Dalton Transactions

Cite this: Dalton Trans., 2011, 40, 1401

PAPER

Oximate-substituted zirconium alkoxides*

Stefan O. Baumann, Michael Puchberger and Ulrich Schubert*

Received 28th April 2010, Accepted 21st November 2010 DOI: 10.1039/c0dt00384k

The reaction of acetoxime, ethyl methyl ketoxime or cyclohexanone oxime with zirconium *iso*-propoxide gave dimeric alkoxo oximate derivatives $[Zr(OiPr)(oximate)_3]_2$. The oximate ligands are side-on coordinated and the alkoxo groups bridge the two metal centres. NMR spectroscopy revealed dynamic behaviour of the compounds in solution. When exposing a reaction mixture of zirconium butoxide and cyclohexanone oxime to ambient moisture, the oxo-alkoxo derivative $Zr_4O(OBu)_8(ON=C_6H_{10})_6$ was obtained.

Introduction

Modification of transition metal alkoxides, $M(OR)_n$, by bi- or tridentate organic ligands allows decreasing the high reaction rates during sol–gel processing as well as introducing functional groups in metal-based sol–gel materials. Effects of these modifications on the derived gels have been discussed elsewhere.¹ Acetic acid or acetylacetone is most commonly used for modification, but also other compounds, such as α -amino acids, hydroxycarboxylic acids, phosphonic and phosphinic acids, sulfonic acids, as well as various β -diketones and β -ketoesters, amino alcohols, *etc*. The protic compounds can substitute one or more OR groups of $M(OR)_n$ with concomitant ROH elimination. This results in modified precursors $M(OR)_{n,x}(BL)_x$, where BL is an anionic bi- or tri-dentate ligand which is more strongly bonded than alkoxo ligands.

The structural chemistry of $Ti(OR)_{4x}(BL)_x$ derivatives with various bidentate ligands and their primary hydrolysis products,² to a smaller extent also that of $Al(OR)_{3-x}(BL)_x$, has been well investigated. The reason for the better knowledge on Ti and Al derivatives is their higher crystallization tendency and simpler structures, compared with other metal alkoxides. Both can be traced back to the lower coordination numbers of Ti (six, rarely five) and Al (4-6) which results in a smaller number of possibilities how the coordination polyhedra can be connected with each other. For this reason, the structures of zirconium alkoxide derivatives cannot be extrapolated from the corresponding titanium derivatives. A particularly illustrative example are the compounds " $M(OR)_3(OCH_2CH_2NH_2)$ " (M = Ti, Zr). While titanium derivatives (OR = $O_i Pr$, OEt) are alkoxobridged dimers with chelating aminoethanolate ligands, the Zr compound is in fact Zr₆(OBu)₁₈(OCH₂CH₂NH₂)₆, assembled from two $Zr_2(OBu)_5(OCH_2CH_2NH_2)_3$ and two $Zr(OBu)_4$ sub-units, which are associated by alkoxo bridges.⁴

When used in sol-gel processes, the organically modified metal alkoxide derivatives are the building blocks for the obtained hybrid inorganic-organic gels. Since the latter are usually non-crystalline, structural information must be extrapolated from the structures of the building blocks. In this respect, partially hydrolyzed compounds are also important, as they allow conclusions on how the gel structures develop in the early stages of the hydrolysis and condensation processes. Each of the structures is just a snapshot, but common features can be extracted when comparing all snapshots. For example, comparison of partially hydrolyzed carboxylate- or aminoalcoholate-substituted titanium alkoxide derivatives showed, *inter alia*,^{2,4} (i) that μ_3 -oxygen atoms are already formed in the very early stages of the hydrolysis process, and (ii) that the degree of substitution (average number of BL ligands per metal atom) and the degree of hydrolysis (average number of oxo groups per metal atom) have a mutual influence on the observed structural features.

Because of the lower crystallization tendency of Zr derivatives, only few structural data on $Zr(OR)_{4x}(BL)_{x}$ derivatives or their partial hydrolysis products are available. Apart from "Zr(OBu)₃(OCH₂CH₂NH₂)", the structures of $[Zr(OiPr)_2(OOC-CCO_3(CO)_9)_2]_2$ (one bridging carboxylate and OiPr ligand per zirconium atom each)⁵ and polymeric $[Zr(OPr)(O_3SMe)_3]_{\infty}^6$ (two bridging and one chelating sulfonate group per zirconium atom and a terminal OPr group) are known. Structurally characterized BL-substituted oxo-alkoxo derivatives are Zr₄O(OMe)₄(acac)₄(3,5-di*tert*-butylcatecholate)₃(MeOH) $(acac = acetylacetonate),^7$ $Zr_4O(OPr)_{10}(acac)_4$,^{8,9} $Zr_{10}O_6(OH)_4(OPr)_{18}(allylacetoacetate)_6$,⁹ [Zr₃O(OBu)₅(methacrylate)₅]₂ and [Zr₃O(OMe)₂(OBu)(methacry- $[ate)_7]_2$ ¹⁰ (oxo derivatives without residual OR groups are disregarded here). The β -diketonate ligands are all chelating, while the methacrylate derivatives contain both chelating and bridging carboxylate ligands, the two Zr₃O units being bridged by OR groups.

Institute of Materials Chemistry, Vienna University of Technology, Getreidemarkt 9, A-1060, Vienna, Austria. E-mail: uschuber@ mail.zserv.tuwien.ac.at; Fax: +43-1-58801-16599

[†] CCDC reference numbers 775285 (for 1), 775286 (for 2), 775287 (for 3), and 775288 (for 4). For crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt00384k

Own recent work dealt with the modification of titanium alkoxides with oximes,¹¹ and the use of the oximate-substituted precursors for sol–gel processing.¹² We were able to show that the chemistry and structures of $Ti(OiPr)_{4-x}(oximate)_x$ derivatives are less straightforward than has been reported in the literature. The preferentially formed derivatives, independent of the employed stoichiometric ratio of $Ti(OiPr)_4$ and oxime, were the dimeric, alkoxo-bridged compounds $[Ti(OiPr)_2(oximate)_2]_2$. In this article, we report the results of our investigations of the corresponding zirconium oximate derivatives.

Results and discussion

It was claimed in the early literature, that the whole series of compounds $Zr(OiPr)_{4x}(oximate)_x$ was obtained when Zr(OiPr)₄ was reacted with simple ketoximes.¹³ Buyuktas et al. reported recently the formation of Zr(OBu)₂(acetoximate)₂ and Zr(OBu)₃(acetoximate) from Zr(OBu)₄.¹⁴ They postulated from spectroscopic data, that both derivatives are oximate-bridged dimers with terminal butoxo groups. Contrary to this report, we only obtained the dimeric, tri-substituted derivatives $[Zr(OiPr)(oximate)_3]_2$ (1: acetoximate, 2: ethyl methyl ketoximate, 3: cyclohexanone oximate, Fig. 1) when $Zr(OiPr)_4$ was reacted with small ketoximes, viz. acetoxime, ethyl methyl ketoxime or cyclohexanone oxime, in a 1:2 ratio. Mono- or di-substituted compounds (i.e., one or two oximate ligands per zirconium atom) could not be isolated even with smaller proportions of oxime. The crystalline compounds were investigated by X-ray structure analyses.

Fig. 1 Schematic structure of the $[Zr(OiPr)(oximate)_3]_2$ derivates 1–3.

The zirconium alkoxide derivatives 1-3 are centrosymmetric dimeric compounds. The structure of **3** is shown in Fig. 2 as an example; important bond lengths and angles are compared in Table 1. Each zirconium atom is coordinated by three oximate ligands (side-on) and two bridging OiPr groups. The zirconium atoms are thus surrounded by three nitrogen and five oxygen atoms in a distorted dodecahedron. The preference of Zr for coordination number (c.n.) 8 may be the reason for (i) the substitution by three oximate ligands and (ii) the formation of OR bridges. A lower degree of substitution or formation of monomeric Zr(OR)(oximate)₃ would result in a lower c.n. For the same reason, the di-substituted derivatives $[Ti(OiPr)_2(oximate)_2]_2$ (one terminal and one bridging OR ligand per Ti atom) are preferentially formed from Ti(OiPr)₄ under comparable conditions, viz. room temperature reaction of the metal alkoxides with two molar equivalents of the respective oxime. The smaller size and therefore

 Table 1
 Selected distances (pm) and angles (deg) in 1–3 (atoms with an asterisk denote inversion-related atoms)

	1	2	3
Zr(1)–O(1)	218.6(3)	215.4(2)	219.2(2)
$Zr(1) - O(1)^*$	214.6(3)	218.2(2)	215.0(2)
Zr(1) - O(2)	212.7(3)	210.3(3)	212.0(3)
Zr(1) - O(3)	210.1(3)	209.4(3)	209.9(3)
Zr(1) - O(4)	208.4(3)	208.6(2)	208.0(3)
Zr(1) - N(1)	218.0(4)	221.5(4)	220.1(3)
Zr(1)-N(2)	223.3(4)	224.2(3)	223.4(3)
Zr(1) - N(3)	226.7(4)	226.4(3)	229.0(3)
O(1) - Zr(1) - N(2)	166.72(12)	168.98(10) (O1*)	167.78(10)
O(2) - Zr(1) - N(3)	167.49(13)	165.77(9)	163.94(10)
N(1) - Zr(1) - N(3)	130.45(14)	129.48(11)	128.94(11)
O(1) - Zr(1) - O(3)	156.50(11)	154.39(10) (O1*)	155.37(10)
O(2) - Zr(1) - O(4)	130.90(12)	130.53(10)	129.91(10)



Fig. 2 Molecular structure of $[Zr(ON=C_6H_{10})_3(OiPr)]_2$ (3) as an example. Thermal ellipsoids were drawn at 50% probability.

smaller c.n. of Ti is the reason for the lower degree of substitution compared to Zr.

Two of the oximate groups in 1–3 are coordinated to the metal centre by forming a nearly linear N–Zr–O axis (N–Zr–O 164–169°) similar to what was previously found for one isomer of di-substituted titanium alkoxides [Ti(OR)₂(oximate)₂]₂ (the other isomer has nearly linear N–Ti–N axes).^{11,15} The corresponding N(1)–Zr–N(3) and O(2)–Zr–O(4) angles are around 130°. The coordination sphere of the zirconium atoms is completed by a third oximate ligand enclosing a O_{alkoxo}–Zr–O_{oximate} angle of ~156° while the associated nitrogen is slightly twisted out of the central Zr₂(O*i*Pr)₂ plane.

Metal alkoxides and their derivatives sometimes undergo complex equilibria in solution. Any structural investigation must therefore be complemented by NMR spectroscopy in solution. As shown in Fig. 3 for [Zr(O*i*Pr)(ON=C(Me)₂)₃]₂ (1) as an example, more than one CH signal for the methine proton of the bridging O*i*Pr group, as expected for a compound with C_i symmetry, was observed in CD₂Cl₂ solution. In this chemical shift range, an additional signal at $\delta = 3.99$ ppm (d) was present in addition to the expected signal at $\delta = 4.55$ ppm (b). Furthermore, two weaker, broad signals were observed at 4.68 ppm (c) and 4.36 (a) ppm. The EXSY spectrum (Fig. 3) shows exchange between the different O*i*Pr species. One possible explanation for the observed spectrum is, that the dynamic behavior arises from site exchange



Fig. 3 EXSY spectrum of the region of the OiPr methine protons of 1 in CD_2Cl_2 at room temperature.

or rotation of the oximate ligands while the OiPr ligands are only "observing" this process (the exchange signals originate from the changed symmetry). This would explain why there are only two resonances for the methyl groups of the oximate ligands (between 1-2 ppm) instead of six which would be expected for a C_i symmetric compound. Unfortunately, these resonances also partially overlap with the methyl groups of the OiPr groups. Therefore, no further information can be derived from this part of the spectrum.

When the CD_2Cl_2 solution of 1 was cooled to -80 °C, the signal pattern changed. The signals at 4.55 ppm and 3.99 ppm became sharper between 0 °C and -40 °C (Fig. 4) before the two weak

signals almost disappeared at -80 °C, *i.e.* one of the exchange processes is slowed down or terminated at this temperature. While the number of methine signals was reduced, splitting of the peaks was observed in the methyl group region upon cooling. At -80 °C three sets of signals were observed for the methyl groups of the O*i*Pr ligands and five (larger) signals for the acetoximate protons.

The additional resonances can be explained by slowing down the site exchange (or rotation) of the oximate ligand and thus observation of a mixture of a C_i and a C_1 symmetric species. An alternative explanation of the observed exchange process might be that an equilibrium between different oximate-substituted zirconium iso-propoxide species is observed. This would be supported by a tentative assignment of the two more intensive CH signals from the HSOC spectrum: The signal a 3.99 ppm shows a carbon correlation at 64.1 ppm, whereas the signal at 4.55 ppm shows a correlation at 71.6 ppm. Therefore it appears possible that this is an equilibrium between bridging and coordinating isopropoxo ligands. Other examples for such equilibria in solution are known, such as $Ti(OR)_3(\beta$ -diketonate) derivatives, where monomeric and dimeric species are in equilibrium.¹⁶ In addition to that, $[Ti(OR)_3(\beta - diketonate)]_n$ is in equilibrium with $Ti(OR)_4$ and Ti(OR)₂(β -diketonate)₂.¹⁷ Two isomers were found in the disubstituted titanium alkoxides derivatives $[Ti(OR)_2(oximate)_2]_2$, which differ by the mutual orientation of the oximate ligands (parallel or antiparallel arrangement of the N-O vectors) but interconvert in solution.¹¹ The many possible equilibria explain the complex NMR spectra, even if an assignment of the resonances to specific compounds is currently not possible.

As mentioned before, we were not able to crystallize a monoor di-substituted derivative $[Zr(OR)_{4,x}(ON=C(Me)_2)_x]_n$ (x = 1 or 2). However, when ambient moisture was allowed to diffuse slowly into a reaction solution containing two molar equivalents of cyclohexanone oxime and one equivalent of $Zr(OBu)_4$, crystals of $Zr_4O(OBu)_8(ON=C_6H_{10})_6$ (4, Fig. 5) were obtained. In this compound, half of the zirconium atoms are substituted by one or two oximate ligands, respectively. The core of this partial hydrolysis



Fig. 4 Temperature-dependent ¹H NMR spectra of 1 in CD_2Cl_2 at three different temperatures: 25 °C (top), -20 °C (centre) and -80 °C (bottom). The region of the methine protons of the OiPr ligand (left) and the methyl group region (right) is shown.

Table 2 Selected d	istances (pm) an	d angles (°) in 4	
Zr(1)–O(1)	221.2(2)	Zr(4)–O(13)	210.7(3)
Zr(2) - O(1)	222.9(2)	Zr(4) - O(14)	208.7(3)
Zr(3) - O(1)	220.7(2)	Zr(1)-N(1)	223.2(3)
Zr(4) - O(1)	220.8(2)	Zr(2)-N(2)	224.6(3)
Zr(1) - O(3)	211.3(3)	Zr(3) - N(3)	224.6(3)
Zr(2) - O(6)	210.3(3)	Zr(3)–N(4)	228.0(3)
Zr(3)–O(9)	207.3(3)	Zr(4) - N(5)	226.4(3)
Zr(3)–O(10)	210.4(3)	Zr(4) - N(6)	222.1(3)
Zr(1) - O(1) - Zr(2)	91.28(9)	Zr(2)-O(1)-Zr(3)	104.90(9)
Zr(1) - O(1) - Zr(3)	136.54(11)	Zr(2)-O(1)-Zr(4)	132.68(11)
Zr(1) - O(1) - Zr(4)	105.68(9)	Zr(3)-O(1)-Zr(4)	92.54(9)



Fig. 5 Molecular structure of $Zr_4O(O^nBu)_8(ON=C_6H_{10})_6$ (4). Thermal ellipsoids were drawn at 50% probability.

product is built by four zirconium atoms which are located around a central μ_4 -oxygen by forming a distorted tetrahedron with Zr–O bond lengths ranging from 221 to 223 pm and Zr–O– Zr– angles from 91.3 to 136.5° (Table 2). The Zr₄O structural motif was already observed in Zr₄O(OMe)₄(acac)₄(3,5-di-*tert*butylcatecholate)₃(MeOH) ⁷ and Zr₄O(OPr)₁₀(acac)₄.^{8,9} In the latter case it was postulated that the compound is formed by condensation of two dimers.⁸ However, other mechanisms are also imaginable.

In contrast to the latter clusters, the Zr_4O core is more strongly distorted. This is probably due to the fact that in the two acac derivatives all edges of the Zr_4 tetrahedron are bridged by organic groups. In **4**, no bridges are present between Zr(1)/Zr(3) and Zr(2)/Zr(4). The two zirconium atoms Zr(1) and Zr(2) which are coordinated by only one oximate each and which are connected by two butoxo bridges have approximately the same distance (317.50(5) pm) as Zr(3) and Zr(4) which both are surrounded by two oximates each and are also connected by two butoxo bridges (319.09(5) pm). The distance between the neighbouring, differently substituted zirconium atoms bridged by one butoxo ligand (Zr(1)-Zr(4) 352.30(5) and Zr(2)-Zr(3) 351.69(5) pm) and the non-bridged zirconium atoms (Zr(1)-Zr(3) 410.6 and Zr(2)- Zr(4) 406.4 pm) is much larger. Coordination of the oximates occurs in side-on fashion as in the derivatives 1–3 exhibiting Zr–O and Zr–N distances of comparable magnitude.

Conclusions

Contrary to analogous reactions of $Ti(OiPr)_4$ with oximes, where mainly the di-substituted derivatives $[Ti(OiPr)_2(oximate)_2]_2$ were obtained, reaction of $Zr(OiPr)_4$ with the oximes of acetone, ethyl methyl ketone and cyclohexanone yielded *tri*-substituted $[Zr(OiPr)(oximate)_3]_2$ (1–3). The Ti and Zr derivatives are structurally related, a terminal *iso*-propoxo group in the Ti derivative being replaced by a side-on coordinated oximate ligand. This appears to be a consequence of the increased coordination number of zirconium. The dimeric structure of $[Zr(OiPr)(oximate)_3]_2$ is in stark contrast to the polymeric structure of $[Zr(OPr)(O_3SMe)_3]_{ac}$.⁶ The structural difference is probably due to the more pronounced tendency of sulfonate ligands for a bridging coordination.

In $Zr_4O(ON=C_6H_{10})_6(OBu)_8$ (4), obtained from partial hydrolysis, both seven- and eightfold coordinated zirconium atoms are present forming a distorted tetrahedron around a central oxygen. The $Zr_4(\mu_4-O)$ motif was already found in two other oxo-alkoxo derivatives (with different arrangements of the organic ligands, although only a few compounds were structurally investigated. There is again a remarkable difference to partially hydrolyzed Ti(OR)_{4-x}(BL)_x derivatives, where Ti₃(μ_3 -O) groups develop in early stages.² Such groups are typical of crystalline titania modifications. By analogy, the $Zr_4(\mu_4-O)$ motif found in **4** and the related compounds is found in crystalline zirconia. Thus, basic building blocks of the corresponding crystalline oxides develop in a very early stage of the hydrolysis reactions.

Experimental

All care was taken to avoid water or other OH species during sample preparation, *viz*. by working in the dry argon atmosphere of a glovebox and silylation of the NMR tubes. The solvents were additionally treated with basic alumina to eliminate acidic species. $Zr(OiPr)_4$, *i*PrOH (ABCR, 99.9%), $Zr(OBu)_4$ (Aldrich, 80% in butanol), acetoxime (Aldrich, 98%), cyclohexanone oxime (Aldrich, 97%) and ethyl methyl ketone (Aldrich, 99%) were used as received. Ethyl methyl ketone *E*-oxime was synthesized from the ketone by usual methods following a modified version of the procedure of Bousquet.¹⁸ All solvents were dried and purified by standard methods. The solvents for NMR spectroscopy (Eurisotop) were degassed prior to use and stored over molecular sieve.

¹H and ¹³C solution NMR spectra were recorded on a Bruker AVANCE 250 (250.13 MHz {¹H}, 62.86 MHz {¹³C}) and a Bruker DPX 300 spectrometer (300.13 MHz {¹H}, 75.47 MHz {¹³C}) equipped with a 5 mm inverse-broadband probe head and a *z*gradient unit. 2D NMR spectra were measured with Bruker standard pulse programs COSY (Correlation Spectroscopy), HSQC (Heteronuclear Single Quantum Correlation), EXSY (Exchange Spectroscopy; t_{mix} = 1 s), and HMBC (Heteronuclear Multiple-Bond Correlation; optimized for *J* = 140 Hz). The numbering scheme for the carbon atoms of the oximate ligands is given in Fig. 6.

Table 3	Crystallographic and	d structural	l parameters of 1-4
---------	----------------------	--------------	---------------------

	1	2	3	$4 \cdot CH_2Cl_2$
Empirical formula	$C_{24}H_{50}N_6O_8Zr_2$	$C_{30}H_{62}N_6O_8Zr_2$	$C_{42}H_{74}N_6O_8Zr_2$	$C_{69}H_{134}Cl_2N_6O_{15}Zr_4$
Formula weight	733.14	817.30	973.51	1723.60
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P\overline{1}$	C2/c	$P\overline{1}$	$P2_1/n$
a/pm	973.44(15)	1454.5(2)	1050.6(3)	1288.58(11)
b/pm	1911.3(3	1825.1(3)	1072.8(3)	2515.8(2)
c/pm	2044.6(3)	1520.8(2)	1095.4(3)	2561.1(2)
α (°)	64.979(2)		100.974(4)	
β (°)	84.170(2)	101.557(2)	112.554(4)	90.299(2)
γ (°)	88.836(2)		91.132(4)	
Volume/pm ³	$3428.2(9) \cdot 10^{6}$	3955.4(11)·10 ⁶	$1113.5(5) \cdot 10^{6}$	8302.5(12).106
Ζ	4	4	1	4
$D_{\rm c}/{\rm g~cm^{-3}}$	1.420	1.372	1.452	1.379
Abs. coeff. μ/mm^{-1}	0.656	0.577	0.525	0.613
Crystal size/mm	$0.19 \times 0.16 \times 0.09$	$0.55 \times 0.26 \times 0.25$	$0.23 \times 0.13 \times 0.05$	$0.90 \times 0.50 \times 0.30$
Θ range/°	1.10-25.00	2.73-25.00	2.86-28.33	2.26-28.29
Reflections coll./unique	26145/11936	14184/3477	14723/5509	55967/20481
Data/parameters	11936/753	3477/227	5509/264	20481/900
GOF on F^2	1.069	1.065	1.007	1.075
$R[I > 2\sigma(I)]$	0.046	0.043	0.050	0.050
0.1317	0.132	0.117	0.109	0.113
Largest diff. peak/hole/e Å ⁻³	1.647/-1.005	0.771/-0.625	1.390/-1.041	1.036/-1.681



Fig. 6 Numbering of the carbon atoms of cyclohexanone and acetoximate ligands.

FT-IR spectra were recorded on a Bruker Tensor 27 working in ATR MicroFocusing MVP-QL with a ZnSe crystal or in CH_2Cl_2 solution, using OPUS version 4.0 software for analysis. Because of the high moisture sensitivity of the complexes, elemental analysis could not be obtained.

Syntheses

[Zr(ON=C(Me)₂)₃(OiPr)]₂ (1). A solution of 94.6 mg (1.29 mmol) of acetoxime in 1.0 mL of toluene was added dropwise to a solution of 242 mg (0.63 mmol) of Zr(OiPr)₄ in 2.0 mL of toluene. The reaction mixture was stirred for 3 min. Slow evaporation of the solvent gave colourless crystals of 1 after three days of storage at room temperature which were washed with several portions of pentane at -20 °C and dried *in vacuo*. Yield 132 mg (58%, rel. Zr(OiPr)₄, 84% rel. oxime). ¹H NMR (CDCl₃, 20 °C): δ 4.50/3.95 (q, br, J 5.9 Hz, 1H, CHMe₂), 1.95 (s, 3H, C²H), 1.91 (s, 3H, C³H), 1.13 (d, br, J 5.2 Hz, 3H, CH(CH₃)₂) ppm. ¹³C{¹H} NMR (CDCl₃, 20 °C): δ 147.0 (C–N), 77.2 (CHMe₂), 25.3/23.9 (CH(CH₃)₂), 22.0 (C²H), 18.0 (C³H) ppm. IR (CH₂Cl₂, cm⁻¹):v 2973 (s), 2919 (s), 1684 (w), 1645 (m), 1495 (m), 1438 (m), 1378 (s), 1367 (m), 1344 (m), 1159 (m), 1128 (m), 1082 (s), 970 (s), 947 (vs), 846 (w), 814 (w), 609 (m), 590 (m).

 $[Zr(ON=C(Me)Et)_3(OiPr)]_2$ (2). An amount of 160 mg (1.80 mmol) of ethyl methyl ketoxime was added dropwise to a

solution of 356 mg (0.92 mmol) of Zr(OiPr)₄ in 3.0 mL of toluene. The reaction mixture was refluxed for 5 min. Evaporation of the solvent gave colourless crystals of **2** after one day of storage at room temperature which were washed with several portions of pentane at -20 °C and dried *in vacuo*. Yield 134 mg (39% rel. Zr(OiPr)₄). ¹H NMR (CDCl₃, 20 °C): δ 4.54/3.95 (q, br, *J* 6.2 Hz, 1H, CHMe₂), 2.44/2.29 (q, *J* 7.6 Hz, 6H, CH₂Me), 1.87 ((s), 9H, CCH₃), 1.13 ((s), 6H, CH(CH₃)₂), 0.99 (d, br, *J* 6.7 Hz, 9H, CH(CH₃)₂) ppm. ¹³C{¹H} NMR (CDCl₃, 20 °C): δ 151 (*C*==N), 77.2 (CHMe₂), 29.1 (CH₂Me), 24.0 (CHMe₂), 15.6 (CCH₃), 9.8 (CH₂CH₃) ppm. IR (CH₂Cl₂, cm⁻¹):v 2873 (s), 2861 (s), 1683 (w), 1649 (w), 1494 (m), 1438 (w), 1375 (m), 1331 (w), 1161 (m), 1128 (m), 1083 (w), 972 (s), 942 (m), 851 (w), 813 (w), 617 (m), 592 (m).

[Zr(ON=C₆H₁₀)₃(OiPr)]₂ (3). A solution of 428 mg (1.10 mmol) of Zr(OiPr)₄ in 5.0 mL toluene was added dropwise to a solution of 250 mg (2.21 mmol) of acetoxime in 1.0 mL of toluene. The reaction mixture was stirred for 3 min. Colourless crystals of **3** were obtained from the yellow solution after one day which were washed with several portions of pentane at $-20 \,^{\circ}$ C and dried *in vacuo*. Yield 136 mg (25% rel. Zr(OiPr)₄). ¹H NMR (CDCl₃, 20 °C): δ 4.51/3.95 (q, br, *J* 6.1 Hz, 1H, CHMe₂), 2.45 (t, br, *J* 7.2 Hz, 6H, C²H), 2.29 (t, br, *J* 5.8 Hz, 6H, C⁶H), 1.51 ((s), 18H, C³⁻⁵H), 1.14 (d, br, *J* 6.2 Hz, 6H, CH₃) ppm. ¹³C{¹H} NMR (CDCl₃, 20 °C): δ 152.0 (*C*=N), 77.2 (*C*HMe₂), 32.3 (*C*⁶), 27.7 (*C*²), 26.7/25.9/25.6 (*C*³⁻⁵), 24.3 (CH₃) ppm. IR (CH₂Cl₂, cm⁻¹): v 2936 (s), 2859 (s), 1683 (w), 1651 (w), 1608 (w), 1451 (m), 1372 (m), 1332 (w), 1123 (m), 1089 (w), 999 (m), 968 (m), 934 (m), 884 (m), 854 (w), 558 (s).

 $Zr_4O(ONC_6H_{10})_6(OBu)_8$ (4). An amount of 444 mg (3.92 mmol) of cyclohexanone oxime was dissolved in 0.63 mL of dichloromethane before 944 mg (1.97 mmol) of $Zr(OBu)_4$ were added. The reaction mixture was reduced to about three quarters of its original volume by evaporation of the solvent *in vacuo*. Storage of the yellow viscous liquid at 2 °C yielded crystals of 4 after three weeks upon slow diffusion of ambient moisture into

the reaction mixture through a perforated rubber seal. The crystals were recrystallized from dichloromethane.

X-Ray structure analyses†

Single crystal X-ray diffraction measurements were performed on a Siemens SMART and a Bruker-AXS KAPPA APEX II diffractometer with CCD area detectors and a crystal-to-detector distance of 5.5 cm using graphite-monochromated Mo-K α radiation ($\lambda = 71.073$ pm). The data collection at 100 K in a stream of cold nitrogen covered at least a hemisphere of the reciprocal space by recording three or more sets of exposures, each of them exhibiting a different Φ angle. The times for each exposure were 5 to 20 s, each of them covering 0.3° in ω . The data were corrected for polarization and Lorentz effects, and an empirical absorption correction (SADABS) was applied. The structures were solved with direct methods (SHELXS97) and refinement to convergence was carried out with the full-matrix least-squares method based on F^2 (SHELXL97) with anisotropic structure parameters for all nonhydrogen atoms. The hydrogen atoms were placed on calculated positions and refined riding on their parent atoms.

A methyl group of one of the oximate ethyl groups of **2** is disordered as well as two of the terminal butoxy groups in **4**.

Acknowledgements

This work was supported by the Austrian *Fonds zur Förderung der* wissenschaftlichen Forschung (FWF) (Project P20750).

References

- 1 U. Schubert, Acc. Chem. Res., 2007, 40, 730; U. Schubert, J. Sol-Gel Sci. Technol., 2003, 26, 47.
- 2 Review: U. Schubert, J. Mater. Chem., 2005, 15, 3701.
- 3 Review: R. Lichtenberger and U. Schubert, J. Mater. Chem., 2010, 20, 9287.
- 4 H. Fric, F. R. Kogler, M. Puchberger and U. Schubert, Z. Naturforsch B, 2004, 59, 1241; H. Fric, M. Puchberger and U. Schubert, Eur. J. Inorg. Chem., 2008, 1452.
- 5 X. Lei, M. Shang and T. P. Fehlner, Organometallics, 1997, 16, 5289.
- 6 A. Lorenz, G. Kickelbick and U. Schubert, *Chem. Mater.*, 1997, 9, 2551.
- 7 Y. Chi, J.-W. Lan, W.-L. Ching, S.-M. Peng and G.-H. Lee, *J. Chem. Soc., Dalton Trans.*, 2000, 2923.
- 8 P. Toledano, M. In and C. Sanchez, C. R. Acad. Sci. Ser. II, 1990, 311, 1161.
- 9 C. Sanchez, M. In, P. Toledano and P. Griesmar, *Mat. Res. Soc. Symp. Proc.*, 1992, **271**, 669.
- 10 B. Moraru, S. Gross, G. Kickelbick, G. Trimmel and U. Schubert, Monatsh. Chem., 2001, 132, 993.
- 11 S. O. Baumann, M. Bendova, H. Fric, M. Puchberger, C. Visinescu and U. Schubert, *Eur. J. Inorg. Chem.*, 2009, 3333.
- 12 M. Lomoschitz, S. O. Baumann, K. Zorn, S. Pabisch, H. Peterlik and U. Schubert, J. Mater. Chem., 2010, 20, 5527; J. Yang, H. Peterlik, M. Lomoschitz and U. Schubert, J. Non-Cryst. Solids, 2010, 356, 1217.
- 13 A. Singh and R. C. Mehrotra, Inorg. Chim. Acta, 1973, 7, 450.
- 14 B. S. Buyuktas and O. Aktas, Transition Met. Chem., 2006, 31, 56.
- 15 M. G. Davidson, A. L. Johnson, M. D. Jones, M. D. Lunn and M. F. Mahon, *Polyhedron*, 2007, 26, 975.
- 16 A. Léaustic, F. Babonneau and J. Livage, Chem. Mater., 1989, 1, 240.
- 17 J. Blanchard, S. Barboux-Doueff, J. Maquet and C. Sanchez, New J. Chem., 1995, 19, 929; R. J. Errington, J. Ridland, W. Clegg, R. A. Coxall and J. M. Sherwood, Polyhedron, 1998, 17, 659.
- 18 E. W. Bousquet, Organic Syntheses (Coll. Vol.), 1943, 2, 313.