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Synthesis and Structural Characterization of Tetra- and Pentanuclear Lanthanide Hydroxido Clusters

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Tetra- and pentanuclear lanthanide clusters having dibenzoylmethanido and *o*-nitrophenolato as ligands in the coordination sphere were prepared. Treating $[LnCl_3\cdot 6H_2O]$ (Ln = Er, Tm) with dibenzoylmethane and *o*-nitrophenol in the presence of triethylamine yielded the pentanuclear lanthanide clusters $HNEt_3^+[Ln_5(\mu_3\text{-}OH)_4(\mu_4\text{-}OH)(Ph_2acac)_7(o\text{-}O_2NC_6H_4O)_3Cl]^-$ (Ln = Er, Tm). Under the same reaction conditions but using Yb and Lu as center metals, tetranuclear lanthanide clusters $[Ln_4(\mu_3\text{-}OH)_2(Ph_2acac)_8(o\text{-}O_2NC_6H_4O)_2]$ (Ln = Yb, Lu) were obtained. The structures of all new compounds were confirmed by single-crystal X-ray diffraction. The anions of the pentanuclear lanthanide cores are square pyramidal. Each triangular face of the square pyramid is capped by one μ_3-O moiety. In the square base, four lanthanide atoms are linked by one μ_4-O atom. The formation of the hydroxido bridges can be explained by deprotonation of the coordinated water molecules.

Introduction

Inorganic clusters continue to attract considerable attention, as they represent the bridge linking molecular and solid-state chemistry, and also because they act as useful tools to understand the size-dependent physical properties of electronic materials.[1] While the cluster chemistry of the d-block transition metals is now firmly established, and huge clusters (especially of molybdenum,[2] copper,[3] silver,[4] and gold[5]) have been isolated, the analogous chemistry of the lanthanides is virtually undeveloped.[6,7] This is even more surprising, since oligomeric lanthanide structures are proposed to play a key role in some catalytic transformations.[8,9] It is well known that the most stable lanthanide clusters are oxido/hydroxido clusters.[10] Recently, we, along with others, synthesized new tetradeca- and pentadecanuclear lanthanide oxido/hydroxido clusters.[7,11] Basically, two different approaches towards the preparation of oxido/hydroxido clusters were investigated. One way to obtain these compounds is the hydrolysis of moisture-sensitive starting material,[11,12] whereas the other approach is a hydrolytic one in which the water molecules are deprotonated in a controlled way.[13–18] Most of the oxido/hydroxido clusters are stabilized by ligands such as alkoxides,[19,20] phenoxides,[21] diketones,[22,23] and more recently amino acids[7,24] and the *o*-nitrophenolato ligand.[11]

In a recent communication, we reported the synthesis and structure of a pentanuclear yttrium cluster, $H_5[Y_5(\mu_4\text{-}O)(\mu_3\text{-}O)_4(\mu\text{-}\eta^2\text{-}Ph_2acac)_4\eta^2\text{-}(Ph_2acac)_6]$. It was obtained by treating $[YCl_3\cdot 6H_2O]$ with dibenzoylmethane (Ph$_2$acacH) in the presence of triethylamine.[14] The cluster was found to catalyze the oxidation of aldehydes to the corresponding carboxylic acids in the presence of air. An isostructural cluster having europium as the center metal was reported.[13] In contrast, by using the larger lanthanides, tetranuclear clusters of composition $[Ln_4(\mu_3\text{-}OH)_2(Ph_2acac)_{10}]$ (Ln = Pr, Nd, and Sm) were obtained in a similar manner.[15] Single-crystal X-ray analysis of these compounds revealed that each cluster consists of four lanthanide atoms, two μ_3-oxygen atoms, and ten Ph$_2$acac ligands, which make up the peripheral part of the cluster. Three types of coordination modes [η^2-, (μ-O)-η^2-, and (μ-O)$_2$-η^2] are observed for the ligation of Ph$_2$acac to the metal centers.

The second ligand that we successfully introduced in the synthesis of lanthanide clusters is *o*-nitrophenolato.[11] Infinite chains of composition $[(thf)_4\{K(o\text{-}O_2NC_6H_4O)_4\text{-}Ln\}_4]_n$ (Ln = Y, Er, Lu), infinite layers of composition $[\{K_2(o\text{-}O_2NC_6H_4O)_5Tb\}_n]$ and $[\{K_2(o\text{-}O_2NC_6H_4O)_5Ln)\}_n]$ (Ln = Sm, Eu), as well as tetradecanuclear clusters of composition $H_{18}[Ln_{14}(\mu\text{-}\eta^2\text{-}o\text{-}O_2NC_6H_4O)_8(\eta^2\text{-}o\text{-}O_2NC_6H_4O)_{16}\text{-}(\mu_4\text{-}O)_2(\mu_3\text{-}O)_{16}]$ (Ln = Dy, Er, Tm, Yb), were obtained by using *o*-nitrophenolato as a ligand under different reaction conditions. Thus, *o*-nitrophenolato is a ligand that features different coordination modes and is thus able to stabilize different sorts of coordination polymers and oligomers.

We are now interested in synthesizing lanthanide clusters having both the dibenzoylmethanido and *o*-nitrophenolato ligands in the coordination sphere. Herein, we report on the synthesis and structure of a series of novel tetra- and

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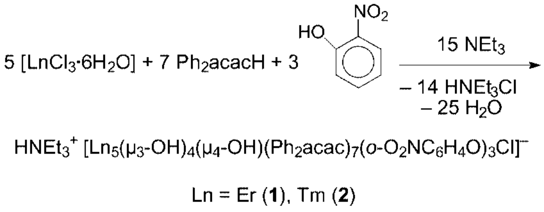
pentanuclear clusters of composition $HNEt_3^+[Ln_5(\mu_3\text{-}OH)_4(\mu_4\text{-}OH)(Ph_2acac)_7(o\text{-}O_2NC_6H_4O)_3Cl]^-$ (Ln = Er, Tm), and $[Ln_4(\mu_3\text{-}OH)_2(Ph_2acac)_8(o\text{-}O_2NC_6H_4O)_2]$ (Ln = Yb, Lu).



Scheme 1.

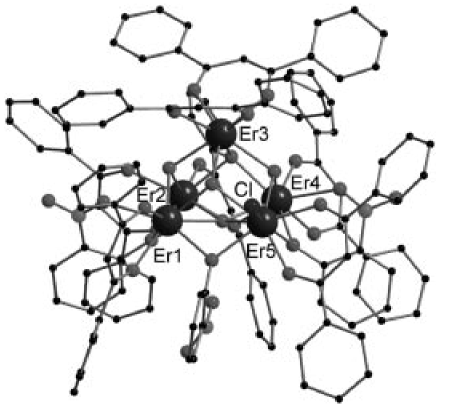


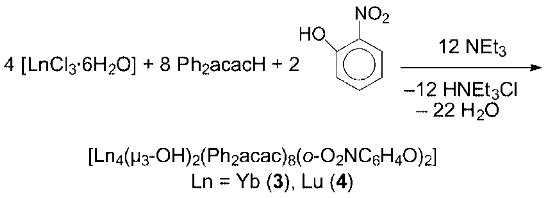
Figure 1. Solid-state structure of the anion of **1** showing the atom labeling scheme, with omission of hydrogen atoms. The small and larger dark spheres indicate carbon and oxygen atoms, respectively, and the lighter spheres stand for nitrogen atoms. Selected bond lengths [pm] (also given for the isostructural compound **2**): Er1–O1 222.8(2), Er1–O2 223.6(2), Er1–O3 229.2(2), Er1–O4 246.2(2), Er1–O21 228.9(2), Er1–O24 232.7(2), Er1–O25 250.0(3), Er1–O26 227.0(2), Er2–O3 230.6(2), Er2–O6 224.8(2), Er2–O7 222.1(2), Er2–O8 230.6(2), Er2–O9 230.5(2), Er2–O24 231.0(2), Er2–O25 250.6(2), Er2–O27 232.9(2), Er3–O10 227.1(2), Er3–O11 228.7(2), Er3–O12 227.8(2), Er3–O13 230.8(2), Er3–O24 235.6(2), Er3–O26 236.6(2), Er3–O28 237.4(2), Er3–O27 236.3(2), Er4–O9 234.3(2), Er4–O14 223.5(2), Er4–O15 224.1(2), Er4–O16 227.7(2), Er4–O17 244.2(2), Er4–O25 243.6(2), Er4–O27 227.8(2), Er4–O28 232.9(2), Er5–O16 234.5(3), Er5–O19 224.8(2), Er5–O20 222.8(2), Er5–O21 229.7(2), Er5–O25 263.7(2), Er5–O26 232.0(2), Er5–O28 230.3(2), Er5–Cl 272.2(4). **2**: Tm1–O1 225.31(11), Tm1–O2 223.63(11), Tm1–O3 229.00(13), Tm1–O4 247.13(13), Tm1–O21 230.68(14), Tm1–O24 232.59(13), Tm1–O26 226.34(12), Tm1–O25 248.56(10), Tm2–O3 232.16(13), Tm2–O6 226.65(12), Tm2–O7 223.77(13), Tm2–O8 230.99(12), Tm2–O9 230.17(13), Tm2–O24 229.68(12), Tm2–O25 250.59(12), Tm2–O27 231.60(12), Tm3–O10 228.69(12), Tm3–O11 232.36(13), Tm3–O12 228.49(11), Tm3–O13 230.87(12), Tm3–O24 235.50(12), Tm3–O26 235.79(13), Tm3–O27 235.37(12), Tm3–O28 236.22(12), Tm4–O9 234.68(13), Tm4–O14 225.27(13), Tm4–O15 224.96(10), Tm4–O16 228.58(14), Tm4–O17 245.18(12), Tm4–O25 242.31(10), Tm4–O27 228.14(13), Tm4–O28 231.56(12), Tm5–O16 234.86(13), Tm5–O19 226.76(13), Tm5–O20 226.54(13), Tm5–O21 229.54(14), Tm5–O25 262.70(11), Tm5–O26 230.26(13), Tm5–O28 230.37(13), Tm5–Cl 272.6(2).

Results and Discussion

Reaction of $[LnCl_3{\cdot}6H_2O]$[25] with dibenzoylmethane and *o*-nitrophenol in methanol, in the presence of triethylamine as a base, yielded the pentanuclear lanthanide clusters $HNEt_3^+[Ln_5(\mu_3\text{-}OH)_4(\mu_4\text{-}OH)(Ph_2acac)_7(o\text{-}O_2NC_6H_4O)_3Cl]^-$ [Ln = Er (**1**), Tm (**2**)] (Scheme 1). As the clusters were soluble in methanol, we used toluene to extract them from the reaction mixture. The clusters have been characterized by standard analytical and spectroscopic techniques. The solid-state structures of compounds **1** and **2** were established by single-crystal X-ray diffraction. They crystallize in the monoclinic space group $P2_1/c$ and have four molecules in the unit cell. Crystals of compounds **1** and **2** that consist of an ion pair composed of a $HNEt_3^+$ cation and a $[Ln_5(\mu_3\text{-}OH)_4(\mu_4\text{-}OH)(Ph_2acac)_7(o\text{-}O_2NC_6H_4O)_3Cl]^-$ anion are isomorphous (Figure 1). The anions consist of pentanuclear lanthanide cores in a square pyramidal arrangement. This pentanuclear arrangement of the Ln core in compounds **1** and **2** is a common structural motif for lanthanide oxido/hydroxido clusters[13,14,26] and is observed in compounds such as $[Y_9O_2(OH)_8(aacac)_{16}]^-$[10] (aacac = allylacetoacetate), $[Ln_9O_2(OH)_8(ba)_{16}]^-$[12] (ba = benzoylacetone and Ln = Sm, Eu, Gd, Dy, Er), $H_{18}[Ln_{14}(\mu\text{-}\eta^2\text{-}o\text{-}O_2NC_6H_4O)_8(\eta^2\text{-}o\text{-}O_2NC_6H_4O)_{16}(\mu_4\text{-}O)_2(\mu_3\text{-}O)_{16}]$ (Ln = Dy, Er, Tm, Yb), and related compounds.[11,13] In contrast to these neutral clusters, compounds **1** and **2** contain anionic species. Each triangular face of the square pyramid is capped by one μ_3-O moiety. In the square base, four lanthanide atoms are linked by one μ_4-O atom. The pentanuclear Ln core is surrounded by ten peripheral ligands and a chlorine atom. A comparison with the pure dibenzoylmethanido clusters $[Ln_5(OH)_5(Ph_2acac)_{10}]$ is quite interesting. In $[Ln_5(OH)_5(Ph_2acac)_{10}]$, six ligands are terminal chelates and four are bridging chelates bonding to two metal ions that belong to the base of the polyhedron. In compounds **1** and **2**, three of the four bridging dibenzoylmethanido ligands are formally substituted by *o*-nitrophenolato ligands. The phenolate oxygen atoms always bridge two lanthanide atoms. Two of the three *o*-nitrophenolato ligands also bind a lanthanide atom through one oxygen atom of the NO_2 group, whereas the NO_2 group of the third *o*-nitrophenolato ligand, located between Ln1 and Ln5, is turned away from the cluster core. This generates a free coordination site on Ln5, which is occupied by a chlorine atom, and results in a negatively charged cluster core.

The formation of the hydroxido bridges can be explained by the presence of water in the solvents[27] and by the six water molecules coordinated to the metal center through the oxygen atom in the starting material $[LnCl_3{\cdot}6H_2O]$.[25] Addition of base leads only to the deprotonation of the coordinated water molecules. The bridging oxygen atoms in the core of the cluster are parts of hydroxy groups; this is confirmed by a broad peak around 3425 cm^{-1} in the IR spectra. The Ln–O bond lengths to the dibenzoylmethanido and to the *o*-nitrophenolato ligands are in the expected range of 222.8(2) to 246.2(2) pm for compound **1** and 223.63(11) to 247.13(13) pm for compound **2**. Each triangular face of the square pyramid is capped by one μ_3-O group, whereas the square plane is capped by one μ_4-bonded oxygen atom. The Ln–O bond lengths of the μ_4-oxygen atoms are in the range of 243.6(2) to 263.7(2) pm in **1** and 242.31(10) to 262.70(11) pm in **2**. The Ln–Cl bond lengths are 272.2(4) pm in **1** and 272.6(2) pm in **2**. Selected metric parameters are given in the caption of Figure 1.

Since it is well known that dramatic changes in the microstructure of lanthanide clusters are observed by altering the ionic radius of the center metal, we were also interested in using smaller lanthanides. Under the same reaction conditions as those used to prepare compounds **1** and **2**, but using Yb and Lu as center metals, tetranuclear lanthanide clusters of composition $[Ln_4(\mu_3\text{-}OH)_2(Ph_2acac)_8(o\text{-}O_2NC_6H_4O)_2]$ [Ln = Yb (**3**), Lu (**4**)] were obtained (Scheme 2). The solid-state structures of compounds **3** and **4** were established by single-crystal X-ray diffraction, which revealed that they are tetranuclear (Figure 2). A comparable Ln_4 core was observed earlier in $[Nd_4(\mu_3\text{-}OH)_2(\mu_2\text{-},\mu_1\text{-}acac)_6(acac)_4]$ (acac = acetylacetonate)[28] and $[Ln_4(\mu_3\text{-}OH)_2(Ph_2acac)_{10}]$ (Ln = Pr, Nd, and Sm).[15] Compounds **3** and **4** are pseudopolymorphic to each other, because the amount of noncoordinated solvent (toluene) in the unit cell differs for each compound. Two types of coordination modes are observed for the ligation of Ph_2acac to the metal centers in the clusters. Of the eight Ph_2acac ligands, six chelate the metal centers in η^2 fashion, and two more both chelate and bridge two metal centers, thus they are $(\mu\text{-}O)_2\text{-}\eta^2$-coordinating. The *o*-nitrophenolato ligands chelate one metal atom and bridge another metal atom through one oxygen atom, thus they are $(\mu\text{-}O)\text{-}\eta^2$-coordinating. A comparison with the pure dibenzoylmethanido clusters $[Ln_4(\mu_3\text{-}OH)_2(Ph_2acac)_{10}]$ (Ln = Pr, Nd, and Sm)[15] shows the same interesting features as those observed for compounds **1** and **2**. The tetranuclear Ln core in $[Ln_4(\mu_3\text{-}OH)_2(Ph_2acac)_{10}]$ is similar to that in compounds **3** and **4**. Moreover, the Ph_2acac ligands coordinate in a similar η^2- and $(\mu\text{-}O)_2\text{-}\eta^2$ fashion. The only difference between compounds **3** and **4** and $[Ln_4(\mu_3\text{-}OH)_2(Ph_2acac)_{10}]$ is the presence of the two *o*-nitrophenolato ligands. In $[Ln_4(\mu_3\text{-}OH)_2(Ph_2acac)_{10}]$, the positions of the *o*-nitrophenolato ligands are formally replaced by two more Ph_2acac ligands, which bind in the same arrangement [$(\mu\text{-}O)\text{-}\eta^2$-coordination]. A significant difference arises with respect to the ionic radius of the center metal. Whereas in the pure Ph_2acac clusters the cluster size decreases from penta- to tetranuclear by increasing the ionic radius, the opposite trend is observed for the mixed Ph_2acac/*o*-nitrophenolato compounds. In compounds **3** and **4**, the two μ_3-oxygen atoms in the core of the cluster are parts of hydroxy groups, as revealed by a broad peak around 3430 cm^{-1} in the IR spectra. This is supported by the Ln–O12–Ln bond angles, which are close to tetrahedral (e.g. for compound **4**: Lu1–O12–Lu1′ 108.20(6)°, Lu1–O12–Lu2 108.75(8)°, and Lu1–O12–Lu2′ 103.54(7)°). Each metal is coordinated to eight oxygen atoms in a square antiprismatic arrangement. The metal-to-oxygen distances of the coordinated ligands range from 230.1(5) to 240.7(6) pm (**3**) and from 234.5(2) to 243.6(2) pm (**4**) for the *o*-nitrophenolato ligands; for the Ph_2acac ligands, the distances range from 223.1(5) to 257.6(7) pm in **3** and from 222.8(2) to 272.0(2) pm in **4**. Selected metric parameters are given in the caption of Figure 2.



Scheme 2.

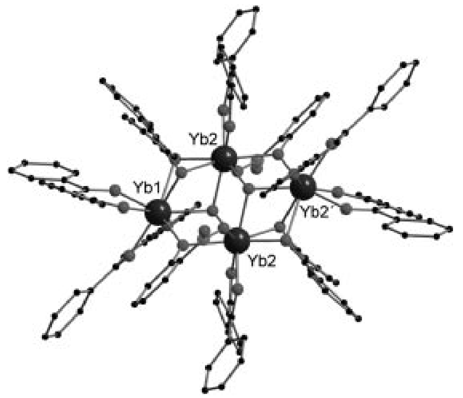


Figure 2. Solid-state structure of **3** showing the atom labeling scheme, with omission of hydrogen atoms. The small and larger dark spheres indicate carbon and oxygen atoms, respectively, and the lighter spheres stand for nitrogen atoms. Selected bond lengths [pm] (also given for the similar compound **4**): Yb1–O1 223.2(5), Yb1–O2 223.6(6), Yb1–O3 223.5(6), Yb1–O4 224.1(5), Yb1–O5 235.5(5), Yb1–O8 245.8(5), Yb1–O9 257.6(7), Yb1–O12 231.7(5), Yb2–O5′ 230.1(5), Yb2–O7 240.7(6), Yb2–O8 238.0(5), Yb2–O9 233.8(6), Yb2–O10 223.1(5), Yb2–O11 223.4(5), Yb2–O12 227.8(5), Yb2–O12′ 225.3(5). **4**: Lu1–O1 224.63(15), Lu1–O2 222.8(2), Lu1–O3 231.1(2), Lu1–O4 235.34(15), Lu1–O5 227.5(2), Lu1–O6 239.1(2), Lu1–O12 227.4(2), Lu1–O12′ 229.43(15), Lu2–O3 235.54(15), Lu2–O4 272.0(2), Lu2–O5′ 235.9(2), Lu2–O8 224.0(2), Lu2–O9 222.8(2), Lu2–O10 223.40(15), Lu2–O11 223.4(2), Lu2–O12′ 229.6(2), Lu3–O13 222.7(2), Lu3–O14 222.7(2), Lu3–O17 226.9(2), Lu3–O24 228.1(2), Lu3–O24′ 227.5(2), Lu3–O15 233.1(2), Lu3–O16 237.4(2), Lu3–O18 243.6(2), Lu4–O15 254.2(2), Lu4–O16 242.50(14), Lu4–O17′ 234.5(2), Lu4–O20 223.1(2), Lu4–O21 224.8(2), Lu4–O22 224.2(2), Lu4–O23 222.62(14), Lu4–O24 229.8(2).

Conclusion

In summary, a series of tetra- and pentanuclear lanthanide clusters having dibenzoylmethanido and *o*-nitrophenolato as ligands in the coordination sphere were synthesized. By using the larger lanthanides as center metals, ionic clusters of composition $HNEt_3^+[Ln_5(\mu_3\text{-}OH)_4(\mu_4\text{-}OH)(Ph_2acac)_7(o\text{-}O_2NC_6H_4O)_3Cl]^-$ (Ln = Er, Tm) were obtained. In contrast, by using the smaller center metals Yb and Lu, clusters of composition $[Ln_4(\mu_3\text{-}OH)_2(Ph_2acac)_8(o\text{-}O_2NC_6H_4O)_2]$ were isolated. The formation of the hydroxido bridges can be explained by the six water molecules, which are coordinated through the oxygen atom to the metal center of the starting material, [$LnCl_3{\cdot}6H_2O$]. Addition of base leads only to deprotonation of the coordinated water molecules. The bridging oxygen atoms in the cores of the clusters are parts of hydroxy groups, as revealed by the broad band in the IR spectra.

A comparison of the new mixed dibenzoylmethanido/*o*-nitrophenolato clusters with pure dibenzoylmethanido clusters shows the relationship between the two classes of clusters. Formally, the dibenzoylmethanide groups, which act in the pure dibenzoylmethanido clusters as tridentate ligands and bind in a (μ-O)-η^2 mode, are replaced by *o*-nitrophenolato ligands.

Experimental Section

General Considerations: Deuterated solvents were obtained from Chemotrade or Euriso-Top GmbH (99% D atoms). NMR spectra were recorded with a Jeol JNM-LA 400 FT-NMR spectrometer. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane. Raman spectra were recorded with a Bruker RFS 100. IR spectra were recorded with a Shimadzu FTIR-8400s. Elemental analyses were carried out with an Elementar vario EL. The lanthanide starting materials were synthesized from the corresponding oxides by neutralizing with concentrated hydrochloric acid, followed by concentration to dryness. Dibenzoylmethane, triethylamine, and the solvents were used as purchased from commercial sources without further purification.

General Procedure for the Preparation of $HNEt_3^+[Ln_5(\mu_3\text{-}OH)_4(\mu_4\text{-}OH)(Ph_2acac)_7(o\text{-}O_2NC_6H_4O)_3Cl]^-$ [Ln = Er (1), Tm(2)] and $[Ln_4(\mu_3\text{-}OH)_2(Ph_2acac)_8(o\text{-}O_2NC_6H_4O)_2]$ [Ln = Yb (3), Lu (4)]: Ph_2acacH (292 mg, 1.30 mmol) and *ortho*-nitrophenol (181 mg, 1.30 mmol) were combined in methanol (20 mL). Excess triethylamine (5.20 mmol) was slowly added to the resulting solution, and the reaction mixture was stirred for 1 h at room temp. To this was added a solution of the corresponding lanthanide trichloride hydrate (1.30 mmol) in methanol (20 mL), and the resulting yellow solution was stirred overnight at room temp. A crimson–yellow precipitate formed and was filtered off before the solvent was removed in vacuo. The residue was dissolved in toluene (5 mL) and stirred for 2 h, at which point the solution was filtered. Slow evaporation of toluene at room temp. yielded yellow crystals.

$HNEt_3^+[Ln_5(\mu_3\text{-}OH)_4(\mu_4\text{-}OH)(Ph_2acac)_7(o\text{-}O_2NC_6H_4O)_3Cl]^-$ [Ln = Er (1), Tm (2)]

1: Yield (single crystals): 100 mg (13%). IR (KBr): 3610 (m), 3525 (m), 3427 (m) (νOH), 3060 (m), 3026 (m), 1603 (s) (νCO), 1552 (s), 1521 (s) (νC$\cdots$C), 1479 (s), 1454 (s), 1441 (w), 1397 (s), 1341 (w), 1329 (w), 1315 (w), 1289 (w), 1253 (w), 1223 (w), 1180 (w), 1156 (w), 1137 (w), 1069 (w), 1023 (w), 1000 (w), 942 (w), 910 (w), 885 (w), 859 (w), 835 (w), 812 (w), 784 (w), 749 (m), 721 (m) (νC-H def), 687 (m), 618 (w), 610 (w), 526 (w) cm^{-1}. Raman (solid): 402 (w), 617 (w), 687 (w), 786 (w), 941 (m), 1000 (s), 1031 (w), 1062 (w), 1156 (w), 1181 (w), 1287 (s), 1315 (s), 1442 (w), 1490 (w), 1596 (s), 3064 (s) cm^{-1}. $C_{146.50}H_{130}ClEr_5N_4O_{28}$ (= **1**·2.5toluene) (3263.75): calcd. C 53.86, H 3.98, N 1.71; found C 53.75, H 3.52, N 1.75.

2: Yield (single crystals): 100 mg (13%). IR (KBr): 3601 (m), 3519 (m), 3426 (m) (νOH), 3060 (m), 3026 (m), 1603 (s) (νCO), 1553 (s), 1521 (s) (νC$\cdots$C), 1479 (s), 1454 (s), 1441 (w), 1399 (s), 1341 (w), 1329 (w), 1315 (w), 1289 (w), 1253 (w), 1224 (w), 1181 (w), 1157 (w), 1137 (w), 1070 (w), 1023 (w), 1000 (w), 942 (w), 885 (w), 859 (w), 836 (w), 812 (w), 784 (w), 750 (m), 721 (m) (νC–H def), 687 (m), 618 (w), 610 (w), 527 (w) cm^{-1}. Raman (solid): 402 (w), 579 (w), 617 (w), 688 (w), 785 (w), 942 (m), 1000 (s), 1033 (w), 1064 (w), 1157 (w), 1182 (w), 1224 (w), 1242 (w), 1289 (s), 1321 (s), 1442 (w), 1490 (m), 1596 (s), 3065 (s) cm^{-1}. $C_{146.50}H_{130}ClN_4O_{28}Tm_5$ (= **2**·2.5toluene) (3272.10): calcd. C 53.72, H 3.97, N 1.71; found C 53.09, H 3.65, N 1.67.

$[Ln_4(\mu_3\text{-}OH)_2(Ph_2acac)_8(o\text{-}O_2NC_6H_4O)_2]$ [Ln = Yb (3), Lu (4)]

3: Yield (single crystals): 220 mg (25%). IR (KBr): 3587 (m), 3429 (m) (νOH), 3058 (m), 3025 (m), 1597 (s) (νCO), 1553 (s), 1522 (s) (νC$\cdots$C), 1479 (s), 1455 (s), 1441 (w), 1404, 1341 (w), 1330 (w), 1316 (w), 1298 (w), 1290 (w), 1243 (w), 1223 (w), 1181 (w), 1156 (w), 1143 (w), 1069 (w), 1023 (w), 1000 (w), 942 (w), 925 (w), 885 (w), 862 (w), 836 (w), 819 (w), 812 (w), 785 (w), 750 (m), 721 (m) (νC–H def), 686 (m), 618 (w), 610 (w), 527 (w) cm^{-1}. Raman (solid): 525 (w), 617 (w), 688 (w), 705 (w), 749 (w), 790 (w), 810 (w), 842 (w), 942 (m), 1000 (s), 1024 (w), 1063 (w), 1126 (w), 1156 (w), 1181 (w), 1223 (w), 1284 (s), 1316 (s), 1377 (m), 1443 (w), 1490 (m), 1507 (w), 1552 (w), 1569 (w), 1596 (s), 3062 (s) cm^{-1}. $C_{132}H_{98}N_2O_{24}Yb_4$ (2786.16): calcd. C 56.85, H 3.51, N 1.00; found C 55.85, H 3.43, N 1.18.

4: Yield (single crystals): 100 mg (11.1%). ^1H NMR (400 MHz, [D_8]thf, 25 °C): δ = 2.29 (s), CH), 7.30–7.39 (m, 58 H, PhH), 8.07 (d, 30 H, PhH) ppm. IR (KBr): 3601 (m), 3430 (m) (νOH), 3059 (m), 3026 (m), 1598 (s) (νCO), 1554 (s), 1522 (s) (νC$\cdots$C), 1479 (s), 1455 (s), 1441 (m), 1405 (s), 1331 (m), 1316 (m), 1245 (m), 1224 (m), 1181 (w), 1156 (w), 1143 (w), 1069 (w), 1024 (w), 1000 (w), 988 (w), 971 (w), 942 (w), 926 (w), 885 (w), 868 (w), 837 (w), 812 (w), 785 (w), 750 (m), 720 (m) (νC–H def), 687 (m), 618 (w), 610 (w), 578 (w), 526 (w) cm^{-1}. Raman (solid): 402 (w), 578 (w), 617 (w), 688 (w), 789 (w), 836 (w), 886 (w), 942 (m), 1000 (s), 1026 (w), 1033 (w), 1065 (w), 1156 (w), 1182 (w), 1224 (w), 1243 (w), 1288 (s), 1319 (s), 1442 (w), 1490 (m), 1520 (w), 1561 (w), 1597 (s), 3066 (s) cm^{-1}. $C_{132}H_{98}Lu_4N_2O_{24}$ (2793.87): calcd. C 56.69, H 3.51, N 1.00; found C 56.16, H 3.42, N 1.43.

X-ray Crystallographic Studies of 1–4: Suitable crystals of **1**–**4** were covered in mineral oil (Aldrich) and mounted onto a glass fiber. The crystal was transferred directly to the cold (–73 °C or –100 °C) N_2 stream of a Stoe IPDS 2T or Bruker Smart 1000 CCD. Subsequent computations were carried out with an Intel Pentium IV PC.

Data Collection and Refinement: Data were processed with SHELXS-97[29] and SHELXL-97.[30]

$HNEt_3^+[Er_5(\mu_3\text{-}OH)_4(\mu_4\text{-}OH)(Ph_2acac)_7(o\text{-}O_2NC_6H_4O)_3Cl]^-{\cdot}$2.5toluene (1): Monoclinic, space group $P2_1/c$ (No. 14); lattice constants a = 2165.5(9) pm, b = 1976.2(6) pm, c = 3312(3) pm, β = 95.50(5)°, V = 14109(13) × 10^6 pm^3, Z = 4; μ(Mo-K_α) = 3.031 mm^{-1}; $2\theta_{max.}$ = 50.0°; 13128 (R_{int} = 0.1037) independent reflections were measured, 13128 of which, observed with $I > 2\sigma(I)$, were considered; max. residual electron density 1.328 and –1.122 e/A^{-3}; 1385 parameters (all non-hydrogen atoms except those in the thf molecules were calculated anisotropically; for H atoms, the idealized positions were calculated) R_1 = 0.0592; wR_2 = 0.1637.

$HNEt_3^+[Tm_5(\mu_3\text{-}OH)_4(\mu_4\text{-}OH)(Ph_2acac)_7(o\text{-}O_2NC_6H_4O)_3Cl]^-{\cdot}$2.5toluene (2): Monoclinic, space group $P2_1/c$ (No. 14); lattice constants a = 2166.89(7) pm, b = 1989.77(5) pm, c = 3308.94(10) pm, β = 95.741(3)°, V = 14195.3(7) × 10^6 pm^3, Z = 4; μ(Mo-K_α) = 3.182 mm^{-1}; $2\theta_{max.}$ = 53.6°; 29856 (R_{int} = 0.0703) independent reflections were measured, 20804 of which, observed with $I > 2\sigma(I)$, were considered; max. residual electron density 1.686 and –2.017 e/A^{-3}; 1384 parameters (all non-hydrogen atoms except those in the thf molecules were calculated anisotropically; for H atoms, the idealized positions were calculated) R_1 = 0.0548; wR_2 = 0.1551.

$[Yb_4(\mu_3\text{-}OH)_2(Ph_2acac)_8(o\text{-}O_2NC_6H_4O)_2]\cdot$6toluene (3): Triclinic, space group $P\bar{1}$ (No. 2); lattice constants a = 1392.42(8) pm, b = 1613.72(10) pm, c = 1820.81(10) pm, α = 84.901(5)°, β = 74.180(4)°, γ = 73.985(5)°, $V = 3783.2(4) \times 10^6$ pm^3, Z = 1; $\mu(\text{Mo-}K_\alpha)$ = 2.519 mm^{-1}; $2\theta_{\text{max.}}$ = 58.5°; 19861 (R_{int} = 0.0713) independent reflections were measured, 14450 of which, observed with $I > 2\sigma(I)$, were considered; max. residual electron density 2.245 and –3.913 e/A^{-3}; 887 parameters (all non-hydrogen atoms except those in the thf molecules were calculated anisotropically; for H atoms, the idealized positions were calculated) R_1 = 0.0731; wR_2 = 0.2427.

$[Lu_4(\mu_3\text{-}OH)_2(Ph_2acac)_8(o\text{-}O_2NC_6H_4O)_2]\cdot$2toluene (4): Triclinic, space group $P\bar{1}$ (No. 2); lattice constants a = 1419.7(5) pm, b = 1440.7(5) pm, c = 3090.1(5) pm, α = 83.974(5)°, β = 84.109(5)°, γ = 81.588(5)°, $V = 6193(3) \times 10^6$ pm^3, Z = 2; $\mu(\text{Mo-}K_\alpha)$ = 3.235 mm^{-1}; $2\theta_{\text{max.}}$ = 50.2°; 21707 (R_{int} = 0.0633) independent reflections were measured, 14033 of which, observed with $I > 2\sigma(I)$, were considered; max. residual electron density 1.434 and –1.717 e/A^{-3}; 1356 parameters (all non-hydrogen atoms except those in the thf molecules were calculated anisotropically; for H atoms, the idealized positions were calculated) R_1 = 0.0505; wR_2 = 0.1400.

CCDC-641082 to CCDC-641085 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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