Acknowledgment. I thank Professor Walter Klemperer and Mr. Omar Yaghi for the ^{17}O-enriched $[CH_3CN\subset(V_{12}O_{32}{}^{4-})]$ sample and also for many helpful discussions. Discussions with Dr. Vera Mainz are also gratefully acknowledged.

Registry No. $[CH_3CN\subset(V_{12}O_{32}{}^{4-})]$, 132699-16-2; ^{17}O, 13968-48-4; ^{51}V, 7440-62-2.

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Intramolecular O–H···Cl Hydrogen Bonding in Titanium Chloride Alkoxides of the Formula $[TiCl_2(OCH_2CH_2X)_2 \cdot HOCH_2CH_2X]_2$ (X = Cl, Br, I). Crystal Structure of $[TiCl_2(OCH_2CH_2Cl)_2 \cdot HOCH_2CH_2Cl]_2$

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Despite the fact that titanium alkoxides have been known for over 50 years, relatively little is known about their molecular geometries due to a paucity of structural data.[1] The limited solid-state studies that are available point to an impressive array of possible molecular compositions, including polymers,[1,2a] hexamers,[2b] tetramers,[2c] dimers,[3,4] and monomers.[1,5] The general picture is further clouded by the existence of complex equilibria that can occur *in solution*.[6] As part of our program relating to the development of new routes to early-transition-metal materials, we have been exploring the synthesis of new titanium complexes that contain oxygen ligands. We now report the preparation and properties of titanium chloride alkoxides of the general formula $[TiCl_2(OCH_2CH_2X)_2 \cdot HOCH_2CH_2X]_2$ (X = Cl, Br, I), which exist as dimers in the solid state. The dimeric structure appears to be strongly favored by intramolecular O–H···Cl hydrogen bonding, which constitutes a general structural feature of these complexes.

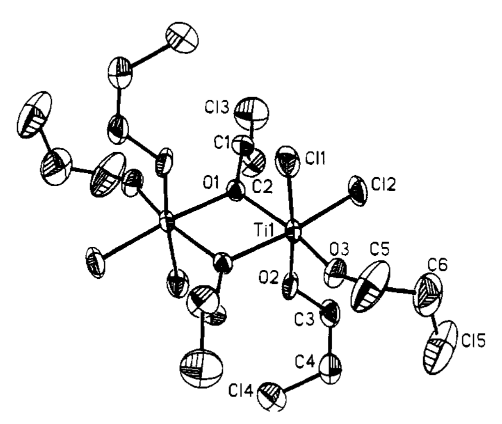

Figure 1. Perspective view of **1**.

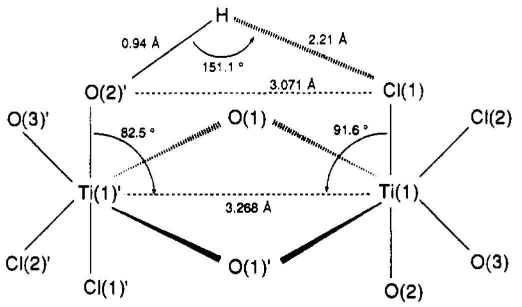

Figure 2. Bond lengths and angles about the Ti_2O_2 core of **1**.

Table I. Crystallographic Data for **1**

chem formula	$C_{12}H_{26}Cl_{10}O_6Ti_2$	fw	716.67
a, Å	8.9659 (7)	space group	$P\bar{1}$
b, Å	9.2748 (8)	*T*, °C	15
c, Å	10.515 (1)	λ, Å	1.541 78
α, deg	98.186 (7)	ρ_{calcd}, g cm^{-3}	1.667
β, deg	111.001 (7)	μ, cm^{-1}	139.0
γ, deg	112.435 (6)	transm coeff	0.493–0.160
V, Å^3	714.0 (1)	$R(F_o)$	0.061
Z	1	$R_w(F_o)$	0.070

Table II. Bond Lengths and Angles for **1**

Ti(1)–C(1)	2.326 (2)	C(1)–C(2)	1.499 (8)
Ti(1)–Cl(2)	2.284 (2)	C(2)–Cl(3)	1.754 (6)
Ti(1)–O(1)	2.087 (5)	O(2)–C(3)	1.455 (9)
Ti(1)–O(2)	2.102 (4)	C(3)–C(4)	1.48 (1)
Ti(1)–O3	1.746 (5)	C(4)–Cl(4)	1.78 (1)
Ti(1)–O(1)′	1.956 (4)	O(3)–C(5)	1.41 (1)
O(1)–C(1)	1.440 (6)	C(5)–C(6)	1.40 (2)
Ti(1)···Ti(1)′	3.268 (3)	C(6)–Cl(5)	1.73 (1)
O(2)···Cl(1)′	3.071 (6)		
Ti(1)–O(1)–C(1)	127.3 (4)	O(1)–Ti(1)–O(2)	86.0 (2)
Ti(1)–O(1)–Ti(1)′	107.9 (1)	O(1)–Ti(1)–O(3)	170.3 (2)
Ti(1)–O(2)–C(3)	130.9 (5)	O(1)–Ti(1)–O(1)′	72.1 (2)
Ti(1)–O(3)–C(5)	154.2 (4)	O(1)–C(1)–C(2)	108.7 (4)
Cl(1)–Ti(1)–Cl(2)	95.50 (7)	C(1)–O(1)–Ti(1)′	124.3 (5)
Cl(1)–Ti(1)–O(1)	88.5 (1)	C(1)–C(2)–Cl(3)	110.7 (4)
Cl(1)–Ti(1)–O(2)	174.0 (2)	O(2)–Ti(1)–O(3)	93.4 (2)
Cl(1)–Ti(1)–O(3)	91.6 (1)	O(2)–Ti(1)–O(1)′	81.8 (2)
Cl(1)–Ti(1)–O(1)′	94.3 (1)	O(2)–C(3)–C(4)	111.0 (6)
Cl(2)–Ti(1)–O(1)	91.7 (1)	C(3)–C(4)–Cl(4)	111.7 (7)
Cl(2)–Ti(1)–O(2)	87.0 (1)	O(3)–Ti(1)–O(1)′	98.2 (2)
Cl(2)–Ti(1)–O(3)	98.0 (2)	O(3)–C(5)–C(6)	114.9 (7)
Cl(2)–Ti(1)–O(1)′	160.8 (1)	C(5)–C(6)–Cl(5)	116.5 (7)
O(2)–H(O(2))···Cl(1)′	151.1 (4)		
Cl(1)–Ti(1)···Ti(1)′	91.61 (8)		
O(2)–Ti(1)···Ti(1)′	82.5 (2)		

Results and Discussion

In the course of our studies pertaining to the deposition of titanium dioxide thin films, we required titanium complexes that contained both chloride and alkoxide ligands. Our attention was

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Table III. Atomic Positional Parameters for **1**

atom	*x*	*y*	*z*
Ti(1)	0.7852 (2)	−0.1003 (2)	0.9576 (2)
Cl(1)	0.7617 (3)	0.1422 (3)	0.9844 (3)
Cl(2)	0.6689 (3)	−0.1847 (3)	1.1104 (3)
O(1)	1.0469 (7)	0.0320 (6)	1.1263 (6)
C(1)	1.099 (1)	0.086 (1)	1.2779 (9)
C(2)	1.140 (1)	−0.036 (1)	1.342 (1)
Cl(3)	1.2333 (4)	0.0369 (4)	1.5303 (3)
O(2)	0.8359 (8)	−0.3039 (7)	0.9438 (7)
C(3)	0.720 (1)	−0.477 (1)	0.917 (1)
C(4)	0.661 (1)	−0.578 (1)	0.769 (1)
Cl(4)	0.8486 (4)	−0.5687 (4)	0.7414 (4)
O(3)	0.5839 (8)	−0.2022 (7)	0.7978 (6)
C(5)	0.422 (2)	−0.218 (2)	0.693 (2)
C(6)	0.263 (2)	−0.340 (2)	0.684 (2)
Cl(5)	0.2316 (5)	−0.5399 (4)	0.6405 (5)

turned toward complexes of the stoichiometry $Cl_2Ti(OR)_2{\cdot}ROH$ that have been prepared by treatment of titanium tetrachloride with excess alcohol.[7,8] Accordingly, we have examined the reaction of 2-haloethanols (chosen to promote crystallinity) with titanium tetrachloride in dichloromethane. Addition of titanium tetrachloride to a solution of excess 2-chloroethanol (3–4 equiv) in dichloromethane at −78 °C, followed by warming to ambient temperature and removal of the volatile organic materials, provided a white crystalline solid (eq 1). Crystallization of this solid from dichloromethane/hexane afforded $[Cl_2Ti(OCH_2CH_2Cl)_2{\cdot}HOCH_2CH_2Cl]_2$ (**1**, 74%) as large, well-formed colorless crystals. In a similar manner, treatment of titanium tetrachloride with 2-bromoethanol and 2-iodoethanol afforded $[Cl_2Ti(OCH_2CH_2Br)_2{\cdot}HOCH_2CH_2Br]_2$ (**2**, 54%) and $[Cl_2Ti(OCH_2CH_2I)_2{\cdot}HOCH_2CH_2I]_2$ (**3**, 46%) respectively, as pale yellow crystalline solids (eq 1). The complexes have been characterized by ^1H and ^{13}C NMR and infrared spectroscopy, elemental analysis, and a crystal structure determination of **1**.

$$TiCl_4 \quad + \quad \geq 3\ HOCH_2CH_2X \xrightarrow[\substack{-78\ ^\circ C\ \text{to RT} \\ 0.5\ h \\ -2\ HCl}]{CH_2Cl_2}$$

$$0.5\ [Cl_2Ti(OCH_2CH_2X)_2{\cdot}HOCH_2CH_2X]_2 \qquad (1)$$

X = Cl **1** 74%
X = Br **2** 54%
X = I **3** 46%

In order to obtain a thorough understanding of the bonding and structural characteristics of this class of complexes, the X-ray crystal structure of **1** was determined. Figure 1 shows a perspective view of **1**, while Figure 2 describes details of the bond lengths and angles about the Ti_2O_2 core. Table I provides the details of the data collection, Table II lists bond distances and angles, and Table III gives the atomic positional parameters. Molecule **1** lies on a crystallographic inversion center, which makes the halves of the molecule identical. The chlorines on each titanium adopt a cis-orientation, with Cl(1) being trans to the coordinated alcohol and Cl(2) being trans to the bridging alkoxide. The short terminal titanium–alkoxide bond (Ti(1)–O(3)) is trans to the long bridging titanium alkoxide (Ti(1)–O(1)). A central feature of the structure is the planar Ti_2O_2 core, with unsymmetrical Ti(1)–O(1) and Ti(1)′–O(1) distances of 1.956 and 2.087 Å, respectively. The titanium–alkoxide Ti(1)–O(3) distance is 1.746 Å, while the coordinated alcohol Ti(1)–O(2) distance is 2.102 Å. A titanium–oxygen single-bond length of 2.08 Å is predicted on the basis of the covalent radii of oxygen and titanium.[9] Hence, the shorter titanium–oxygen bond distances, coupled with the wide Ti(1)–O(3)–C(5) angle of 154.2°, are indicative of multiple titanium–oxygen bond character. The longer titanium–oxygen distances are consistent with single bonds. The Ti(1)–Cl(1) and Ti(1)–Cl(2) distances are 2.326 and 2.284 Å, while the titanium–titanium distance is 3.268 Å.

The angles about the titanium centers indicate an approximate octahedral geometry. With the exception of the O(1)–Ti(1)–O(1)′ angle (72.1°), which is constrained to be less than 90° by the Ti_2O_2 ring, the cis-ligand angles range from 87 to 98°. The trans-ligand angles span 161–174°. Closer inspection of the bond angles about the titanium center reveals an interesting finding. The Cl(1)–Ti(1)–Ti(1)′ angle is 91.6°, as expected for octahedral geometry. However, the O(2)–Ti(1)–Ti(1)′ angle is 82.5°, which indicates that the oxygen atom of the coordinated alcohol (O(2)) is bent toward the chlorine atom Cl(1)′. Such bond angle deformation is further revealed in the O(2)–Cl(1)′ distance of 3.071 Å, which is considerably shorter than the Ti(1)–Ti(1)′ distance of 3.268 Å. In view of the spatial arrangement of the 2-chloroethyl group of the coordinated alcohol, leaning of the oxygen atom O(2) toward Cl(1)′ was highly suggestive of O(2)–H(O(2))···Cl(1)′ hydrogen bonding. Indeed, the final difference map revealed electron density in the region between O(2) and Cl(1)′, which is consistent with a hydrogen atom bonded to O(2), with an O(2)–H(O(2)) bond length of 0.94 Å, an H(O(2))···Cl(1)′ bond length of 2.21 Å, and a O(2)–H(O(2))–Cl(1)′ angle of 151°. While H(O(2)) was assigned a position and not refined and therefore possesses an ill-defined estimated standard deviation, its position is chemically reasonable and fits in with the proposed hydrogen bonding.

The infrared spectra of **1**–**3** corroborated the presence of O–H···Cl hydrogen bonding. A Nujol mull spectrum of **1** showed a medium-intensity, broad hydroxyl absorption at 3215 cm^{-1}. Complexes **2** (3214 cm^{-1}) and **3** (3205 cm^{-1}) showed similar hydroxyl stretches. Free hydroxyl groups generally exhibit a weak, sharp absorption between 3580 and 3650 cm^{-1}, while hydrogen bonded hydroxyl groups show broad, more intense bands in the region from 3200 to 3550 cm^{-1}.[10] Hence, intramolecular O–H···Cl hydrogen bonding is clearly established for **1**–**3**.

We next sought to probe the structure of **1**–**3** in solution using NMR methods to determine if the solid-state O–H···Cl hydrogen bonding was maintained in solution. At room temperature in dichloromethane-d_2, the ^1H NMR spectrum of **1** showed broad resonances at δ 5.0 (4 OCH_2), 4.4 (2 OCH_2), and 3.9 (6 CH_2Cl). However, when the sample was cooled to −80 °C, the coordinated alcohol proton was clearly evident at δ 7.24 (t, J = 5.7 Hz), while multiplets were observed at δ 5.09 (2 OCH_2), 4.84 (2 OCH_2), 4.39 (2 OCH_2), and 3.82 (6 CH_2Cl). The chemical shift of the hydrogen-bonded proton (δ 7.24) was essentially independent of temperature between −90 and −25 °C, which is consistent with a static hydrogen-bonded structure on the NMR time scale. At −20 °C, the hydrogen-bonded proton resonance became extremely broad and was not observed above this temperature. The large downfield chemical shift of the alcohol proton observed when the sample was cooled to ≤−20 °C is consistent with the maintenance of a hydrogen-bonded structure in solution. Unfortunately, **2** and **3** were not soluble enough at low temperature to obtain NMR data. However, analogous structures are proposed from the similarity of their ^1H NMR spectra and from the fact that the infrared spectra of **2** and **3** are nearly identical with that of **1**.

The $^{13}C\{^1H\}$ NMR spectrum of **1** at −80 °C revealed resonances due to oxygenated carbons at 85.67, 78.24, and 68.97 ppm, while chloromethyl carbon resonances were observed at 44.19, 44.06, and 43.14 ppm. The fact that three types of carbons are observed is compatible with the retention of a dimeric structure in solution, at least at low temperature.

This study represents the first structure determination of a titanium chloride alkoxide of the empirical formula $Cl_2Ti(OR)_2{\cdot}HOR$. Since the results clearly indicate that the complexes adopt a dimeric structure in the solid state (which is probably retained in solution), they are better represented by the dimeric

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formulation $[\mathrm{Cl_2Ti(OR)_2{\cdot}HOR}]_2$. A novel feature of these complexes concerns the observed intramolecular O–H···Cl hydrogen bonding, which until now has been an unrecognized feature of titanium chloride alkoxides containing coordinated alcohols. This hydrogen bonding was initially established by the structural distortions observed in the structure of **1**. It was further corroborated by the ν_{OH} infrared stretches of the coordinated alcohols in **1**–**3** and from low-temperature NMR studies of **1**. On the basis of the hydrogen bond classification system of Novak,[11] the hydrogen bonding in **1**–**3** should be classified as weak, since the infrared ν_{OH} occurs at >3200 cm^{-1}. These interactions probably involve O–H···Cl bond strengths of <5 kcal/mol.[11]

Several examples of intramolecular E–H···X hydrogen bonding (X = Cl,[12,13] OR,[14] NR[15]) have been reported. In a particularly relevant recent study, Caulton has described the intramolecular O–H···O hydrogen bonding that occurs in the complex $[\mathrm{Zr(O^iPr)_4{\cdot}HO^iPr}]_2$.[14] Such hydrogen bonding is very similar to that encountered in **1**, except that an oxygen atom is acting as the acceptor, rather than a chlorine atom.

In summary, the complexes $[\mathrm{TiCl_2(OCH_2CH_2X)_2{\cdot}HOCH_2CH_2X}]_2$, which are prepared by treatment of titanium tetrachloride with the appropriate 2-haloethanol in dichloromethane, are dimeric with intramolecular O–H···Cl hydrogen bonding as a central feature of the structures. This study further substantiates the idea that metal–chlorine bonds should be regarded as reasonable hydrogen-bond acceptors in situations where hydrogen bonding is feasible.

Experimental Section

General Considerations. The compounds reported in this work were extremely moisture-sensitive. All manipulations were performed under an atmosphere of argon or nitrogen by using a glovebox or Schlenk techniques. Dichloromethane was distilled from calcium hydride. Hexane was distilled from sodium. Dichloromethane-d_2 was purified by vacuum transfer from activated 4-Å molecular sieves. Titanium tetrachloride and the 2-haloalcohols were used as received from the Aldrich Chemical Co.

^{1}H NMR and ^{13}C{^{1}H} NMR spectra were obtained on a General Electric QE-300 or GN-300 spectrometer for samples in dichloromethane-d_2. Infrared spectra were obtained on a Nicolet DX20 spectrophotometer using Nujol as the medium. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN. Melting points were obtained on a Haake Buchler HBI digital melting point apparatus and are uncorrected.

Preparation of $[\mathbf{Cl_2Ti(OCH_2CH_2Cl)_2{\cdot}HOCH_2CH_2Cl}]_2$ (1). A 100-mL Schlenk flask was charged with 2-chloroethanol (3.0 mL, 45 mmol), dichloromethane (20 mL), and a stir bar and was fitted with a rubber septum. The solution was cooled to −78 °C, and then titanium tetrachloride (1.23 mL, 11.2 mmol) was added by syringe. The mixture was allowed to warm to ambient temperature over 0.5 h. The reaction solution was filtered through a 1-cm pad of Celite on a medium glass frit to afford a clear, yellow solution. Hexane (80 mL) was carefully layered on the dichloromethane layer. The system was allowed to equilibrate for 24 h. The solvent was decanted by cannula and the crystals were vacuum dried to afford **1** as large colorless rhomboids (2.96 g, 74% based upon titanium tetrachloride): mp 127–134 °C dec; IR (Nujol, cm^{-1}) 3215 (m, ν_{OH}), 1300 (m), 1221 (m), 1191 (s), 1098 (vs), 1061 (s), 1041 (s), 1019 (s), 993 (s), 942 (s), 891 (s), 849 (m), 752 (m); ^{1}H NMR (dichloromethane-d_2, −80 °C, δ) 7.24 (t, J = 5.7 Hz, $\mathrm{TiO(\mathit{H})(CH_2CH_2Cl)}$, 5.09 (m, 2 $\mathrm{OC\mathit{H}_2}$), 4.84 (m, 2 $\mathrm{OC\mathit{H}_2}$), 4.39 (m, 2 $\mathrm{OC\mathit{H}_2}$), 3.82 (m, 6 $\mathrm{C\mathit{H}_2Cl}$); ^{13}C{^{1}H} NMR (dichloromethane-d_2, −80 °C, ppm) 85.67 (s, 2 $\mathrm{TiO(\mathit{C}H_2CH_2Cl)Ti}$), 78.24 (s, 2 $\mathrm{TiO(H)(\mathit{C}H_2CH_2Cl)}$, 68.97 (s, 2 $\mathrm{TiO\mathit{C}H_2CH_2Cl}$), 44.19 (s, 2 $\mathrm{\mathit{C}H_2Cl}$), 44.06 (s, 2 $\mathrm{\mathit{C}H_2Cl}$), 43.14 (s, 2 $\mathrm{\mathit{C}H_2Cl}$).

Anal. Calcd for $\mathrm{C_{12}H_{26}Cl_{10}O_6Ti_2}$: C, 20.11; H, 3.66. Found: C, 20.11; H, 3.52.

Preparation of $[\mathbf{Cl_2Ti(OCH_2CH_2Br)_2{\cdot}HOCH_2CH_2Br}]_2$ (2). In a manner similar to the preparation of **1**, treatment of 2-bromoethanol (0.258 mL, 3.64 mmol) with titanium tetrachloride (0.100 mL, 0.910 mmol) afforded **2** as pale yellow square rods (0.24 g, 54% based upon titanium tetrachloride): mp 134–137 °C dec; IR (Nujol, cm^{-1}) 3214 (m, ν_{OH}), 1277 (s), 1171 (s), 1097 (vs), 1056 (s), 1015 (s), 974 (s), 933 (s), 867 (m); ^{1}H NMR (dichloromethane-d_2, 22 °C, δ) 5.2 (broad, 2 $\mathrm{OC\mathit{H}_2}$), 4.2 (broad, 4 $\mathrm{OC\mathit{H}_2}$), 3.6 (6 $\mathrm{C\mathit{H}_2Br}$).

Anal. Calcd for $\mathrm{C_{12}H_{26}Br_6Cl_4O_6Ti_2}$: C, 14.66; H, 2.67. Found: C, 14.86; H, 2.72.

Preparation of $[\mathbf{Cl_2Ti(OCH_2CH_2I)_2{\cdot}HOCH_2CH_2I}]_2$ (3). In a manner similar to the preparation of **1**, treatment of 2-iodoethanol (0.10 mL, 1.28 mmol) with titanium tetrachloride (0.070 mL, 0.641 mmol) afforded **3** as pale yellow needles (0.120 g, 46% based upon 2-iodoethanol): mp 123–125 °C dec; IR (Nujol, cm^{-1}) 3205 (m, ν_{OH}), 1261 (s), 1162 (s), 1089 (vs), 1039 (s), 990 (s), 957 (s), 925 (s), 835 (m); ^{1}H NMR (dichloromethane-d_2, 22 °C, δ) 5.0 (broad, 4 $\mathrm{OC\mathit{H}_2}$), 4.2 (broad, 2 $\mathrm{OC\mathit{H}_2}$), 3.5 (6 $\mathrm{C\mathit{H}_2I}$).

Anal. Calcd for $\mathrm{C_{12}H_{26}Cl_4I_6O_6Ti_2}$: C, 11.39; H, 2.07. Found: C, 11.29; H, 2.04.

X-ray Crystal Structure of $[\mathbf{Cl_2Ti(OCH_2CH_2Cl)_2{\cdot}HOCH_2CH_2Cl}]_2$ (1). A suitable diamond-shaped plate was grown by slow diffusion of hexane into a dichloromethane solution of **1** at ambient temperature. The crystal was mounted in a thin-walled capillary under an argon atmosphere. The capillary was flame-sealed to maintain the inert atmosphere. Details of the data collection are given in Table I. Lattice constants were obtained from 25 high angle (2θ > 40°) reflections. Absorption corrections were empirical, based upon a number of ψ scans.[16a] *Lp* corrections were applied, and neutral atom scattering factors and corrections for anomalous dispersion were taken from ref 16b. One reflection (−1,2,0) was omitted on the basis of secondary extinction.

The structure was solved by Patterson methods and refined in a full-matrix with the programs of SHELX-76.[16c] All non-hydrogen atoms were refined anisotropically; hydrogen atoms were placed in a combination of observed and calculated positions and were held invariant. All atoms occupy general positions in the unit cell, but the center of the dimer is coincident with an inversion center. Final positional parameters are given in Table III. Further data are contained in the supplementary material.

Acknowledgment. We thank Rajesh Kumar for his expert help with crystal mounting.

Supplementary Material Available: Tables SI–SIII, listing thermal parameters, hydrogen positional parameters, and full experimental details for data collection and refinement for **1** (3 pages); Table SIV, listing calculated and observed structure factors for **1** (12 pages). Ordering information is given on any current masthead page.

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