nm, assignable to charge-transfer transitions in the Cu(II) chromophores and/or intraligand $\pi-\pi^*$ interactions.[6a] A relatively stronger band centered at 520 nm was observed and can be attributed to the d−d transitions of Cu(II) in an environment close to square planar.[24] The hypersensitive transition bands of the rare earth metal ions were not observed.[26]

Magnetic Properties. The magnetic susceptibilities were measured in the temperature range 5−300 K on a Quantum Design MPMS-7 SQUID magnetometer in an applied magnetic field of 10000 G (Figure 2). The $\chi_M T$ (where χ_M is the molar magnetic susceptibility) values are equal to 4.63 (**1**) and 5.05 (**2**) cm^3 mol^{-1} K at room temperature. These values of $\chi_M T$ are lower than those expected if the metal centers are not interacting (for **1**, 5.45 cm^3 mol^{-1} K; for **2**, 5.52 cm^3 mol^{-1} K, assuming $g_{Cu} = 2.0$, $g_{Pr} = {}^4/_5$, and $g_{Nd} = {}^8/_{11}$). For **1** (**2**), this value declines gradually between 300 and 50 K, where the $\chi_M T$ value is 3.68 (4.17) cm^3 mol^{-1} K; below 50 K, it falls sharply to 2.12 (2.50) cm^3 mol^{-1} K at 5 K. Fitting the data to the Curie−Weiss law gave $C = 4.5$, $\theta = -12.1$ K (**1**) and $C = 2.62$, $\theta = -10.8$ K (**2**). The θ values are large, indicating the importance of ligand field effects in these compounds.

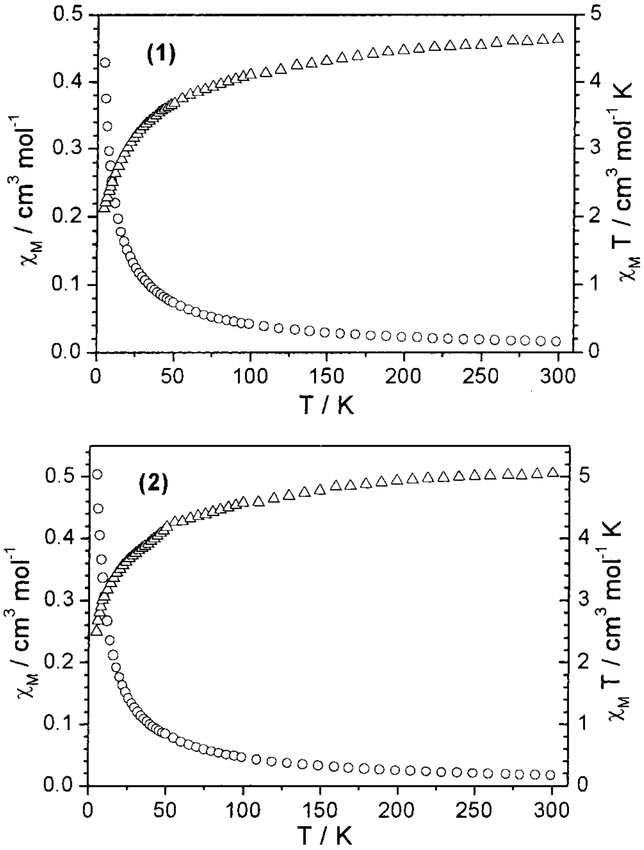

Figure 2. χ_M(○) versus T and $\chi_M T$(△) versus T plots for the nonanuclear species **1** and **2**.

In contrast to the Gd(III)−Cu(II) case, when a lanthanide (III) ion with an orbital contribution is involved in the interaction, the temperature dependence of $\chi_M T$ for the compound is due to both the $\chi_{Ln}T$ (χ_{Ln} stands for the magnetic susceptibility of Ln(III) ion) and the coupling between the Ln(III) ion and the other paramagnetic species. Consequently, the nature of the interactions between a Ln(III) ion with a first-order orbital momentum (such as Pr(III), Nd(III)) and the second paramagnetic species (such as Cu(II)) cannot be unambiguously deduced only from the shape of the $\chi_M T$ versus T curve or θ values.[27]

To gain some information concerning the interaction between Ln(III) ions with a first-order orbital momentum and the second paramagnetic ions, Kahn et al. have developed an experimental approach. However, it appeared necessary to synthesize an isostructural Ln(III) complex with a diamagnetic surrounding.[27] Unfortunately, for the two [NaLn$_2$Cu$_6$] compounds involved in this study, we have been unable to crystallize isostructural series of the present

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compounds. On the other hand, there are only a few studies addressing the strength of the interaction between Ln(III) with orbital momentum and the other paramagnetic species.[12a] Preliminary treatment of the magnetic data using an approximate approach, where Ln(III) is considered as free ions (Pr(III) and Nd(III)),[12a] cannot give reasonable results. As pointed out by Lloret et al.,[12a] this approach should be inappropriate, especially at low temperatures, where the energy gaps induced by ligand field effects are larger than KT, because the J values so obtained would include ligand field effects such as a selective depopulation of the low-lying levels. Thus, to get insight into the strength of these interactions, accurate models involving both the orbital contribution and ligand field effect have to be developed.

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Supporting Information Available: X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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