Metal Complexes in Inorganic Matrices. 13.[1] Nickel Complexes with Lysinate-Substituted Titanium Alkoxides as Ligands. X-ray Structure Analysis of $[(EtO)_3Ti(glycinate)]_2$

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Introduction

Organically substituted alkoxysilanes of the type $(RO)_3Si-X-A$ in which two reactive centers (the functional organic group A and the $Si(OR)_3$ moiety) are connected by a hydrolytically stable spacer X, mostly a $(CH_2)_n$ chain, have found widespread industrial applications.[2] Upon addition of water, functionalized polysiloxanes $O_{3/2}Si-X-A$ are formed.

There are interesting potential applications for compounds $(RO)_nE-X-A$ with $E \neq Si$. However, only very few derivatives of this type are known. This is partly because the functional group A cannot be linked to the alkoxide moiety by a hydrocarbon group, due to the hydrolytic cleavage of most relevant E−C bonds. Therefore, the grouping E−X−A must have another chemical composition for $E \neq Si$ than for $E = Si$.

When non-silicon alkoxides are reacted with carboxylic acids or β-diketones (or related compounds), part of the alkoxide groups is substituted by carboxylate or β-diketonate groups. Upon addition of water, the remaining alkoxy groups are preferentially hydrolyzed.[3]

Our interest in compounds of the general type $[(RO)_nE-X-A]_mML_x$,[4a] with ML_x being a transition metal complex fragment or a transition metal ion (for $x = 0$) and A a substituent capable of binding metal atoms (for example, NH_2, $NHCH_2CH_2NH_2$, or PR_2), prompted us to investigate the possibility of preparing such compounds with E = Al, Ti, or Zr. They could bind metal ions or metal complexes to alumina, titania, or zirconia, respectively, analogous to the well-investigated silicon compounds $[(RO)_3Si(CH_2)_nA]_mML_x$.[4b] We have previously shown that phosphanyl-substituted carboxylic acids[5] or functional β-diketones[6] can be used for this purpose.

In this paper we report a first example on the use of diamino acids to link $E(OR)_n$ moieties with $E \neq Si$ and transition metal ions.

Results and Discussion

Our initial observation was that amino carboxylate ligands in metal alkoxides are considerably more stable toward hydrolytic cleavage than, for instance, acetate ligands. Since spectroscopic data gave no clear evidence for the coordination mode of the amino carboxylate groups, we searched for a derivative suitable for X-ray crystallography.

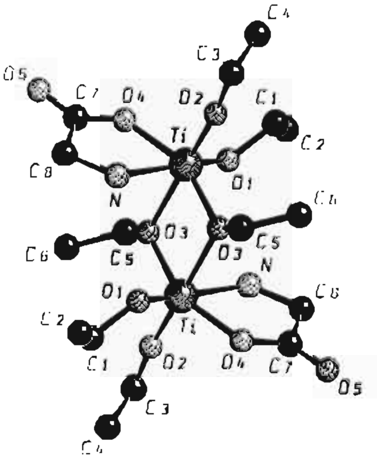
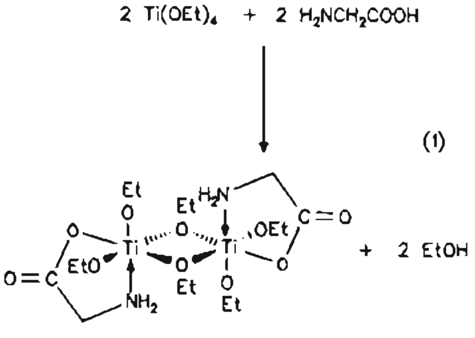


Figure 1. Molecular structure of **1**. Selected bond distances (pm) and angles (deg): Ti−O(1) = 181.3(6), Ti−O(2) = 176.5(6), Ti−O(3) = 208.7(5), Ti−O(3)* = 195.5(5), Ti−O(4) = 198.1(6), Ti−N = 223.6(6), C(7)−O(4) = 129(1), C(7)−O(5) = 121(1), C(8)−N = 147(1); N−Ti−O(1) = 166.3(3), N−Ti−O(2) = 91.2(3), N−Ti−O(3) = 81.6(3), N−Ti−O(3)* = 84.8(3), N−Ti−O(4) = 75.4(3), O(1)−Ti−O(2) = 100.1(3), O(1)−Ti−O(3) = 88.0(3), O(1)−Ti−O(3)* = 101.1(3), O(1)−Ti−O(4) = 95.3(3), O(2)−Ti−O(3) = 170.1(3), O(2)−Ti−O(3)* = 98.1(3), O(2)−Ti−O(4) = 97.0(3), O(3)−Ti−O(4) = 155.3(2), O(3)*−Ti−O(4) = 87.9(3), O(3)−Ti−O(3)* = 74.5(3), Ti−O(4)−C(7) = 125.3(6), O(4)−C(7)−C(8) = 116.3(8), C(7)−C(8)−N = 109.8(7), C(8)−N−Ti = 112.4(6).

When $Ti(OEt)_4$ and glycine were reacted in a 1:1 ratio in ethanol at 70 °C, the IR bands at 1600 and 1612 cm^{-1}, typical for the $-NH_3^+$ and $-COO^-$ group of the amino acid, disappeared. After cooling, colorless crystals were obtained. Analytical data indicated the formation of the monoglycinate derivative (eq 1).



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The X-ray structure analysis of **1** (Figure 1) showed that one ethoxy substituent of the starting alkoxide was replaced by a glycinate ligand. The usual coordination mode of carboxylate groups to metal alkoxide moieties is chelating or bridging via the two RCOO oxygen atoms.[7] Contrary to this, only one oxygen atom of the carboxylate unit and the α-amino group coordinate to the titanium center in **1**. This is the most common coordination mode of α-amino carboxylates to transition metal centers, due to the formation of a thermodynamically favored five-membered ring.[8]

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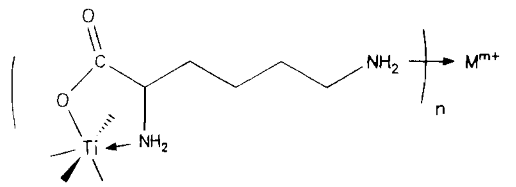

Figure 2. Schematic view of the coordination of Ni^{2+} by $Ti(OR)_3$(lysinate).

Each titanium atom in **1** reaches an octahedral coordination by dimerization. The ethoxide bridges are slightly unsymmetric, probably due to different *trans*-ligands (carboxylate oxygen *trans* to C(3) and ethoxide *trans* to C(3)*).

The structure of **1** shows that this is not a compound of the type $(RO)_3Ti-X-A$, because the α-amino group is engaged in coordination to the titanium atom (i.e., it is part of the spacer X) and therefore not available for the coordination of transition metal ions. However, the result of the structure analysis suggested that amino acids of the type $A-Y-CH(NH_2)COOH$, with a second functional group (A), would be suitable. With the same kind of coordination of the $-CH(NH_2)COO$ group to the $E(OR)_n$ unit as in **1**, the dangling group A could be available for further chemical reactions.

Reaction of $Ti(OEt)_4$ with lysine in ethanol at room temperature resulted in the formation of the lysinate complex $H_2N(CH_2)_4CH(NH_2)COOTi(OEt)_3$ (**2**), which was not isolated analytically pure. The degree of association was not determined, but spectroscopic evidence suggests that it is the same as in **1**, as well as the coordination mode of the α-amino carboxylate group to the $Ti(OEt)_3$ moiety. Contrary to the glycinate derivative **1**, the solubility of the lysinate **2** in ethanol is high.

When a freshly prepared solution of **2** was reacted with water-free nickel acetate (1 mol of $Ni(OAc)_2$/4 mol of **2**) in ethanol at 60 °C, the color of the solution turned blue within 30 min. The UV spectrum of this solution showed a broad absorption at 600 nm. Approximately the same UV spectrum (absorption at 636 nm) was obtained when $Ni(OAc)_2$ and *n*-butylamine were reacted in a 1:4 molar ratio in ethanol. This shows that the dangling amino end of the lysinate-modified alkoxide **2** reacted with metal salts as primary amines to give the amine complex $\{Ni[NH_2(CH_2)_4CH(NH_2)COOTi(OEt)_3]_4\}^{2+}$ (**3**) (Figure 2).

Complex **3** can be employed as an alkoxytitanate precursor for sol–gel processing. Complete condensation occurred within 72 h at 60 °C when a 7.5-fold excess of water (relative to all Ti–OEt groups) was added. A blue powder was obtained after removal of the solvent. It showed a UV absorption similar to that of **3** (616 nm), and in its IR spectrum no bands were observed which could be attributed to an uncoordinated amino acid. The spectra indicate that only the Ti–OEt groups were hydrolyzed, but the nickel complex (Figure 2), including its link to the $TiO_{3/2}$ moiety, was not affected. Washing of the blue solid with water did not result in a noticeable leaching of either Ni^{2+} or lysine. The composition of the blue solid was the same before and after washing.

Conclusions

We have shown in this article that reaction of $Ti(OR)_4$ with diamino acids results in alkoxide carboxylate derivatives, in which coordination of the carboxylate ligand to the $Ti(OR)_3$ moiety is improved compared with simple carboxylic acids. This is due to the participation of the α-amino group and formation of a five-membered chelate ring. Simple carboxylic acids, such as acetic or propionic acid, are often used in sol–gel chemistry to moderate the reactivity of metal alkoxides. Although the alkoxide ligands are preferentially hydrolyzed, part of the carboxylate is sometimes also lost. In most materials syntheses this does not matter too much. However, in those cases where partial hydrolytic cleavage of the carboxylate ligand(s) has to be avoided for some reason, we propose to use amino acids instead of simple carboxylic acids.

A second advantage of using amino acids to modify metal alkoxides is the ready availability of compounds having an additional functional group at one of the more distant carbon atoms. Metal alkoxides modified with such amino acids correspond to the general type of precursors $(RO)_nE-X-A$, discussed in the Introduction. As shown in this article, the lysinate-substituted alkoxytitanate **2** is fully equivalent to $H_2N(CH_2)_3Si(OR)_3$ with regard to its use in sol–gel processing or related reactions. The same is true for **3**, which is analogous to the complexes $\{Ni[NR'_2(CH_2)_3Si(OR)_3]_n\}^{2+}$.

In this article lysine was used to demonstrate the principle. However, there is no reason why other diamino acids or amino acids with other functional groups should not be used in the same way.

Experimental Section

All operations were performed in an atmosphere of dry and oxygen-free nitrogen, using dried solvents. Instrumentation: FTIR spectra, Bruker IFS 25; ^{13}C NMR spectra, Bruker AC 400; UV spectra, Hewlett Packard 8452 A and Shimadzu UV 3100 with MPC 3100.

Preparation of $[Ti(OEt)_3(glycinate)]_2$ (1). A 0.74 g amount (10 mmol) of glycine was added to an ethanolic (50 mL) solution of 2.28 g (10 mmol) of $Ti(OEt)_4$. On being heated to 70 °C, the glycine dissolved. Heating was continued until a clear solution was obtained (about 45 min). Then the solution was slowly cooled to ambient temperature. The glycinate derivative crystallized as colorless crystals, which were filtered off and dried *in vacuo*. Yield: 1.70 g (67%). Mp: 222 °C. Anal. Found (calcd): C, 37.66 (37.37); H, 8.04 (7.45); N, 5.43 (5.45). IR (Nujol): 3288 (m, NH), 3244 (m, NH), 1660 (s), 1132 (s, C–OEt terminal), 1098 (s, C–OEt terminal), 1068 (s, C–OEt terminal), 1036 (m, C–OEt bridging), 920 (s, C–OEt terminal), 888 (m, C–OEt bridging), 653 (m, C–OEt terminal), 608 (m, C–OEt terminal), 536 (m, C–OEt terminal), 512 (m, C–OEt bridging) cm^{-1} (assignment of the bands according to ref 9).

X-ray Structure Analysis of 1. Colorless crystals (0.5 × 0.4 × 0.3 mm) were obtained from a EtOH solution: Monoclinic, space group $P2_1/c$; $a = 921.2(3)$, $b = 957.4(2)$, $c = 1528.2(5)$ pm; $\beta = 98.9(1)°$; $V = 1331 \times 10^6$ pm^3; $Z = 2$; $d_{ber} = 1.28$ g/cm^3. Data collection: The cell constants were determined by refinement of 25 reflections with high diffraction angles from different parts of the reciprocal space. The reflection intensities were measured in the range $3° \le 2\theta \le 48°$ at an Enraf-Nonius CAD4 diffractometer at 298 K with Mo Kα radiation ($\lambda = 71.069$ pm) using the ω/θ scan method. Following Lorentz, polarization, empirical absorption (ω scan, $\mu = 6.36$ cm^{-1}; minimum transmission 88.4%), and linear decay correction (intensity decay 4.7%), 1784 independent reflections were measured. A total of 1268 reflections with $F_o > 3\sigma(F_o)$ were used for the solution of the structure by direct methods (SHELX86). The positions of the hydrogen atoms were partially located from difference Fourier maps and partially calculated according to an ideal geometry. During refinement they were kept riding on the carbon (nitrogen) atoms. The ethyl groups at O(1) and O(2) are disordered; they were only isotropically refined without hydrogen atoms. The other heavy atoms were refined with anisotropic thermal parameters by full-matrix least-squares methods with the full matrix. $R = 0.055$; $R_w = 0.067$. The residual electron density was 0.31×10^6 e/pm^3.

Preparation of $[Ti(OEt)_3(lysinate)]_2$ (2). A 1.46 g amount (10 mmol) of lysine was added to an ethanolic (50 mL) solution of 2.28 g (10 mmol) of $Ti(OEt)_4$. While the suspension was stirred at room temperature for 2 h, the lysine dissolved. After removal of the solvent *in vacuo* a yellowish solid was obtained, which was used without further purification. IR (Nujol): 3270 (m, NH), 3125 (br, NH), 1644 (vs, CO),

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1146 (s, C−OEt terminal), 1098 (s, C−OEt terminal), 1066 (sh, C−OEt terminal), 1051 (sh, C−OEt bridging), 905 (s, C−OEt terminal), 879 (m, C−OEt bridging), 659 (m, C−OEt terminal), 559 (m, C−OEt terminal) cm^{-1}. ^{13}C NMR (200 MHz, CD_3OD, δ): 184.0 (COO), 79.5 (CH), 58.3 ($TiOCH_2$), 41.4, 34.4, 31.1, 24.3 (CH_2, lysinat), 18.4 (CH_3).

Reaction of 2 with Nickel Acetate and Subsequent Hydrolysis. A 10 mmol amount of lysine and 10 mmol of $Ti(OEt)_4$ were reacted in 400 mL of ethanol as described above. After formation of **2**, 440 mg (2.5 mmol) of $Ni(OAc)_2$ was added, and the solution was heated to 60 °C for 30 min, while the color of the solution changed from green to blue. UV (ethanol): λ 600 nm.

To the clear solution 4.05 mL (225 mmol) of water was added, and heating was continued for 72 h. The solvent was then removed *in vacuo*. The obtained blue solid was washed with water. The washing solutions did neither contain Ni^{2+} nor lysine. After drying, the elemental analysis of the solid was the same as before. UV: λ 616 nm. IR (Nujol): 1576 (br), 1634 (sh), 3167 (m), 3260 (m), 3314 (m) cm^{-1}. Anal. Found (calcd for $[TiO_{3/2}(OOCCH(NH_2)(CH_2)_4NH_2]_4$-$Ni(OAc)_2$): C, 31.84 (32.18); H, 5.59 (5.55); N, 9.98 (10.73).

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Supplementary Material Available: Tables of the final atomic coordinates, thermal parameters, bond lengths, and bond angles (7 pages). Ordering information is given on any current masthead page.

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