ARTICLES

Organically Modified Transition Metal Alkoxides: Chemical Problems and Structural Issues on the Way to Materials Syntheses

ULRICH SCHUBERT

Institute of Materials Chemistry, Vienna University of Technology, Getreidemarkt 9/165, A-1060 Wien, Austria

Received October 30, 2006

ABSTRACT

Metal or semimetal alkoxides substituted with nonhydrolyzable organic groups are important precursors for inorganic–organic hybrid materials. Understanding the chemistry and structural issues of such precursors is a prerequisite for a rational materials design. Examples are given in this Account, mainly from the chemistry of titanium and zirconium alkoxides, which show that modified metal alkoxide precursors sometimes have an unexpected and unpredictable stuctural chemistry. Furthermore, chemical consequences of the Lewis acidity of the metal alkoxides are discussed, such as adduct formation, ligand exchange reactions, or organic side reactions.

Introduction

The development of inorganic–organic hybrid materials, which have already found numerous applications,[1] is one of the big achievements of sol–gel science. The notion is to create materials with new combinations of properties by combining inorganic and organic building blocks on a molecular level. In the so-called class I materials,[2] the organic and inorganic entities interact only weakly, while they are linked through strong chemical bonds in class II hybrid materials. Preparation of class II sol–gel materials requires precursors being substituted with hydrolytically stable organic groups which either provide a chemical link between the inorganic and organic network structures or introduce pending organic groups.

The development of class II hybrid sol–gel materials was fostered by the availability of alkoxysilanes of the type R′Si(OR)$_3$, where the organic group R′ is directly bonded to the silicon atom. R′ groups may range from simple alkyl or aryl groups to coupling sites or polymerizable groups and complex organic or organometallic units, such as chromophores, catalytically active groups, biomolecules,

etc.[3] Upon sol–gel processing, the Si(OR)$_3$ unit is integrated into the gel network to which the organic group R′ is grafted (eq 1).

$$Si(OR)_4 + R'\text{-}Si(OR)_3 \xrightarrow[-\ ROH]{+\ H_2O} \quad (1)$$
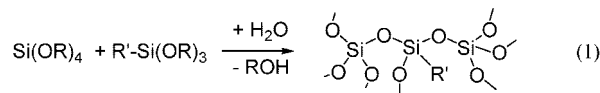
The development of inorganic–organic hybrid materials is often labeled as "materials design", because a certain level of rationality is possible via an appropriate combination of precursors (molecular building blocks). The number of possibilities for such materials design would be tremendously increased by the broader availability of hydrolyzable inorganic groups carrying functional or nonfunctional organic groups, based on elements other than silicon but with otherwise similar chemical properties, viz. compounds of the type R′-M(OR)$_n$.

As opposed to alkoxysilanes, the organic R′ groups cannot be linked to the metal atom by metal–carbon bonds, because most of these bonds are not hydrolytically stable. However, the development of such precursors can be based on what is known as "chemical additives" to moderate the reactivity of nonsilicate metal alkoxides during sol–gel processing. Acetic acid or acetylacetone is mainly used, but also other compounds, such as α-amino acids, hydroxycarboxylic acids, phosphonic and phosphinic acids, sulfonic acids, and various β-diketones and β-ketoesters, amino alcohols, oximes, etc. The common feature of such additives is that they are protic compounds and are thus able to substitute one or more OR groups of M(OR)$_m$ with concomitant ROH elimination. Furthermore, the corresponding anions act as bidentate (or multidentate) ligands, which are more strongly bonded than monodentate ligands because of the chelate effect. Reaction of such protic compounds (BL-H) with metal alkoxides results in new, modified precursors M(OR)$_{m-x}$(BL)$_x$, where BL is the (anionic) bidentate ligand (eq 2).

$$M(OR)_m + xBL\text{-}H \rightarrow M(OR)_{m-x}(BL)_x + xROH \quad (2)$$

The replacement of one or more OR groups with BL has several chemical and structural consequences for sol–gel processing. (i) The new precursor M(OR)$_{m-x}$(BL)$_x$ has a reactivity different from that of the parent alkoxide M(OR)$_m$. (ii) The degree of cross-linking of the gel network is decreased, because of the smaller proportion of hydrolyzable OR groups. (iii) The substitution of monodentate alkoxy group with bi- or multidentate BL lowers the connectivity of the molecular building blocks. This favors the formation of gels instead of crystalline precipitates. (iv) The polarity change by the organic groups probably has a similar effect on the network structure than changing the polarity of the solvent. (v) The complexing ligands may stereochemically direct the hydrolysis and condensation reactions because the site trans to an organic group has

Ulrich Schubert, born 1946 in Regensburg, Germany, received his diploma (1972) and doctoral degree (1974) at the Technical University in Munich, Germany. He was appointed Associated Professor of Inorganic Chemistry at the University of Würzburg (Würzburg, Germany) in 1982, and Full Professor at Vienna University of Technology in 1994. From 1989 to 1994, he also worked at the Fraunhofer Institute of Silicate Research in Würzburg. He is member of the Austrian Academy of Sciences and the Germany Academy of Sciences Leopoldina.

Scheme 1
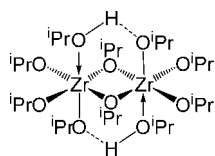
a reactivity different from that of the cis sites. (vi) Organic functionalities could be introduced via the BL, an option which is hardly exploited.

Despite the widespread use of "organically modified metal alkoxides" in sol–gel processes and their huge impact on the formation and structure of the resulting gels, there are few systematic investigations on their basic chemistry, i.e., their structures and the initial reaction steps when water is added. In most practical sol–gel protocols, the modified precursors are just prepared in situ by adding a compound BL-H to the metal alkoxide and are processed without paying attention to what is happening at the molecular level. This Account is about rendering sol–gel processing of organically modified metal alkoxides more rational by better understanding chemical and structural issues of the alkoxide precursors. This is an important and necessary step toward real materials design. The focus is on some of our recent efforts in this area with a strong emphasis on titanium and zirconium alkoxides.[4] It turns out that the chemistry and the structural issues of $M(OR)_{m-x}(BL)_x$ compounds are less straightforward than it may appear on paper and than has been reported in the literature.

Metal Alkoxides as Lewis Acids

The Lewis acidity of the metal in metal alkoxides is much higher than that of silicon in silicon alkoxides, and all the structural and reactivity differences can be traced back to that. A first effect of the higher Lewis acidity is the tendency of metal alkoxides to form oligomers $[M(OR)_m]_n$ with alkoxo bridges between two or three metal atoms, i.e., by interaction of the Lewis basic alkoxo groups with the metal centers. It is well known that the physical properties as well as the chemical reactivity of the metal alkoxides are influenced by the degree of oligomerization.[5]

As a matter of fact, any other Lewis base may also interact with the metal centers. The most obvious Lewis basic molecules in sol–gel systems are solvent molecules, such as alcohols. Complex equilibria may exist due to competition between solvent coordination and formation of alkoxo bridges. A few alcohol adducts were isolated and characterized by single-crystal X-ray diffraction. An example is $Zr_2(O^iPr)_8(^iPrOH)_2$ (Scheme 1),[6] where the metal atoms are octahedrally coordinated because of both formation of alkoxo bridges and coordination of alcohol molecules.

The coordinated alcohol in $Zr_2(O^iPr)_8(^iPrOH)_2$ undergoes hydrogen bonding with the neighboring alkoxo ligand. This turned out to be more important with regard to the stability of the adducts than originally thought. We recently isolated a series of amine adducts $M_2(O^iPr)_8(NH_2R)_2$ (M = Ti or Zr) which have the same

overall structure as $Zr_2(O^iPr)_8(^iPrOH)_2$ (Scheme 1) (eq 3). One might expect that stability of the adducts increases with an increase in the basicity of the amine. However, adduct stability depends to a large extent also on the hydrogen-donor ability of the amine.[7] Thus, secondary amines R_2NH result in less stable adducts; although they are more basic than primary amines, they are weaker hydrogen donors in NH $\cdots$ O bonds.

$$M(O^iPr)_4 + RNH_2 \longrightarrow \qquad\qquad (3)$$
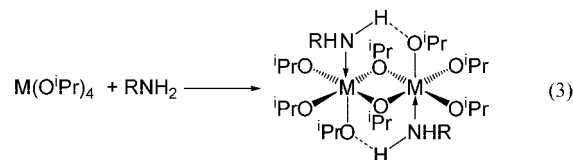
The seemingly simple fact that adducts can be formed has several far-reaching chemical consequences. First, when several bases are present at the same time, the bases compete with each other. For example, $Ti(OR)_4$ can reach its preferred coordination number of six either by addition of two Lewis base molecules (LB), i.e., formation of $Ti(OR)_4(LB)_2$, or by addition of one base molecule per titanium atom with concomitant formation of alkoxo bridges, i.e., formation of $Ti_2(OR)_8(LB)_2$. For simple alkoxo ligands, only the latter has been observed so far. However, when the basicity of the alkoxo groups is lowered by using fluoroalkoxo groups, the monomeric bis adducts $Ti[OCH(CF_3)_2]_4(LB)_2$ (LB = NCMe or THF) were obtained; i.e., addition of a second solvent molecule becomes more favorable than formation of alkoxo bridges.[8]

Second, adduct formation must be taken into account, whenever Lewis basic compounds are co-reacted with metal alkoxides in sol–gel processes. A particularly illustrative example is the adduct $Ti_2(O^iPr)_6(OEt)_2[NH_2(CH_2)_3Si(O^iPr)_3]_2$ [eq 3, where M = Ti and R = $(CH_2)_3Si(O^iPr)_3$] obtained from $Ti(O^iPr)_4$ and $(EtO)_3SiCH_2CH_2CH_2NH_2$ [Figure 1; adduct formation is accompanied by an alkoxo group exchange between $Si(OEt)_3$ and $Ti(O^iPr)_4$].[9] The amino-substituted alkoxysilane is sometimes co-reacted with metal alkoxides in sol–gel formulations. If this is done, one must be aware of adduct formation which may "neutralize" the amino group and, furthermore, influence the hydrolysis and condensation rates of the metal alkoxide. The same is true for base "catalysts" sometimes used in sol–gel reactions involving metal alkoxides. Due to the fact that such molecules will coordinate to the metal alkoxides, they will hardly exhibit any catalytic activity.

Third, adduct formation may result in a proton exchange reaction, if the added base contains an exchangeable proton, such as alcohols, primary and secondary amines, etc. The alcohol adducts (Scheme 1) are probably intermediates in alkoxo group exchange reactions, where addition of R'OH to the metal center of $M(OR)_m$ is followed by transfer of a proton from R'OH to OR and elimination of ROH. Although hydrogen bridges are also observed in the amine adducts, the proton remains bonded to the nitrogen (i.e., H is not transferred to OR), because the HNR_2 group is less acidic than the HOR group. However, such addition–proton transfer–elimination reactions are the basis for the modification
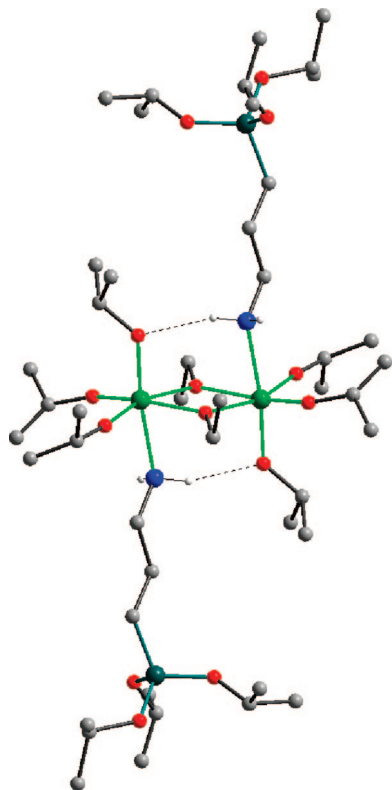
FIGURE 1. Molecular structure of $Ti_2(O^iPr)_6(OEt)_2[NH_2(CH_2)_3Si(O^iPr)_3]_2$ (green for Ti, blue for nitrogen, red for oxygen, and gray for carbon).

of metal alkoxides by bidentate ligands (BL), which are discussed in the next section. When metal alkoxides, $M(OR)_m$ are reacted with compounds BL-H, which are more acidic than the ROH group to be eliminated, modified precursors $M(OR)_{m-x}(BL)_x$ are obtained. The anionic BL ligand is more strongly bonded (due to the bidentate coordination) and thus retained at the metal.

Adduct formation can result in coordination polymers, when compounds with more than one Lewis basic center are employed, such as diamines (eq 4) or triamines.[7,10] The general structure of the titanium alkoxide groups is the same as that shown in eq 3, with the di- or triamine ligands bridging the $Ti_2(O^iPr)_8$ units. An example of a chain structure (where $X = C_6H_4$) is shown in Figure 2. The polymeric structures can be extended in a second dimension when triamines are used. Thus, puckered layers of condensed six-membered rings of $[Ti_2(O^iPr)_8]_3$-$[N(CH_2CH_2NH_2)_3]_2$ were formed when $Ti(O^iPr)_4$ was reacted with tris(2-aminoethyl)amine.[10]

At this point the questions of whether coordination of the amines is retained in solution and the extent to which the solid-state structure of the amine adducts represents the solution chemistry of metal alkoxides arise. This is not just an academic question, but also important for sol–gel processes, where coordination of amines may influence the reactivity of the metal alkoxides, or where metal alkoxides might be pre-organized prior to hydrolytic polycondensation by di- and triamines. Most amine adducts can be recrystallized, which is already a strong indication that they are relatively stable. However, this
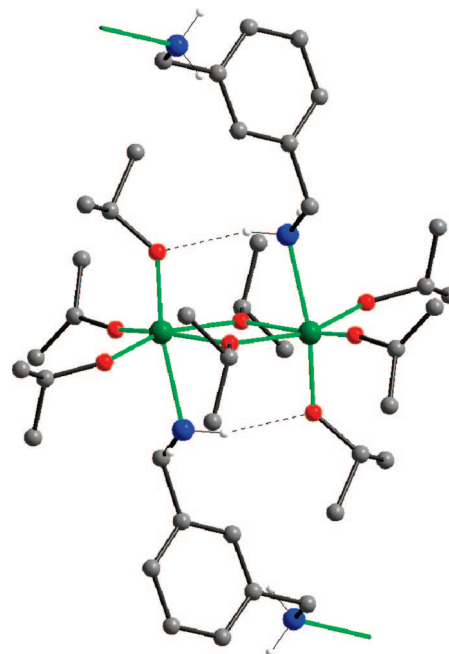

FIGURE 2. Polymeric structure of $[Ti_2(O^iPr)_8(H_2NCH_2C_6H_4CH_2NH_2)]_\infty$.
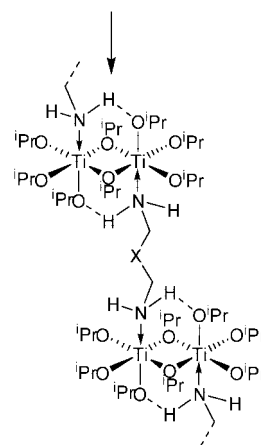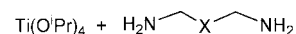
(4)

does not exclude the existence of coordination equilibria in solution. A clearer picture was obtained from two-dimensional (2D) NMR experiments for several $Ti(O^iPr)_4$/amine combinations.[10] For example, when bis(2-aminoethyl)amine was added to a CD_2Cl_2 solution of 2 molar equiv of $Ti(O^iPr)_4$, the initial NMR spectra were those of the precursors. However, over a period of 2 weeks, the NMR spectra changed completely (Figure 3). The resonances of the starting compounds decreased in intensity and eventually disappeared, and new NMR signals evolved, the number and intensity of which corresponded to the symmetry of crystalline $[Ti_2(O^iPr)_8(H_2NCH_2CH_2NHCH_2CH_2NH_2)]_\infty$ (this compound has the same overall structure as that shown in Figure 2; only the NH_2 groups are coordinated to Ti, but not the NH group).

Although CD_2Cl_2 solutions certainly do not completely model the situation in sol–gel systems (where ROH is present), the NMR results clearly show that the amine
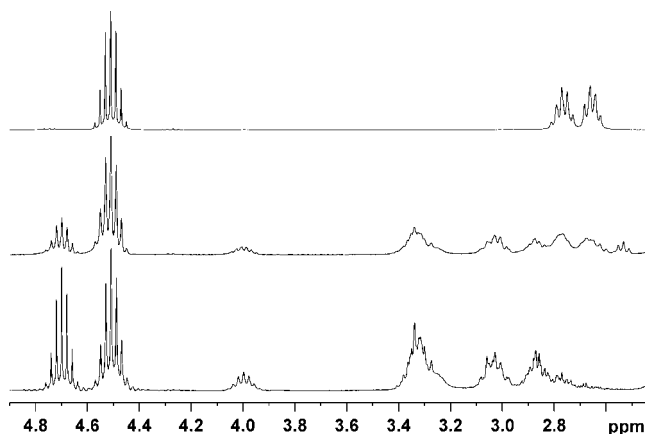
FIGURE 3. ^{1}H NMR spectra of Ti$_2$(O^{i}Pr)$_8$(NH$_2$CH$_2$CH$_2$NHCH$_2$CH$_2$NH$_2$) in CD$_2$Cl$_2$: (top) mixture of Ti$_2$(O^{i}Pr)$_8$ and NH$_2$CH$_2$CH$_2$NHCH$_2$CH$_2$NH$_2$, (middle) solution after 1 week, and (bottom) solution after 2 weeks. Reprinted with permission from ref 10. Copyright 2007 Wiley-VCH.

adducts are persistent enough that they could play a role in the sol–gel chemistry of metal alkoxides.

The formation of either adducts or oligomers by alkoxo bridging is one consequence of the Lewis acidity of metal alkoxides. Another is that organic side reactions may be catalyzed. For example, hydrodeacylation of β-diketones may occur (eq 5). This reaction is especially likely if the β-diketone is substituted in the 3-position,[11] but it was also observed in rare cases for unsubstituted acetylace-tone.[12,13] The extent of this side reaction also depends on the Lewis acidity of the metal alkoxide; the cleavage reaction can be suppressed when the reaction of β-dike-tone with the metal alkoxide is carried out in an alcoholic solution. Another example for an organic side reaction is metal alkoxide-catalyzed lactame formation from lysine competing with coordination of the amino acid to the metal alkoxide.[14]
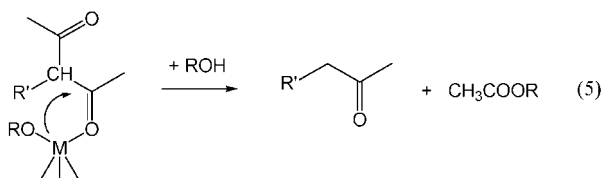
## Modification of Metal Alkoxides by Nitrogen-Containing Bidentate Ligands

While the modification of metal alkoxides by β-diketonate, β-keto ester, or carboxylate ligands has been investigated well, less attention has been paid to derivatives with nitrogen-containing anionic ligands, such as aminoalco-holate, oximate, or hydroxamate ligands, although such derivatives were prepared rather early, mainly by the group of R. C. Mehrotra.[5] These ligands could be interest-ing alternatives to the use of oxygen-containing ligands, and some of the chemical problems encountered there can be possibly avoided. We therefore started to investi-gate the structural chemistry of group IV alkoxide deriva-tives with aminoethanolate and oximate ligands, which turned out to be less straightforward than anticipated.

It was claimed that all OR groups of Ti(OR)$_4$ can successively be replaced with dialkylaminoethanolate
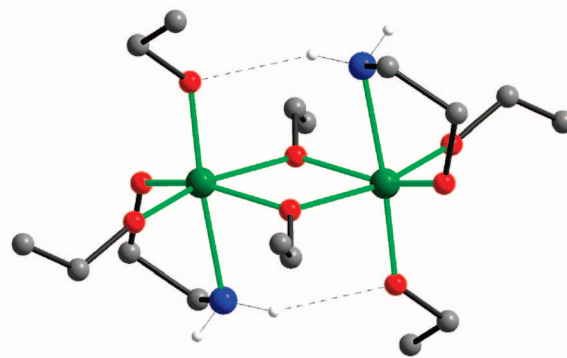
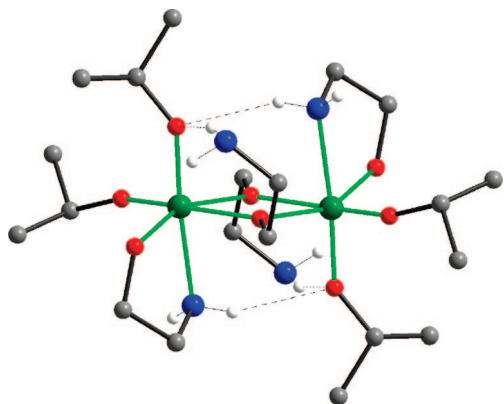FIGURE 4. Molecular structure of Ti$_2$(OEt)$_6$(OCH$_2$CH$_2$NH$_2$)$_2$.

ligands, i.e., that the whole series of Ti(OR)$_{4-x}$(OCH$_2$CH$_2$-NR$_2$)$_x$ derivatives (x = 1–4) can be obtained.[5] Variable-temperature NMR spectra indicated a monomer–dimer equilibrium for Ti(O^{i}Pr)$_3$(OCH$_2$CH$_2$NMe$_2$) in a benzene solution.[15] We were able to crystallize several NH$_2$-substituted derivatives Ti(OR)$_3$(OCHR'CHR''H$_2$) (x = 1), viz., Ti$_2$(OR)$_6$(OCH$_2$CH$_2$NH$_2$)$_2$ (R = ^{i}Pr or Et),[16] Ti$_2$(O^{i}Pr)$_6$(OCHMeCH$_2$NH$_2$)$_2$, and Ti$_2$(O^{i}Pr)$_6$(OCH$_2$CH-MeNH$_2$)$_2$ (eq 6).[17] The compounds turned out to be dimeric in the solid state, and the structures were related to that of Ti$_2$(OR)$_8$(NH$_2$R)$_2$ discussed above. The NH$_2$ group of the aminoalcoholate ligands occupies the same position as the amine ligands in the amine adducts and is again stabilized by NH$\cdots$O hydrogen bonding to neighboring OR ligands (Figure 4).
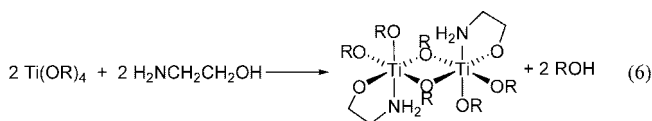

The bis-substituted derivative Ti(O^{i}Pr)$_2$(OCH$_2$CH$_2$-NMe$_2$)$_2$ was shown to be monomeric both in solution and in the gas phase.[15] We were not able to obtain the corresponding NH$_2$ derivative Ti(O^{i}Pr)$_2$(OCH$_2$CH$_2$NH$_2$)$_2$ by reaction of Ti(O^{i}Pr)$_4$. Even with an excess of ethanolamine, the dimer Ti$_2$(O^{i}Pr)$_6$(OCH$_2$CH$_2$NH$_2$)$_2$, with a Ti:aminoeth-anolate ratio of 1, crystallized from the reaction mixture. However, the bis-substituted derivative Ti$_2$(O^{i}Pr)$_4$(OCH$_2$-CH$_2$NH$_2$)$_4$ was formed, when NaTi(O^{i}Pr)$_5$ was reacted with an excess of aminoethanol.[17] From simple structural considerations, one would expect monomeric compounds Ti(OR)$_2$(OCH$_2$CH$_2$NR'$_2$)$_2$, where the titanium atom reaches its preferred coordination number of six by two chelating aminoethanolate ligands. However, as discussed above, monomeric structures Ti(OR)$_4$L$_2$ where R = alkyl and L = R'NH$_2$ are apparently not stable. Thus, "Ti(O^{i}Pr)$_2$(OCH$_2$-CH$_2$NH$_2$)$_2$" is dimeric with only *one* chelating OCH$_2$CH$_2$-NH$_2$ ligand per Ti atom (Figure 5). The alkoxo bridge is formed by the second OCH$_2$CH$_2$NH$_2$ ligand, the amino group of which does not coordinate to the titanium atoms.

When Zr(O^{i}Pr)$_4$ was reacted with aminoethanol under the same conditions as Ti(O^{i}Pr)$_4$, a colorless precipitate was obtained in an exothermic reaction. From the CH$_2$Cl$_2$ solution of this precipitate, only small amounts of

FIGURE 5. Molecular structure of $Ti_2(O^iPr)_4(OCH_2CH_2NH_2)_4$.

$Zr(OCH_2CH_2NH_2)_4$ crystallized after extended periods. The Zr atom in this compound is eight-coordinate due to four chelating aminoethanolate ligands.[17] However, when $Zr(O-Bu)_4$ was reacted instead, a crystalline compound of the overall composition "$Zr(OBu)_3(OCH_2CH_2NH_2)$" was obtained (eq 7).[17] While the mono-aminoethanolate derivative of $Ti(OR)_4$ (R = Et or ^iPr) is dimeric, viz., $Ti_2(OR)_6(OCH_2CH_2NH_2)_2$ (see above), the corresponding derivative of $Zr(OBu)_4$ has a completely different structure. The compound turned out to be a hexamer $Zr_6(OBu)_{18}$-$(OCH_2CH_2NH_2)_6$ (Figure 6) with a complicated centrosymmetric structure. The outer Zr atoms of the hexamer are not substituted with aminoethanolate ligands; they are instead $Zr(OBu)_4$ units which interact with the central part of the structure by two OBu bridges each. The compound is thus better represented by the formula $Zr_4(OBu)_{10}(OCH_2CH_2NH_2)_6 \cdot 2Zr(OBu)_4$. All $OCH_2CH_2NH_2$ ligands are μ,η^2, with bridging oxygen atoms. The reason for the surprising difference between the structure of $Ti(OR)_3(OCH_2CH_2NH_2)$ and $Zr(OR)_3(OCH_2CH_2NH_2)$ could be that the Zr atoms in the $Zr_4(OBu)_{10}(OCH_2CH_2NH_2)_6$ part of the structure become seven-coordinate in this particular arrangement.
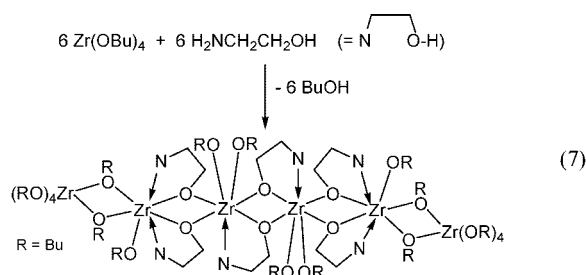
Oximes R_2C=N-OH are characterized by a protic OH group and a weakly basic nitrogen atom. Oximate ligands are ambidentate with the possibility of end-on coordination of the oxygen, side-on coordination of the NO group, or bridging coordination. Although several derivatives $Ti(OR)_{4-x}(ON{=}CR_2)_x$ were reported in the early literature,[5] no structural information was available. We now isolated crystals of the bis-substituted compound $Ti_2(O^iPr)_4$-$(ON{=}C_5H_8)_4$ (Figure 7) when $Ti(O^iPr)_4$ was reacted with 1 or 2 equiv of $C_5H_8{=}NOH$ (in the 1:1 reaction, only the yield was lower) (eq 8).[18] Both oximate ligands are side-on coordinated, with Ti–N distances [209.2(5) and 211.6(5)

pm] that are longer than Ti–O distances [194.9(4) and 195.9(4) pm]. The structure of $Ti_2(O^iPr)_4(ON{=}C_5H_8)_4$ is similar to that of dimeric $Ti_2(O^iPr)_8$,[10] with all axial O^iPr groups replaced with side-on coordinated oximate ligands. The nitrogen atoms are approximately trans [N–Ti–N angle = 164.3(2)°], and the five oxygen atoms are arranged in a distorted trigonal bipyramid around the Ti atom, with the terminal and one bridging O^iPr group in the apical positions [169.5(2)°].
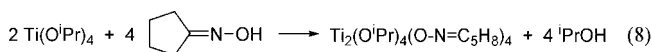
Although we were not yet able to isolate an alkoxide derivative with a Ti:oximate ratio of 1, i.e., $Ti(OR)_3$-$(ON{=}CR'_2)$, we obtained a partial hydrolysis product with this metal:ligand ratio. Surprisingly, all oximate ligands in $Ti_6O_6(OBu)_6(ON{=}C_5H_8)_6$ are bridging (Figure 8).[18] The structure of the oxo cluster is related to that of the carboxylate derivatives $Ti_6O_6(OR)_6(OOCR')_6$,[4] where the Ti_6O_6 core is a hexagonal prism of alternating titanium and oxygen atoms, and the bridging ligands (oximate or carboxylate) span the four-membered Ti_2O_2 rings of the prism.

Comparison of the structures of $Ti_2(O^iPr)_4(ON{=}C_5H_8)_4$ (Figure 7) and $Ti_6O_6(OBu)_6(ON{=}C_5H_8)_6$ (Figure 8) shows that oximes could be especially interesting for the modification and functionalization of metal alkoxides. They are easily prepared, and oximate ligands exhibit coordination behavior much more versatile and adaptable than that of any other simple ligand.

Modification of Metal Alkoxides by Carboxylate Ligands

Reaction with carboxylic acids is a common way of modifying metal alkoxides for sol–gel processing. However, this reaction is considerably more complex that the reactions with other acidic compounds discussed before. The reason is that one or more OR groups can be substituted with carboxylate ligands, but in addition, the Lewis acidic metal alkoxides catalyze formation of an ester between the employed carboxylic acid and the eliminated alcohol. The thus generated water gives rise to partial hydrolysis of the metal alkoxides, and carboxylate-substituted oxo/hydroxo clusters $M_aO_b(OH/OR)_c(OOCR')_d$ may be obtained instead of carboxylate-substituted metal alkoxide derivatives $M_a(OR)_b(OOCR')_c$ (eq 9). Since two carboxylic acid-consuming reactions (substitution and ester formation) compete with each other, the relative reaction rates determine the kind of product that is obtained. Another point to be considered is that the substitution reactions are equilibria while the hydrolysis reactions are not. Thus, even if the equilibrium is on the side of the substituted metal alkoxide $M_a(OR)_b(OOCR')_c$, a lower solubility of the clusters could shift the substitution equilibrium.

$$M(OR)_m + R'COOH \rightarrow M_aO_b(OH/OR)_c(OOCR')_d + R'COOR \quad (9)$$
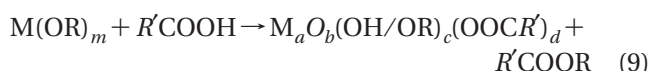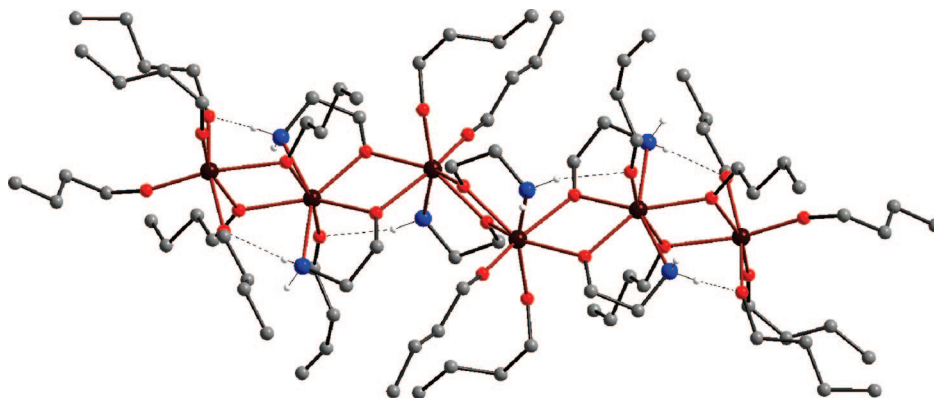
FIGURE 6. Molecular structure of $Zr_6(OBu)_{18}(OCH_2CH_2NH_2)_6 \cdot 2BuOH$.
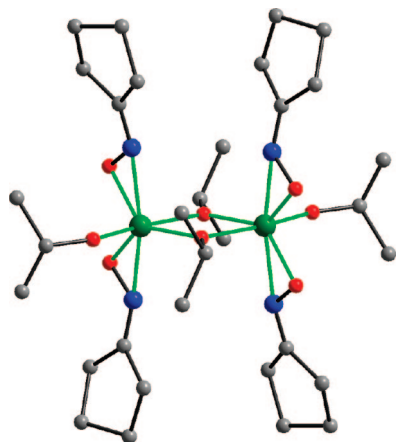

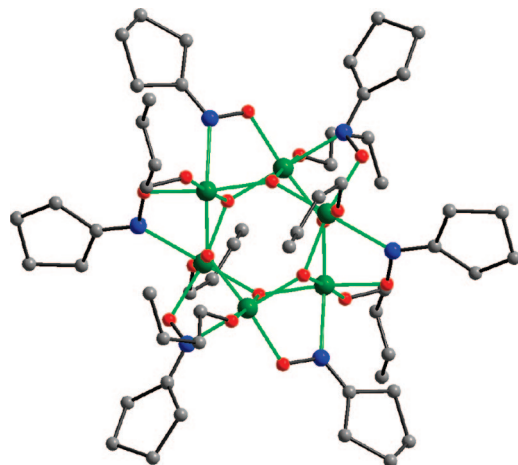**FIGURE 7.** Molecular structure of $Ti_2(O^iPr)_4(ON{=}C_5H_8)_4$.

FIGURE 8. Molecular structure of $Ti_6O_6(OBu)_6(ON{=}C_5H_8)_6$.

Two contrary examples may illustrate the complexity of the carboxylic acid reactions. When $Y(OCH_2CH_2OMe)_3$ was reacted with methacrylic or acetic acid, the crystalline yttrium carboxylate $Y(OMc)_3$ (OMc = methacrylate) or $Y(acetate)_3 \cdot 0.5H_2O$, respectively, was obtained; i.e., the OR groups were completely substituted with carboxylate groups, and no oxo cluster was formed.[19] The fact that the acetate was obtained as a hemihydrate shows that despite the formation of water in the reaction of the yttrium alkoxide this was not consumed by hydrolysis reactions. This could be due to the insolubility of the carboxylates. Although no carboxylate-substituted yttrium

Scheme 2
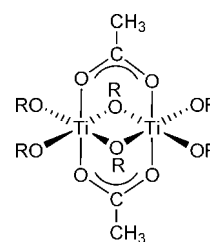
oxo/alkoxo clusters were obtained, mixed-metal clusters with yttrium as one of the components, viz., $Ti_4Y_2O_4$-$(OMc)_{14}L_2$ (L = $MeOCH_2CH_2OH$ or McOH) and $Ti_4Y_2O_4(OMc)_{12}(OCH_2CH_2OMe)_2(McOH)_2$, were formed when a mixture of $Ti(OPr)_4$ and $Y(OCH_2CH_2OMe)_3$ was reacted with methacrylic acid.[20]

The situation is quite different for the reaction of titanium or zirconium alkoxides with carboxylic acids. A spectroscopic analysis of the reaction of $Ti(OBu)_4$ with an *equimolar* quantity of acetic acid revealed that the acid was completely consumed and that butanol was formed. No ester was observed.[21] Spectroscopic evidence suggested that the acetate ligands in $Ti(OBu)_3(OOCMe)$ are bridging. With the given preference of titanium for an octahedral coordination, the smallest possible structure is the dimer $Ti_2(OR)_6(OOCR')_2$ with bridging carboxylate ligands (Scheme 2), although cyclic or linear trimers with OBu and acetate bridges would also be in line with the spectroscopic data. Only a single compound of this type was structurally characterized, viz., $Ti_2(OCH_2CMe_3)_6(OOC$-$CMe_3)_2$.[22] Apart from this exceptional case, only oxo/alkoxo clusters $Ti_aO_b(OR)_c(OOCR')_d$ of various composition were isolated from reactions of titanium alkoxides with carboxylic acids, especially when more than 1 molar equiv of R'COOH was used. The rich structural chemistry of the clusters was recently reviewed.[4]

The influence of the two competing acid-consuming reactions on cluster formation, i.e., substitution of OR ligands and ester formation, is impressively seen in a series of methacrylate-substituted oxo zirconium clusters. Different cluster types, viz., $Zr_6O_2(OBu)_{10}(OMc)_{10}$,[23] $Zr_6(OH)_4O_4$-$(OMc)_{12}$, and $Zr_4O_2(OMc)_{12}$ (Figure 9),[24] were obtained when only the methacrylic acid:$Zr(OBu)_4$ ratio was varied (from 1.6 to 4 and 7, respectively). The Zr_6O_2 cluster is only formed in small yields, and the latter two clusters
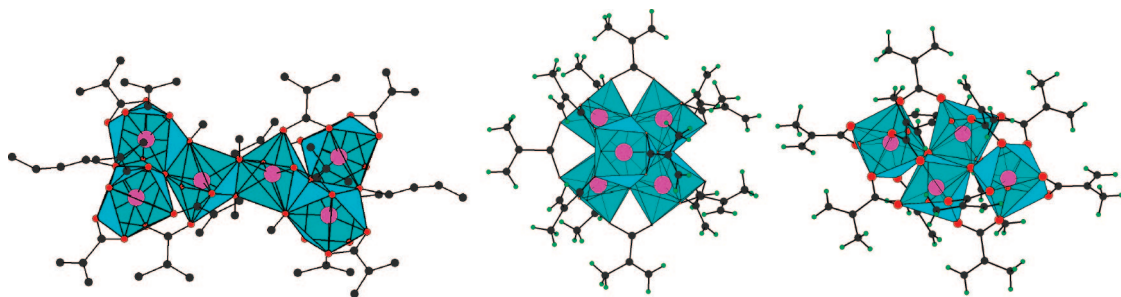
FIGURE 9. Structures of the clusters $Zr_6O_2(OBu)_{10}(OMc)_{10}$ (left), $Zr_6(OH)_4O_4(OMc)_{12}$ (middle), and $Zr_4O_2(OMc)_{12}$ (right) emphasizing the condensed Zr coordination polyhedra.

are formed in quantitative yields. The three clusters differ (i) by the average number of methacrylate ligands per Zr atom, which increases from 1.67 in $Zr_6O_2(OBu)_{10}(OMc)_{10}$ to 3 in $Zr_4O_2(OMc)_{12}$, and (ii) by the degree of condensation (the number of oxo groups per Zr atom), which has a maximum for $Zr_6(OH)_4O_4(OMc)_{12}$, i.e., for a medium acid:$Zr(OBu)_4$ ratio. When only a small proportion of acid is employed, most of the acid is consumed for substitution of part of the OR groups. A relatively open cluster with residual OR ligands is thus formed, i.e., $Zr_6O_2(OBu)_{10}(OMc)_{10}$, because only a small amount of acid is available for ester + water formation. An open structure is also obtained with a large excess of acid, but for a different reason. Each Zr atom in $Zr_4O_2(OMc)_{12}$ is substituted with an average of three bidentate carboxylate groups. Due to the high degree of substitution, only a few coordination sites are left for condensation reactions (formation of oxo bridges). The most highly condensed cluster, i.e., $Zr_6(OH)_4O_4(OMc)_{12}$, is thus obtained for a medium acid:$Zr(OBu)_4$ ratio. Under these conditions, the substitution of the Zr atoms with two methacrylate ligands still leaves enough coordination sites empty to allow the condensation of the Zr polyhedra by oxo bridges, and a sufficient amount water can be generated in situ by ester formation.

The carboxylic acid:metal alkoxide ratio is thus the key parameter that determines which kind of cluster is formed in a given system. If this parameter is kept constant, the same cluster is reliably obtained even in reactions on a larger scale, and mostly in very high yields. Vice versa, changing this parameter allows synthesis of clusters of different size and shape. However, as the example of the above-discussed yttrium alkoxides has shown, the relation between substitution of OR groups with carboxylate groups and ester formation is difficult to foresee. Furthermore, it is different for different metal alkoxides and/or acids (most probably also for different OR ligands). Therefore, a rational control or prediction of the cluster size and shape is not yet possible.

Although cluster formation may appear to be a complication in the chemistry of metal alkoxides and mostly prevents the formation of simple carboxylate derivatives of metal alkoxides, the formed clusters are themselves valuable (nanosized) building blocks for materials syntheses. When the carboxylate groups covering the cluster surface contain reactive organic groups, the clusters can be employed in organic polymerization reactions. A new type of inorganic–organic hybrid material is obtained, where the clusters are preformed nanosized building blocks. Thus, several acrylate- or methacrylate-substituted mono- or bimetallic oxo clusters were co-reacted with unsaturated organic monomers, such as styrene, methyl methacrylate, or methacrylic acid, in free radical polymerizations.[25] The resulting inorganic–organic hybrid polymers have interesting thermal, thermomechanical, and mechanical properties, due to an interplay of efficient cross-linking and inorganic (nano-)filler properties of the clusters.[26,27] An alternative polymerization method involving organic double bonds is ring-opening metathesis polymerization (ROMP). ROMP of norbornene in the presence of the cluster $Zr_6O_4(OH)_4$(5-norbornene-2-carboxylate)$_{12}$ also resulted in highly cross-linked polymers.[28] Core-shell morphologies with the cluster as the inorganic core were obtained by atom transfer radical polymerization (ATRP) using the clusters $Ti_6O_4(OOCR)_8(O^iPr)_8$, $Zr_5O_4(OOCR)_{10}(OPr)_2(PrOH)_4$, and $V_3O_3(OOCR)_6(HO^iPr)$ where R = $CBrMe_2$ as macro-initiators.[29]

Conclusion and Outlook

The substitution of metal alkoxides with chelating or bridging organic ligands offers tremendous, largely unexploited possibilities for the development of new functional precursors for sol–gel processing. However, as the examples in this Account have shown, many chemical issues are still unresolved. Open questions beyond the ones addressed in this article are, for example, how the partly complex precursor structures or the complex equilibria in solution influence the structural evolution of the networks formed during sol-gel processing, or how organic functions can be integrated in the organic part of the modified precursors. Thus, the structures of (partial) hydrolysis products need to be studied in detail. Precursors with functional organic groups must be prepared, and potential interactions of organic functionalities with the metal centers must be investigated, etc.

One may argue that these issues are not important for materials developments. This is true for simple materials, which can be empirically developed and where the structural organization on a molecular level may not have an overly strong influence on the materials properties. However, these issues will play a role for the next generation of sol–gel materials which can be rationally designed for highly specialized applications. The dream

is to construct materials according to a chemical blueprint by connecting specially designed molecular or nanoscale building blocks in a deliberate manner. To achieve this, a sufficiently large set of chemical Lego pieces must be developed, where each piece has a special shape, connectivity, and function and is equipped with suitable sites that allow connection (bonding) to other chemical Lego pieces.

References

(1) Haas, K.-H. Hybrid inorganic-organic polymers based on organically modified Si-alkoxides. *Adv. Eng. Mater.* **2000**, *2*, 571–582. Sanchez, C.; Julián, B.; Belleville, P.; Popall, M. Applications of hybrid organic–inorganic nanocomposites. *J. Mater. Chem.* **2005**, *15*, 3559–3592.

(2) Sanchez, C.; Ribot, F. Design of hybrid organic-inorganic materials synthesized via sol-gel chemistry. *New J. Chem.* **1994**, *18*, 1007–1047.

(3) Schubert, U.; Hüsing, N.; Lorenz, A. Hybrid inorganic-organic materials by sol-gel processing of organofunctional metal alkoxides. *Chem. Mater.* **1995**, *7*, 2010–2027.

(4) Schubert, U. Chemical modification of titanium alkoxides for sol-gel processing. *J. Mater. Chem.* **2005**, *15*, 3701–3715. Rozes, L.; Stenou, N.; Fornasieri, G.; Sanchez, C. Titanium-oxo clusters, versatile nanobuilding blocks for the design of advanced hybrid materials. *Monatsh. Chem.* **2006**, *137*, 501–528.

(5) Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. *Metal Alkoxides*; Academic Press: London, 1978. Bradley, D. C.; Mehrotra, R. C.; Rothwell, I. P.; Singh, A. *Alkoxo and Aryloxo Derivatives of Metals*; Academic Press: London, 2001. Turova, N. Ya.; Turevskaya, E. P.; Kessler, V. G.; Yanovskaya, M. I. *The Chemistry of Metal Alkoxides*; Kluwer: Boston, 2002.

(6) Vaartstra, B. A.; Huffman, J. C.; Gradeff, P. S.; Hubert-Pfalzgraf, L. G.; Daran, J. C.; Parraud, S.; Yunlu, K.; Caulton, K. G. Alcohol adducts of alkoxides: Intramolecular hydrogen bonding as a general structural feature. *Inorg. Chem.* **1990**, *29*, 3126–3131.

(7) Fric, H.; Puchberger, M.; Schubert, U. Coordination of mono- and diamines to titanium and zirconium alkoxides. *J. Sol-Gel Sci. Technol.* **2006**, *40*, 155–162.

(8) Campbell, C.; Bott, S. G.; Larsen, R.; van der Sluys, W. G. Preparation of Titanium Fluoroalkoxides by Alcoholysis of Titanium Alkoxides. *Inorg. Chem.* **1994**, *33*, 4950–4958.

(9) Fric, H.; Schubert, U. Amine adducts of titanium tetraalkoxides. *New J. Chem.* **2005**, *29*, 232–236.

(10) Fric, H.; Puchberger, M.; Schubert, U. Two- and three-dimensional coordination polymers by reaction of bis- and tris(2-aminoethyl)amine with titanium and zirconium alkoxides. *Eur. J. Inorg. Chem.* **2007**, 376–383.

(11) Puchberger, M.; Rupp, W.; Bauer, U.; Schubert, U. Reaction of metal alkoxides with 3-alkyl-substituted acetylacetone derivatives–coordination vs. hydroacylation. *New J. Chem.* **2004**, *28*, 1289–1294.

(12) Poncelet, O.; Hubert-Pfalzgraf, L.; Daran, J.-C. Unexpected cleavage of acetylacetone induced by yttrium oxoisopropoxide: Synthesis and molecular structure of $Y_2(\mu_2\text{-OAc})_2(acac)_4(H_2O)_2$. *Polyhedron* **1990**, *9*, 1305–1310.

(13) Seisenbaeva, G. A.; Suslova, E. V.; Kritikos, M.; Kessler, V. G.; Rapenne, L.; Andrieux, M.; Chassagneux, F.; Parola, S. Purposeful construction versus self-assembly in approaches to single source precursors of spinel materials. Synthesis, structure and stability studies of $M^{II}Al_2(acac)_3(O^iPr)_4(OAc)$, M^{II} = Mn, Co, Zn: A new class of heterometallic heteroleptic alkoxide complexes. *J. Mater. Chem.* **2004**, *14*, 3150–3157.

(14) Metelkina, O.; Schubert, U. Reaction of metal alkoxides with lysine: Substitution of alkoxide ligands vs. lactam formation. *Monatsh. Chem.* **2003**, *134*, 1065–1069.

(15) Jones, A. C.; Leedham, T. J.; Wright, P. J.; Crosbie, M. J.; Fleeting, K. A.; Otway, D. J.; O'Brien, P.; Pemble, M. E. Synthesis and characterisation of two novel titanium isopropoxides stabilised with a chelating alkoxide: Their use in the liquid injection MOCVD of titanium dioxide thin films. *J. Mater. Chem.* **1998**, *8*, 1773–1778.

(16) Fric, H.; Kogler, F. R.; Puchberger, M.; Schubert, U. Structural chemistry of titanium alkoxides substituted by the chelating bidentate ligands isoeugenolate or 2-aminoethanolate. *Z. Naturforsch. B* **2004**, *59*, 1241–1245.

(17) Fric, H.; Schubert, U. Unpublished results.

(18) Visinescu, C.; Fric, H.; Schubert, U. Unpublished results.

(19) Fric, H.; Jupa, M.; Schubert, U. The solid-state structures of a non-hydrated yttrium carboxylate and a yttrium carboxylate hemihydrate obtained by reaction of yttrium alkoxides with carboxylic acids. *Monatsh. Chem.* **2006**, *137*, 1–6.

(20) Jupa, M.; Kickelbick, G.; Schubert, U. Methacrylate-substituted titanium-yttrium mixed-metal oxo clusters. *Eur. J. Inorg. Chem.* **2004**, 1835–1839.

(21) Barboux-Doeuff, S.; Sanchez, C. Synthesis and characterization of titanium oxide-based gels synthesized from acetate modified titanium butoxide precursors. *Mater. Res. Bull.* **1994**, *29*, 1–13.

(22) Boyle, T. J.; Tyner, R. P.; Alam, T. M.; Scott, B. L.; Ziller, J. W.; Potter, B. G., Jr. Implications for the thin-film densification of TiO_2 from carboxylic acid-modified titanium alkoxides. Syntheses, characterizations, X-ray structures of $Ti_3(\mu_3\text{-O})(O_2CH)_2(ONep)_8$, $Ti_3(\mu_3\text{-O})(O_2CMe)_2(ONep)_8$, $Ti_6(\mu_3\text{-O})_6(O_2CCHMe_2)_6(ONep)_6$, $[Ti(\mu\text{-}O_2CCMe_3)(ONep)_3]_2$, and $Ti_3(\mu_3\text{-O})(O_2CCH_2CMe_3)_2(ONep)_8$ (ONep = OCH_2CMe_3). *J. Am. Chem. Soc.* **1999**, *121*, 12104–12112.

(23) Moraru, B.; Gross, S.; Kickelbick, G.; Trimmel, G.; Schubert, U. A new type of methacrylate-substituted oxozirconium clusters: $[Zr_3O(OR)_5(OMc)_5]_2$ and $[Zr_3O(OR)_3(OMc)_7]_2$. *Monatsh. Chem.* **2001**, *132*, 993–999.

(24) Kickelbick, G.; Schubert, U. Oxozirconium methacrylate clusters $Zr_6(OH)_4O_4(OMc)_{12}$ and $Zr_4O_2(OMc)_{12}$ (OMc = methacrylate). *Chem. Ber.* **1997**, *130*, 473–477.

(25) Schubert, U. Polymers reinforced by covalently bonded inorganic clusters. *Chem. Mater.* **2001**, *13*, 3487–3494.

(26) Kogler, F. R.; Koch, Th.; Peterlik, H.; Seidler, S.; Schubert, U. Mechanical, thermomechanical and thermal properties of polystyrene crosslinked with a multifunctional zirconium oxo cluster. *J. Polym. Sci., Part B: Polym. Phys.*, in press.

(27) Koch, Th.; Kogler, F. R.; Schubert, U.; Seidler, S. Mechanical properties of organic-inorganic hybrid materials determined by indentation techniques. *Monatsh. Chem.* **2007**, *138*, 293–299.

(28) Gao, Y.; Kogler, F. R.; Peterlik, H.; Schubert, U. Ring-opening metathesis polymerizations with norbornene carboxylate-substituted metal oxo clusters. *J. Mater. Chem.* **2006**, *16*, 3268–3276.

(29) Kickelbick, G.; Holzinger, D.; Brick, C.; Trimmel, G.; Moons, E. Hybrid inorganic-organic core-shell particles from surface-functionalized titanium, zirconium and vanadium oxo clusters. *Chem. Mater.* **2002**, *14*, 4382–4389.

AR600036X