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Heterometallic Group 4–Lanthanide Oxo-alkoxide Precursors for Synthesis of Binary Oxide Nanomaterials

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ABSTRACT: In this study, an efficient procedure for the synthesis of uncommon group 4–lanthanide oxo-alkoxide derivatives was developed. Heterometallic clusters with the structures $[La_2Ti_4(\mu_4-O)_2(\mu_3-OEt)_2(\mu-OEt)_8(OEt)_6(Cl)_2(HOEt)_2]$ (1), $[La_2Zr_2(\mu_3-O)(\mu-OEt)_5(\mu-Cl)(OEt)_2(HOEt)_4(Cl)_4]_n$ (3), $[Nd_2Ti_4(\mu_4-O)_2(\mu_3-OEt)_2(\mu-OEt)_8(OEt)_6(HOEt)_2(Cl)_2]$ (4), $[Nd_4Zr_4(\mu_3-O)_2(\mu-OEt)_{10}(\mu-Cl)_4(OEt)_8(HOEt)_{10}(Cl)_2]$ (5), and $[Nd_4Hf_4(\mu_3-O)_2(\mu-OEt)_{10}(\mu-Cl)_4(OEt)_8(HOEt)_{10}(Cl)_2]$ (6) were synthesized via the reaction of a metallocene dichloride, $Cp_2M'Cl_2$ (where M' = Ti, Zr, and Hf), and metallic lanthanum or neodymium in the presence of excess ethanol. This procedure gave crystalline precursors with molecular stoichiometries suitable for obtaining group 4–lanthanide oxide materials. Compounds 1–6 were examined by analytical and spectroscopic techniques and single-crystal X-ray diffraction. The magnetic properties of **5** and **6** were investigated by using direct and alternating current (dc and ac) susceptibility measurements. The results indicated weak antiferromagnetic interactions between Nd^{III} ions and a field-supported slow magnetic relaxation. Lanthanum–titanium compound 1 decomposed at 950 °C to give the perovskite compound $La_{0.66}TiO_3$ and small amounts of rutile TiO_2. Under the same conditions, 4 decomposed to give a mixture of Nd_4Ti_9O_{24} and Nd_{0.66}TiO_3. When 4 was calcined at 1300 °C, decomposition of Nd_4Ti_9O_{24} to Nd_{0.66}TiO_3 and TiO_2 was observed. Calcination of **2**, **3**, **5**, and **6** at 950–1500 °C led to the selective formation of heterometallic $La_2Zr_2O_7$, $La_2Hf_2O_7$, $Nd_2Zr_2O_7$, and $Nd_2Hf_2O_7$ phases, respectively.

■ INTRODUCTION

Over the last four decades, structurally authenticated group 4 heterometallic alkoxides have been intensively investigated because of their numerous practical applications in catalysis, as well as material and polymer chemistry. Various combinations of titanium group metals with alkali,¹⁻⁴ alkaline earth,⁵⁻⁸ and transition metal elements⁹⁻¹³ have been reported. Most of these compounds involve alkaline earth derivatives. Heterometallic alkoxides composed of group 4 ($M^{\prime 4+}$) and lanthanide (Ln^{2+}/Ln^{3+}) ions are uncommon and have not been widely studied. Until now, the structures of only 31 such compounds have been deposited in the Cambridge Structural Database.¹⁴ Most of them (29) are isopropoxide or ethoxide derivatives of formula [$Ln_4Ti(O)(O^{\dagger}Pr)_{14}$] (Ln = Sm and Tb),^{15,16} [$Ln_2Zr_4(O^{\dagger}Pr)_{18}(Cl)_4$] (Ln = Nd, Ho, and Ce), [CpLnZr_2(O^{\dagger}Pr)_9] (Ln = Yb and Sm),¹⁷ [$LnZr_2(O^{\dagger}Pr)_9$ ($X)_2$] (Ln = Tm, Er, and Yb; X = Cl and I),¹⁸ [$La_2Zr_3(O)(O^{\dagger}Pr)_{16}$],¹⁹

 $[Ln_2Ti_4(O)_2(OEt)_{16}(HOEt)_2(Cl)_2]$ (Ln = Ce, Eu, and Nd),²⁰⁻²² $[LnTi_8(O)_7(OEt)_{21}(HOEt)_x]$ (Ln = Ce and Er and x = 0 and 1),^{22,23} $[PrTi_{29}(O)_{38}(OEt)_{40}(Br)]$,²⁴ $[LnTi_{28}(O)_{36}(OEt)_{40}(OH)_2(Cl)]$ (Ln = Ce and La),²⁰ and $[LnTi_{11}(O)_{16}(NO_3)_2(O^iPr)_{17}]$ (Ln = Sm, Eu, and Gd).²⁵ Of these heterometallic clusters, 15 are zirconium, and 16 are titanium derivatives. There are no known hafnium–lanthanide-based compounds. The significant number of zirconium derivatives reflects the availability of a simple and efficient

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Scheme 1. Synthesis of 1-3



method for their synthesis, i.e., the substitution of the halogen ions in LnX₃ by $[Zr_2(O'Pr)_9]^-$. Heterometallic group 4– lanthanide carboxylates form a much larger family of coordination compounds than metal alkoxides. For example, $[LnTi_6O_3(O^iPr)_9(salicylate)_6]$ for Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, and Er were investigated as a platform for the in-depth study of the NMR behavior of paramagnetic Ln³⁺ ions.²⁶ The ion-size-dependent formation of mixed titaniumlanthanide oxo clusters $[LnTi_4(O)_3(O^iPr)_2(OMc)_{11}]$ (Ln = La and Ce; OMc = methacrylate), $[Ln_2Ti_6O_6(OMc)_{18}(HO^iPr)]$ (Ln = La, Ce, Nd, and Sm) and $[Ln_2Ti_4O_4(OMc)_{14}(HOMc)_2]$ (Ln = Sm, Eu, Gd, and Ho) was observed during the reaction of titanium isopropoxide, lanthanide acetate, and methacrylic acid.²⁷ Titanium group–lanthanide compounds are of particular interest for use as catalysts in various photochemical reactions²⁸ and as magnetic and luminescent molecular materials.²⁹⁻³¹ They are also attractive single-source molecular precursors for advanced multicomponent oxide ceramics.

The compounds Ln₂M'₂O₇ are a family of heterometallic materials with a wide range of chemical and physical properties, which depend on oxygen vacancies, chemical composition, and ordering-disordering of the Ln³⁺ and M'⁴⁺ ions. These oxides can exist in two closely related structures, i.e., cubic pyrochlore or disordered fluorite. The fluorite structure is favored when the ionic radii of the Ln³⁺ and M'⁴⁺ ions are comparable $[r(Ln^{3+})/$ $r(M'^{4+}) < 1.46$]. The ordered pyrochlore structure is not stable and can be transformed into the fluorite structure by the actions of temperature or pressure and by chemical doping. $Ln_2M'_2O_7$ oxides are of considerable interest because of their excellent thermal stabilities, high radiation stabilities, high melting points, high thermal expansion coefficients, low thermal conductivities, and chemical resistance. Because of their high electrical conductivities, they are promising candidates for use as hightemperature solid electrolytes in solid-oxide fuel cells.³² They are also excellent host lattices for lanthanide-doped (Er^{3+} , Tb^{3+} , Pr^{3+} , and Eu^{3+}) phosphor materials for use in light-emitting devices, fiber amplifiers, lasers, color displays, brand anti-counterfeiting, and temperature sensors.³³⁻³⁵ Lanthanide titanates are promising ferroelectric materials for the construction of metal-ferroelectric-insulator semiconductor structures.³⁶ La₂Ti₂O₇ has been intensively investigated as a photocatalyst for water splitting, decomposition of organic waste,³⁷ \dot{CO}_2 reduction, and H_2 production. Lanthanide zirconates have been mainly investigated as materials for thermal barrier coating (TBC) of turbine components for thermal insulation and protection against hot and corrosive gas streams.³⁸ La₂Zr₂O₇ is particularly useful in this context and has many advantages compared to traditional TBC systems based on 8 wt % yttria-stabilized zirconia (Y_2O_3/ZrO_2) , such as no phase transformation from room temperature to its melting temperature, high sintering resistance, low thermal conductivity, and low oxygen ion diffusivity.³⁹ Because of its high density (7.84 g/cm^3) , large effective atomic number, and high stopping power for X- and γ -rays, La₂Hf₂O₇ is technologically important in radiation-resistant materials.⁴⁰ The development of efficient and inexpensive methods for the synthesis of group 4lanthanide oxide ceramics is therefore important for increasing their range of applications.

Several of our previous studies showed that heterometallic alkoxides are attractive starting materials for the preparation of high-purity group 4–alkaline earth oxides.⁴¹ The molecular precursors were synthesized by protonolysis of the cyclopentadienyl ligand in Cp₂M'Cl₂ in the presence of an alcohol (2-methoxyethanol or ethanol) and M(OR)₂ (M = Mg, Ca, Sr, and Ba).^{42,43} The current study aimed to use this approach for the synthesis of group 4–lanthanide alkoxides and their conversion to binary metal oxide materials.

RESULTS AND DISCUSSION

Syntheses and Structural Study. Treatment of Cp₂TiCl₂ with lanthanum powder (1 equiv) in an ethanol/toluene mixture (3:1) at ambient temperature (Scheme 1) gave crystalline cyclopentadienyl-free $[La_2Ti_4(\mu_4-O)_2(\mu_3-OEt)_2(\mu-OE-t)_8(OEt)_6(Cl)_2(HOEt)_2]$ (1, 36%). When the same reaction was performed with zirconocene or hafnocene dichloride, the isostructural compounds $[La_2M'_2(\mu_3-O)(\mu-OEt)_5(\mu-Cl)-(OEt)_2(HOEt)_4(Cl)_4]_n$, where M' = Zr (2, 42%) or Hf (3, 33%), were obtained. In these reactions, Cp₂M'Cl₂ (M' = Ti, Zr,

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and Hf) undergoes protonolysis of the cyclopentadienyl ligands, which leads to the release of CpH and formation of group 4 ethoxide or chloro-ethoxide species. This process is accompanied by the elimination of Cl^- from $Cp_2M'Cl_2$, which results in the generation of chloro or dichloro lanthanum ethoxide derivatives.

These species were involved in the formation of heterometallic clusters 1-3. Analytical methods, infrared (IR) spectroscopy, and single-crystal X-ray diffraction (XRD) were used to characterize 1-3 (Figures S1-S6). These compounds were isolated as crystalline materials. They are insoluble in most conventional solvents. The crystallographic data in Figure 1



Figure 1. Molecular structure of $[La_2Ti_4(\mu_4-O)_2(\mu_3-OEt)_2(\mu-OE-t)_8(OEt)_6(Cl)_2(HOEt)_2]$ (1). Displacement ellipsoids are drawn at the 30% probability level. Solvent molecules and hydrogen atoms of alkyl groups are omitted for clarity [symmetry code: (i) -x + 1, -y + 1, -z + 1].

show that 1 is a centrosymmetric hexanuclear cluster in which lanthanum centers surrounded by O₇Cl donors adopt a square antiprismatic geometry, and titanium atoms coordinated with O₆ donors form distorted octahedrons. The La–O, La–Cl, and Ti-O bond lengths for 1, i.e., 2.445(2)-2.641(2), 2.803(2), and 1.774(2)-2.182(2) Å, respectively, are similar to those reported for $[La_5(O)(O^iPr)_{13}(HO^iPr)_2]$,⁴⁴ $[La_2Cl_6(HO^iPr)_2]$,⁴⁵ and $[Ti_4(OH)(OEt)_{15}]$.²¹ The structure of 1 corresponds well to that previously reported for titaniuml an than i de alkoxides of formula $[Ln_2Ti_4(O)_2(OEt)_{16}(HOEt)_2(Cl)_2]^{20-23}$ (Ln = Ce, Eu, and Nd) or $[Er_2Ti_4(O)_2(OEt)_{18}(HOEt)_2]^{46}$ The central core structure of these compounds contains the double oxo-bridged dilanthanide unit $\{Ln_2(O)_2X\}$ (X = Cl and OEt) capped by four $Ti(OEt)_4$ molecules through two μ_4 -O oxo atoms. The metric parameters of 1 and the four other hexanuclear clusters are very similar with the bond lengths of 2.368-2.495 Å for Ln-O, 2.412-2.653 Å for Ln-OEt, 2.684-2.803 Å for Ln-Cl, 1.905-2.183 Å for Ti–OEt_(bridging), 1.774–1.876 Å for Ti–OEt_(terminal), and 1.938–2.012 Å for Ti–O. The XRD study (Figure 2) shows that 2 and 3 are linear 1D coordination polymers based on tetranuclear $[La_2M'_2(\mu_3-O)(\mu-OEt)_5(\mu-Cl) (OEt)_2(HOEt)_4(Cl)_4$] units. The lanthanum atoms are surrounded by one oxo, three chloro, and four ethoxo ligands and adopt a triangular dodecahedral geometry; the M' atoms coordinated by one chloro, one oxo, and four ethoxo groups form distorted octahedrons.



Figure 2. Molecular structures of $[La_2M'_2(\mu_3-O)(\mu-OEt)_5(\mu-Cl)-(OEt)_2(HOEt)_4(Cl)_4]_n$ for M' = Zr (2) and Hf (3). Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms of alkyl groups are omitted for clarity [symmetry code: (i) $x_1 - y + 0.5$, z + 0.5; (ii) $x_1 - y + 0.5$, z - 0.5].

The continuous shape measure (CShM) method was used to investigate the geometric distortions around the metal atoms in $[La_2M'_2(\mu_3-O)(\mu-OEt)_5(\mu-Cl)(OEt)_2(HOEt)_4(Cl)_4]_n$. These calculations showed similar deformations of the coordination environments around La atoms, with metric parameters S(TDD-8) equal to 1.99 and 1.36 for 2 and 2.08 and 1.38 for 3. For the Zr and Hf atoms, the values of S(Oh) vary from 3.57 to 3.73. The bond lengths La–O (2.471(6)–2.580(6) Å), La–Cl (2.890(2)–2.967(2) Å), M'–O (1.901(8)–2.137(6) Å), and M'–Cl (2.603(3)–2.636(3) Å) in 2 and 3 are similar and lie in the expected ranges for lanthanum and group 4 chloro-alkoxo derivatives.^{47,48} Note that 3 is the first reported example of a heterometallic lanthanide–hafnium alkoxide.

When Cp₂M'Cl₂ was reacted with Nd (1 equiv) and excess ethanol, heterometallic alkoxide clusters were obtained, i.e., $[Nd_2Ti_4(\mu_4-O)_2(\mu_3-OEt)_2(\mu-OEt)_8(OEt)_6(HOEt)_2(Cl)_2]$ (4, 3 2 %) and $[Nd_4M'_4(\mu_3-O)_2(\mu-OEt)_{10}(\mu-Cl)_4(OEt)_8(HOEt)_{10}(Cl)_2]$, M' = Zr (5, 51%) and M' = Hf (6, 42%; Scheme 2).

Compound 4 is isostructural with 1 and had been previously obtained from the reaction of NdCl₃ with Ti(OEt)₄.²⁰ Compounds 5 and 6 are octanuclear clusters formed by two $\{Nd_2M'_2(\mu_3-O)(\mu-OEt)_5(\mu-Cl)(OEt)_4(HOEt)_5(Cl)\}$ units bridged by two μ -Cl groups (Figure 3). These structural units are similar to those observed in 2 and 3, but with the M' atoms bonded to OEt anions rather than to Cl ligands. The coordination of additional ethanol solvent molecules to the peripheral Nd atoms prevents the formation of polymeric structures.

The Nd ions in **5** and **6** surrounded by O_5Cl_3 or O_6Cl_2 donor atoms adopt a triangular dodecahedral geometry, and the M' atoms coordinated with five ethoxo and one oxo groups form distorted octahedrons. CShM calculations showed similar distortions in the neodymium coordination geometries in **5** and **6**, with measurement parameters from 0.973 to 1.174. For the M' atoms, a slightly larger deformation of the octahedral geometry was observed around the zirconium atoms in **5**, as shown by the *S*(Oh) parameters of 1.921 and 2.041 for Zr ions and 1.741 and 1.800 for Hf ions. The Nd–O and Nd–Cl bond

Scheme 2. Synthesis of 4-6





Figure 3. Molecular structures of $[Nd_4M'_4(\mu_3-O)_2(\mu-OEt)_{10}(\mu-Cl)_4(OEt)_8(HOEt)_{10}(Cl)_2]$ (5, M' = Zr) and (6, M' = Hf). Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms of alkyl groups are omitted for clarity [symmetry code: (i) -x + 1, -y + 1, -z + 1].

lengths of 2.387(4)-2.559(4) and 2.827(3)-2.885(3) Å, are similar to those reported for $[Nd_5(O)(O^iPr)_{13}(HO^iPr)_x]^{49,50}$ (x = 0 and 2) and $[Nd_2(Cl)_6(HO^iPr)_2]^{.51}$ The geometric parameters for the M' atoms correlate well with those for 2 and 3. In 2/3 and 5/6 the stoichiometry of metal elements Ln:M' = 1:1 differs from those usually observed for group 4lanthanide alkoxides with Ln:M' ratio of 1:2. The double chlorobridged Ln atoms found in 2/3 and 5/6 have been before observed only in the clusters $[Ln_2Zr_4(O^iPr)_{18}(Cl)_4]$ (Ln = Nd, Ho, and Ce).¹⁷ The comparison of bond lengths of lanthanidezirconium alkoxides 2 and 5 with the data available for compounds $[Ln_2Zr_4(O^iPr)_{18}(Cl)_4]$ revealed the expected values for this type of coordination compounds with Ln-OR distances of 2.330-2.520 Å, Ln-Cl_(bridging) distances of 2.729-2.967 Å, and Zr-OR distances of 1.908-2.169 and 2.068-2.302 Å for terminal and bridging alkoxide groups.

In addition to compound 5, we isolated crystals of a nonanuclear cluster $[Nd_5Zr_4(\mu_4-O)_2(\mu_4-Cl)(\mu_3-OH)_2(\mu_3-OEt)_2(\mu-OEt)_{10}(\mu-Cl)_2(OEt)_{10}(HOEt)_6]$ (7, 2%) when the

products of the reaction of Cp₂ZrCl₂ with metallic Nd were recrystallized from ethanol/tetrahydrofuran solution. However, separation of the two compounds in quantitative yield was impossible, and only a few crystals of 7 for XRD studies were isolated manually. The presence in 7 of two bridging μ_3 -OH groups, which arise from moisture present in the solution, shows that the use of an ethanol/H₂O mixture as the solvent for these reactions could provide a promising method for the synthesis of a new group of coordination compounds based on group 4 and lanthanide ions (Figure 4). The zirconium atoms in 7 are octahedrally coordinated with oxygen atoms from six ethoxy or five ethoxy and one oxo ligands. Neodymium ions coordinated with O₇Cl or O₈ donor atoms adopt a triangular dodecahedral (Nd1) or biaugmented trigonal prismatic (Nd2-Nd5) geometry. The presence of four peripheral $Zr(OEt)_4$ units in 7 suggests that it is formed by the coordination of $Zr(OEt)_4$ molecules with a pentanuclear neodymium unit, i.e., $[Nd_5(O)_2(OH)_2(OEt)_6(Cl)_3(HOEt)_6]$, which prevents further aggregation in the solid state. A similar nonanuclear central core



Figure 4. Molecular structure of $[Nd_5Zr_4(\mu_4-O)_2(\mu_4-Cl)(\mu_3-OH)_2(\mu_3-OH)_2(\mu_0-Cl)_10(\mu-Cl)_2(OEt)_{10}(HOEt)_6]$ (7). Displacement ellipsoids are drawn at the 20% probability level. The second disordered counterpart of alkoxy group and hydrogen atoms of alkyl groups are omitted for clarity.

structure was previously reported for $[Nd_4Na_5(L)_4(OH)-(OMe)_4(dme)_3(HOMe)]$ (LH₃ = 2-oxidopropane-1,3-diylbis-(nitrilomethylylidene)diphenol, dme = 1,2-dimethoxy-ethane).⁵²

Synthesis and Powder XRD (PXRD) Characterization of Heterometallic Oxide Materials. A combination of thermogravimetry and differential scanning calorimetry/differential thermal analysis (TG-DSC/DTA) coupled with quadrupole mass spectrometry, and PXRD was used to study the thermal decomposition of 1–6 to identify appropriate temperatures for removing organic ligands and formation of heterometallic oxide phases. Calcination of 1–6 from 20 to 1300 °C in a N₂ atmosphere was investigated. Representative thermograms for the isostructural compounds 2, 3, 5, and 6 are shown in Figure 5. The results indicate that the heterometallic compounds underwent multistep decomposition. All the compounds were thermally stable up to 78 °C with mass losses not exceeding



Figure 5. TGA curves (dashed lines) for 2, 3, 5, and 6 recorded at a heating rate of 10 °C min⁻¹ in nitrogen atmosphere over a temperature range 25-1300 °C.

several percent. At temperatures above 80 °C, traces of the ethanol ligands were eliminated from the lanthanum or neodymium coordination sphere. The ethanol ligands were weakly coordinated to the Ln atoms and were removed from the samples during vacuum drying. At 120–310 °C, ethoxide ligands were removed as C_2H_4 , H_2O , and CO_2 . In the range of 400–950 °C, only CO_2 and HCl were removed. The presence in the DSC curve of single endothermic peaks at 858 and 758 °C, which correspond to the melting points of LaCl₃ and NdCl₃, respectively, together with the overall mass losses of 25.1% for 2, 22.9% for 3, 32.5% for 5, and 27.2% for 6 suggest that in a N_2 atmosphere these compounds decompose to a mixture of $M'O_2$, LnCl₃, and Ln₂O₃.

When TG/DTA measurements were performed under N₂ in the temperature range of 20–1500 °C, LaCl₃ and NdCl₃ vaporized above 1000 and 1500 °C, respectively, and were removed from the sample. When thermal degradation was performed in air, LnCl₃ was oxidized to LnOCl and then to Ln₂O₃. These species together with M'O₂ are involved in the formation of heterobimetallic phases.

Oxides were synthesized by heating precursors 1–6 at 950 °C and between 1300 and 1500 °C for 3 h in air. The phase purities of the resulting materials were determined by PXRD; the data are shown in Figures 6–11. Treatment of 1 at 950 and 1300 °C resulted in the formation of La_{0.66}TiO₃ as the main product, but a small amount of TiO₂ was also detected because of the stoichiometry of 1 (Figure 6). The PXRD patterns of the oxides synthesized by heating 2 at 950 and 1500 °C (Figure 7) clearly show the formation of only one pure phase, namely, $La_2Zr_2O_7$. Calcination of 3 at 950 °C gave La₂Hf₂O₇ as the main phase, but small diffraction peaks from La₂O₃ and HfO₂ were also detected. When the calcination temperature was increased to 1500 °C, only La₂Hf₂O₇ was formed (Figure 8). Figure 9 shows that calcination of 4 at 950 °C gave a mixture of Nd₄Ti₉O₂₄ and $Nd_{0.66}TiO_3$. When 4 was heated at 1300 °C, the intensities of the Nd₄Ti₉O₂₄ phase peaks decreased with simultaneous increases in the Nd_{0.66}TiO₃ and rutile TiO₂ peak intensities. The PXRD patterns of the oxides prepared by heating 5 and 6 at 950 and

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Figure 6. PXRD patterns of oxide materials prepared by calcination of 1 at 950 °C [blue] (a) and 1300 °C [red] (b), $La_{0.66}$ TiO₃ [Powder Diffraction File 4 (PDF-4) no. 04–019–9846 (2018) green] (c), and TiO₂ reference pattern [01–072–4815, brown] (d).



Figure 7. PXRD patterns of oxide materials prepared by calcination of 2 at 950 °C [blue] (a) and 1500 °C [red] (b), and $La_2Zr_2O_7$ reference pattern [PDF-4+ no. 04–006–2370, 2018; green] (c).



Figure 8. PXRD patterns of oxide materials prepared by calcination of **3** at 950 °C [blue] (a) and 1500 °C [red] (b), $La_2Hf_2O_7$ [PDF-4+ 04– 016–6623, 2018; green] (c), HfO₂ [04–002–5353, brown] (d), and La_2O_3 reference pattern [04–014–8421, cyan] (e).

1500 °C showed selective crystallization of the $Nd_2Zr_2O_7$ or $Nd_2Hf_2O_7$ phases (Figures 10 and 11).

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Figure 9. PXRD patterns of oxide materials prepared by calcination of 4 at 950 °C [blue] (a) and 1300 °C [red] (b), Nd₄Ti₉O₂₄ [PDF-4+ 04– 010–7646, 2018; green] (c), Nd_{0.66}TiO₃ [04–013–3633, brown] (d), and TiO₂ reference pattern [01–079–6031, cyan] (e).



Figure 10. PXRD patterns of oxide materials prepared by calcination of 5 at 950 °C [blue] (a) and 1500 °C [red] (b), and Nd₂Zr₂O₇ reference pattern [PDF-4+ 04–001–9352, 2018; green] (c).



Figure 11. PXRD patterns of oxide materials prepared by calcination of 6 at 950 °C [blue] (a) and 1500 °C [red] (b), and Nd₂Hf₂O₇ reference pattern [PDF-4+ 04–006–1654, 2018; green] (c).

Figures 12 and 13 show transmission electron microscopy (TEM) photographs of materials prepared by thermal

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Figure 12. TEM images of oxide materials prepared by calcination of 1 (a), 2 (b), and 3 (c) at 950 °C.

decomposition of molecular precursors 1-6 at 950 °C. The crystallites prepared from 1 had a regular morphology and a particle size of 50-100 nm (Figure 12a). The La₂Zr₂O₇ particles obtained from precursor 2 had irregularly shaped particles that varied significantly in size, with a mean particle size varying from 30 to 200 nm (Figure 12b). Similar shape and size properties to those of the product obtained from 2 were observed for La₂Hf₂O₇, which was derived from 3 (Figure 12c). The obtained Nd₄Ti₉O₂₄ had an interesting morphology; the material consisted of round and elongated crystallites of diameter 50–200 nm (Figure 13a). Nd₂Zr₂O₇ was obtained as regular crystallites of diameter 10–30 nm (Figure 13b). Nd₂Hf₂O₇ was obtained as highly aggregated irregularly shaped particles (Figure 13c).

Direct and Alternating Current Susceptibilities. The molar magnetic susceptibility was converted to the $\chi_M T$ product (or effective magnetic moment). The temperature dependence of $\chi_M T$ is shown in Figure 14 (left). The field dependence of the magnetization per formula unit, $M_1 = M_{mol}/N_A\mu_B$, at constant temperature is shown in Figure 14 (right).

The octanuclear $Nd^{III}_{4}Zr^{IV}_{4}$ (5) and $Nd^{III}_{4}Hf^{IV}_{4}$ (6) complexes behaved magnetically as homonuclear tetramers with $S_{Nd} = 3/2$ because Zr^{IV} and Hf^{IV} ions are diamagnetic. The values of $\chi_M T$ at room temperature, i.e., 7.99 cm³ mol⁻¹ K for 5 and 7.10 cm³ mol⁻¹ K for 6, are slightly higher than those

expected for formula units consisting of four noninteracting Nd^{III} species (4f³, S = 3/2, J = 9/2, L = 6, ${}^{4}I_{9/2}$; $\chi_{\rm M}T = 6.59$ cm³ mol⁻¹ K), possibly because of the effect of strong spin–orbit coupling. The product function $\chi_{\rm M}T$ (Figure 14) decreased gradually at 300–150 K, decreased greatly below 150 K, and reached values of 3.33 and 3.01 cm³ mol⁻¹ K for compounds **5** and **6**, respectively, at 2 K. The magnetic features of both these complexes indicate antiferromagnetic exchange interactions together with thermal depopulation of the Stark levels of the Nd^{III} ion.

Fitting of the magnetic data of **5** and **6** were performed using the PHI program,⁵³ which enables simultaneous fitting of the $\chi T(T)$ and $M(\mu_0 H)$ dependences, by taking account of the two different exchange pathways, i.e., via a double symmetric chloride bridge (J_1) and a double, heterogeneous chloridooxide bridge (J_2) . The intermolecular interactions between Nd^{III} ions in neighboring molecules are omitted because of the long Nd…Nd distances (the shortest one is 10.303 Å in **5**, and then 10.421 Å in **6**). In the fitting procedure, we also considered the terms of the spin—orbit constant λ of paramagnetic Nd^{III} ions. The least-squares fit of the experimental data by this expression leads to the following results: g = 2.07, $J_1 = -0.87$ cm⁻¹, $J_1 =$ -14.18 cm⁻¹ for **5**; g = 2.03, $J_1 = -0.81$ cm⁻¹, $J_1 = -13.82$ cm⁻¹ for **6**. The discrepancy factors are 3.48×10^{-7} and 2.83×10^{-7} for **5** and **6**, respectively. The calculated curve matches the



Figure 13. TEM images of oxide materials prepared by calcination of 4 (a), 5 (b), and 6 (c) at 950 °C.



Figure 14. Direct current (dc) magnetic data for **5** and **6**. Left: temperature dependences of χ_M (O, black and blue, respectively) and $\chi_M T$ (\bigcirc , black and blue, respectively). Right: field dependence of magnetization per formula unit. Solid lines (in both graphs) were calculated using the HDVV spin Hamiltonian and PHI program.

magnetic data well (solid lines in Figure 14). The obtained J values confirm antiferromagnetic properties of similar magnitudes for both complexes and show good agreement with magnetostructural correlations parameters, e.g., the large bridging angles of Nd–Cl–Nd (107.9° for 5 and 108.31° for

6) and Nd–O–Nd (126.5° for **5** and 126.6° for **6**), and Nd···Nd distances (4.27 or 4.60 Å for **5** and 4.28 or 4.63 Å for **6**). Isothermal magnetization curves, M(H), were recorded at 2 and 5 K (Figure 14, left). Both curves show a sharp increase in magnetization at the lower field before reaching $\mu_{\rm B}$ values of 6.14

for **5** and 6.51 for **6** at 5.0 T and 2 K. The reduced curves are not perfectly superimposed, which suggests contributions from excited levels.

Although no hysteresis was observed for 5 and 6, the slow magnetization relaxation dynamics were probed by performing alternating current (ac) susceptibility measurements. The first result obtained at T = 2.0 K for a set of representative frequencies of the alternating field (f = 1.0, 11, 111, and 1116 Hz) by ramping the magnetic field from zero to $B_{dc} = 1.0 \text{ T}$ (working amplitude $B_{ac} = 0.3 \text{ mT}$) showed that there was no absorption signal for either complex (out-of-phase susceptibility component χ'') at zero field because of fast magnetic tunneling. For 6, this component increased with increasing external field passed through a maximum and then attenuated. This behavior confirms that the 6 shows field-supported slow magnetic relaxation. The position of the maximum depends on the frequency f of the oscillating field (Figure S7). Subsequent experiments for 6 were done for a fixed external magnetic field $B_{\rm dc} = 0.4 \text{ T}$ (at which there is a maximum of the high-frequency signal) by changing frequency in the range of f = 0.1 - 1500 Hz for a set of temperatures ranging between T = 1.8 and 7 K (Figure S8). The in-phase (χ_M') and out-of-phase (χ_M'') components exhibit small-frequency dependences with the application of an external field of 0.4 T, indicative the possibility of slow relaxation of magnetization, although the maxima in χ' are missing. The absence of the maxima precludes the direct extraction of the energy barrier but it can be estimated if the relaxation process is dominated by a single relaxation time and the additive constant to the real part χ' is vanishing. Further precise ac measurements and analysis based on theoretical calculations are needed to explain the effects of diamagnetic ions on the presence and dynamics of relaxation processes and will be performed in the nearest future.

CONCLUSIONS

We developed a simple and efficient strategy for the synthesis of heterometallic oxide nanomaterials based on lanthanide and group 4 elements. The nanomaterials were synthesized by thermal decomposition of single-source molecular precursors derived from the reaction of $Cp_2M'Cl_2$ (M' = Ti, Zr, and Hf) with metallic lanthanum or neodymium in the presence of ethanol as a protonation agent. The six obtained compounds are new examples of heterometallic group 4-lanthanide alkoxides, 31 examples of which have been previously reported. Compounds 3 and 6 are the first reported heterometallic alkoxide clusters of hafnium and lanthanide ions. The dc susceptibility measurements on 5 and 6 showed the presence of diamagnetic Zr^{IV} and Hf^{IV} ions and weak antiferromagnetic interactions between neighboring paramagnetic Nd^{III} ions in the Nd₄O₈Cl₄ core together with thermal depopulation of the Stark levels. A preliminary ac study indicated field-supported slow magnetic relaxation. The obtained heterometallic compounds, which have three different central core coordination arrangements, were used as molecular models for investigation of solidstate structural effects on the phase compositions, homogeneities, and morphologies of the synthesized nanomaterials. Thermal decomposition of the isostructural compounds $[Ln_2Ti_4(\mu_4-O)_2(\mu_3-OEt)_2(\mu-OEt)_8(OEt)_6(Cl)_2(HOEt)_2]$ (Ln = La and Nd) at 950 °C gave $La_{0.66}TiO_3$ or a mixture of Nd₄Ti₉O₂₄ and Nd_{0.66}TiO₃. We showed that above 950 °C, $Nd_4Ti_9O_{24}$ decomposes to $Nd_{0.66}TiO_3$ and $TiO_2.$ Calcination of $[La_2M'_2(\mu_3-O)(\mu-OEt)_5(\mu-Cl)(OEt)_2(HOEt)_4(Cl)_4]_n$ and $[Nd_4M'_4(\mu_3-O)_2(\mu-OEt)_{10}(\mu-Cl)_4(OEt)_8(HOEt)_{10}(Cl)_2]$ (M'

= Zr and Hf) at 950–1500 °C gave the heterobimetallic oxide nanomaterials La₂Zr₂O₇, La₂Hf₂O₇, Nd₂Zr₂O₇, and Nd₂Hf₂O₇. The results of this study show that group 4–lanthanide ethoxides are attractive starting materials for the production of numerous advanced multicomponent oxide ceramics with a large variety of chemical and physical properties. These properties will enable further applications of these compounds in energy storage and conversion, photocatalysis, electronic devices, electrochemical components, thermal coatings, and surface protection.

EXPERIMENTAL SECTION

All reactions were performed under N2 and using standard Schlenk and vacuum-line techniques. All reagents were obtained from commercial sources: Ethanol, hexane, tetrahydrofuran, toluene, HgCl₂, lanthanum, and neodymium powder were obtained from Sigma-Aldrich, and $Cp_2M'Cl_2$ (M' = Ti, Zr, and Hf) was obtained from Alfa Aesar. Solvents were purified using standard methods and distilled under N₂ before use. Hexane and toluene were purified by refluxing over sodium. Tetrahydrofuran was distilled from sodium/benzophenone, and ethanol was distilled over metallic magnesium. FTIR-ATR spectroscopy was performed with an FT-IR Nicolet 6700 (Thermo Scientific) spectrometer. Elemental analysis was performed with a PerkinElmer 2400 CHN elemental analyzer. Chlorine analysis was performed by the Schöninger method using an Elementar Micro K analyzer. Metal ion concentrations were determined by inductively coupled plasma optical emission spectrometry (-iCAP 7400 Duo spectrometer, Thermo Scientific). The observed slight differences between the theoretical and found values of the elemental analysis for the received compounds are due to the presence of EtOH ligands, which can be easily removed during vacuum drying. TG-DSC/DTA was performed with a Netzsch STA 449 F1 Jupiter system coupled with Bruker FTIR Tensor 27 and QMS Aeolos spectrometers in an N₂ atmosphere at a heating rate of 10 °C min⁻¹. Thermal decomposition of the metal alkoxide precursors was performed with an NT 1313 furnace (Neotherm) equipped with a KXP4 thermostat in atmospheric air. The resulting oxide materials were investigated by powder XRD (Empyrean, PANalytical); the powder diffraction database PDF-4+ was used. The morphologies of the resulting oxide materials were examined with an FEI Tecnai G² 20 X-Twin TEM microscope equipped with a field-emission gun and integrated energy-dispersive spectrometer (EDAX). For the TEM observations, 200-mesh copper grids with lacey carbon films were used. Signals from both copper and carbon (from the grids) were observed in the TEM-EDX spectra. Variable-temperature (2-300 K) DC magnetic susceptibility measurements under applied fields of 0.1 (T < 20 K) and 1.0 ($T \ge 20$ K) kG and variable-field (0–5 T) magnetization measurements at low temperatures (2 and 5 K) were performed with a Quantum Design SQUID magnetometer. Raw magnetic susceptibility data were corrected for the effects of underlying diamagnetism and the sample holder.⁵⁴ Magnetic measurements were performed by crushing the crystals and restraining the sample to prevent displacement caused by magnetic anisotropy. Single-crystal XRD data were collected using an Xcalibur or Xcalibur Ruby diffractometer at 100 K for 1-5, 190 K for 6, and 150 K for 7.55 The experimental details and crystal data are summarized in Tables S1 and S2. The structures were solved by direct methods and refined by the full-matrix least-squares method on F^2 , using the SHELXTL package.⁵⁶ Non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were positioned geometrically and added to the structure factor calculations, but were not refined. Molecular graphics for the resulting structures were created using Diamond (version 3.1e).⁵

Synthesis of $[La_2Ti_4(\mu_4-O)_2(\mu_3-OEt)_2(\mu-OE-t)_8(OEt)_6(CI)_2(HOEt)_2]$ (1). A 150 mL Schlenk flask equipped with a stir bar was charged with Cp₂TiCl₂ (0.75 g, 3.01 mmol), La powder (0.4 g; 2.9 mmol), HgCl₂ (0.008 g; 0.029 mmol), ethanol (70 mL), and toluene (20 mL). Then the reaction mixture was stirred under reflux for 35 h. During the reaction progress, the dark red solution slowly changed color to green and finally light yellow. Then the resulting solution was

filtered, and the filtrate was concentrated under vacuum to 20 mL. Hexane (15 mL) was added and formed a layer over the solution. Colorless crystals of **1** were grown at room temperature after 8 weeks. The crystals were filtered off, washed with hexane (3×5 mL), and dried under vacuum. Overall yield: 0.38 g (0.27 mmol, 36%). Anal. Calcd for C₃₆H₉₂O₂₀Cl₂La₂Ti₄: C, 31.21; H, 6.69; Cl, 5.12; La, 20.05; Ti, 13.82. Found: C, 32.07; H, 6.75; Cl, 5.16; La, 21.12; Ti, 13.59. IR (cm⁻¹, ATR diamond): 3331 (s), 2972 (s), 2929 (m), 2904 (m), 2871 (m), 1634 (w), 1476 (w), 1456 (w), 1380 (w), 1260 (m), 1095 (s), 1050 (vs), 915 (s), 881 (s), 799 (vs), 541 (s). Compound **1** is not soluble in most conventional solvents or crystallizes immediately upon dissolution and therefore was not investigated by NMR spectroscopy.

Synthesis of $[La_2Zr_2(\mu_3-O)(\mu-OEt)_5(\mu-CI)(OEt)_2(HOEt)_4(CI)_4]_n$ (2). A 150 mL Schlenk flask was charged with Cp₂ZrCl₂ (0.75 g, 2.57 mmol), ethanol (70 mL), and toluene (20 mL). The mixture was stirred at room temperature within 1 h, and La powder (0.4 g; 2.9 mmol) and HgCl₂ (0.008 g; 0.029 mmol) were introduced. Then the reaction mixture was stirred under reflux for an additional 36 h and was filtered off. The yellow filtrate was concentrated under vacuum to 20 mL. Then hexane (10 mL) was added, forming a layer over the solution. Colorless blocklike crystals of 2 were grown at room temperature after 6-7 weeks. The crystals were filtered off, washed with hexane $(3 \times 5 \text{ mL})$, and dried under vacuum. Overall yield: 0.62 g (0.54 mmol, 42%); Anal. Calcd for C₂₂H₅₉O₁₂Cl₅La₂Zr₂: C, 22.91; H, 5.16; Cl, 15.37; La, 24.09; Zr, 15.82. Found: C, 23.14; H, 5.21; Cl, 15.49; La, 24.99; Zr, 14.97. IR (cm⁻¹, ATR diamond): 3324 (vs), 2976 (w), 1609 (s), 1447 (vw), 1398 (vw), 1264 (vw), 1084 (vw), 1035 (w), 872 (vw), 802 (w), 653 $(\mathbf{v}\mathbf{w})$

Synthesis of $[La_2Hf_2(\mu_3-O)(\mu-OEt)_5(\mu-CI)(OEt)_2(HOEt)_4(CI)_4]_n$ (3). A 150 mL Schlenk flask was charged with Cp₂HfCl₂ (0.82 g, 2.16 mmol), ethanol (70 mL), and toluene (20 mL). The mixture was stirred at room temperature within 1 h, and La powder (0.37 g; 2.66 mmol) and HgCl₂ (0.007 g; 0.025 mmol) were introduced. Then the reaction mixture was stirred under reflux for an additional 48 h and was filtered off. The light yellow filtrate was concentrated under vacuum to 30 mL, and 10 mL of hexane was slowly added to the solution. Colorless blocklike crystals of 3 were grown at room temperature after 4 weeks. The crystals were filtered off, washed with hexane $(3 \times 5 \text{ mL})$, and dried under vacuum. Overall yield: 0.47 g (0.35 mmol, 33%). Anal. Calcd for C₂₂H₅₉O₁₂Cl₅La₂Hf₂: C, 19.90; H, 4.48; Cl, 13.35; La, 20.92; Hf, 26.89. Found: C, 20.15; H, 4.56; Cl, 13.49; La, 21.12; Hf, 27.54. IR (cm⁻¹, ATR diamond): 3570 (m), 3555 (m), 3344 (vs), 1623 (m), 1262 (w), 1091 (w), 1017 (vw), 800 (w), 700 (m), 529 (w), 456 (vw). Crystalline 3 was not soluble in most conventional solvents and therefore it was not possible to carry out an NMR study.

Synthesis of $[Nd_2Ti_4(\mu_4-O)_2(\mu_3-OEt)_2(\mu-OE-t)_8(OEt)_6(HOEt)_2(CI)_2]$ (4). A 150 mL Schlenk flask equipped with a stir bar was charged with Cp2TiCl2 (0.75 g, 3.01 mmol), Nd powder (0.42 g; 2.9 mmol), HgCl₂ (0.008 g; 0.029 mmol), ethanol (70 mL), and toluene (20 mL). Then the reaction mixture was stirred under reflux for 28 h. During the reaction progress, the dark red solution slowly changed color to light yellow. Then the resulting solution was filtered, and the filtrate was concentrated under vacuum to 20 mL. Hexane (10 mL) was added and formed a layer over the solution. Colorless crystals of 4 were grown at room temperature after several weeks. The crystals were filtered off, washed with hexane $(3 \times 5 \text{ mL})$, and dried under vacuum. Overall yield: 0.34 g (0.24 mmol, 32%). Anal. Calcd for C₃₆H₉₂O₂₀Cl₂Nd₂Ti₄: C, 30.97; H, 6.64; Cl, 5.08; Nd, 20.67; Ti, 13.72. Found: C, 31.17; H, 6.69; Cl, 5.19; Nd, 21.23; Ti, 13.66. IR (cm⁻¹, ATR diamond): 3568 (s), 3548 (s), 3366 (vs), 2974 (s), 2933 (m), 1634 (m), 1508 (w), 1489 (w), 1475 (w), 1459 (vw), 1380 (w), 1260 (w), 1094 (m), 1048 (s), 943 (m), 881 (m), 799 (m), 720 (s), 556 (vs). Compound 4 for the same reason as 1 was not investigated by NMR spectroscopy.

Synthesis of $[Nd_4Zr_4(\mu_3-O)_2(\mu-OEt)_{10}(\mu-Cl)_4(OEt)_8(HOEt)_{10}(Cl)_2]$ (5). A Schlenk flask was charged with Cp₂ZrCl₂ (0.75 g, 2.57 mmol), ethanol (70 mL), and toluene (20 mL) and stirred by 0.5 h. Then Nd powder (0.38 g; 2.66 mmol) and HgCl₂ (0.008 g; 0.025 mmol) were added, and the mixture was stirred under reflux for 56 h. The resulting cloudy solution was cooled to room

temperature and filtered. The filtrate was concentrated to 15–20 mL, and 5 mL of hexane was added. Crystals of **6** were formed after 12 weeks of crystallization at room temperature. Overall yield: 0.81 g (0.33 mmol, 51%). Anal. Calcd for $C_{56}H_{150}O_{30}Cl_6Nd_4Zr_4$: C, 27.36; H, 6.15; Cl, 8.65; Nd, 23.47; Zr, 14.84. Found: C, 27.54; H, 6.27; Cl, 8.73; Nd, 23.54; Zr, 14.76. IR (cm⁻¹, ATR diamond): 3326 (vs), 2965 (m), 1614 (m), 1447 (w), 1402 (w), 1381 (w), 1260 (m), 1148 (w), 1071 (m), 1038 (m), 873 (w), 795 (m), 655 (w). Compound **5** is not soluble in most conventional solvents or crystallizes immediately upon dissolution and therefore was not investigated by NMR spectroscopy.

Synthesis of $[Nd_4Hf_4(\mu_3-O)_2(\mu-OEt)_{10}(\mu-CI)_4(OEt)_8(HOEt)_{10}(CI)_2]$ (6). A 150 mL Schlenk flask equipped with a stir bar was charged with Cp₂HfCl₂ (0.82 g, 2.16 mmol), ethanol (70 mL), and toluene (20 mL). The mixture was stirred at room temperature within 0.5 h, and Nd powder (0.38 g; 2.66 mmol) and HgCl₂ (0.007 g; 0.025 mmol) was added. Then the reaction was stirred under reflux for an additional 45 h and then was filtered off. The yellow filtrate was concentrated under vacuum to 30 mL, and 10 mL of hexane was slowly added to the solution. Colorless crystals of 6 were grown at room temperature after 6 weeks. The crystals were filtered off, washed with hexane (3 × 5 mL), and dried under vacuum. Overall yield: 0.63 g (0.22 mmol, 42%). Anal. Calcd for C₅₆H₁₅₀O₃₀Cl₆Nd₄Hf₄: C, 23.96; H, 5.39; Cl, 7.58; Nd, 20.55; Hf, 25.43. Found: C, 24.22; H, 5.43; Cl, 7.71; Nd, 20.95; Hf, 25.13. IR (cm⁻¹, ATR diamond): 3333 (m), 2969 (m), 2930 (w), 2904 (w), 2873 (w), 1614 (w), 1476 (vw), 1445 (w), 1383 (w), 1260 (m), 1154 (w), 1080 (m), 1037 (vs), 874 (w), 797 (m).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c02478.

IR spectroscopic and crystallographic data for 1-7 and field dependence of the ac susceptibility for 5 and 6 (PDF)

Accession Codes

CCDC 2014396–2014401 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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The manuscript was written through the contributions of all authors. All authors have approved the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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