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Synthesis, spectroscopic and X-ray single-crystal structure study of bis(2-methoxy-ethanolato)-bis(8-quinolinato)titanium(IV)

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Reaction of $Ti(OCH_2CH_2OR)_4$ (R=CH_3 and C_2H_5) with 8-hydroxyquinoline in benzene at room temperature resulted in the formation of $Ti(C_9H_6NO)_2(OCH_2CH_2OR)_2$, characterized by IR, ^{1}H-NMR, UV and mass spectroscopies. The molecular structure of $Ti(C_9H_6NO)_2(OCH_2CH_2OCH_3)_2$ has been determined by single-crystal X-ray structure analysis. The geometry at titanium is a distorted octahedron, with the nitrogen atoms of quinolinate occupying the *trans* position with respect to oxygens of the 2-methoxyethoxy groups. The prepared quinolinate derivatives of titanium alkoxides are very stable towards hydrolysis and harsh conditions are required for hydrolytic cleavage. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: coordination; 8-hydroxyquinoline; titanium alkoxide; X-ray structure

INTRODUCTION

Metal alkoxides have been investigated extensively due to their potential application as precursors for oxide base ceramic materials, catalyst supports, thin films and fibers via sol–gel processing.[1] However, the majority of metal alkoxides are very unstable towards hydrolysis and their stabilization with chelating functionalities is interesting and desired in the sol–gel processing of material. Various chelating ligands have been used for the stabilization of metal alkoxides, such as carboxylates,[2] β-diketonates[3] and alkanolamines, and a variety of structural types have been isolated.[4] In addition to the higher stability advantage of modified metal alkoxides, the low solubility problems of the late transition-metal alkoxides of the first row can be overcome by introducing chelating ligands.[5] Interestingly, the stabilized metal alkoxides show a different behavior in the hydrolysis–condensation process and this is reflected in the properties of the final materials.[6] This approach has been used in industry for tailoring metal oxides with well-defined specifications for catalytic applications and the fabrication of advance ceramics.[7] Evidently, the solubility and stability of modified metal alkoxides depend on the type of ligand and its coordination status. Recent studies show that due to the lability of metal alkoxides, their alkoxy groups can be replaced quite readily by a wide variety of ligands containing hydroxyl groups.[8,9] Apparently, the hydrolytic stability of metal alkoxides increases on replacing the number of alkoxy groups with other ligands, and consequently their alkoxy character vanishes; this means that their hydrolysis requires acidic media.[10,11]

During the course of stabilization of metal alkoxides for the fabrication of metal oxides and because of the interest in how structural change would alter the final texture of the metal oxides, we have synthesized $Ti(C_9H_6NO)_2(OCH_2CH_2OR)_2$ complexes, where R=CH_3 (**1**) and R=C_2H_5 (**2**), and characterized them using various spectroscopic techniques, in addition to X-ray single-crystal structure determination of compound **1**.

EXPERIMENTAL

Materials and methods

All manipulations were carried out under nitrogen, using standard Schlenk techniques. Solvents were dried and distilled under nitrogen prior to use. Titanium(IV) tetraisopropoxide, 2-methoxyethanol, 2-ethoxyethanol and 8-hydroxyquinoline were purchased from Fluka and used without further purification. Both $Ti(OCH_2CH_2OCH_3)_4$ and

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$Ti(OCH_2CH_2OCH_2CH_3)_4$ were prepared by the alcohol exchange method according to a previous report.[12]

Infrared spectra were recorded on a Shimadzo 470 instrument at 4 cm^{-1} resolution, using KBr pellets. The ^1H NMR spectrum was obtained in $CDCl_3$ (vs. Me_4Si in ppm) using a Bruker DRX-500 spectrometer. The mass spectroscopy was performed on a Varian Matt 44 instrument (electron impact, 20 eV) and UV–Vis spectra were recorded on a Shimadzo 2100 spectrophotometer.

Synthesis of compound 1

Compound **1** was prepared by reaction of 8-hydroxyquinoline (0.56 g, 4 mmol) with $Ti(OCH_2CH_2OCH_3)_4$ (1.34 g, 4 mmol) in benzene (10 ml). The mixture was stirred for 1 day and the solvent was removed under reduced pressure to leave an orange solid. The solid was crystallized from dichloromethane–hexane; single crystals of complex were isolated from solution after several days at −5 °C, m.p. 175–177 °C. Anal. (calc.) for $C_{24}H_{26}N_2O_6Ti$: C, 59.27; H, 5.39; N, 5.76%. Found: C, 59.72; H, 5.45; N, 5.42%. UV (CH_2Cl_2, nm): 233 (LMCT), 254 (π–π^*), 386 (n–π^*). IR (cm^{-1}): 3035 (C–H, aromatic), 2875 (C–H, aliphatic), 1592 (C=N), 1564 (C=C), 1264 (C–O), 626 (Ti–O–C, symmetric), 532 (Ti–O–C, asymmetric). ^1H NMR ($CDCl_3$, ppm): 3.41 (3H, s, OCH_3), 3.51 (2H, t,–CH_2O–), 3.74 (2H, t, –OCH_2–). C_9H_6NO ligand protons: 6.58 (1H, dd), 6.80 (1H, dd), 7.11 (1H, m), 7.40 (1H, m), 8.10 (1H, dd), 8.76 (1H, dd). Mass spectral data, titanium-bearing fragments (*m/e*): 486 $[Ti(OCH_2CH_2OCH_3)_2(C_9H_6NO)_2]^+$, 411 $[Ti(OCH_2CH_2OCH_3)(C_9H_6NO)_2]^+$, 366 $[Ti(OCH_2)(C_9H_6NO)_2]^+$, 352 $[Ti(O)(C_9H_6NO)_2]^+$, 342 $[Ti(OCH_2CH_2OCH_3)_2(C_9H_6NO)]^+$, 336 $[Ti(C_9H_6NO)_2]^+$, 297 $[Ti(OCH_2CH_2OCH3)(OCH_2)(C_9H_6NO)]^+$, 252 $[Ti(OCH_2)_2(C_9H_6NO)]^+$, 208 $[Ti(O)(C_9H_6NO)]^+$, 192 $[Ti(C_9H_6NO)]^+$. Mass numbers are based upon ^1H, ^{12}C, ^{14}N, ^{16}O and ^{48}Ti.

Synthesis of compound 2

Compound **2** was prepared by reaction of 8-hydroxyquinoline (0.72 g, 5 mmol) with $Ti(OCH_2CH_2OCH_2CH_3)_4$ (2.00 g, 5 mmol) in benzene (10 ml). The mixture was stirred for 1 day and the solvent was removed under reduced pressure to leave an orange solid. The solid was crystallized from dichloromethane–diethyl ether at −5 °C, m.p. 119–120 °C. Anal. (calc.) for $C_{26}H_{30}N_2O_6Ti$: C, 61.70; H, 5.88; N, 5.45%. Found: C, 62.12; H, 5.95; N, 5.24%. UV (CH_2Cl_2, nm): 235.5 (LMCT), 258.5 (π–π^*), 388 (n–π^*). IR (cm^{-1}): 3040 (C–H, aromatic), 2915 (C–H, aliphatic), 1599 (C=N), 1569 (C=C), 1266 (C–O), 629 (Ti–O–C, symmetric), 521 (Ti–O–C, asymmetric). ^1H NMR ($CDCl_3$, ppm): 1.0 (3H, t, CH_3), 3.30 (2H, q, –OCH_2–), 3.40 (2H, t, –CH_2O–), 4.44 (2H, t, $TiOCH_2$–). C_9H_6NO ligand protons: 7.05 (1H, dd), 7.09 (1H, dd), 7.16 (1H, dd), 7.46 (1H, m), 8.04 (1H, dd), 8.53 (1H, dd). Mass spectral data, titanium-bearing fragments (*m/e*): 514 $[Ti(OCH_2CH_2OCH_2CH_3)_2(C_9H_6NO)_2]^+$, 425 $[Ti(OCH_2CH_2OCH_2CH_3)(C_9H_6NO)_2]^+$, 381 $[Ti(OCH_2CH_2)(C_9H_6NO)_2]^+$, 370 $[Ti(OCH_2CH_2OCH_2CH_3)_2(C_9H_6NO)]^+$, 352 $[Ti(O)(C_9H_6NO)_2]^+$, 336 $[Ti(C_9H_6NO)_2]^+$, 326 $[Ti(OCH_2CH_2OCH_2CH_3)(OCH_2CH_2)(C_9H_6NO)]^+$, 252 $[Ti(OCH_2)_2(C_9H_6NO)]^+$, 208 $[Ti(O)(C_9H_6NO)]^+$.

X-ray crystallography

An orange prism-shaped crystal of **1**, air stable at room temperature, was used for the crystallographic measurements. The data were collected at 20 °C on a Bruker SMART 1000 CCD area detector diffractometer. Crystal data and details of structure determination for compound **1** are presented in Table 1. Unit cell parameters were determined using SAINT-PLUS software.[13] The structure was solved by a direct method and refined with full matrix least-squares on F2 to a final *R* value of 0.0558; $R_w = 0.1214$ with SHELXTL program.[14] The positions of the hydrogen atoms were found from the difference Fourier maps. The hydrogen temperature factors were constrained whereas those of the other atoms were refined anisotropically.

Table 1. Crystal data and structure refinement for compound **1**

Empirical formula	$C_{24} H_{26} N_2 O_6 Ti$
Formula weight	486.37
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P 2_1/n$
Unit cell dimensions	$a = 11.208(2)$Å, $\alpha = 90°$ $b = 14.445(3)$Å, $\beta = 107.901(5)°$ $c = 15.236(4)$Å, $\gamma = 90°$
Volume	2347.2(9) Å^3
Z	4
Density (calculated)	1.376 mg m^{-3}
Absorption coefficient	0.407 mm^{-1}
F(000)	1016
Crystal size	0.30 × 0.20 × 0.20 mm^3
θ range for data collection	1.99–28.05°
Index ranges	$-14 <= h <= 14$, $-18 <= k <= 18$, $-20 <= l <= 10$
Reflections collected	12 129
Independent reflections	5539 [R(int) = 0.0331]
Completeness to $\theta = 28.05°$	97.2%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8426 and 0.7531
Refinement method	Full matrix least-squares on F^2
Data/restraints/parameters	5539/0/300
Goodness-of-fit on F^2	1.082
Final R indices for 3292 refl. with $[I > 2\sigma(I)]$	$R_1 = 0.0558$, $wR_2 = 0.1214$
R indices (all data)	$R_1 = 0.0948$, $wR_2 = 0.1334$
CCDC deposition number	229 784

RESULTS AND DISCUSSION

The room temperature reactions of $Ti(OCH_2CH_2OCH_3)_4$ and $Ti(OCH_2CH_2OCH_2CH_3)_4$ with 8-hydroxyquinoline are quite fast and their progress was followed readily by the appearance of a yellow fluorescence color. Such lability of metal alkoxides towards reaction with 8-hydroxyquinoline has been reported also for other metal alkoxides.[8,9] The formation of the isolated compounds was established by observing the presence of their parent ions using mass spectroscopy, which is quite rare in the mass spectra of metal alkoxides. Observation of the parent ions can be attributed to the stability of the compounds and a drastic change in their alkoxide character. The ^1H NMR spectra of the complexes exhibit the expected aromatic and aliphatic protons. However, it is interesting to note that there is considerable deshielding of the proton bonded to the carbon atom adjacent to the nitrogen and shielding of the proton bonded to the carbon atom adjacent to the oxygen (phenolate ring) in comparison to the free ligand. Such a shift has been observed previously in the 8-quinolinolate vanadium complex.[15]

Because the coordination mode of the quinolinate group was ambiguous from spectroscopic data and because of the similarity between the two compounds, only compound **1** was subject to X-ray single-crystal structure analysis.

Crystal structure of compound 1

The molecular structure of **1** has been determined by X-ray single-crystal structure analysis. The selected bond distances and angles of **1** are listed in Table 2 and the ORTEP drawing is shown in Fig. 1. The titanium is six-coordinated in distorted octahedron geometry by two phenolate oxygens, two nitrogens and two methoxyethoxy group oxygens, with band angles ranging from 75.85(7) to 104.20(8)°. Both nitrogen atoms are *trans* to the oxygen of the 2-methoxyethoxy ligand. The two $Ti{-}O_{phenolate}$ distances of 1.9546(17) and 1.9526(17) Å are nearly identical but much longer than the other two Ti–O distances of 1.801(2) and 1.8072(19) Å. It seems that the oxygen atom of the alkoxy group carrying the most coordination burden of ligand weakness in other side. The Ti–O distances are similar to those found in the four centrosymmetric dimeric complexes: $[Ti(quinolinate)(C_2H_5O)_3]_2$, 1.819(1) and 1.779(1) Å;[16] $[Ti(glycinate)(C_2H_5O)_3]_2$, 1.813(6) and 1.765(6) Å;[17] $[Ti(acetylacetonate)\ (C_2H_5O)_3]_2$, 1.805(1) and 1.796(1) Å;[18] and $[Ti(maltolate)(C_2H_5O)_3]_2$, 1.809(3) and 1.778(3) Å.[19] The Ti–N band distances 2.233(2) and 2.241(2) Å are in the expected range for the titanium alkoxide quinolinate derivatives.[16,20] The O1′–Ti1–O1, O2′–Ti1–N1′ and O2–Ti1–N1 angles of 155.30(80), 165.95(9) and 164.42(8)°, respectively, are bent severely and distortion from ideal geometry is seen in the sum of the O–Ti1–O and O–Ti1–N angles in the equatorial plane 356.72(8)°. The O1′–Ti1–O1, O2–Ti1–N1 and O2′–Ti1–N1′ angles are similar to those reported for bis(8-quinolinolato)bis(2,6-diispropylphenoxo)titanium(IV) (155.5(3) and 165.4(2)°)[20] and bis(2-methyl-8-quinolinolato)bis(2,6-diisopropylphenoxo)titanium(IV) (151.6(3), 168.1(3) and 167.4(3)°).[20] The quinoline bite angles of 76.32(7) and 75.85(7)° are nearly identical and comparable to that in the centrosymmetric dimeric of $[Ti(quinolinate)(C_2H_5O)_3]_2$ and $[Ti(glycinate)(C_2H_5O)_3]_2$,[16,17] and also monomeric $Ti(quinolinate)_2Cl_2$.[21] Apparently, the structure features of 8-hydroxyquinoline complexes of titanium alkoxides depend on the type of alkoxy ligands. It seems that the sterically hindered alkoxy groups, such as 2-methoxyethoxy or 2,6-diisopropylphenoxy, favor formation of the monomeric species.[16,19] Consistent with this, in the β-diketonate derivatives of titanium alkoxides only monomeric species have been observed for the *tert*-butoxy

Table 2. Bond lengths (Å) and angles (deg) for compound **1**

Ti1–O2	1.801(2)	Ti1–O1	1.9546(17)
Ti1–O2′	1.8072(19)	Ti1–N1′	2.233(2)
Ti1–O1′	1.9526(17)	Ti1–N1	2.241(2)
O2–Ti1–O2′	102.46(9)	O1′–Ti1–N1	85.50(7)
O2–Ti1–O1′	104.20(8)	O1–Ti1–N1	75.85(7)
O2′–Ti1–O1′	93.01(8)	N1′–Ti1–N1	81.21(7)
O2–Ti1–O1	91.17(8)	C8–O1–Ti1	121.22(15)
O2′–Ti1–O1	102.56(8)	C1–N1–Ti1	130.71(16)
O1′–Ti1–O1	155.30(8)	C9–N1–Ti1	111.22(16)
O2–Ti1–N1′	89.18(8)	C8′–O1′–Ti1	120.49(15)
O2′–Ti1–N1′	165.95(9)	C1′–N1′–Ti1	130.45(19)
O1′–Ti1–N1′	76.32(7)	C9′–N1′–Ti1	110.77(15)
O1–Ti1–N1′	84.83(8)	C10–O2–Ti1	136.68(19)
O2–Ti1–N1	164.42(8)	C10′–O2′–Ti1	143.4(2)
O2′–Ti1–N1	88.95(8)		

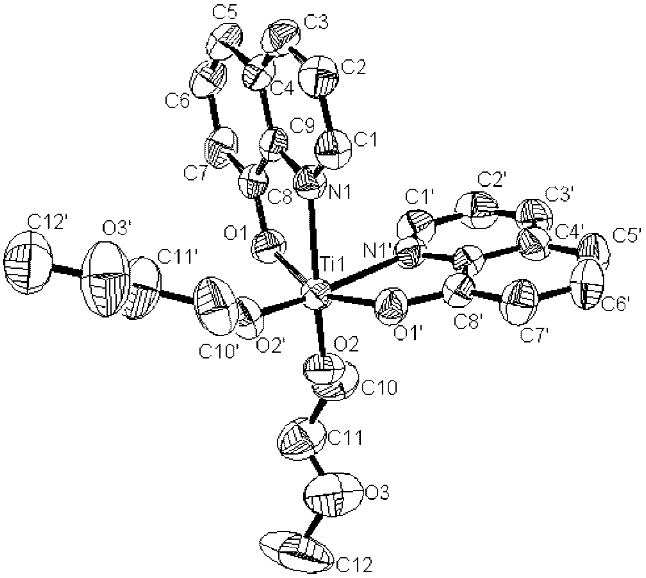

Figure 1. An ORTEP diagram of compound **1**. Thermal ellipsoids are at the 50% probability level.

ligand.[18] Apparently, the type of alkoxide ligand is more influential in the structural features than the chelating ligand.

The isolated complexes are air stable and soluble in benzene, toluene, dichloromethane and chloroform, which make them attractive precursors for the preparation of titanium oxide by the sol–gel process. However, it must be mentioned that our preliminary study shows that the quinolinate derivatives of titanium alkoxides are more stable towards hydrolysis in comparison to acetate ligands and thus harsh conditions are required for hydrolytic cleavage.

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