Synthesis and Characterizations of Heterometallic Lanthanide-Zinc Complexes $[La_2Zn_2(O_2CEt)_8(C_9H_7N)_2(NO_3)_2(H_2O)_2]$ and $[Yb_2Zn_2(O_2CEt)_8(C_9H_7N)_2(NO_3)_2]$

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Heterotetranuclear complexes $[La_2Zn_2(O_2CEt)_8(C_9H_7N)_2(NO_3)_2(H_2O)_2]$ and $[Yb_2Zn_2(O_2CEt)_8(C_9H_7N)_2(NO_3)_2]$ have been prepared and structurally characterized by X-ray crystallography. Magnetic measurement of the latter case shows that there exists weak antiferromagnetic exchange interaction between a pair of Yb^{3+} ions.

Heterometeallic complexes comprising both lanthanide (Ln) and transition metal ions have been actively investigated in the last few years.[1-8] Research in this area ranges from magnetical modeling applications to material and biological chemistry. Polynuclear lanthanide-group 12 metal complexes have been known to have a broad range of potential applications in the fields of Ln-doped semiconductor technology and photoluminescent materials.[8,9] Complexes of this type have been extensively studied in solid state.[9] By contrast, only relatively few such species have been synthesized and structurally characterized in molecular system by so far.[8] Herein we described the synthesis and crystal structures of $[La_2Zn_2(O_2CEt)_8(C_9H_7N)_2(NO_3)_2(H_2O)_2]$ and $[Yb_2Zn_2(O_2CEt)_8(C_9H_7N)_2(NO_3)_2]$, together with the magnetic properties of the latter complex. To the best of our knowledge, the present cases are the first two examples of carboxylate-bridged lanthanide-zinc complexes.[3-7]

Complex 1 and 2 were prepared and crystallized in the similar procedure. A mixture of $Zn(O_2CEt)_2$ (2 mmol), prepared according to the literature method,[10] and $Ln(NO_3)_3 \cdot 6H_2O$ (Ln = La 1, Yb 2) (1 mmol) was dissolved in EtOH (80 mmol), followed by addition of quinoline (2 cm^3). The resulting mixture was refluxed for 12 h, filtered while hot, and then concentrated to 20 mL. The filtrate was kept at room temperature for about two weeks to give well-shaped colorless crystals. Satisfactory element analyses were obtained for both complexes.[11] The IR spectra of 1 and 2 are similar and each shows two strong bands at *ca.* 1566 and 1558 cm^{-1} due to νasym(CO_2), and one broad and strong bands at *ca.* 1440 cm^{-1} due to νsym(CO_2), indicative of the presence of two different geometries of the coordinated propionate ligands, and characteristic absorptions corresponding to bidentate nitrate anions (1468 and 1309 cm^{-1}) and quinoline groups (1510, 811, 790 and 725 cm^{-1}).

X-ray crystallography[12] has established that complex **1** consists of a centrosymmetric tetranuclear $[La_2Zn_2(O_2CEt)_8(C_9H_7N)_2(NO_3)_2(H_2O)_2]$ molecule, the inversion residing on the midpoint of the La-La vector, as shown in Figure 1. Two zinc atoms are each coordinated by three carboxyl oxygen atoms and a quinoline molecule to form a distorted tetrahedron where the most distorted angles are 96.57(14)° for O22-Zn-N2. Each terminal Zn^{II} atoms is triply linked to the neighboring La^{3+} ion *via* three bidentate propionate bridges in a *syn-syn* fashion with the Zn-La distance of 4.1337(11) Å, and a pair of La^{3+} ions in two centrosymmetrically related dinuclear Zn-La subunits are linked together by two tridentate propionate bridges in both *syn-syn* and *syn-anti* fashions with the La-La distance of 4.3976(3) Å. As a result, the sequence of atoms Zn-La-La-Zn makes a broke line with a Zn-La-La angle of 161.61(2)°. The La^{3+} ion is nine coordinate, with six of the sites filled by three bidentate and two tridentate propionate ligands, two sites by a chelating nitrate anion and one site by a water molecule. The geometry of the La center is irregular, but it still can be related to a a tricapped trigonal prism with the two outer triangular faces formed by atoms O11, O21, O31 and O1, O41, O41a, and the three capping positions occupied by atoms Ow, O2 and O42a.

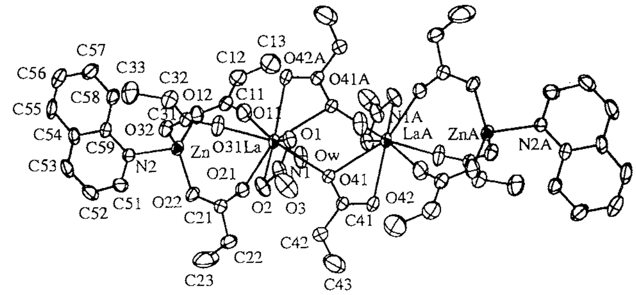

Figure 1. Molecular structure of complex 1. Selected bond distances (Å): La-Ow 2.568(4), La-O1 2.660(3), La-O2 2.651(3), La-O11 2.428(3), La-O21 2.425(3), La-O31, 2.427(3), La-O41 2.559(3), La-O41A^{i} 2.631(3), La-O42A^{i} 2.583(3), Zn-O12 1.942(3), Zn-O22 1.932(3), Zn-O32 1.936(3), Zn-N2 2.085(3). Symmetry code: ^{i} -x, -y, -z.

As shown in Figure 2, the structure[13] of complex **2** is similar to that of **1**. The only observed difference is in the lanthanide coordination sphere; the water molecule attached to La^{3+} in **1** has been lost, giving a coordination sphere consisting of eight oxygen atoms from three bidentate and two tridentate propionate ligands and a chelating nitrate anion. This change in coordination number is clearly caused by the smaller ionic radii of the heavier f-block metals associated with the lanthaniod contraction. Similar effects have been observed previously.[1c] The geometry of the ytterbium ion is based on a dodecahedron, with the two trapezia defined by O1, O2, O21, O31 and O11, O41, O41a, O42 intersecting at an angle of 90.2°. The arrangement of the two zinc and two ytterbium ions is also a broken line, but the angle of Zn-Yb-Yb angle, being 140.06(4)°, is substantially smaller than that observed for 1. The Zn-Yb and Yb-Yb separation distances are 3.850(2) and 3.922(2) Å, respectively.

Since Zn^{2+} ion has no unpaired electron and is diamagnetic, the tetranuclear Yb_2Zn_2 complex containing a pair of adjacent Yb^{3+} ions, is a very good and useful mode complex for investigation on the magnetic exchange interaction between Yb^{3+} ions. So the magnetic properties of complex 2 in the solid state have been investigate in the temperature range of 5-280 K. The observed magnetic moment at 300 K is 6.37 μ_B ($\mu_B \approx 9.27 \times 10^{-24}$ J·T^{-1}), which is nearly identical to that expected for two isolated Yb^{3+} ions (6.36 μ_B). Below this temperature, the moment decreases slightly with

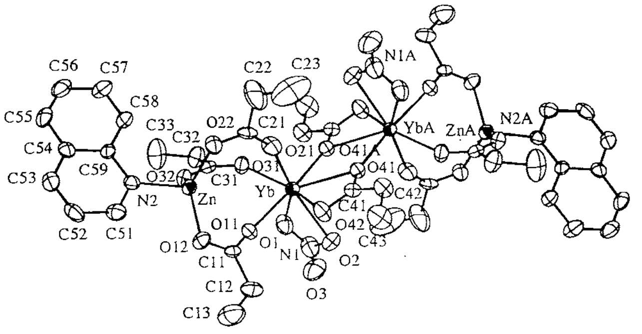

Figure 2. Molecular structure of complex **2**. Only one part of the disordered nitrate oxygen atoms is shown. Selected bond distances (Å): Yb-O1 2.38(1),Yb-O2 2.35(1), Yb-O11 2.188(9), Yb-O21 2.20(1), Yb-O31, 2.232(9), Yb-O41 2.425(6), Yb-O41A^{i} 2.253(9),Yb-O42 2.38(1), Zn-O12 1.97(1), Zn-O22 1.922(8), Zn-O32 1.94(1), Zn-N2 2.056(9). Symmetry code: ^{i}-x, -y, -z.

decreasing temperature, reaching a value of 5.15 μ_B at 5.0 K. This magnetic behavior suggests there exists weak anti-ferromagnetic exchange interaction between a pair of Yb^{3+} ions in the molecule. Further study on the synthesis, magnetic and other properties of series carboxylate-bridged lanthanide-zinc complexes is in progress.

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11 Elemental analyses: **1**. Found: C, 35.58; H, 4.16; N, 4.00%. Calcd for $C_{42}H_{58}N_4La_2Zn_2O_{24}$: C, 35.74; H, 4.14; N, 3.97%. **2**. Found: C, 34.82; H, 3.95; N, 3.88%. Calcd for $C_{42}H_{54}N_4Yb_2Zn_2O_{22}$: C, 34.94; H, 3.77; N, 3.88%

10 Crytal data for **1**: $C_{42}H_{58}N_4La_2Zn_2O_{24}$, F.W = 1411.48, triclinic, P-1(#2), a = 8.1705(2), b = 11.7024(2), c = 16.4877(1) Å, α = 108.601(1), β = 102.572(1), γ = 95.156(1)°, V = 1436.5(1) $Å^3$, Z = 1, D_c = 1.632 g·cm^{-3}, μ(Mo-Kα) = 2.360 mm^{-1}. Measurements were carried out on a SMART CCD diffractometer. The structures was solved by direct methods and refined by full-matrix least squares (on F^2). The final R1 = 0.033 and wR = 0.078 for 4094 observed reflections (I > 2.00σ(I)).

10 Crytal data for **2**: $C_{42}H_{54}N_4Yb_2Zn_2O_{22}$, F.W = 1443.74, triclinic, P-1(#2), a =11.169(3), b = 11.698(4), c = 11.761(3) Å, α = 63.40(2), β = 73.28(2), γ = 84.20(2)°, V = 1315(2) $Å^3$, Z = 1, D_c = 1.82 g·cm^{-3}, μ(Mo-Kα) = 4.51 mm^{-1}. Measurements were carried out on an Enraf-Nonius CAD4 diffractometer. The structure was solved by direct methods and refined by full-matrix least squares (on F). The atom O3 of the chelating nitrate is disordered over two sites having relative occupancies 0.60/0.40. The final R1 = 0.052 and Rw = 0.062 for 3340 observed reflections (I > 3.00σ(I)).