

Zirconium mixed ligand isopropoxide/aminoalkoxide complexes: crystal structures of $[\text{Zr}_2(\text{OPr}^i)_6(\text{L})_2]$ and $[\text{Zr}_2(\text{OBu}^t)_3(\text{bdmap})_4(\text{OH})]$ {where L = dmap, 1-dimethylaminopropan-2-olate and bdmap, 1,1-bis(dimethylamino)propan-2-olate}

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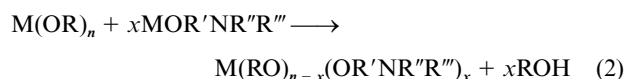
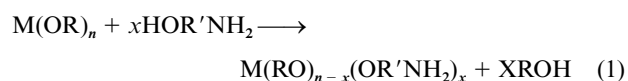
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The reactions of the homoleptic zirconium alkoxides $[\text{Zr}_2(\text{OPr}^i)_8(\text{Pr}^i\text{OH})_2]$ and $\text{Zr}(\text{OBu}^t)_4$ in *n*-hexane suspensions or solutions with two equivalents of the aminoalcohols 2-dimethylaminoethanol (Hdmae), 1-dimethylaminopropan-2-ol (Hdmap), or 1,1-bis(dimethylamino)propan-2-ol (Hbdmap) have been studied. Products with the formula $[\text{Zr}(\text{OR})_2(\text{dmae})_2]$ (R = Prⁱ **1** or Bu^t **2**), $[\text{Zr}_2(\text{OPr}^i)_6(\text{L})_2]$ (L = dmap **3** or bdmap **4**), and $[\text{Zr}_2(\text{OBu}^t)_3(\text{bdmap})_4(\text{OH})]$ **5** have been isolated. Compounds **3** and **4** have been shown by single crystal X-ray crystallography to be asymmetric binuclear complexes in the solid state. The two metal centres are bridged *via* the two aminoalkoxide oxygen atoms and one isopropoxide ligand. The remaining co-ordination spheres of the binuclear molecules are completed by 3 terminal isopropoxide ligands on one metal centre, and 2 terminal isopropoxide ligands on the other. Compound **5** was found to be binuclear, but instead of a μ -isopropoxide bridge a μ -OH group was observed which intra-molecularly hydrogen bonds to one of the free NMe₂ groups on a terminal bdmap ligand. The remaining sites in the co-ordination spheres are filled by 3 terminal *tert*-butoxide ligands on one metal centre and two terminal aminoalkoxide ligands on the other. These are the first binuclear 6/7 co-ordinate zirconium compounds. The structural studies are helpful in understanding the behaviour of these and related complexes as precursors in the MOCVD of ZrO₂ films.

Introduction

The chemistry of metal alkoxides has only been seriously and systematically studied and developed in the last 50 years. Although Ebelman and Bouquet¹ first synthesized some alkoxy-derivatives of silicon and boron in 1846, until the 1950s the alkoxides of only a dozen elements were known.² A large number of synthetic routes to compounds of empirical formula $\text{M}(\text{OR})_n$ and $\text{L}_x\text{M}(\text{OR})_y$ (where R is an alkyl group, L a neutral or anionic ligand and *n* and *y* are integers) have been developed.³ Much of the later developing of this work has coincided with an interest in designing better precursors for the deposition of metal oxides by methods such as the sol-gel route or MOCVD.⁴

The chemistry of zirconium alkoxides has been studied over a number of years^{2,5} and recently we have carried out studies⁶ into new potential precursors for ZrO₂ and related ferroelectric oxides. In this paper we report on the modification of zirconium alkoxides by their reaction with aminoalcohols. Aminoalcohols are simple derivatives of alcohols from which the hydrogen atoms of the alkyl or alkene groups have been replaced by amino or N-alkyl substituted amino groups. There are many examples of metal mixed isopropoxide/aminoalcohol complexes in the literature for a large number of metals, leading to Bradley *et al.*² to summarise these reactions as in eqns. (1) and (2). Specifically, in 1974 Bharara⁷ investigated the reactions of



$[\text{Zr}_2(\text{OPr}^i)_8(\text{Pr}^i\text{OH})_2]$ with *N*-methyl- and *N,N*-dimethylaminoalcohols and aminopropanol in refluxing benzene, but only managed to obtain unstable white pasty solids or yellow viscous liquids. The reactions of zirconium alkoxides with other ligands, such as pinacol,⁸ β -diketonates,⁶ *etc.* has received some attention, but few structures have been determined. The vast majority of the work is concerned with the sol-gel method.⁸⁻¹¹

In the present paper we report the successful isolation and spectroscopic analyses of a series of zirconium mixed alkoxide/alkanamine compounds **1–5**, and the structural characterisation of the compounds $[\text{Zr}_2(\text{OPr}^i)_6(\text{dmap})_2]$ **3** (dmap = 1-dimethylaminopropan-2-olate), $[\text{Zr}_2(\text{OPr}^i)_6(\text{bdmap})_2]$ **4** and $[\text{Zr}_2(\text{OBu}^t)_3(\text{bdmap})_4(\text{OH})]$ **5** [bdmap = 1,1-bis(dimethylamino)propan-2-olate] all of which are asymmetric binuclear complexes with zirconium metal centres with different co-ordination numbers (6 and 7).

Binuclear zirconium compounds with co-ordination numbers of six and six, or seven and seven, are well documented and many have been structurally characterised.^{2,8,12,13} Compounds of zirconium with mixed co-ordination numbers of four and five are also known.^{14,15} Calderazzo *et al.*^{16,17} have synthesized and structurally characterised a number of trinuclear zirconium species as toluene solvates, with metal co-ordination numbers of 6:6:7, for example $[\text{Zr}_3\text{Cp}_2(\text{O}_2\text{CNPr}^i)_6(\mu_3\text{-O})(\mu\text{-CCO})]$. The structures reported here are the first binuclear zirconium complexes with six- and seven-co-ordinate metal centres.

Experimental

General methods

All manipulations were carried out under an atmosphere of dry (molecular sieves) nitrogen using standard glove-box (Miller-Howe FF 160 with double-recirculator system) and Schlenk techniques. All alcohols were distilled, and stored over molecular sieves under nitrogen. The microanalytical department of Imperial College performed elemental analyses. The melting points were measured under argon in sealed capillaries and are uncorrected.

Physical techniques

Infrared spectra were recorded on a Matteson Polaris FT-IR spectrometer as Nujol mulls between 25×4 mm NaCl plates. The Nujol was dried with 4 Å molecular sieves prior to use. The NMR spectra were recorded on a JEOL GS 270 MHz spectrometer, using the proton impurities of the deuteriated solvent as a reference for ^1H and the ^{13}C resonance of the solvent as a reference for ^{13}C - $\{^1\text{H}\}$ spectra. All chemical shifts are reported positive to high frequency of the standard. Mass spectrometric studies were performed on a VG Autospec-Q (Imperial College Mass Spectrometry Service) operating in Electron Impact (positive) mode (70 eV) using a direct insertion probe and over the temperature range 50–200 °C.

Synthesis

All reactions were performed using dry solvents obtained from Aldrich Chemical Co, and all reagents were obtained from Inorgtech of Mildenhall, Suffolk, UK.

[Zr(OPrⁱ)₂(dmae)₂] 1. The compound [Zr₂(OPrⁱ)₈(PrⁱOH)₂] (1.55 g, 2.00 mmol) was dissolved in *n*-hexane (30 cm³) and 2-dimethylaminoethanol (Hdmae) (8.02 cm³, 8.00 mmol) added. The solution was stirred at reflux for 1 h, after which time all volatiles were removed *in vacuo* to yield a viscous colourless liquid. Yield: 1.08 g, 70%. Calc for C₁₄H₃₄O₄Zr: C, 43.4; H, 8.8; N, 7.2. Found: C, 43.1; H, 8.6; N, 7.2%. Sublimation temperature: 45 °C/0.1 mmHg.

[Zr(Obu^t)₂(dmae)₂] 2. The compound Zr(Obu^t)₄ (1.33 g, 3.47 mmol) was dissolved in *n*-hexane (30 cm³) and Hdmae (0.70 cm³, 6.95 mmol) added. The solution was stirred at reflux for 1 h, after which time all volatiles were removed *in vacuo* to yield a viscous colourless liquid. This was redissolved in the minimum of hot *n*-hexane (*ca.* 8 cm³), and left to stand at 0 °C for a week. Opaque crystals of **2** were filtered off. Yield: 1.27 g, 89%. Calc. for C₁₆H₃₈N₂O₄Zr: C, 46.3; H, 9.2; N, 6.8. Found: C, 47.2; H, 9.3; N, 7.2%. Melting point: 93–97 °C. Sublimation temperature: 200 °C/0.1 mmHg.

[Zr₂(OPrⁱ)₆(dmap)₂] 3. The compound [Zr₂(OPrⁱ)₈(PrⁱOH)₂] (3.76 g, 4.85 mmol) was dissolved in *n*-hexane (30 cm³) and Hdmap (2.36 cm³, 19.40 mmol) added. The solution was stirred at reflux for 1 h, after which time all volatiles were removed *in vacuo* to yield a very viscous colourless liquid. This was redissolved in a 1 : 1 solution of hot *n*-hexane and PrⁱOH (*ca.* 10 cm³), and left to stand at 0 °C for a week. Colourless crystals of **3** were filtered off. Yield: 4.37 g, 61%. Calc. for C₁₄H₃₃N₂O₄Zr: C, 45.5; H, 8.7; N, 3.8. Found: C, 45.4; H, 8.7; N, 3.7%. Melting point: 107–110 °C. Sublimation temperature: 205 °C/0.1 mmHg.

[Zr₂(OPrⁱ)₆(bdmap)₂] 4. The compound [Zr₂(OPrⁱ)₈(PrⁱOH)₂] (3.25 g, 4.19 mmol) was dissolved in *n*-hexane (30 cm³) and Hbdmap (2.73 cm³, 16.76 mmol) added. The reaction conditions and work-up were as for **3**. Colourless crystals of **4** were filtered off. Yield: 3.95 g, 57%. Calc. for C₁₆H₃₈N₂O₄Zr: C, 46.5;

H, 9.2; N, 6.8. Found: C, 46.4; H, 8.8; N, 6.6%. Melting point: 176–180 °C. Sublimation temperature: 145 °C/0.1 mmHg.

[Zr₂(Obu^t)₃(bdmap)₄(OH)] 5. The compound Zr(Obu^t)₄ (8.51 g, 22.18 mmol) was dissolved in *n*-hexane (50 cm³) and Hbdmap (7.23 cm³, 44.35 mmol) added. The reaction conditions and work-up were as for **2**. Colourless crystals of **5** were filtered off. Yield: 19.51 g, 88%. Calc. for C₂₀H₄₈N₄O₄Zr: C, 48.1; H, 9.7; N, 11.2. Found: C, 48.0; H, 9.4; N, 11.3. Melting point: 120–124 °C. Sublimation temperature: 190 °C/0.1 mmHg.

X-Ray crystallography of [Zr₂(OPrⁱ)₆(dmap)₂] **3**, [Zr₂(OPrⁱ)₆(bdmap)₂] **4**, and [Zr₂(Obu^t)₃(bdmap)₄(OH)] **5**

Table 1 provides a summary of the crystal data, data collection and refinement parameters for the compounds [Zr₂(OPrⁱ)₆(dmap)₂] **3**, [Zr₂(OPrⁱ)₆(bdmap)₂] **4** and [Zr₂(Obu^t)₃(bdmap)₄(OH)] **5a** and **5b**. The structures were solved by direct methods and refined by full matrix least-squares based on F^2 . In **3** all of the five, and in **4** one of the five, terminal isopropoxide ligands were found to have disorder in the positions of their carbon atoms. In **5b** one of the terminal *tert*-butoxides and one of the monodentate (Me₂NCH₂)₂CHO[−] ligands were found to be disordered (though in both cases the co-ordinating oxygen atoms were ordered). In all these instances the disorder was resolved into two partial occupancy orientations with the non-hydrogen atoms of the major occupancy orientations being refined anisotropically. All of the remaining non-hydrogen atoms in all four structures were refined anisotropically. In each structure the C–H hydrogen atoms were placed in calculated positions, assigned isotropic thermal parameters, and allowed to ride on their parent atoms. The O–H hydrogen atom in **5a** and **5b** was located from a ΔF map and refined isotropically subject to an O–H distance constraint. Computations were carried out using the SHELXTL PC program system.¹⁸

CCDC reference number 186/1525.

See <http://www.rsc.org/suppdata/dt/1999/2853/> for crystallographic files in .cif format.

Results and discussion

The zirconium alkoxides [Zr₂(OPrⁱ)₈(PrⁱOH)₂] and Zr(Obu^t)₄ when dissolved in *n*-hexane react rapidly under reflux conditions with the aminoalcohols Hdmae, Hdmap or Hbdmap to give clear yellow solutions. On removal of the solvent the crude products of the reactions were viscous colourless liquids. The microanalysis results of the crude liquids **1–4** were found to be consistent with the empirical formula [Zr(OPrⁱ)₂L₂]. On storage of liquids **3**, **4** and **5** at room temperature large colourless crystals formed, indicating two or more products in the reaction mixtures. As time progressed more of the liquids became crystalline, suggesting a complex equilibrium to be present. Crystallisation of the crude products from *n*-hexane at 0 °C also gave colourless crystals (except in the case of **1**, which did not crystallise but remained a viscous liquid).

Compounds **1–5** were found to be soluble in hydrocarbon solvents (pentane, hexane), and exceptionally soluble in THF; solubility was found to be poorer in aromatic solvents (benzene, toluene). They were moisture sensitive, but less so than the parent alkoxides. The reduced atmospheric sensitivity may be attributed to the compounds having a more saturated co-ordination sphere. The melting points show the compounds are all relatively low melting solids (below 250 °C), and sublime under reduced pressure with very little residue (<5%) at relatively low temperatures.

Crystals of compounds **3**, **4** and **5** were suitable for single crystal X-ray analysis, and in an effort to obtain more detailed structural information their structures were determined.

Table 1 Crystal data, data collection and refinement parameters^a

| | [Zr ₂ (OPr ⁱ) ₆ (dmap) ₂] 3 | [Zr ₂ (OPr ⁱ) ₆ (bdmap) ₂] 4 | [Zr ₂ (OBu ^t) ₃ (bdmap) ₄ (OH)] 5a | [Zr ₂ (OBu ^t) ₃ (bdmap) ₄ (OH)] 5b |
|---|--|---|--|--|
| Formula | C ₂₈ H ₆₆ N ₂ O ₈ Zr ₂ | C ₃₂ H ₇₆ N ₄ O ₈ Zr ₂ | C ₄₀ H ₉₆ N ₈ O ₈ Zr ₂ | C ₄₀ H ₉₆ N ₈ O ₈ Zr ₂ |
| Formula weight | 741.3 | 827.4 | 999.7 | 999.7 |
| Colour, habit | Clear blocks | Clear rhombs | Clear blocky plates | Clear prisms |
| Crystal size/mm | 1.00 × 0.83 × 0.50 | 1.00 × 0.90 × 0.73 | 0.83 × 0.53 × 0.23 | 0.67 × 0.33 × 0.33 |
| Crystal system | Triclinic | Monoclinic | Monoclinic | Triclinic |
| Space group | <i>P</i> $\bar{1}$ (no. 2) | <i>C</i> 2/ <i>c</i> (no. 15) | <i>P</i> 2 ₁ / <i>n</i> (no. 14) | <i>P</i> $\bar{1}$ (no. 2) |
| <i>a</i> /Å | 10.146(1) | 22.066(2) | 20.949(2) | 12.589(1) |
| <i>b</i> /Å | 12.412(1) | 12.339(1) | 12.276(2) | 14.147(2) |
| <i>c</i> /Å | 17.585(2) | 32.591(3) | 23.485(3) | 17.062(1) |
| <i>α</i> /° | 104.85(1) | — | — | 86.48(1) |
| <i>β</i> /° | 92.93(1) | 101.16(1) | 111.49(7) | 70.62(1) |
| <i>γ</i> /° | 113.76(1) | — | — | 85.23(1) |
| <i>V</i> /Å ³ | 1929.0(3) | 8706(1) | 5620(1) | 2854.8(5) |
| <i>Z</i> | 2 | 8 | 4 | 2 |
| <i>D</i> /g cm ⁻³ | 1.276 | 1.263 | 1.182 | 1.163 |
| <i>F</i> (000) | 784 | 3520 | 2144 | 1072 |
| Radiation used | Mo-Kα | Cu-Kα ^b | Mo-Kα | Mo-Kα |
| <i>μ</i> /mm ⁻¹ | 0.58 | 4.29 | 0.42 | 0.41 |
| <i>θ</i> range/° | 1.9–25.0 | 2.8–62.5 | 1.9–25.0 | 1.8–25.0 |
| No. unique reflections | | | | |
| measured | 6656 | 6937 | 9871 | 9526 |
| observed, <i> F_o </i> > 4σ(<i> F_o </i>) | 5164 | 5510 | 7323 | 5785 |
| No. variables | 451 | 428 | 528 | 571 |
| <i>R</i> 1 | 0.038 | 0.054 | 0.045 | 0.056 |
| <i>wR</i> 2 | 0.085 | 0.136 | 0.095 | 0.114 |
| Largest difference peak, hole/e Å ⁻³ | 0.48, −0.33 | 0.78, −1.62 | 0.81, −0.37 | 0.48, −0.31 |

^a Details in common: graphite monochromated radiation, *ω* scans, Siemens P4 diffractometer, 203 K. ^b Rotating anode source.

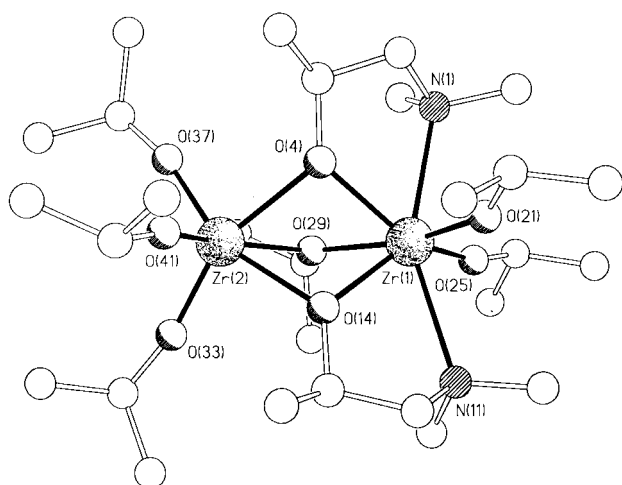
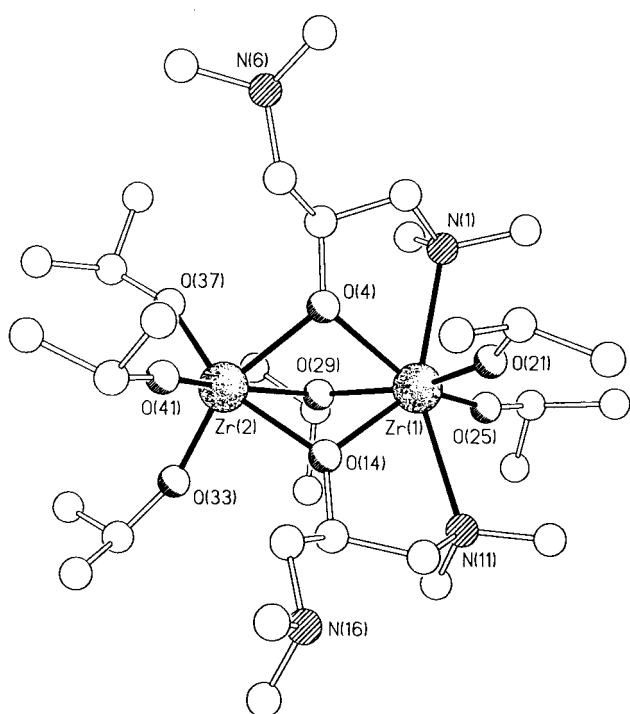


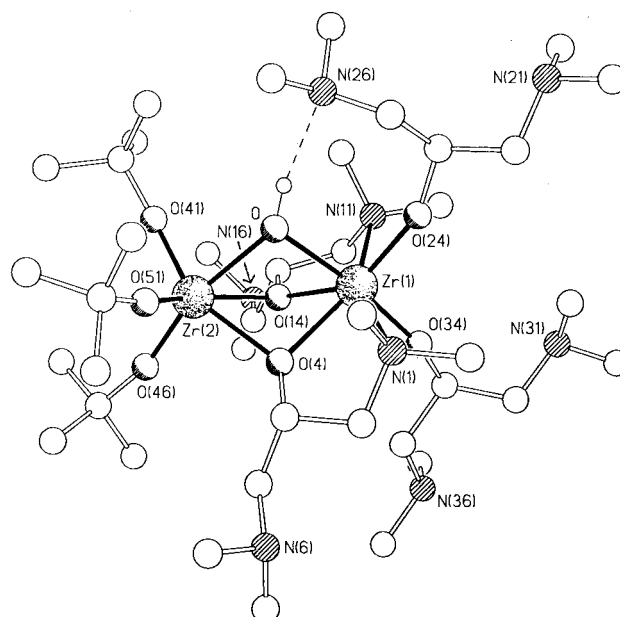
Table 2 Selected bond lengths (Å) and angles (°) for $[\text{Zr}_2(\text{OPr}^i)_6(\text{dmap})_2]$ **3** and $[\text{Zr}_2(\text{OPr}^i)_6(\text{bdmap})_2]$ **4**

| | 3 | 4 | | 3 | 4 |
|-------------------|------------|-----------|-------------------|------------|------------|
| Zr(1)–O(4) | 2.206(2) | 2.204(3) | Zr(1)–O(14) | 2.161(2) | 2.165(4) |
| Zr(1)–O(21) | 1.953(2) | 1.951(4) | Zr(1)–O(25) | 1.978(2) | 1.967(4) |
| Zr(1)–O(29) | 2.189(2) | 2.176(3) | Zr(1)–N(1) | 2.490(3) | 2.502(4) |
| Zr(1)–N(11) | 2.540(3) | 2.516(5) | Zr(2)–O(4) | 2.212(2) | 2.217(3) |
| Zr(2)–O(14) | 2.214(2) | 2.216(4) | Zr(2)–O(29) | 2.291(2) | 2.280(3) |
| Zr(2)–O(33) | 1.946(2) | 1.943(4) | Zr(2)–O(37) | 1.964(2) | 1.953(4) |
| Zr(2)–O(41) | 1.937(3) | 1.946(4) | Zr(1)···Zr(2) | 3.2936(6) | 3.2900(6) |
| O(4)–Zr(1)–O(14) | 68.31(9) | 68.54(13) | O(4)–Zr(1)–O(21) | 91.40(10) | 90.84(14) |
| O(4)–Zr(1)–O(25) | 144.57(10) | 145.4(2) | O(4)–Zr(1)–O(29) | 72.52(9) | 72.47(12) |
| O(4)–Zr(1)–N(1) | 69.67(10) | 69.16(14) | O(4)–Zr(1)–N(11) | 134.91(10) | 134.52(14) |
| O(14)–Zr(1)–O(21) | 97.55(10) | 99.0(2) | O(14)–Zr(1)–O(25) | 137.70(10) | 136.4(2) |
| O(14)–Zr(1)–O(29) | 74.03(9) | 73.96(13) | O(14)–Zr(1)–N(1) | 137.97(10) | 137.65(14) |
| O(14)–Zr(1)–N(11) | 68.55(10) | 68.19(14) | O(21)–Zr(1)–O(25) | 104.57(10) | 104.5(2) |
| O(21)–Zr(1)–O(29) | 163.63(9) | 163.2(2) | O(21)–Zr(1)–N(1) | 84.01(11) | 83.7(2) |
| O(21)–Zr(1)–N(11) | 81.77(11) | 82.7(2) | O(25)–Zr(1)–O(29) | 90.72(9) | 90.54(14) |
| O(25)–Zr(1)–N(1) | 80.62(11) | 81.7(2) | O(25)–Zr(1)–N(11) | 79.39(11) | 78.9(2) |
| O(29)–Zr(1)–N(1) | 92.93(10) | 91.4(2) | O(29)–Zr(1)–N(11) | 107.22(10) | 107.8(2) |
| N(1)–Zr(1)–N(11) | 151.63(11) | 152.7(2) | O(4)–Zr(2)–O(14) | 67.28(9) | 67.44(13) |
| O(4)–Zr(2)–O(29) | 70.48(8) | 70.28(12) | O(4)–Zr(2)–O(33) | 156.82(10) | 156.8(2) |

**Fig. 2** Molecular structure of $[\text{Zr}_2(\text{OPr}^i)_6(\text{bdmap})_2]$ **4**.**Crystal structure of $[\text{Zr}_2(\text{OPr}^i)_6(\text{bdmap})_2]$ **4****

The structure of $[\text{Zr}_2(\text{OPr}^i)_6(\text{bdmap})_2]$ **4** is depicted in Fig. 2. This structure resembles that of the dmap compound **3**, comprising two zirconium metal centres that are bridged by two bdmap ligands and one isopropoxide ligand. The $\text{Zr} \cdots \text{Zr}$ distance is non-bonding at 3.2900(6) Å, and shorter than that observed in **3**. The zirconium metal centres of **4** have very similar geometries to those in **3**, but are here bridged by two chelating η^2 -bdmap ligands.

The Zr–O bond distances fall into the same three distinct groups as in compound **3**. The first set, to the terminally bonded isopropoxide molecules, are in a narrower range than those in **3** [1.943(4)–1.967(4) Å], though with a similar average (1.952 Å). The second set (for the bridging μ -isopropoxide ligand) are also comparable in that the Zr(2)–O bond is longer [2.280(3) Å] than the Zr(1)–O [2.176(3) Å], averaging 2.228 Å, which again is slightly longer than those reported. The third set of Zr–O bonds involves the bridging μ -bdmap ligands. Again,

**Fig. 3** Molecular structure of $[\text{Zr}_2(\text{OBu}^i)_3(\text{bdmap})_4(\text{OH})]$ **5**.

the Zr(2)–O bonds are longer than the Zr(1)–O (average 2.217 and 2.185 Å respectively), and slightly larger than those to the bridging oxygens in $[\text{Zr}_2(\text{OPr}^i)_8(\text{Pr}^i\text{OH})_2]$ [average $\text{Zr}(\mu\text{-OPr}^i)$ 2.170 Å].¹²

The Zr–N bonds are 2.516(5) and 2.502(4) Å (average 2.509 Å), slightly shorter than those in compound **3**. The Zr–O–Zr bond angles are again all obtuse, though the $\text{Zr}-\text{O}_{\text{bdmap}}-\text{Zr}$ angles are slightly smaller than those in **3**, at 97.4(1) and 96.2(1)°, and $\text{Zr}-\text{O}_{\text{OPr}}-\text{Zr}$ of 95.2(1)° is larger than that in **3**.

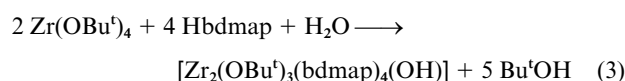
Crystal structure of $[\text{Zr}_2(\text{OBu}^i)_3(\text{bdmap})_4(\text{OH})]$ **5**

The molecular structure of $[\text{Zr}_2(\text{OBu}^i)_3(\text{bdmap})_4(\text{OH})]$ **5** is shown in Fig. 3. This compound is entirely different from the isopropoxide analogue **4**. It was synthesized repeatedly, and despite extreme efforts to exclude moisture a μ -hydroxo bridged compound always crystallised. Indeed in the process of these multiple experiments two different polymorphs of **5** (**5a** and **5b**) were crystallised and their structures analysed. The geometries of the central cores in the two polymorphs differ only slightly with an r.m.s. deviation of 0.05 Å and a maximum deviation of 0.11 Å for O(41). In this complex four bdmap ligands and three

Table 3 Selected bond lengths (Å) and angles (°) for complexes [Zr₂(OBu^t)₃(bdmap)₄(OH)] **5a** and **5b**

| | 5a | 5b | | 5a | 5b |
|-------------------|------------|-----------|-------------------|------------|-----------|
| Zr(1)–O | 2.125(3) | 2.123(4) | Zr(1)–O(4) | 2.195(3) | 2.173(4) |
| Zr(1)–O(14) | 2.190(2) | 2.182(4) | Zr(1)–O(24) | 1.993(3) | 1.991(5) |
| Zr(1)–O(34) | 1.968(3) | 1.984(4) | Zr(1)–N(1) | 2.488(4) | 2.485(5) |
| Zr(1)–N(11) | 2.499(3) | 2.481(5) | Zr(2)–O | 2.238(3) | 2.232(4) |
| Zr(2)–O(4) | 2.222(3) | 2.228(4) | Zr(2)–O(14) | 2.232(3) | 2.233(4) |
| Zr(2)–O(41) | 1.968(3) | 1.959(5) | Zr(2)–O(46) | 1.951(3) | 1.943(5) |
| Zr(2)–O(51) | 1.948(3) | 1.939(4) | Zr(1)···Zr(2) | 3.2714(6) | 3.2731(9) |
| O–Zr(1)–O(4) | 73.76(10) | 74.5(2) | O–Zr(1)–O(14) | 74.99(10) | 73.3(2) |
| O–Zr(1)–O(24) | 86.36(11) | 86.1(2) | O–Zr(1)–O(34) | 171.02(11) | 168.8(2) |
| O–Zr(1)–N(1) | 98.27(12) | 101.6(2) | O–Zr(1)–N(11) | 95.96(11) | 94.6(2) |
| O(4)–Zr(1)–O(14) | 66.47(9) | 67.2(2) | O(4)–Zr(1)–O(24) | 139.39(11) | 137.6(2) |
| O(4)–Zr(1)–O(34) | 100.30(10) | 99.0(2) | O(4)–Zr(1)–N(1) | 68.24(11) | 68.5(2) |
| O(4)–Zr(1)–N(11) | 135.04(10) | 136.4(2) | O(14)–Zr(1)–O(24) | 141.90(11) | 142.1(2) |
| O(14)–Zr(1)–O(34) | 96.56(10) | 95.8(2) | O(14)–Zr(1)–N(1) | 134.27(11) | 135.1(2) |
| O(14)–Zr(1)–N(11) | 68.59(10) | 69.2(2) | O(24)–Zr(1)–O(34) | 102.37(11) | 104.5(2) |
| O(24)–Zr(1)–N(1) | 80.47(12) | 79.4(2) | O(24)–Zr(1)–N(11) | 80.99(11) | 81.5(2) |
| O(34)–Zr(1)–N(1) | 85.42(12) | 84.1(2) | O(34)–Zr(1)–N(11) | 83.48(11) | 83.7(2) |
| N(1)–Zr(1)–N(11) | 155.78(11) | 153.9(2) | O–Zr(2)–O(4) | 71.10(10) | 71.4(2) |
| O–Zr(2)–O(14) | 71.98(9) | 70.3(2) | O–Zr(2)–O(41) | 89.58(12) | 91.2(2) |
| O–Zr(2)–O(46) | 164.51(11) | 163.2(2) | O–Zr(2)–O(51) | 90.89(13) | 92.2(2) |
| O(4)–Zr(2)–O(14) | 65.29(9) | 65.4(2) | O(4)–Zr(2)–O(41) | 153.82(11) | 156.8(2) |
| O(4)–Zr(2)–O(46) | 96.60(12) | 95.6(2) | O(4)–Zr(2)–O(51) | 93.67(12) | 93.1(2) |
| O(14)–Zr(2)–O(41) | 92.43(12) | 94.9(2) | O(14)–Zr(2)–O(46) | 94.56(12) | 94.9(2) |
| O(14)–Zr(2)–O(51) | 156.00(13) | 155.4(2) | O(41)–Zr(2)–O(46) | 98.84(13) | 98.2(2) |
| O(41)–Zr(2)–O(51) | 104.42(14) | 103.0(2) | O(46)–Zr(2)–O(51) | 99.5(2) | 99.2(2) |

tert-butoxide ligands are present, whereas both isopropoxide (**3** and **4**) compounds have two aminoalkoxide ligands and six isopropoxide ligands. It is possible that due to steric restraints on the system the observed OH moiety arises from cleavage of the Bu^t–OH bond in one of the ligands, or more likely that adventitious water assists the reaction, eqn. (3).



The structure is binuclear, consisting of two zirconium metal centres that are bridged by two bdmap ligands and one hydroxide ligand. For the purposes of comparison between the two polymorphs the first value given is that for structure **5a** and the second in square brackets that for **5b**. The Zr···Zr distance of 3.2714(6) [3.2731(9) Å] (Table 3) is significantly shorter than previously reported values. Again, one zirconium centre [Zr(2)] has a distorted octahedral geometry, whereas the other [Zr(1)] is distorted pentagonal bipyramidal, as observed in **3** and **4**. Here the inner co-ordination sphere at Zr(2) comprises three terminal *tert*-butoxide ligands, two O-bonded μ -bdmap ligands and the μ -hydroxide ligand. The Zr(1) centre has two chelating η^2 -bdmap ligands [which bridge *via* oxygen to Zr(2)], two terminal bdmap ligands and the bridging hydroxide.

The Zr–O bond distances fall into four distinct groups. The first set involves the *tert*-butoxide ligands bonded terminally to the six-co-ordinate Zr(2), and is in the range 1.939(4)–1.968(3) Å (average 1.951 Å). The accompanying Zr–O–C angles are nearly linear²¹ (average Zr–O–C 166.0°). This combination of short Zr–O bonds and near linear Zr–O–C angles has been observed for a variety of compounds, [(tritox)Zr]₅(μ_5 -N)-(μ_5 -NH)₄(μ -NH₂)₄] (1.927 Å, 177°),²² (tritox = ^tBu₃CO) [ZrCl₃-(tritox)₂·Li(OEt)₂] (1.895 Å, 169°),²¹ [Cp₂W=C(H)OZr(H)(η^5 -C₅(CH₃)₅)₂] (1.970 Å, 166°),²³ and [(Cp₂ZrCH₃)₂O] (1.945 Å, 174°),²⁴ and can be interpreted as reflecting strong O_(pr)→Zr_(dr) bonding.^{21,25} The second set of Zr–O bond distances are for the μ -bridging η^2 -bdmap ligands. The bridging Zr(2)–O_{bdmap} bond lengths (average 2.185 Å) are longer than their Zr(1) counterparts (average 2.229 Å). The third group comprises the terminal Zr–O_{bdmap} bonds, which are significantly shorter at 1.968(3) [1.984(4)] and 1.993(3) [1.991(5) Å] (average 1.981 Å), but com-

parable with those of other related terminally bonded ligands. The fourth type of Zr–O bond distance is that to the hydroxyl group; the Zr(2)–O bond is substantially longer than the Zr(1)–O, 2.238(3) [2.232(4)] and 2.125(3) [2.123(4) Å] respectively. These distances are similar to those of other Zr– μ -OH containing compounds, for example [(ZrCp(NO₃)₂(μ -OH))₂·2THF (average 2.13 Å).¹³ In both polymorphs the bridging hydroxyl group is involved in an intramolecular hydrogen bond to one of the non-co-ordinated dimethylamino nitrogen atoms [N(26)]; the O···N and H···N distances are 2.91 [2.90] and 2.02 [2.05 Å] with an associated O–H···N angle of 170 [158°] (the O–H distances were fixed at 0.90 Å).

The Zr–N bonds lengths of 2.499(3) [2.481(5)] and 2.488(4) [2.485(5) Å] are shorter than those in compounds **3** and **4**, but longer than would be expected on the basis of the sum of the atomic radii reflecting the dative nature of these interactions.

The co-ordination of bdmap generates a chiral centre at the α -hydroxyl carbons in compounds **4**, **5** and **5b**. In each, two such ligands are co-ordinated in enantiomorphic pairs leading to molecules of the binuclear complexes best described as *meso* compounds.

Spectroscopic characterisation

The infrared spectra of complexes **1–5** were studied as Nujol mulls between NaCl windows. Selected bands are listed in Table 4. They are tentatively assigned on the basis of data of previously characterised alkoxides and aminoalcohols.²⁰ The asymmetric and symmetric ν (C–O) stretches were observed in the region 1030–1070 cm^{−1}, and the ν (C–N) absorption frequencies corresponding to the aminoalcohols in the region 1165–1180 cm^{−1}.

Multinuclear NMR spectroscopy (¹H and ¹³C-{¹H}) studies were undertaken; the ¹H NMR data are detailed in Table 5, and the ¹³C-{¹H} NMR data in Table 6. There is no evidence of any free alcohol remaining in the lattice of any of the compounds, unlike the parent alkoxide [Zr₂(OPrⁱ)₈(PrOH)₂]. The ¹H and ¹³C-{¹H} NMR spectra of the aminoalcohol compounds **1** and **2** (which have the stoichiometry [Zr(OR)₂-(dmae)₂]) do not differ significantly with the nature of the alkoxide, which may be due to the less bulky nature of Hdmae when compared to the β -diketone Htmhd.⁶

Table 4 Characteristic IR assignments for compounds **1–5**

| Compound | $\tilde{\nu}(\text{C}=\text{O})/\text{cm}^{-1}$ | $\tilde{\nu}(\text{C}=\text{N})/\text{cm}^{-1}$ | $\tilde{\nu}(\text{O}=\text{H})/\text{cm}^{-1}$ | $\tilde{\nu}(\text{M}=\text{O})/\text{cm}^{-1}$ |
|---|---|---|---|---|
| 1 $[\text{Zr}(\text{OPr}^i)_2(\text{dmae})_2]$ | 1030–1070 | 1165–1180 | — | 459, 453, 437, 434, 419, 413, 403 |
| 2 $[\text{Zr}(\text{OBu}^t)_2(\text{dmap})_2]$ | 1030–1070 | 1160–1175 | — | 461, 443, 434, 420, 413, 405 |
| 3 $[\text{Zr}_2(\text{OPr}^i)_6(\text{dmap})_2]$ | 1020–1065 | 1140–1160 | — | 464, 451, 436, 426, 419, 411, 407 |
| 4 $[\text{Zr}_2(\text{OPr}^i)_6(\text{bdmap})_2]$ | 1010–1050 | 1150–1175 | — | 462, 450, 444, 435, 426, 409, 403 |
| 5 $[\text{Zr}_2(\text{OBu}^t)_3(\text{bdmap})_4(\text{OH})]$ | 1020–1080 | 1160–1180 | 3450 | 467, 461, 443, 437, 430, 414, 408, 401 |

Table 5 ^1H NMR data (δ) for compounds **1–5** at room temperature in C_6D_6

| Compound | OR | | Aminoalkoxide | | |
|---|-------------------------|-----------|----------------|-----------------------|----------------|
| | OR_{Me} | OCH | NMe_2 | OCH_n | NCH_2 |
| 1 $[\text{Zr}(\text{OPr}^i)_2(\text{dmae})_2]$ | 1.25 | 4.47 | 2.23 | 4.17 ($n = 2$) | 2.48 |
| 2 $[\text{Zr}(\text{OBu}^t)_2(\text{dmap})_2]$ | 1.58 | — | 2.16 | 4.26 ($n = 2$) | 2.38 |
| 3 $[\text{Zr}_2(\text{OPr}^i)_6(\text{dmap})_2]$ | 1.28–1.49 | 4.28–4.67 | 2.17–2.51 | 3.74 ($n = 1$) | 2.17–2.51 |
| 4 $[\text{Zr}_2(\text{OPr}^i)_6(\text{bdmap})_2]$ | 0.97 | 4.58 | 2.08–2.52 | 3.51–3.63 ($n = 1$) | 2.08–2.52 |
| 5 $[\text{Zr}_2(\text{OBu}^t)_3(\text{bdmap})_4(\text{OH})]$ | 1.52–1.59 | — | 2.12–2.34 | 4.40–4.72 ($n = 1$) | 2.12–2.34 |

Table 6 $^{13}\text{C}\{-^1\text{H}\}$ NMR data (δ) for compounds **1–5** at room temperature in C_6D_6

| Compound | OR | | Aminoalkoxide | | |
|----------|--------------------------|-------|----------------|-------------------|----------------|
| | $\text{OC}(\text{Me})_n$ | Me | NMe_2 | OCH_n | NCH_2 |
| 1 | 75.98 | 22.65 | 46.53 | 69.64 ($n = 2$) | 62.63 |
| 2 | 73.0 | 31.1 | 33.6 | 68.00 ($n = 2$) | 46.4 |
| 3 | 69.65 | 25.47 | 45.25 | 67.26 ($n = 1$) | 63.65 |
| 4 | 72.91 | 17.63 | 45.73 | 68.52 ($n = 1$) | 45.73 |
| 5 | 67.88 | 23.00 | 31.50 | 67.88 ($n = 1$) | 31.50 |

The spectra show only minor shifts in each peak between the compounds. The integration for each peak was as expected. However, the signals for $\text{OCH}(\text{CH}_3)_2$ and $\text{OCH}_2\text{CH}_2\text{N}$ of **1** and the $\text{OCH}_2\text{CH}_2\text{N}$ signal of **2** are not fully resolved in the ^1H NMR spectra. $^{13}\text{C}\{-^1\text{H}\}$ NMR experiments show only 5 distinct carbon environments, which is consistent with the monomeric species. If the dimeric species $[\text{Zr}_2(\text{OR})_4(\text{dmae})_4]$ was present one would expect to see a larger number of signals due to the carbon environments in the bridging backbone being slightly different to the terminal carbon environments. There is no evidence in the ^1H or the $^{13}\text{C}\{-^1\text{H}\}$ NMR spectra to suggest an equilibrium is present for either compound in solution. Similar results were observed for the titanium analogue $[\text{Ti}(\text{OPr}^i)_2(\text{dmae})_2]$.²⁶

The ^1H and $^{13}\text{C}\{-^1\text{H}\}$ NMR spectra of both compounds **3** and **4** are very complex, because of their nature. The crystal structure determinations have helped with the interpretation of these spectra; in both compounds there are 3 isopropoxide environments, with evidence of *cis-trans* isomerisation. The CH_2N and $\text{N}(\text{CH}_3)_2$ region is very crowded for **3**, and even more so for **4**, therefore only tentative assignments have been made for each peak; however, the integration across each region is as expected for compounds with a formula of $[\text{Zr}_2(\text{OPr}^i)_6\text{L}_2]$.

The ^1H and $^{13}\text{C}\{-^1\text{H}\}$ NMR spectra of compound **5** are even more complex. It can be seen that there are four bdmap ligands, giving rise to eight different CH_2N and CH_3N environments, and four CHO environments. Owing to the complexity of the ^1H NMR spectrum only tentative assignments have been made, but the overall integrations are as expected for each region.

Electron impact mass spectrometric studies were performed for all compounds, and the major ions observed are shown in Table 7. The data for **1** and **2** demonstrate that, in the instrument, the binuclear compounds $[\text{Zr}_2(\text{OR})_6(\text{dmae})_2]$ and fragments of the monomer are present, as found for the titanium

isopropoxide analogue.²⁶ Compounds **3** and **4**, although structurally similar, behave differently under mass spectrum conditions; both exhibited ions of binuclear composition and subsequently a distinct pattern of decomposition due to their monomeric fragments; however **3** ‘loses’ its aminoalcohol ligands more readily than **4**, which preferentially fragments by ‘losing’ isopropoxide ligands. The fragments $[\text{Zr}_2(\text{OPr}^i)_5\text{L}_2]$ and $[\text{Zr}_2(\text{OPr}^i)_3]$ were observed in both spectra. Compound **5** also exhibited binuclear ions, and a distinct pattern of decomposition to its monomeric fragments, yet behaves in a similar manner to **3** in the instrument, by ‘losing’ its *tert*-butoxide ligands first.

Conclusion

The use of donor functionalised ligands in the modification of zirconium alkoxides has enabled us to isolate a series of new zirconium compounds, three of which have been structurally characterised. The dmae analogues $[\text{Zr}(\text{OR})_2(\text{dmae})_2]$ [$\text{R} = \text{Pr}^i$ **1** or Bu^t **2**] are monomeric probably due to the less ‘bulky’ nature of the chelating ligand in comparison to the Hdmap, Hbdmap and Htmhd⁶ ligands.

Compounds **3** and **4** have the same empirical formula $[\text{Zr}_2(\text{OPr}^i)_6(\text{L})_2]$, and are asymmetric, with in both cases the zirconium centres having different co-ordination numbers of 6 and 7, which is unusual. One half of each molecule can be viewed as being derived from the alkoxide, the other half from the aminoalkoxide. The structure of $[\text{Zr}_2(\text{OBu}^t)_3(\text{bdmap})_4(\text{OH})]$ **5**, is also asymmetric, and its zirconium metal centres also have the same mixed co-ordination as found in **3** and **4**, but is unusual due to the presence of a μ -hydroxy bridge.

The single crystal structures of the compounds we have determined are useful in interpreting some of the observations made in growth studies.²⁷ The parent alkoxides “ $[\text{Zr}(\text{OR})_4]$ ” are

Table 7 Selected mass spectrometric data (m/z^+) for compounds **1–5**, value of x in parentheses and percentage heights in square brackets

| Compound | Zr(OR) _x | Zr(OR) _x (L) ₂ | Zr(OR) _x (L) | Zr ₂ (OR) _x (L) ₂ | Zr ₂ (OR) _x L | Zr ₂ (OR) ₂ (L) _x |
|----------|------------------------------|--|------------------------------|--|--|--|
| 1 | 209 (2) [10] | 267 (0) [12] 326 (1) [96] 385 (2) [20] | 238 (1) [15] | 712 (6) [11] | — | — |
| 2 | 164 (1) [8] | 267 (0) [10] 340 (1) [91] 413 (2) [27] | 252 (1) [11] 325 (2) [19] | 796 (6) [9] | — | — |
| 3 | 209 (2) [12] 268 (3) [28] | 354 (1) [67] | — | 681 (5) [14] | 637 (6) [98] 578 (5) [10] 519 (4) [29] | — |
| 4 | 209 (2) [19] 268 (3) [17] | 381 (0) [61] 499 (2) [32] | 354 (2) [37] | 826 (6) [25] 767 (5) [96] 708 (4) [42] 649 (3) [34] | — | — |
| 5 | 237 (2) [13] | 454 (1) [98] 527 (2) [37] | — | — | — | 908 (4) [21] 763 (3) [42] 618 (2) [29] |

poor precursors for the deposition of zirconium containing materials by MOCVD and, in particular, are prone to adventitious decomposition reactions in the vapour phase. In contrast to the symmetrical $[\text{Zr}_2(\text{OPr}^i)_6(\text{tmhd})_2]$, the present compounds **3** and **4** contain longer and weaker $[\text{Zr}-\text{O}-\text{Zr}]$ bridging bonds, which will cleave on heating and yield “ $[\text{Zr}(\text{OPr}^i)_4]$ ”. Any vapour containing this species will have the properties of the parent alkoxide, which is very sensitive to water and/or oxygen and readily pre-reacts in the reactor leading to homogeneous precipitation.²⁷

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