DALTON

Di-zirconium-nona-isopropoxide as a cyclopentadienyl replacement: synthesis and crystal structure of the di-zirconium-nona-isopropoxide lanthanide halides $\{[Zr_2(OPr^i)_9]Eu(\mu\text{-}I)\}_2$, $\{[Zr_2(OPr^i)_9]NdCl(\mu\text{-}Cl)\}_2$ and $\{[Zr_2(OPr^i)_9]Nd(\mu\text{-}O_2CBu^t)(\mu\text{-}Cl)\}_2$ †

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Structural evidence has been obtained which suggests that the monoanionic polydentate moiety, $Zr_2(OPr^i)_9^-$, obtainable from $KZr_2(OPr^i)_9$ and $Zr_2(OPr^i)_8(Pr^iOH)_2$, can function as a replacement for cyclopentadienyl-containing ligand sets in established types of organolanthanide compounds. The $Zr_2(OPr^i)_9^-$ unit has been found to replace the ligand set $[(C_5Me_5)(thf)_2]^-$ (thf = tetrahydrofuran) in $[(C_5Me_5)(thf)_2Sm(\mu\text{-}I)]_2$ and the ligand set $[(C_5H_5)_2]^{2-}$ in $[(C_5H_5)_2Nd(thf)(\mu\text{-}Cl)]_2$. The complex $KZr_2(OPr^i)_9$ reacts with $LnI_2(thf)_2$ (Ln = Eu or Sm) in toluene to form the isostructural, isomorphous complexes $\{[Zr_2(OPr^i)_9]Ln(\mu\text{-}I)\}_2$, which crystallize from toluene (**1**: $\{[Zr_2(OPr^i)_9Eu(\mu\text{-}I)\}_2$, $P2_1/n$, $a = 12.082(2)$, $b = 19.309(3)$, $c = 17.294(3)$ Å, $\beta = 92.805(11)°$, $U = 4029.4(12)$ Å^3 and $D_c = 1.637$ g cm^{-3} for $Z = 2$; **2**: $\{[Zr_2(OPr^i)_9]Sm(\mu\text{-}I)\}_2$, $P2_1/n$, $a = 12.071(2)$, $b = 19.273(3)$, $c = 17.279(2)$ Å, $\beta = 92.679(12)°$, $U = 4015.4(8)$ Å^3 and $D_c = 1.640$ Mg m^{-3} for $Z = 2$). The face-sharing bioctahedral $Zr_2(OPr^i)_9^-$ unit uses two of its central isopropoxide ligands and one additional isopropoxide on each zirconium to attach to the lanthanide metal, which has a distorted octahedral co-ordination environment completed by two bridging iodide ligands. The complex $Zr_2(OPr^i)_8(Pr^iOH)_2$ reacts with $NdCl_3$ in thf to form $\{[Zr_2(OPr^i)_9]NdCl(\mu\text{-}Cl)\}_2$ **3**, which crystallizes from toluene [$C2/c$, $a = 25.283(5)$, $b = 12.505(3)$, $c = 18.162(2)$ Å, $\beta = 119.802(9)°$, $U = 8553.6(22)$ Å^3 and $D_c = 1.515$ Mg m^{-3} for $Z = 4$]. In **3** the $Zr_2(OPr^i)_9^-$ unit again functions as a tetradentate ligand as in **1** and **2**. Two bridging and one terminal chloride complete the pentagonal bipyramidal environment of Nd. A derivative of **3** in which the terminal chlorides are replaced by bridging pivalate groups is obtained by reacting $NdCl_3$ with KO_2CBu^t and $Zr_2(OPr^i)_8(Pr^iOH)$ in thf to form $\{[Zr_2(OPr^i)_9]Nd(\mu\text{-}O_2CBu^t)(\mu\text{-}Cl)\}_2$ **4**, which crystallizes from toluene [$P\bar{1}$, $a = 12.267(3)$, $b = 14.217(4)$, $c = 14.700(3)$ Å, $\alpha = 88.08(2)$, $\beta = 71.98(2)$, $\gamma = 78.37(2)°$, $U = 2386.7(10)$ Å^3 and $D_c = 1.485$ Mg m^{-3} for $Z = 1$].

Convergence of interests in developing ancillary ligands alternative to cyclopentadienyl groups[1] and in synthesizing heteropolymetallic compounds[2] has led to an investigation of the utility of the di-zirconium-nona-isopropoxide unit as a polydentate monoanionic ligand. Currently, many groups are searching for alternatives to cyclopentadienyl ligands which are prominent solubilizing and stabilizing ligands in many areas of organometallic chemistry. Replacement of cyclopentadienyl ligands is difficult since these ligands have a rather special combination of properties.[1] Many groups are also investigating the designed synthesis of heteropolymetallic compounds using alkoxide ligands since these compounds may be useful precursors to solid-state materials *via* sol–gel processes.[3] Recent studies in heterometallic alkoxide chemistry have shown that mixed-metal complexes can readily be made with zirconium using isopropoxide ligation. For example, complexes of formula $\{[Zr_2(OPr^i)_9]Ba(\mu\text{-}OPr^i)\}_2$,[4] $[Zr_2(OPr^i)_9]Li(HOPr^i)$,[4] $[Zr_2(OPr^i)_9]K(dme)$ (dme = 1,2-dimethoxyethane),[5] $[Zr_2(OPr^i)_9]_2Ba$,[6] $[Zr_2(OPr^i)_9]CuCl$,[7] $[Zr_2(OPr^i)_9]Cu_2(OPr^i)$,[7] $\{[Zr_2(OPr^i)_9]Cu_2\}(\mu\text{-}O)$,[8] $\{[Zr_2(OPr^i)_9]Pb(\mu\text{-}OPr^i)\}_2$,[9] $\{[Zr_2(OPr^i)_9]CdCl\}_2$,[10] $\{[Zr_2(OPr^i)_9]SnI\}_2$,[11] $\{[Zr_2(OPr^i)_9]CdI\}_2$,[12] and $\{[Zr_2(OPr^i)_9]Ba(\mu\text{-}OPr^i)_2Cd(\mu\text{-}OPr^i)\}_2$[12] have been structurally characterized. In each case, a monoanionic $Zr_2(OPr^i)_9^-$ subunit attaches to the other metal centers *via* either 2, 3 or 4 oxygen atoms of bridging isopropoxides. This subunit can be viewed as a derivative of $Zr_2(OPr^i)_8(HOPr^i)_2$, Fig. 1, which has a $(HOPr^i)(Pr^iO)_3Zr(\mu\text{-}OPr^i)_2Zr(OPr^i)_3(HOPr^i)$ structure[13] in which each zirconium atom is surrounded by six oxygen atoms which form a distorted edge-sharing bioctahedron. Deprotonation of one of the alcohols and dissociation of the other leads to the distorted *face*-sharing bioctahedron of formula $[(Pr^iO)_3Zr(\mu\text{-}OPr^i)_3Zr(OPr^i)_3]^-$, Fig. 1. This monoanion binds as a polydentate unit by converting up to two of the central $\mu\text{-}OPr^i$ groups to $\mu_3\text{-}OPr^i$ moieties and by changing one or two of the formerly terminal isopropoxide groups into $\mu\text{-}OPr^i$ moieties.

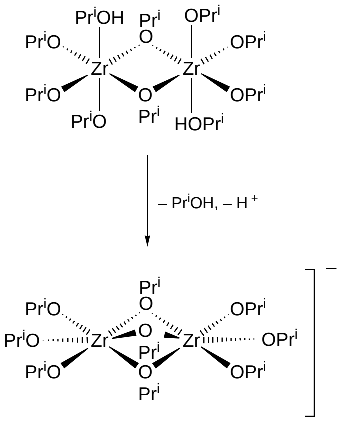

Fig. 1 Formation of $Zr_2(OPr^i)_9^-$ from $Zr_2(OPr^i)_8(HOPr^i)_2$

As a polydentate monoanion, $Zr_2(OPr^i)_9^-$ is potentially similar to cyclopentadienyl ligands and could stabilize and solubilize lanthanide halides as is done by cyclopentadienyl ligands. Accordingly, we have examined the formation of both divalent and trivalent lanthanide halide derivatives of di-zirconium-nona-isopropoxide and we report on the synthesis and structures of four examples which demonstrate the ligating ability of this unit. A literature search revealed a previous report of reactions of $SmCl_3{\cdot}3Pr^iOH$ with $KZr_2(OPr^i)_9$, but no structural

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† *Non-SI unit employed*: $\mu_B \approx 9.274 \times 10^{-24}$ J T^{-1}.

data were obtained to allow direct comparisons with cyclopentadienyl compounds.[14]

Experimental

All compounds described below were handled under nitrogen using standard Schlenk, vacuum line and glovebox techniques. Solvents were dried and physical measurements were made as previously described.[15] The NMR spectra were acquired and magnetic moments were measured by the method of Evans [16] on a General Electric GN500 or QE300 NMR spectrometer. Elemental analyses were performed by Analytische Laboratorien, Lindlar, Germany.

{$[Zr_2(OPr^i)_9]Eu(\mu\text{-}I)\}_2$ **1**

In a glovebox, a solution of $KZr_2(OPr^i)_9$ (295 mg, 0.392 mmol) in toluene (2 cm^3) was added to a stirred suspension of $EuI_2(thf)_2$ (thf = tetrahydrofuran) (216 mg, 0.393 mmol) in toluene (3 cm^3). The mixture was gently heated and stirred for 20 min, after which time the cloudy yellow-green solution was centrifuged to remove KI. Solvent was then removed from the supernatant by rotary evaporation to give a final solution volume of approximately 2 cm^3. From this solution, X-ray quality crystals of **1** (320 mg, 67%) were grown over 12 h at ambient conditions in the glovebox (Found: C, 32.4; H, 6.25; Eu, 15.5; Zr, 18.7. Calc. for: $C_{27}H_{63}EuIO_9Zr_2$ C, 32.7; H, 6.39; Eu, 15.3; Zr, 18.4%). $\chi_G^{298K} = 2.44 \times 10^{-5}$, $\mu_{eff}^{298K} = 7.6\ \mu_B$. IR (KBr): 2973s, 2927s, 2863s, 2626w, 2365w, 2334w, 1463m, 1376m, 1361m, 1339m, 1260w, 1169s, 1128s, 1022s, 1007s, 963s, 936s, 847m, 830m, 815s, 560s, 530m cm^{-1}. UV/VIS (toluene) λ_{max} 326 nm. Fluorescence (toluene, 328 nm excitation) λ_{max} 494 nm.

X-Ray data collection and solution and refinement for {$[Zr_2(OPr^i)_9]Eu(\mu\text{-}I)\}_2$ **1**

A yellow crystal of approximate dimensions 0.13 × 0.10 × 0.10 mm was mounted on a glass fiber and transferred to the Siemens P4 diffractometer. The determination of symmetry, crystal class, unit cell parameters and the crystal's orientation matrix were carried out according to standard procedures.[17] [$C_{27}H_{63}EuIO_9Zr_2$: *M* 993.07, monoclinic, space group $P2_1/n$, $a = 12.082(2)$, $b = 19.309(3)$, $c = 17.294(3)$ Å, $\beta = 92.805(11)°$, $U = 4029.4(12)$ Å^3, $Z = 4$, $D_c = 1.637$ Mg m^{-3}, $T = 158$ K, $\mu = 2.850$ mm^{-1}.] Intensity data were collected at 158 K using 2θ–ω scan technique with Mo-Kα radiation. The raw data were processed with a local version of CARESS [18] which employs a modified version of the Lehman–Larsen algorithm to obtain intensities and standard deviations from the measured 96-step peak profiles. All 6651 data were corrected for absorption and Lorentz and polarization effects and were placed on an approximately absolute scale. The diffraction symmetry was $2/m$ with systematic absences $h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$. The centrosymmetric monoclinic space group $P2_1/n$ is therefore uniquely defined.

All calculations were carried out using the SHELXL program.[19] The analytical scattering factors for neutral atoms were used throughout the analysis.[20] The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model. Minor disorder in the isopropyl groups was modeled by assigning partial occupancy to components of the disordered groups. Hydrogen atoms were included using a riding model. At convergence, $wR2 = 0.0838$ and goodness of fit = 1.013 for 382 variables refined against all 6320 unique data [for refinement on F, $R1 = 0.0395$ for those 4292 data with $F > 4.0\sigma(F)$].

{$[Zr_2(OPr^i)_9]Sm(\mu\text{-}I)\}_2$ **2**

In a glovebox a solution of $KZr_2(OPr^i)_9$ (269 mg, 0.358 mmol) in toluene (2 cm^3) was added to a stirred suspension of $SmI_2(thf)_2$ (199 mg, 0.362 mmol) in toluene (2 cm^3). After the mixture was gently heated and stirred for 1 h, the cloudy dark purple solution was centrifuged to remove KI. Solvent was removed from the supernatant by rotary evaporation to give a final solution volume of approximately 2 cm^3. From this solution, X-ray quality crystals of **2** (279.6 mg, 79%) were grown over 48 h at −40 °C. Unit cell constants showed that **2** is isomorphous with **1**. ^1H NMR (C_6D_6): δ 18.76 (br, $\Delta\nu_{\frac{1}{2}}$ 30, 12 H), −0.633 (br, $\Delta\nu_{\frac{1}{2}}$ 25, 12 H), −0.768 (br, $\Delta\nu_{\frac{1}{2}}$ 25, 12 H), −2.056 (br, $\Delta\nu_{\frac{1}{2}}$ 15, 6 H), −12.327 (br, $\Delta\nu_{\frac{1}{2}}$ 20 Hz, 12 H). $\chi_G^{298K} = 5.14 \times 10^{-6}$, $\mu_{eff}^{298K} = 3.50\ \mu_B$. IR (KBr): 2968s, 2927m, 2863m, 1458w, 1374m, 1365m, 1341w, 1264w, 1171s, 1130s, 1021s, 1004s, 956m, 938m, 874w, 848m, 832m, 816s, 746w, 696w, 670w, 657w, 642w, 627w, 610w, 587w, 576w, 569m, 560m, 553m, 542m cm^{-1}. UV/VIS (toluene) λ_{max} 370, 481, 581, 697 nm.

{$[Zr_2(OPr^i)_9]NdCl(\mu\text{-}Cl)\}_2$ **3**

In the glovebox, a vial was charged with $NdCl_3$ (250 mg, 1 mmol) and thf (10 cm^3). The suspension was stirred for 30 min and solid $[Zr_2(OPr^i)_4(HOPr^i)]_2$ (788 mg, 1 mmol) was added. The resultant cloudy pale blue solution was stirred overnight and centrifuged to remove a small amount of pale blue solid. As the volume of the supernatant was reduced to half by rotary evaporation, microcrystals started forming. These were recrystallized from toluene over several days to produce diffraction quality crystals of **3** (650 mg, 66%) (Found: C, 34.71; H, 6.65; Nd, 15.68; Zr, 19.93. Calc. for $C_{54}H_{126}Cl_4Nd_2O_{18}Zr_4$: C, 34.89; H, 6.83; Cl, 7.63; Nd, 15.52; Zr, 19.63%). ^1H NMR (C_6D_6): δ 6.14 (br, $\Delta\nu_{\frac{1}{2}}$ 35), 4.87 ($\Delta\nu_{\frac{1}{2}}$ 17), 2.53 ($\Delta\nu_{\frac{1}{2}}$ 40), 2.31 ($\Delta\nu_{\frac{1}{2}}$ 38), 1.36 ($\Delta\nu_{\frac{1}{2}}$ 55 Hz). IR (Nujol): 1596m, 1126m, 1019m, 948w, 920w, 726m cm^{-1}.

X-Ray data collection and solution and refinement for {$[Zr_2(OPr^i)_9]NdCl(\mu\text{-}Cl)\}_2(C_7H_8)$

A pale blue crystal of dimensions 0.50 × 0.43 × 0.40 mm was handled as described above for **1**. [$C_6H_{134}Cl_4Nd_2O_{18}Zr_4$: *M* 1950.84, monoclinic, space group $C2/c$, $a = 25.238(5)$, $b = 21.505(3)$, $c = 18.162(2)$ Å, $\beta = 119.802(9)°$, $U = 8554(2)$ Å^3, $Z = 4$, $D_c = 1.515$ Mg m^{-3}, $T = 163$ K, $\mu = 1.841$ mm^{-1}.] All 10 045 data were corrected for absorption and Lorentz and polarization effects and were placed on an approximately absolute scale. The diffraction symmetry was $2/m$ with systematic absences hkl for $h + k = 2n + 1$ and $h0l$ for $h, l = 2n + 1$. The centrosymmetric monoclinic space group $C2/c$ [C^6_{2h}; no. 15] is therefore uniquely defined.

All calculations were carried out and the analytical scattering factors for neutral atoms were used as described above. Minor disorder in the isopropyl groups was modeled as in **1** above. One molecule of toluene per dimeric formula unit was located. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model. At convergence, $wR2 = 0.1072$ and goodness of fit = 1.039 for 291 variables refined against all 9829 unique data [refinement on F, $R1 = 0.0408$ for those 8206 data with $F > 4.0\sigma(F)$].

{$[Zr_2(OPr^i)_9]Nd(\mu\text{-}O_2CBu^t)(\mu\text{-}Cl)\}_2$ **4**

In the glovebox, a freshly prepared sample of KO_2CBu^t, obtained by reacting KH (40 mg, 1.0 mmol) with HO_2CBu^t (102 mg, 1.0 mmol) in thf (5 cm^3), was added to a solution of $NdCl_3$ (250 mg, 1.0 mmol) in thf (10 cm^3), and the resultant cloudy solution was stirred for 24 h. Solid $[Zr_2(OPr^i)_4(HOPr^i)]_2$ (788 mg, 1 mmol) was added, and the solution was stirred for an additional 48 h. The solution was centrifuged to remove a small amount of insolubles. The solvent was removed from the supernatant by rotary evaporation and the isolated pale blue solids were washed with hexanes to remove unreacted $[Zr_2(OPr^i)_4(HOPr^i)]_2$. The pale blue solids were dissolved in thf

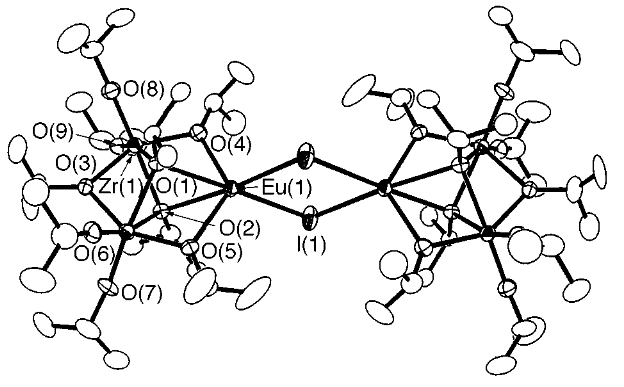

Fig. 2 Thermal ellipsoid plot of $\{[Zr_2(OPr^i)_9]Eu(\mu\text{-}I)\}_2$ **1** drawn at the 50% probability level

and recrystallized at −40 °C to yield **3** (320 mg, 30%). IR (Nujol): 1552m, 1168m, 1073w, 1020w, 950w, 725m cm^{-1}.

X-Ray data collection and solution and refinement for $\{[Zr_2(OPr^i)_9]Nd(\mu\text{-}O_2CBu^t)(\mu\text{-}Cl)\}_2(thf)_2$

A pale blue crystal of approximate dimensions 0.17 × 0.13 × 0.12 mm was handled as described above for **1**. [$C_{72}H_{160}Cl_2Nd_2O_{24}Zr_4$: $M = 2134.26$, triclinic, space group $P\bar{1}$, $a = 12.267(3)$, $b = 14.217(4)$, $c = 14.700(3)$ Å, $\alpha = 88.08(2)$, $\beta = 71.98(2)$, $\gamma = 78.73(2)°$, $U = 2386.7(10)$ Å^3, $Z = 1$, $D_c = 1.485$ Mg m^{-3}, $T = 158$ K, $\mu = 1.607$ mm^{-1}.] All 6583 data were corrected for absorption and Lorentz and polarization effects and were placed on an approximately absolute scale. The diffraction symmetry was $P\bar{1}$ with no systematic absences. The centrosymmetric triclinic space group $P\bar{1}$ [C_1^i; no. 2] was found to be correct by solution and subsequent refinement.

All calculations were carried out and the analytical scattering factors for neutral atoms were used as described above. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. Minor disorder in the isopropyl groups was modeled as in **1** above. Two molecules of tetrahydrofuran per dimeric formula unit were located. Hydrogen atoms were included using a riding model. At convergence, $wR2 = 0.0909$ and goodness of fit = 1.050 for 459 variables refined against all 6235 unique data [refinement on F, $R1 = 0.0363$ for those 4992 data with $F > 4.0\sigma(F)$].

CCDC reference number 186/736.

Results

$\{[Zr_2(OPr^i)_9]Ln(\mu\text{-}I)\}_2$

Addition of $KZr_9(OPr^i)_9$ to a slurry of $LnI_2(thf)_2$ (Ln = Sm or Eu) in toluene with slight heating brings the arene insoluble lanthanide diiodides into solution. A white insoluble by-product of weight appropriate for 1 equivalent of KI per Ln was formed and was readily separated by centrifugation. In the case of Eu, a bright yellow-green supernatant immediately begins to form yellow crystals of paramagnetic $\{[Zr_2(OPr^i)_9]Eu(\mu\text{-}I)\}_2$ **1** which was identified by X-ray crystallography, Fig. 2. With Sm, a dark blue supernatant forms dark blue crystals of paramagnetic $\{[Zr_2(OPr^i)_9]Sm(\mu\text{-}I\}_2$ **2** which was found to be isomorphous with **1**.

The effective magnetic moments of **1** and **2**, 7.6 and 3.5 μ_B, respectively, are consistent with the presence of divalent lanthanide metals.[21] The ^1H NMR spectrum of **1** contained resonances too broad for analysis, but the ^1H NMR spectrum of **2** contained methyl resonances in a ratio of 2 : 2 : 2 : 1 : 2 which is consistent with the solid-state structure (see below). The infrared spectra of **1** and **2** were superimposable. Complex **1** also shows luminescent behavior. The emission spectrum of **1** irradiated at 328 nm in toluene consisted of an intense band at 494 nm with a width of approximately 100 nm. This is red shifted from the 437 nm emission of EuI_2 in a mixture of thf and toluene, but it has approximately the same linewidth.

Table 1 Lanthanide oxygen bond distances (Å) in complexes **1**, **3** and **4**

		$Ln-(\mu\text{-}OPr^i)$	$Ln-(\mu_3\text{-}OPr^i)$
1	$\{[Zr_2(OPr^i)_9]EuI\}_2$	2.506(5), 2.525(5)	2.541(5), 2.600(5)
3	$\{[Zr_2(OPr^i)_9]NdCl_2\}_2$	2.414(3), 2.418(3)	2.486(3), 2.538(3)
4	$\{[Zr_2(OPr^i)_9]NdCl(O_2CBu^t)\}_2$	2.505(4), 2.527(4)	2.529(4), 2.574(4)

As shown in Fig. 2, complexes **1** and **2** crystallize as centrosymmetric dimers with slightly asymmetric bridging iodide ligands connecting the six-co-ordinate lanthanide centers. A cadmium compound of the same formula as **1** and **2** is known, $[Zr_2(OPr^i)_9]CdI$,[12] but it is monomeric in solution and in the solid state. Complexes **1** and **2** may form bridged dimers in the solid state due to their more electrophilic nature compared to Cd and their larger size: the six-co-ordinate radii are 1.31 for Eu^{2+}, 1.33 for Sm^{2+} and 1.09 Å for Cd^{2+}.[22]

From a lanthanide perspective, the overall structure is similar to the bridged lanthanide iodide complexes, $[(C_5Me_5)(thf)_2Sm(\mu\text{-}I)_2$ **5**[23] and $[(L)_3IEu(\mu\text{-}I)]_2$ (L = *N*-methylimidazole) **6**.[24] The $Zr_2(OPr^i)_9^-$ unit in **1** and **2** is identical to those in heterometallic complexes of Ba,[4,6,12] K,[5] Cu,[7,8] Cd[10,12] and Sn.[11] In each case, it attaches to divalent europium and samarium *via* two doubly bridging and two triply bridging isopropoxide units. The co-ordination geometry of each zirconium atom is a severely distorted octahedron of oxygen atoms. The structures of complexes **1** and **2** can also be considered as dimeric versions of the common trimetallic structural unit $M_3(\mu_3\text{-}Z)_2(\mu\text{-}Z)_3$ in which Z = isopropoxide. The M_3Z_5 unit is found with a variety of metals in heterometallic alkoxide complexes.[3b]

The 3.2615(8) and 3.2819(8) Å $Eu-(\mu\text{-}I)$ distances in **1** are quite similar to the 3.306 and 3.263 Å analogs in **6**. The samarium complex **5** is less symmetrical with 3.356(2) and 3.459(2) Å Sm–I distances. All four of the europium and iodide atoms in **1** are coplanar due to the presence of an inversion center. The 84.78(2)° I–Eu–I angle in **1** is similar to the I–Ln–I angles in **6** (83.7°) and **5** [82.04(5)°]. Consequently, the Eu–I–Eu angle in **1** [95.22(2)°] is also similar to those in **6** (96.3°) and **5** [97.96(5)°].

Direct comparisons of the Eu–O distances in **1** with other divalent europium alkoxide complexes cannot be made since this is the first structurally characterized divalent europium alkoxide complex. However, divalent europium complexes with bridging aryloxides have been isolated and the 2.506(5) and 2.525(5) Å $Eu-(\mu\text{-}O)$ distances in **1** (Table 1) are in the ranges of $Eu-(\mu\text{-}OR)$ distances in $Eu_4(\mu\text{-}OC_6H_3Pr^i_2\text{-}2,6)_4(OC_6H_3Pr^i_2\text{-}2,6)_2(\mu_3\text{-}OH)_2(NCMe)_6$ [2.403(6)–2.543(6) Å][2a] and $(dme)_2Eu(\mu\text{-}OC_6H_3Me_2\text{-}2,6)_3Eu(OC_6H_3Me_2\text{-}2,6)(dme)$ [2.447(5)–2.597(5) Å].[2b] As expected, the 2.541(5) and 2.600(5) Å $Eu-(\mu_3\text{-}O)$ distances in **1** are slightly longer than the doubly bridging alkoxide lengths.

The Zr–O distances in **1** are quite normal with the usual progression of increasing length with increasing bridging: 1.927(5)–1.935(5) (Zr–O), 2.071(5)–2.183(5) (Zr–μ-O), and 2.229(5)–2.298(5) Å ($Zr-\mu_3\text{-}O$). As shown in Table 2, these distances are consistent with $Zr-O(OPr^i)$ lengths in other compounds. The Zr···Zr non-bonding distance and the bond angles are also in the normal range.

$\{[Zr_2(OPr^i)_9]NdCl(\mu\text{-}Cl)\}_2$ 3

Direct reaction of an equimolar thf solution of $NdCl_3$ with $Zr_2(OPr^i)_8(HOPr^i)_2$ provides, after centrifugation and solvent removal, $\{[Zr_2(OPr^i)_9]NdCl(\mu\text{-}Cl)\}_2$ **3**, Fig. 3, in 66% yield. The ^1H NMR spectrum of **3** contained broad resonances ($\Delta\nu_{\frac{1}{2}} = 17$–55 Hz) in the range δ 1.36–6.14 which were not structurally

Table 2 Selected bond distances (Å) in structurally characterized heterometallic $Zr_2(OPr^i)_9^-$

Complex	Zr–(OPr^i)	Zr–(μ-OPr^i)	Zr–(μ_3-OPr^i)	Zr···Zr (non-bonding)
1 $\{[Zr_2(OPr^i)_9]EuI\}_2$	1.927(5)–1.935(5)	2.071(5)–2.183(5)	2.229(5)–2.298(5)	3.2967(12)
3 $\{[Zr_2(OPr^i)_9]NdCl_2\}_2$	1.912(4)–1.928(3)	2.069(3)–2.193(5)	2.276(3)–2.296(3)	3.3330(8)
4 $\{[Zr_2(OPr^i)_9]NdCl(O_2CBu^t)\}_2$	1.926(4)–1.931(4)	2.069(4)–2.185(4)	2.247(4)–2.299(4)	3.3350(12)
$\{[Zr_2(OPr^i)_9]CdI\}_2$[12]	1.908(4)–1.926(5)	2.053(5)–2.186(5)	2.263(4)–2.299(4)	
$\{[Zr_2(OPr^i)_9]Ba(OPr^i)_2Cd(OPr^i)\}_2$[12]	1.931(11)–2.189(12)	1.908(10)–2.217(11)	2.230(10)–2.477(10)	
$\{[Zr_2(OPr^i)_9]Ba(OPr^i)\}_2$[4]	1.924(7)–1.940(7)	2.054(7)–2.202(6)	2.219(6)–2.243(6)	
$[Zr_2(OPr^i)_9]CuCl$[7]	1.914(6)–1.936(6)	2.092(6)–2.208(6)	2.221(6)–2.257(6)	3.3102(13)
$[Zr_2(OPr^i)_9]Cu_2(OPr^i)$[7]	1.933(5)–1.942(5)	2.110(5)–2.178(5)	2.206(5)–2.225(5)	3.2269(10)*
$\{[Zr_2(OPr^i)_9]Cu_2\}_2(\mu_4\text{-}O)$[8]	1.921(10)–1.945(10)	2.098(9)–2.238(9)		3.2227(20)–3.2300(20)*
$\{[Zr_2(OPr^i)_9]Pb(OPr^i)\}_2$[9]	1.89(2)–1.97(2)	2.159–2.268	2.226–2.270	3.302
$[Zr_2(OPr^i)_9]Li(HOPr^i)$[4]	1.923(3)–1.945(3)	2.065(3)–2.226(3)	2.229(3)–2.287(3)	
$[Zr_2(OPr^i)_9]K(dme)$[5]	1.945(8)	2.016(8)–2.203(8)	2.224(7)	
$\{[Zr_2(OPr^i)_9]Cd(\mu\text{-}Cl)\}_2$[10]	1.917–1.931	2.064–2.182	2.265–2.295	3.313(1)

* These values may differ because these complexes have two heterometals attached to a single $Zr_2(OPr^i)_9$ unit.

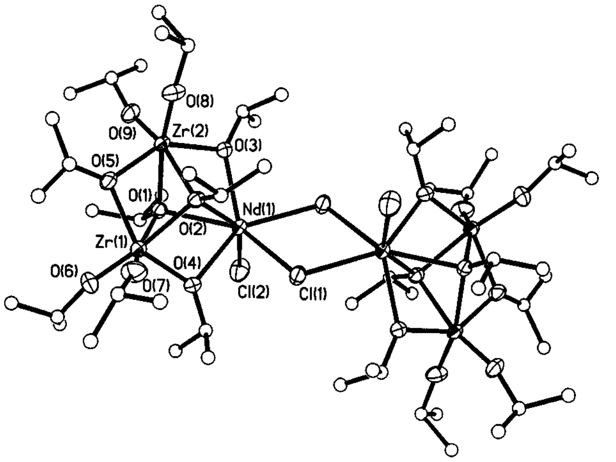

Fig. 3 Ball and stick plot of $\{[Zr_2(OPr^i)_9]NdCl(\mu\text{-}Cl)\}_2$ **3** with the thermal ellipsoids of the heteroatoms drawn at the 50% probability level

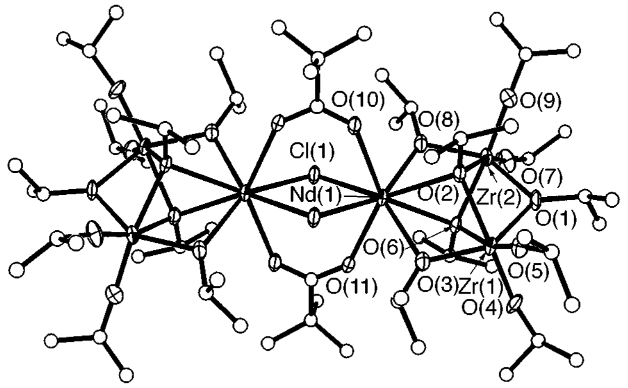

Fig. 4 Ball and stick plot of $\{[Zr_2(OPr^i)_9]Nd(\mu\text{-}O_2CBu^t)(\mu\text{-}Cl)\}_2$ **4** with the thermal ellipsoids of the heteroatoms drawn at the 50% probability level

informative. Accordingly, complex **3** was characterized by X-ray diffraction.

The structure of **3** is similar to that of **1** and **2** in that the $Zr_2(OPr^i)_9^-$ unit is again functioning as a tetradentate monoanionic ligand. Since trivalent neodymium requires two anionic ligands in addition to the $Zr_2(OPr^i)_9^-$ unit, there is more halide ligation in **3** than in **1** and **2**: **3** has terminal as well as bridging halides and a seven-co-ordinate lanthanide center. Seven-co-ordinate lanthanide halides are common and many examples have been crystallographically characterized.[25] The structure of **3** is similar to that of $[(C_5H_5)_2Nd(thf)(\mu\text{-}Cl)]_2$[26] with the $Zr_2(OPr^i)_9^-$ unit taking the place of the $[(C_5H_5)_2]^{2-}$ ligand set and the terminal Cl^- replacing the terminal thf.

The 2.8114(11) and 2.8149(11) Å Nd–(μ-Cl) distances and the 2.6430(13) Å terminal Nd–Cl distance are similar to those previously reported: $[NdCl_2(\mu\text{-}Cl)(HOPr^i)_3]_2$ [terminal: 2.693(2), 2.755(2); μ-Cl: 2.834(3), 2.911(2) Å];[27] $[NdCl_2(\mu\text{-}Cl)(thf)]_n$ [terminal: 2.661(1); μ-Cl: 2.793(1)–2.847(1) Å];[25] $\{[(Me_3C)_3CO]_2Nd(\mu\text{-}Cl)(thf)\}_2$ [2.808(1), 2.883(1) Å];[28] $[(1,3\text{-}Bu^t_2C_5H_3)_2Nd(\mu\text{-}Cl)]_2$ [2.837(1), 2.841(1) Å];[29] $[(C_5H_5)_2Nd(thf)(\mu\text{-}Cl)]_2$ [2.787(4), 2.861(4) Å].[26] The 73.47(3)° Cl(1A)–Nd(1)–Cl(1) angle is also in the 72.1(1)–74.8(1)° range of the (μ-Cl)–Nd–(μ-Cl) angles in the above chloro-bridged complexes.

As shown in Table 2, the Zr–O distances in **3** are similar to those in **1** and other zirconium isopropoxide complexes. The 2.414(3) and 2.418(3) Å Nd–(μ-O) distances in **3** (Table 1) are similar to Nd–(μ-O) distances in the structurally characterized neodymium isopropoxide complexes: $Nd_5(\mu_5\text{-}O)(\mu_3\text{-}OPr^i)_2(\mu\text{-}OPr^i)_6(OPr^i)_5(Pr^iOH)_2$ [2.307(10)–2.463(9) Å][30] and $Nd_6(\mu_6\text{-}Cl)(\mu_3\text{-}OPr^i)_2(\mu\text{-}OPr^i)_9(OPr^i)_6$ [2.27(3)–2.43(4) Å].[31] The 2.486(3) and 2.583(3) Å Nd–(μ_3-O) distances in **3** are in the high range of those in $Nd_5(\mu_5\text{-}O)(\mu_3\text{-}OPr^i)_2(\mu\text{-}OPr^i)_6(OPr^i)_5(Pr^iOH)_2$ [2.450(9)–2.477(9) Å][30] and $Nd_6(\mu_6\text{-}Cl)(\mu_3\text{-}OPr^i)_2(\mu\text{-}OPr^i)_9(OPr^i)_6$ [2.38(3)–2.51(3) Å].[31]

$\{[Zr_2(OPr^i)_9]Nd(\mu\text{-}O_2CBu^t)(\mu\text{-}Cl)\}_2$ 4

In an attempt to make a mixed-ligand $Zr_2(OPr^i)_9^-$ lanthanide complex, $NdCl_3$ was first treated with 1 equivalent of KO_2CBu^t in thf followed by addition of $Zr_2(OPr^i)_8(HOPr^i)_2$. Upon work-up, the chloro pivalate $[Zr_2(OPr^i)_9Nd(\mu\text{-}\eta^1:\eta^1\text{-}Bu^tCOO)(\mu\text{-}Cl)]_2$ **4**, Fig. 4, was isolated. Complex **4** crystallized from thf and is sparingly soluble in toluene and insoluble in hexanes.

The structure of **4** is similar to that of **3** except that the terminal chloride ligands in **3** have been replaced by bridging bidentate $Bu^tCO_2^-$ ligands. The replacement of monodentate chlorides by bidentate carboxylates raises the co-ordination number of neodymium from seven in **3** to eight in **4**. Each carboxylate binds such that its two donor atoms are attached to two different neodymium atoms. The very similar 2.393(4) and 2.415(4) Å Nd–O (O_2CBu^t) distances in **4** indicate that the carboxylates bridge symmetrically. Similar symmetrical carboxylate bridging with similar bond distance was found in $[Nd_2(\mu\text{-}\eta^1:\eta^1\text{-}O_2CMe)(\mu\text{-}O_2CMe)(\eta^2\text{-}O_2CMe)\{CO(NH_2)_2\}_2]_2\cdot 2CO(NH_2)_2\cdot 2H_2O$ which has 2.430 and 2.445 Å Nd–(μ-O) bond lengths and a nine-co-ordinate metal center.[32]

Interestingly, the 2.817(2) and 2.842(2) Å Nd–(μ-Cl) distances in **4** do not differ significantly from the 2.8114(11) and 2.8149(11) Å distances in **3** despite the difference in co-ordination number. The 88.04(5)° Cl(1A)–Nd(1)–Cl(1) angle in **4** is substantially larger than the 73.47(3)° (μ-Cl)–Nd–(μ-Cl) angle in **3**. This increased angle, without significant changes in the Nd–(μ-Cl) distances, requires the two monomer units to be closer together, which is expected with the addition of another set of bridging ligands.

The Zr–O distances in **4** are in the range of those in **1** and **3** despite the differences in the co-ordination environment around Nd. Hence in this complex, as in **1**–**3**, the internal structure of the $Zr_2(OPr^i)_9^-$ ligand is rather invariant.

The 2.505(4) and 2.527(4) Å Nd–(μ-OPr^i) distances in **4** are longer than those in **3** and in general longer than those in other structurally characterized complexes. The 2.529(4) and 2.574(4) Å Nd–(μ_3-OPr^i) distances in **4** are also longer than those in **3** and are in general longer than the Nd–(μ_3-OPr^i) distances in other neodymium isopropoxide complexes in the literature. The longer Nd–(μ-OPr^i) bond lengths in **4** are consistent with a higher co-ordination number. Since the Zr–O distances in **4** are normal, but the Nd–(μ-O) and Nd–(μ_3-O) distances are generally longer, it appears that oxygen donor atoms in the $Zr_2(OPr^i)_9^-$ unit retain a fairly rigid geometry around the zirconium centers in these heterometallic complexes, instead of distorting the zirconium environment to form more normal heterometal–isopropoxide interactions with the other metal.

Discussion

The reactions of $EuI_2(thf)_2$ or $SmI_2(thf)_2$ with $K[Zr_2(OPr^i)_9]$ and $NdCl_3$ with $[Zr_2(OPr^i)_8(HOPr^i)_2]$ show that treatment of both divalent and trivalent thf-soluble lanthanide halides with a source of the *d*i-*z*irconium-*n*ona-*i*sopropoxide (dzni) unit, $Zr_2(OPr^i)_9^-$, provides mixed-metal, toluene-soluble derivatives of the lanthanide halides. In each case, the reactions are facile and form readily crystallizable products in good yield. Hence, chemically there is a direct parallel between dzni and cyclopentadienyl chemistry.

Structurally, there are also similarities. Both ligands are polydentate monoanions which do not change their internal structure from complex to complex. As shown in Table 2, the dzni unit remains relatively invariant in all of the dzni complexes in the literature. In each of the complexes **1**–**4** the monoanionic face-sharing bioctahedral $Zr_2(OPr^i)_9^-$ subunit attaches to the lanthanide metal *via* four oxygen atoms of bridging isopropoxides, but the co-ordination capacity of dzni appears to be quite flexible in terms of which other ligands it can replace. For example, comparison of $\{[Zr_2(OPr^i)_9]Ln(\mu\text{-}I)\}_2$ **1** and **2** with $[(C_5Me_5)(thf)_2Sm(\mu\text{-}I)]_2$ **5** and $[(L)_3IEu(\mu\text{-}I)]_2$ **6** shows that the dzni ligand can replace the ligand sets $[(C_5Me_5)(thf)_2]^-$ and $[L_3I]^-$ directly. Comparison of $\{[Zr_2(OPr^i)_9]NdCl(\mu\text{-}Cl)\}_2$ **3** with $[(C_5H_5)_2Nd(thf)(\mu\text{-}Cl)]_2$[26] shows that the dzni anion is sterically equivalent to the $[(C_5H_5)]^{2-}$ ligand set and can replace it in a lanthanide cyclopentadienide compound if charge balance can be achieved by interchanging a neutral ligand with an anion, *e.g.* thf for Cl^- in this case. Although in these complexes dzni is a tetradentate ligand, it apparently can fill the space of four, five or six formal co-ordination positions and it can replace one or two anionic ligands. Moreover, in this study the dzni ligand is able to stabilize a variety of co-ordination environments for the lanthanides, *e.g.* six-, seven- and eight-co-ordinate **1**, **3** and **4**, respectively. Since the dzni ligand has also been structurally characterized as a tridentate ligand in $[Zr_2(OPr^i)_9]Li(HOPr^i)_2$[4] and $\{[Zr_2(OPr^i)_9]SnI\}_2$[11] and as a bidentate ligand in $\{[Zr_2(OPr^i)_9]Cu_2\}_2(\mu_4\text{-}O)$,[8] it is likely that the dzni ligand will have a more variable type of co-ordination chemistry than cyclopentadienyl ligands.

From the heteropolymetallic viewpoint, these reactions lead to new heterometallic lanthanide complexes and may constitute a general route for molecular precursors to lanthanide-containing zirconia-based materials. Although the dzni ligand has been shown to stabilize monovalent states of copper, potassium and lithium and divalent states of Ba, Pb, Cd and Sn, complexes **3** and **4** are the first structurally characterized cases in which the dzni unit complexes with a trivalent metal. Given the parallels of dzni and cyclopentadienyl ligands, new reactions leading to heterometallic zirconium species may become obvious by examining the cyclopentadienyl chemistry of the heterometal.

Complexes **1**–**4** each adopt the trimetallic structural arrangement, $M_3(\mu_3\text{-}Z)_2(\mu\text{-}Z)_3$, found in many types of polymetallic compounds including yttrium, the lanthanides, uranium, tungsten and molybdenum, and most of the heterometallic zirconium compounds previously reported.[3b] Whereas many of the previously reported $M_3(\mu_3\text{-}Z)_2(\mu\text{-}Z)_3$ complexes are homoleptic or have a mixture of oxide and alkoxide ligands, complexes **1**, **2** and **3** have derivatizable halide ligands as well. The isolation of the mixed alkoxide halide carboxylate complex **4** suggests that these halides can be substituted and this offers possibilities for the addition of other types of metals or ligands to the Zr/Ln systems.[12]

Conclusion

The dzni ligand, $[Zr_2(OPr^i)_9]^-$, has proven to be a useful polydentate monoanionic ancillary ligand for stabilizing and solubilizing divalent and trivalent lanthanide halides. Its demonstrated capacity to form isolable crystalline lanthanide complexes with a variety of co-ordination numbers while maintaining its structural integrity suggests that it may be a useful ligand in lanthanide chemistry. The dzni/cyclopentadienyl ligand equivalence may also be useful in designing heterometallic complexes on the basis of known cyclopentadienyl chemistry.

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