

Covalent Titanium(IV)–Aryloxy Network Materials: 4,4'-Biphenoxide 3D and Polyphenolic 2D Motifs

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The three- and two-dimensional covalent metal–organic network (CMON) compounds $\{[\text{Ti}(\mu_{1,6}:\eta^2,\eta^1\text{-}4,4'\text{-OC}_{12}\text{H}_8\text{O})_{0.5}(\mu_{1,6}:\eta^2,\eta^1\text{-}4,4'\text{-OC}_{12}\text{H}_8\text{O})(\text{O}^i\text{Pr})(\text{HO}^i\text{Pr})]_2 \cdot \text{THF}\}_n$ (1) and $\{[\text{Ti}(\mu_{1,3}\text{-}1,3\text{-OC}_6\text{H}_4\text{O})(\mu\text{-}1,3\text{-OC}_6\text{H}_4\text{OH})(1,3\text{-OC}_6\text{H}_4\text{OH})(\text{HO}^i\text{Pr})]_2\}_n$ (2) were synthesized by treatment of $\text{Ti}(\text{O}^i\text{Pr})_4$ with 4,4'-dihydroxybiphenyl in THF and resorcinol in CS_2 , respectively, at 100°C. Diffraction data was collected at the Cornell High Energy Synchrotron Source (CHESS) because of the small, weakly diffracting nature of the crystals. 1 ($\text{C}_{26}\text{H}_{31}\text{O}_{5.5}\text{Ti}$, monoclinic, $P2_1$, $a = 10.137(2)$, $b = 15.988(3)$, $c = 15.745(3)$, $\beta = 107.76(3)^\circ$, $Z = 4$, $R = 0.0858$) and 2 ($\text{C}_{21}\text{H}_{22}\text{O}_7\text{Ti}$, monoclinic, $P2_1/c$, $a = 11.955(2)$, $b = 16.275(3)$, $c = 11.028(2)$, $\beta = 113.25(3)^\circ$, $Z = 4$, $R = 0.0550$) are both based upon similar edge-sharing bioctahedral dititanium building blocks, (i.e., $\text{Ti}_2(\mu\text{-OAr})_2$). Six connections per dititanium unit constrain the structural motif of 1 to be base-centered. Four $\mu_{1,3}$ -diphenoxides per dititanium core in 2 connect to provide a rectangular net, but the regiochemistry of resorcinol ultimately restricts its dimensionality. The structures suggest design elements based on the number and geometry of connecting organic linkages. © 2000 Academic Press

Key Words: metal-organic networks; coordination polymer, titanium; alkoxides.

INTRODUCTION

The renewed interest in structural aspects of coordination polymers stems from the ability to predict their topology and dimensionality based on utilization of rigid spacers and metals of known coordination tendencies. A growing number of these structurally interesting two- and three-dimensional coordination networks have been characterized (1), and certain structural motifs have been generated based on design (2). Many of these compounds exhibit interesting solid-state properties (3), catalysis (4, 5), or inclusion reactivity (6). The scope of metal–organic networks needs to be further delineated in order to exploit the structural design

features, which exceed those of conventional solid state syntheses, through structure-based properties and reactivity.

Bonding in the great majority of coordination polymers is coordinate covalent, allowing crystallization by methods similar to those of ionic compounds. Common coordination networks typically contain middle to late transition metals or main group metals (6), and aside from research in these laboratories, exploration of early transition metal–alkoxide networks has been limited. Only one other Ti–alkoxide extended structure has been crystallographically characterized (7), and few examples of amorphous systems exist (5, 8).

The formation of rigid, virtually insoluble networks via metal–alkoxide precursor and a dihydroxyaromatic spacer occurs via alcoholysis; thus the crystallization event is fundamentally different than those derived from dative interactions. The solvent donor capacity is a major factor in determining the dimensionality of each network. Poor donors enforce three-dimensionality through μ -alkoxide bridge formation, providing body-centered and hexagonal motifs (9), while good donors tend to disrupt plausible μ -OAr bridges, yielding two-dimensional, sheet-like materials (10). Herein are described the synthesis and characterization of two titanium-aryloxy compounds that extend our understanding of covalent metal–organic network (CMON) materials. In both cases, a titanium-containing building block has been modified by the organic spacer (11) to restrict the nature of the polymerization, thereby affording two new CMON: a 3D network based on dititanium units with six connections and a polyphenolic 2D network derived from resorcinol.

EXPERIMENTAL

General Considerations

All manipulations were performed in an inert atmosphere drybox unless otherwise noted. Tetrahydrofuran was distilled from purple sodium benzophenone ketyl and vacuum transferred from the same into a glass bomb immediately prior to use in the drybox. Carbon disulfide was vacuum transferred and stored onto activated, degassed 4-Å

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molecular sieves. Resorcinol (Aldrich, 99+%) and 4,4'-dihydroxybiphenyl (Aldrich, 97%) were dried by dissolving in dry THF and then removing the volatiles; this procedure was repeated three times. $\text{Ti}(\text{O}^i\text{Pr})_4$ (Aldrich, 97%) was used as received and stored in the drybox. DCl (20 wt% in D_2O , Aldrich) and CD_3OD (Cambridge Isotope Laboratories, D, 99.8%) were used as received; solutions for ^1H NMR were ca. 3 wt% DCl (~ 1 M) and were prepared on the benchtop.

^1H NMR spectra were obtained on a Varian XL-200 spectrometer. Spectra were the product of four transients with a 60-s delay between acquisitions to ensure accurate integrations. Powder diffraction was performed on a Scintag XRD system interfaced to PC with Windows NT. Standard powder patterns were recorded as continuous scans with a chopper increment of $0.03^\circ 2\theta$ and a scan rate of 2° per minute.

Synthesis

(1) *Preparation of* $\{[\text{Ti}(\mu_{1,6}:\eta^2,\eta^1\text{-}4,4'\text{-OC}_{12}\text{H}_8\text{O})_{0.5}(\mu_{1,6}:\eta^2,\eta^1\text{-}4,4'\text{-OC}_{12}\text{H}_8\text{O}) (\text{O}^i\text{Pr}) (\text{HO}^i\text{Pr})]_2 \cdot \text{THF}\}_n$ (**1**). $\text{Ti}(\text{O}^i\text{Pr})_4$ (300 mg, 1.06 mmol) was added to a suspension of 4,4'-dihydroxybiphenyl (372 mg, 2.00 mmol) and THF (~ 3 mL) in a 10-mm-o.d. glass tube to give a red suspension and solution. The tube was sealed under vacuum and heated at 100°C . After 7 weeks small crystals were observed, which continued to grow for 8 more weeks, at which point the product was collected by filtration and washed with THF on a frit. The crystals were dried *in vacuo* for ~ 10 min. Inspection of a sample in Paratone oil under a microscope revealed the crystals to be red-orange flakes of various shapes and about 25% large red blocks. The theoretical powder pattern was calculated from the single crystal data and was compared to the experimental pattern. The large red blocks and chips of **1** are the major crystalline phase, with the remainder of the material being either amorphous or of very poor crystallinity; i.e., all of the peaks in the experimental powder pattern that do not correspond to **1** have very low intensity. A ^1H NMR spectrum of a sample degraded in $\text{CD}_3\text{OD}/\text{DCl}$ did not contain enough $^i\text{PrOD}$ to account for the stoichiometry from the single-crystal structure.

(2) *Preparation of* $\{[\text{Ti}(\mu_{1,3}\text{-}1,3\text{-OC}_6\text{H}_4\text{O})(\mu\text{-}1,3\text{-OC}_6\text{H}_4\text{OH}) (1,3\text{-OC}_6\text{H}_4\text{OH}) (\text{HO}^i\text{Pr})]_2\}_n$ (**2**). $\text{Ti}(\text{O}^i\text{Pr})_4$ (200 mg, 0.70 mmol) was combined with resorcinol (338 mg, 3.07 mmol) in a 10-mm-o.d. glass tube. The tube was freeze-pump-thaw degassed to avoid loss of $\text{Ti}(\text{O}^i\text{Pr})_4$ and ~ 3 mL of CS_2 was vacuum transferred into the tube. A yellow-orange solution and precipitate resulted upon thawing. The tube was heated at 100°C for 10 days, affording yellow crystals. The product was collected by filtration and washed with THF on the benchtop. The crystals were immediately dried *in vacuo* for ~ 10 min. Inspection of a sample in

Paratone oil under a microscope revealed the crystals to be thin diamond plates and flakes of various shapes. Powder XRD matched the theoretical powder pattern with no extraneous peaks. A ^1H NMR spectrum of a sample dissolved in $\text{CD}_3\text{OD}/\text{DCl}$ indicated a 3:1 ratio of $\text{DOC}_6\text{H}_4\text{OD}:\text{HO}^i\text{Pr}$. Anal. Calc'd for $\text{C}_{21}\text{H}_{22}\text{O}_7\text{Ti}$ (Found): C, 58.10 (57.58); H, 5.07 (4.93); N, 0.00 (≤ 0.002), IR (nujol, cm^{-1}): 3523 (m), 3408 (m), 3392 (m, br) 1605 (s), 1586 (s), 1562 (s), 1283 (s), 1255 (s), 1231 (m), 1207 (m), 1168 (s), 1140 (s), 1108 (s), 1070 (m), 979 (s), 940 (m), 871 (m), 856 (m), 844 (s), 823 (m), 806 (m), 787 (m), 763 (s), 681 (s), 648 (s), 619 (m), 585 (m), 499 (m) 484 (m), 439 (s).

Single-Crystal X-ray Structure Determinations

(1) *Structure of* $\{[\text{Ti}(\mu_{1,6}:\eta^2,\eta^1\text{-}4,4'\text{-OC}_{12}\text{H}_8\text{O})_{0.5}(\mu_{1,6}:\eta^2,\eta^1\text{-}4,4'\text{-OC}_{12}\text{H}_8\text{O}) (\text{O}^i\text{Pr}) (\text{HO}^i\text{Pr})]_2 \cdot \text{THF}\}_n$ (**1**). Crystals of **1** were grown from THF as explained above. A few milligrams of red blocks was suspended in Paratone oil on a glass slide. Handling the crystals in Paratone for a few hours in the ambient atmosphere caused no apparent decomposition. Under a microscope, a single block-shaped crystal was isolated in a rayon fiber loop epoxied to a glass fiber (12). On the F2 line at CHESS ($\lambda = 0.9808 \text{ \AA}$), the crystal was frozen in a 110 K nitrogen stream. Using a 0.2-mm collimator, a Quantum 4 CCD was employed to record diffraction (13). Data was collected as 30 s, 5° oscillations in phi, with a total of 360° collected, yielding 15,600 reflections. Observed intensities were corrected for Lorentz and polarization effects, and no absorption correction was applied. The first frame was indexed using the program DENZO (14) and all the data were scaled together with SCALEPACK. Crystal data and structure refinement information are given in Table 1.

(2) *Structure of* $\{[\text{Ti}(\mu_{1,3}\text{-}1,3\text{-OC}_6\text{H}_4\text{O})(\mu\text{-}1,3\text{-OC}_6\text{H}_4\text{OH}) (1,3\text{-OC}_6\text{H}_4\text{OH}) (\text{HO}^i\text{Pr})]_2\}_n$ (**2**). Crystals of **2** were grown in CS_2 as explained above. A few milligrams of yellow plates were suspended in Paratone oil on a glass slide. Under a microscope, a single flat triangular crystal was isolated in a rayon fiber loop epoxied to a glass fiber (12). On the A1 line at CHESS ($\lambda = 0.9134 \text{ \AA}$), the crystal was frozen in a 100 K nitrogen stream. Using a 0.1-mm collimator, a Quantum 4 CCD was used to record diffraction (13). Data were collected as 10 s, 8° oscillations in phi, with a total of 360° collected. Observed intensities were corrected for Lorentz and polarization effects; no absorption correction was applied. The first frame was indexed to a P monoclinic unit cell using the program DENZO (14) and all the data (13,700 reflections) were scaled together with SCALEPACK. The structure was solved with data in the range $\theta = 17.74$ to 30.49° by direct methods (SHELXTL), and all hydrogen atoms were introduced geometrically. The structure was refined by full-matrix

TABLE 1
Crystal Data and Structure Refinement for $\{[\text{Ti}(\mu_{1,6}:\eta^2,\eta^1\text{-4,4'-OC}_{12}\text{H}_8\text{O})_{0.5}(\mu_{1,6}:\eta^2,\eta^1\text{-4,4'-OC}_{12}\text{H}_8\text{O})(\text{O}^i\text{Pr})(\text{HO}^i\text{Pr})]_2 \cdot \text{THF}\}_n$ (1) and $\{[\text{Ti}(\mu_{1,3}\text{-1,3-OC}_6\text{H}_4\text{O})(\mu\text{-1,3-OC}_6\text{H}_4\text{OH})(1,3\text{-OC}_6\text{H}_4\text{OH})(\text{HO}^i\text{Pr})]_2\}_n$ (2)

	1	2
Crystal size (mm)	0.10 × 0.05 × 0.05	0.06 × 0.06 × 0.02
Empirical formula	C ₂₆ H ₃₁ O _{5.5} Ti	C ₂₁ H ₂₂ O ₇ Ti
Formula Weight	479.41	433.26
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ (No. 4)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)
<i>a</i> (Å)	10.137(2)	11.955(2)
<i>b</i> (Å)	15.988(3)	16.275(3)
<i>c</i> (Å)	15.745(3)	11.028(2)
β (°)	107.76(3)	113.25(3)
Volume (Å ³)	2430.2(8)	1971.4(7)
<i>Z</i>	4	4
ρ_{calc} (g cm ⁻³)	1.310	1.543
μ (mm ⁻¹)	0.388	0.475
<i>F</i> (000)	1012	892
<i>T</i> (K)	110	100
λ	0.98080	0.91340
θ Range	3.43° to 29.35°	17.74° to 30.49°
Indices	-10 ≤ <i>h</i> ≤ 9, 0 ≤ <i>k</i> ≤ 14, 0 ≤ <i>l</i> ≤ 15	-13 ≤ <i>h</i> ≤ 11, -18 ≤ <i>k</i> ≤ 0, 0 ≤ <i>l</i> ≤ 12
Reflections collected	15,600	13,700
Indep reflec/restraints/param	2169/1/595	2153/0/262
Absorption corr.	None	None
Refinement method	Full matrix least-sqs. on <i>F</i> ²	Full matrix least-sqs. on <i>F</i> ²
GOF ^a on <i>F</i> ²	2.810	1.315
<i>R</i> indices [<i>I</i> > 2 <i>s</i> (<i>I</i>)] ^b	<i>R</i> ₁ = 0.0797, <i>wR</i> ₂ = 0.2539	<i>R</i> ₁ = 0.0527, <i>wR</i> ₂ = 0.1554
<i>R</i> indices (all data) ^b	<i>R</i> ₁ = 0.0858, <i>wR</i> ₂ = 0.2755	<i>R</i> ₁ = 0.0550, <i>wR</i> ₂ = 0.1637
Largest diff. peak and hole (eÅ ⁻³)	1.295 and -0.669	0.629 and -0.611

^a GOF = $[\sum w(|F_o| - |F_c|)^2 / (n - p)]^{1/2}$; *n*, number of independent reflections; *p*, number of parameters.

^b *R*₁ = $\sum ||F_o| - |F_c|| / \sum |F_o|$; *wR*₂ = $[\sum w(|F_o| - |F_c|)^2 / \sum \omega F_o^2]^{1/2}$.

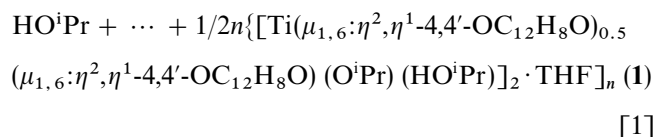
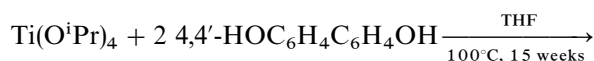
least-squares on *F*² using anisotropic thermal parameters for all nonhydrogen atoms. Crystal data and structure refinement information are given in Table 1.

RESULTS

Synthesis

The synthesis of metal-alkoxide networks can be considered a modified sol-gel procedure, where dihydroxy functionalized aromatics are used instead of water. Initially, the combination of metal-alkoxide with the organic spacer results in a gel, which when dried often yields an amorphous precipitate. Continue heating of the components in a sealed reaction vessel can yield microcrystalline material under the correct conditions, but often the material remains amorphous. In the preparations that follow, residual isopropanol or isopropoxide derived from the starting Ti(O^{*i*}Pr)₄ is evident, illustrating one of the pitfalls of the direct synthesis method employed.

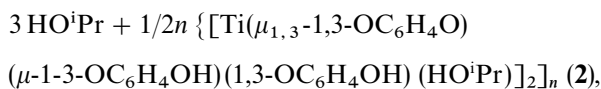
Ti(O^{*i*}Pr)₄ was combined with ~2 equiv 4,4'-biphenol in THF in a sealed tube and heated for 15 weeks at 100°C to afford $[\text{Ti}(\mu_{1,6}:\eta^2,\eta^1\text{-4,4'-OC}_{12}\text{H}_8\text{O})_{0.5}(\mu_{1,6}:\eta^2,\eta^1\text{-4,4'-OC}_{12}\text{H}_8\text{O})(\text{O}^i\text{Pr})(\text{HO}^i\text{Pr})]_2 \cdot \text{THF}]_n$ (**1**), among other unidentified material (Eq. [1]). Powder XRD revealed



minor crystalline components that did not correspond to **1**, whose theoretical powder pattern was calculated from single crystal data. Light microscopy revealed that ~25% of the material was composed of red blocks, one of which was used in the single crystal X-ray diffraction study. The

remaining 75% of the materials was composed of red-orange flakes. Portions of the bulk sample were degraded in CD₃OD/DCl and ¹H NMR spectral analyses of the organic material were inconsistent with an expected 1.5:2:0.5 ratio of 4,4'-DOC₆H₄-C₆H₄OD:DOⁱPr:THF from **1**. Combined with the observation of impurities detected by XRD, the quenching studies suggest that other solid state compositions, both crystalline and amorphous, comprise the remainder of the bulk.

Ti(OⁱPr)₄ was combined with > 4 equiv resorcinol in carbon disulfide in a sealed tube and heated to 100°C for 10 days to afford yellow crystals of {[Ti(μ_{1,3}-1,3-OC₆H₄O)(μ-1-3-OC₆H₄OH)(1,3-OC₆H₄OH)(HOⁱPr)]₂]_n (**2**) (Eq. [2]). The powder XRD of the bulk matched that



[2]

obtained from a single crystal X-ray diffraction study of **2**, and a CD₃OD/DCl quench of the material indicated the expected 3:1 ratio of DOC₆H₄OD:HOⁱPr according to ¹H NMR spectroscopy. As a consequence of these observa-

tions and elemental analysis, production of **2** is considered to be nearly quantitative.

X-Ray Structural Studies

The small, weakly diffracting single crystals {[Ti(μ_{1,6}:η²,η¹-4,4'-OC₁₂H₈O)_{0.5}(μ_{1,6}:η²,η¹-4,4'-OC₁₂H₈O)(OⁱPr)(HOⁱPr)]₂·THF]_n (**1**) and {[Ti(μ_{1,3}-1,3-OC₆H₄O)(μ-1-3-OC₆H₄OH)(1,3-OC₆H₄OH)(HOⁱPr)]₂]_n (**2**) necessitated the use of the high-intensity X-ray beam provided by the Cornell High Energy Synchrotron Source. While crystals of **1** were regular blocks, crystals of the two-dimensional compound **2** were very thin plates, and larger examples were found to be multiply twinned. Furthermore, upon data analysis, frames containing low-angle data caused severe scaling problems; hence the structure solution of **2** was determined solely from high-angle data. Despite the difficulties intrinsic to small crystals and relatively weakly diffracting samples, satisfactory structures were obtained by direct methods. The density of the networks varies according to the efficiency in packing of the ligands and the filling of void space by molecules of solvation. In the case of **2**, which forms irregular, slightly interpenetrating sheets, the density of 1.453 g/cm³ is quite normal (9), whereas in **1** the lower density of 1.301 g/cm³ is consistent with the larger channels supported by the three-dimensional network.

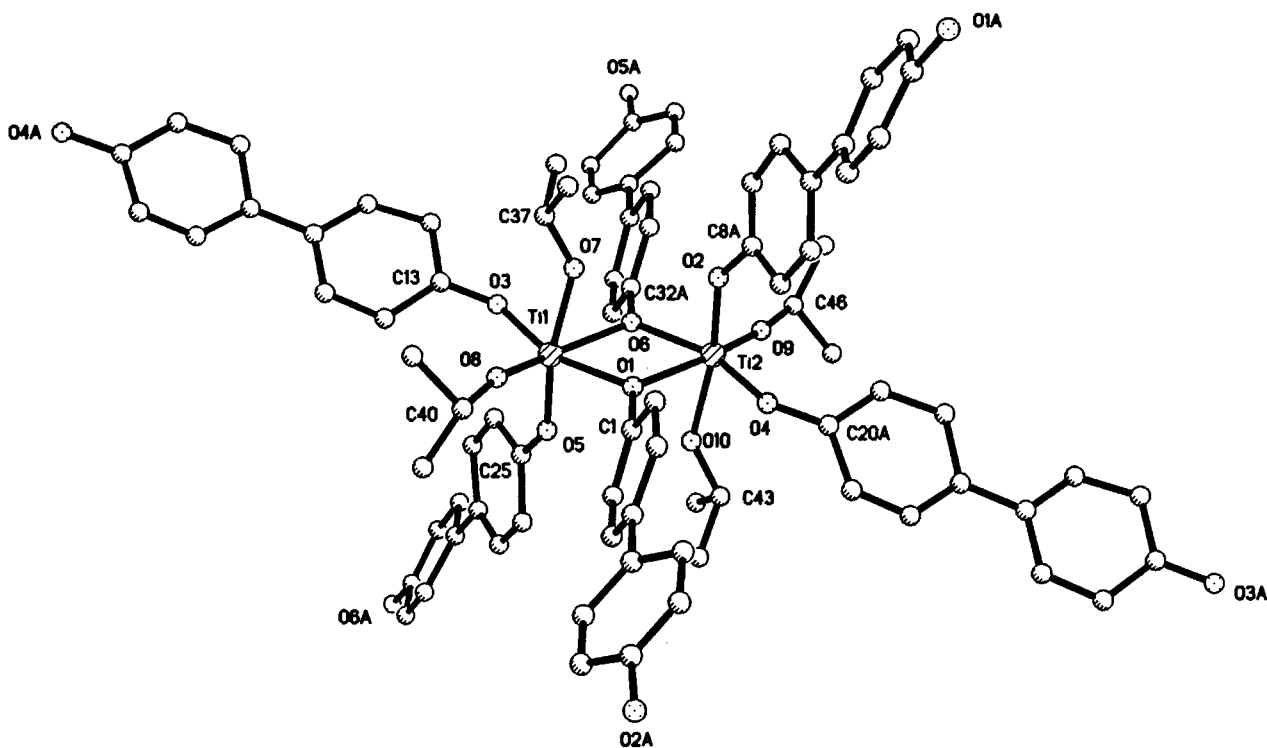


FIG. 1. Biotetrahedral dititanium building block of {[Ti(μ_{1,6}:η²,η¹-4,4'-OC₁₂H₈O)_{0.5}(μ_{1,6}:η²,η¹-4,4'-OC₁₂H₈O)(OⁱPr)(HOⁱPr)]₂·THF]_n (**1**).

TABLE 2
Selected Interatomic Distances (Å) and Angles (°) in $\{[\text{Ti}(\mu_{1,6}:\eta^2,\eta^1\text{-}4,4'\text{-OC}_{12}\text{H}_8\text{O})_{0.5}(\mu_{1,6}:\eta^2,\eta^1\text{-}4,4'\text{-OC}_{12}\text{H}_8\text{O})(\text{O}^i\text{Pr})(\text{HO}^i\text{Pr})]_2 \cdot \text{THF}\}_n$ (1**)**

Ti1–O1	2.055(9)	Ti1 ... Ti2	3.378(3)	O1–C1	1.42(2)
Ti1–O6	2.107(10)	Ti2–O1	2.077(11)	O2–C8	1.38(2)
Ti1–O3	1.873(10)	Ti2–O6	2.055(8)	O3–C13	1.29(2)
Ti1–O8	1.748(10)	Ti2–O9	1.751(12)	O4–C20	1.32(2)
Ti1–O7	2.103(12)	Ti2–O4	1.797(11)	O5–C25	1.34(2)
Ti1–O5	1.861(11)	Ti2–O2	1.893(11)	O6–C32	1.33(2)
		Ti2–O10	2.149(13)	O7–C37	1.34(2)
Aryl (C–C) _{ave}	1.39(4)			O8–C40	1.40(2)
Biphenyl (C–C) _{ave}	1.47(4)			O9–C46	1.44(2)
Pr (C–C) _{ave}	1.5(1)			O10–C43	1.33(3)
O8–Ti1–O3	101.2(5)	O9–Ti2–O4	103.3(5)	O3–Ti1–O1	160.0(5)
O3–Ti1–O5	98.7(4)	O9–Ti2–O2	97.9(5)	O7–Ti1–O1	80.8(5)
O3–Ti1–O7	86.7(4)	O9–Ti2–O6	93.4(4)	O3–Ti1–O6	91.5(4)
O8–Ti1–O1	94.4(5)	O4–Ti2–O2	96.2(5)	O7–Ti1–O6	77.4(5)
O5–Ti1–O1	91.1(5)	O4–Ti2–O6	161.0(5)	O1–Ti1–O6	70.6(4)
O8–Ti1–O6	161.4(5)	O2–Ti2–O6	90.2(5)	O9–Ti2–O10	89.1(5)
O5–Ti1–O6	92.4(5)	O9–Ti2–O1	162.6(4)	O4–Ti2–O10	88.3(5)
O8–Ti1–O5	99.0(5)	O4–Ti2–O1	90.9(4)	O2–Ti2–O10	170.6(6)
O8–Ti1–O7	89.6(5)	O2–Ti2–O1	90.5(5)	O6–Ti2–O10	83.1(5)
O5–Ti1–O7	168.7(5)	O6–Ti2–O1	71.2(4)	O1–Ti2–O10	81.2(5)
Ti1–O6–Ti2	108.5(4)	Ti1–O1–Ti2	109.7(5)	Ti2–O10–C43	136(2)
Ti1–O7–C37	139.7(12)	Ti1–O8–C40	167.0(11)	Ti2–O2–C8A	144.1(11)
Ti1–O5–C25	142.3(9)	Ti1–O3–C13	141.8(9)	Ti2–O9–C46	172.8(11)
Aryl (CCC) _{ave}	120.2(40)	Aryl (OCC) _{ave}	121.4(27)	Ti2–O4–C20A	138.4(8)

The primary building block in the structure of $\{[\text{Ti}(\mu_{1,6}:\eta^2,\eta^1\text{-}4,4'\text{-OC}_{12}\text{H}_8\text{O})_{0.5}(\mu_{1,6}:\eta^2,\eta^1\text{-}4,4'\text{-OC}_{12}\text{H}_8\text{O})(\text{O}^i\text{Pr})(\text{HO}^i\text{Pr})]_2 \cdot \text{THF}\}_n$ (**1**) is the familiar edge-shared bioctahedral dititanium unit (9, 15) illustrated in Fig. 1. Isopropoxides and isopropanols derived from the starting $\text{Ti}(\text{O}^i\text{Pr})_4$ complex remain as part of the extended structure occupying equatorial ($d(\text{Ti1-O8}) = 1.748(10)$ Å, $d(\text{Ti2-O9}) = 1.751(12)$ Å) and axial ($d(\text{Ti1-O7}) = 2.103(12)$, $d(\text{Ti2-O10}) = 2.149(13)$ Å) sites, respectively. The latter hydrogen bond with axial 4,4'-biphenoxide linkages ($d(\text{Ti1-O5}) = 1.861(11)$ Å, $d(\text{Ti2-O2}) = 1.893(11)$ Å) that reconnect to neighboring dititanium units at bridging positions. The isopropanols lean ($\angle\text{O1-Ti1-O7} = 80.8(5)^\circ$, $\angle\text{O6-Ti1-O7} = 77.4(5)^\circ$, $\angle\text{O1-Ti2-O10} = 81.2(5)^\circ$, $\angle\text{O6-Ti2-O10} = 83.1(5)^\circ$ toward the 4,4'-biphenoxides ($\angle\text{O1-Ti1-O5} = 91.1(5)^\circ$, $\angle\text{O6-Ti1-O5} = 92.4(5)^\circ$, $\angle\text{O1-Ti2-O2} = 90.5(5)^\circ$, $\angle\text{O6-Ti2-O2} = 90.2(5)^\circ$) to establish the hydrogen bonds, and the remaining angles about each titanium tend to be greater than 90° in response to this feature, as Table 2 indicates. The equatorial plane of the bioctahedron contains two terminal aryloxide bonds ($d(\text{Ti1-O3}) = 1.873(10)$ Å, $d(\text{Ti2-O4}) = 1.797(11)$ Å) from a single 4,4'-biphenoxide, the isopropoxides and two 4,4'-biphenoxide bridges ($d(\text{Ti1-O1}) = 2.055(9)$ Å, $d(\text{Ti1-O6}) = 2.107(10)$ Å, $d(\text{Ti2-O1}) = 2.077(11)$ Å, $d(\text{Ti2-O6}) = 2.055(8)$ Å) that span the two titaniums ($\angle\text{O6-Ti1-O1} = 70.6(4)^\circ$, $\angle\text{O6-Ti2-O1} = 71.2(4)^\circ$, $\angle\text{Ti1-O6-Ti2} = 108.5(4)^\circ$, $\angle\text{Ti1-O1-Ti2} = 109.7(5)^\circ$).

The secondary structure of three-dimensional **1** is based on the connectivity of three unique 4,4'-biphenoxides bridging dititanium cores, and may be considered a base-centered motif. The O3, O4 4,4'-biphenoxide connects dititanium

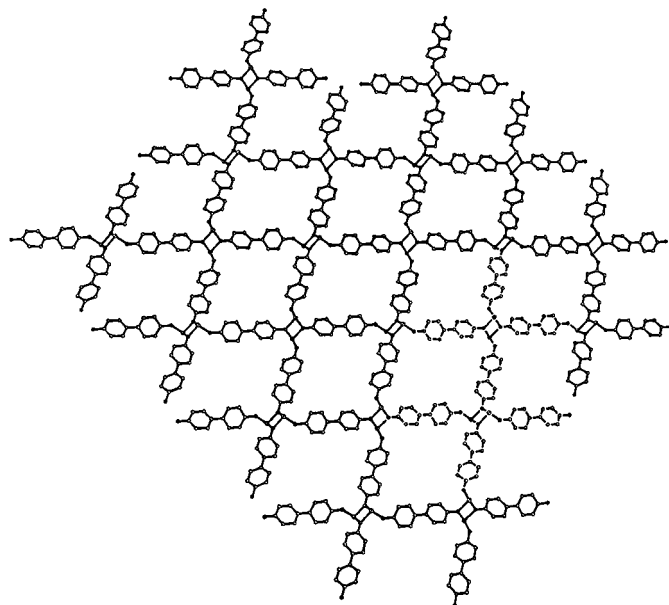


FIG. 2. Two-dimensional network of the bridge-to-axial O1, O2 and O6, O5 4,4'-biphenoxide connections in $\{[\text{Ti}(\mu_{1,6}:\eta^2,\eta^1\text{-}4,4'\text{-OC}_{12}\text{H}_8\text{O})_{0.5}(\mu_{1,6}:\eta^2,\eta^1\text{-}4,4'\text{-OC}_{12}\text{H}_8\text{O})(\text{O}^i\text{Pr})(\text{HO}^i\text{Pr})]_2 \cdot \text{THF}\}_n$ (**1**). All nonconnecting ligands have been removed for clarity.

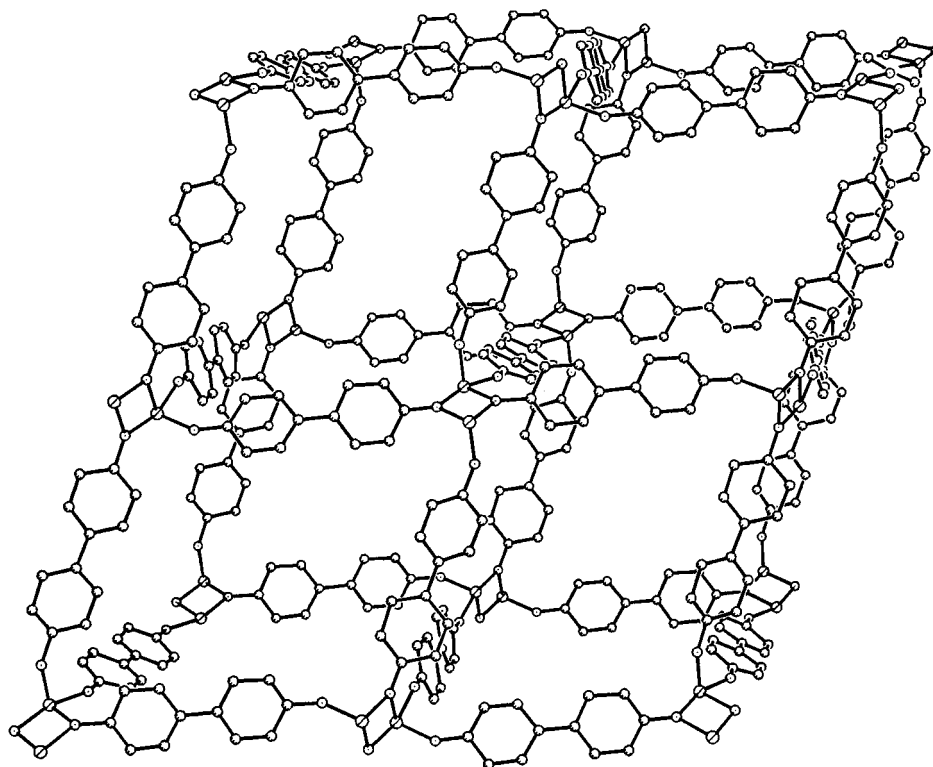


FIG. 3. Three-dimensional lattice of $\{[\text{Ti}(\mu_{1,6}:\eta^2, \eta^1\text{-4,4}'\text{-OC}_{12}\text{H}_8\text{O})_{0.5}(\mu_{1,6}:\eta^2, \eta^1\text{-4,4}'\text{-OC}_{12}\text{H}_8\text{O})(\text{O}^i\text{Pr})(\text{HO}^i\text{Pr})]_2 \cdot \text{THF}\}_n$ (**1**). All nonconnecting ligands have been removed for clarity.

units via terminal equatorial bonds, while the O1, O2, and O6, O5 4,4'-biphenoxides generate linkages from bridging to axial sites in adjacent Ti_2 cores. Figure 2, reveals a network composed of the latter two connections, with the equatorial linkages, isopropoxides, and isopropanol removed for clarity. The network is base-centered, since alternating orientations of Ti_2O_2 cores are evident. Inclusion of the O3–O4, 4,4'-biphenoxide translates the cores to adjacent layers and establishes the three-dimensional network, which Fig. 3. illustrates as viewed down the b axis. Alternatively, if the dititanium units are viewed simply as connecting points, the network can be considered primitive. The isopropanols, isopropoxides, and two disordered molecules of THF per unit cell partially fill the cavities generated by the rigid framework.

The two-dimensional structure of $\{[\text{Ti}(\mu_{1,3}\text{-1,3-OC}_6\text{H}_4\text{O})(\mu\text{-1,3-OC}_6\text{H}_4\text{OH})(1,3\text{-OC}_6\text{H}_4\text{OH})(\text{HO}^i\text{Pr})]_2\}_n$ (**2**) is also based upon a biocahedral dititanium core (Fig. 4), but one exhibiting crystallographic inversion symmetry. The titaniums are spanned by a 3-hydroxyphenoxide ($d(\text{Ti}-\text{O}5) = 2.0433(18) \text{ \AA}$, $d(\text{Ti}-\text{O}5) = 2.0661(18) \text{ \AA}$; $\angle \text{Ti}1-\text{O}5-\text{Ti}1\text{A} = 108.01(8)^\circ$, $\angle \text{O}5-\text{Ti}-\text{O}5\text{A} = 71.99(8)^\circ$) that does not engage in connecting dititanium units, but hydrogen bonds with neighboring layers. The remaining equatorial sites are occu-

pled by a terminal 3-hydroxyphenoxide ($d(\text{Ti}-\text{O}3) = 1.8034(18) \text{ \AA}$) that hydrogen bonds with another layer and a 1,3-diphenoxide ($d(\text{Ti}-\text{O}1) = 1.821(2) \text{ \AA}$) that provides the covalent linkage between dititanium cores, reentering another unit at an axial position ($d(\text{Ti}-\text{O}2) = 1.9002(18) \text{ \AA}$, $\angle \text{O}2-\text{Ti}-\text{O}5 = 89.16(8)^\circ$, $\angle \text{O}2-\text{Ti}-\text{O}5\text{A} = 89.52(7)^\circ$). The axial 1,3-diphenoxide hydrogen bonds with an axial isopropanol ($d(\text{Ti}-\text{O}7) = 2.1800(19) \text{ \AA}$, $\angle \text{O}5-\text{Ti}-\text{O}7 = 79.00(7)^\circ$, $\angle \text{O}5\text{A}-\text{Ti}-\text{O}7 = 79.34(7)^\circ$) on the adjacent titanium, and the angles about each Ti (Table 3) are similar to those of **1** and previous cases (9).

Figure 5 reveals the two-dimensional net described by the equatorial-O1, axial-O2, 1,3-diphenoxide of **2**, with all of the nonbridging ligands removed for clarity. It is basically a rectangular net, with two essentially orthogonal dititanium building blocks per repeat unit. In Fig. 6, all ligands except the isopropanols are illustrated, and the axial, equatorial connectivity is shown in multiple layers. The view perpendicular to the covalent net reveals that phenolic residues from the bridging (O6) and adjacent equatorial (O4) hydroxyphenols engage in hydrogen bonding with the same O4, O6 functionality, respectively, of a neighboring layer ($d(\text{O}4-\text{O}6) = 2.813(4) \text{ \AA}$). With the isopropanols again removed in the related parallel view in Fig. 7, crosslinking by

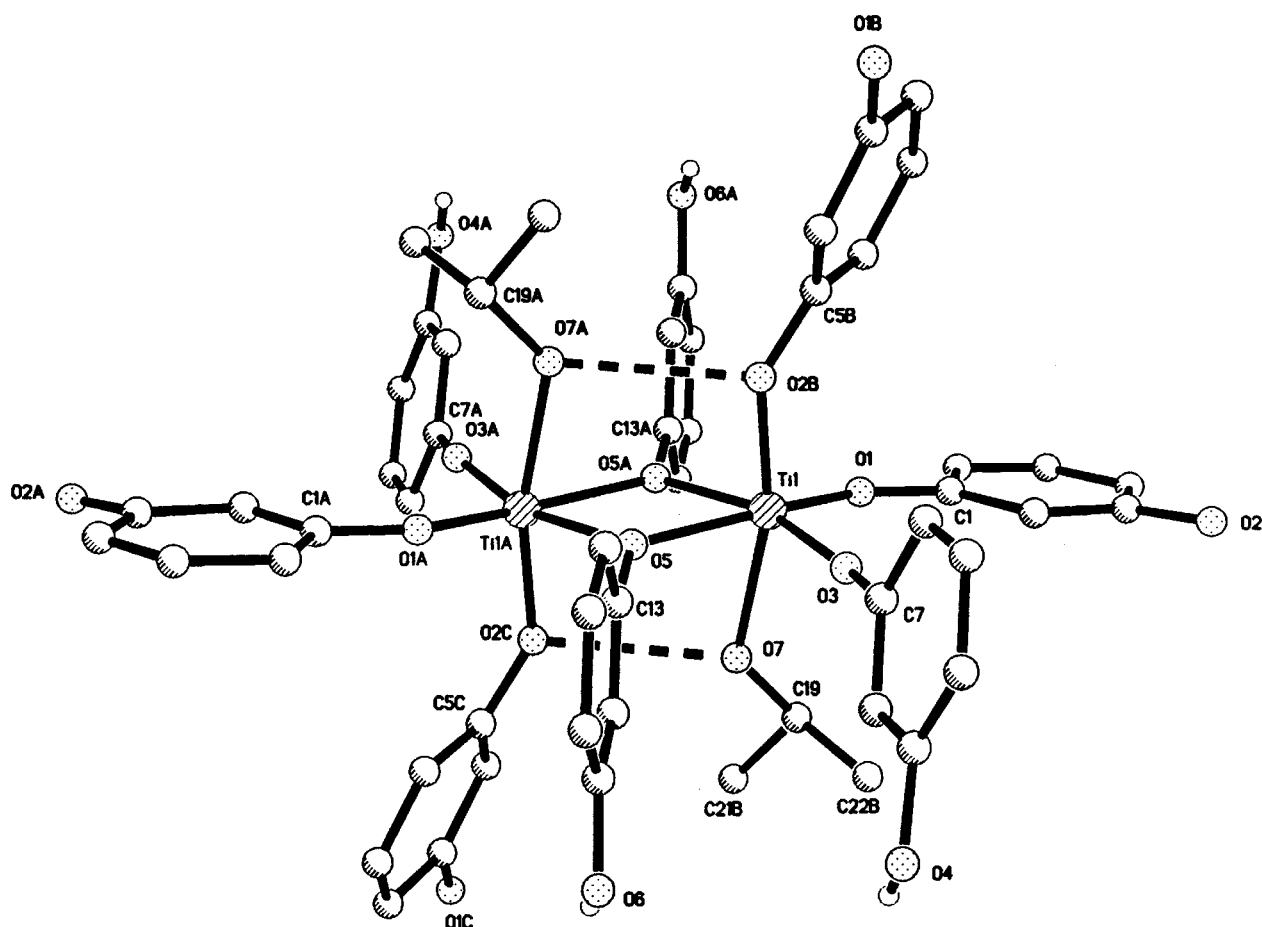


FIG. 4. Biocahedral dititanium building block of $\{[\text{Ti}(\mu_{1,3}\text{-}1,3\text{-OC}_6\text{H}_4\text{O})(\mu\text{-}1,3\text{-OC}_6\text{H}_4\text{OH})(1,3\text{-OC}_6\text{H}_4\text{OH})(\text{HO}^i\text{Pr})]_2\}_n$ (2).

these phenolic residues is again seen to establish the interconnectivity between layers. The strength of this hydrogen bonding interaction is uncertain (16), because the hydrogen donor and acceptor are the same residue, i.e., ArOH. It may

be that the subtle stacking of the hydroxyphenoxide ligands, coupled with dipolar interactions of the hydroxyaryloxo functionalities, provides a greater impetus for the specific layered motif observed.

TABLE 3

Selected Interatomic Distances (Å) and Angles (°) in $\{[\text{Ti}(\mu_{1,3}\text{-}1,3\text{-OC}_6\text{H}_4\text{O})(\mu\text{-}1,3\text{-OC}_6\text{H}_4\text{OH})(1,3\text{-OC}_6\text{H}_4\text{OH})(\text{HO}^i\text{Pr})]_2\}_n$ (2)

Ti-O1	1.821(2)	Ti-Ti	3.3247(10)	O5-C13	1.374(3)
Ti-O2	1.900(2)	O1-C1	1.355(3)	O6-C17	1.355(3)
Ti-O3	1.803(2)	O2-C5	1.352(4)	O7-C19	1.451(4)
Ti-O5	2.043(2)	O3-C7	1.355(4)	Aryl (C-C) _{ave}	1.391(7)
Ti-O5A	2.066(2)	O4-C11	1.387(4)	Pr (C-C) _{ave}	1.505(6)
Ti-O7	2.180(2)				
O1-Ti-O2	99.75(8)	O3-Ti-O7	90.83(8)	Ti-O5-TiA	108.01(8)
O1-Ti-O3	100.59(9)	O5-Ti-O2B	89.16(8)	Ti-O1-C1	155.26(16)
O1-Ti-O5	161.75(8)	O5-Ti-O5A	71.99(8)	Ti-O2-C1	141.15(16)
O1-Ti-O5A	92.05(8)	O5-Ti-O	79.00(7)	Ti-O3-C7	159.30(17)
O1-Ti-O7	89.60(8)	O2B-Ti-O5A	89.52(7)	Ti-O5-C13	125.80(15)
O3-Ti-O2B	97.92(9)	O2B-Ti-O7	165.75(8)	Ti-O7-C19	129.84(15)
O3-Ti-O5	93.84(8)	O5A-Ti-O7	79.34(7)	Ti-O5-C13	125.23(14)
O3-Ti-O5A	163.07(8)	Aryl (CCC) _{ave}	120.0(10)	Aryl (OCC) _{ave}	119.7(16)

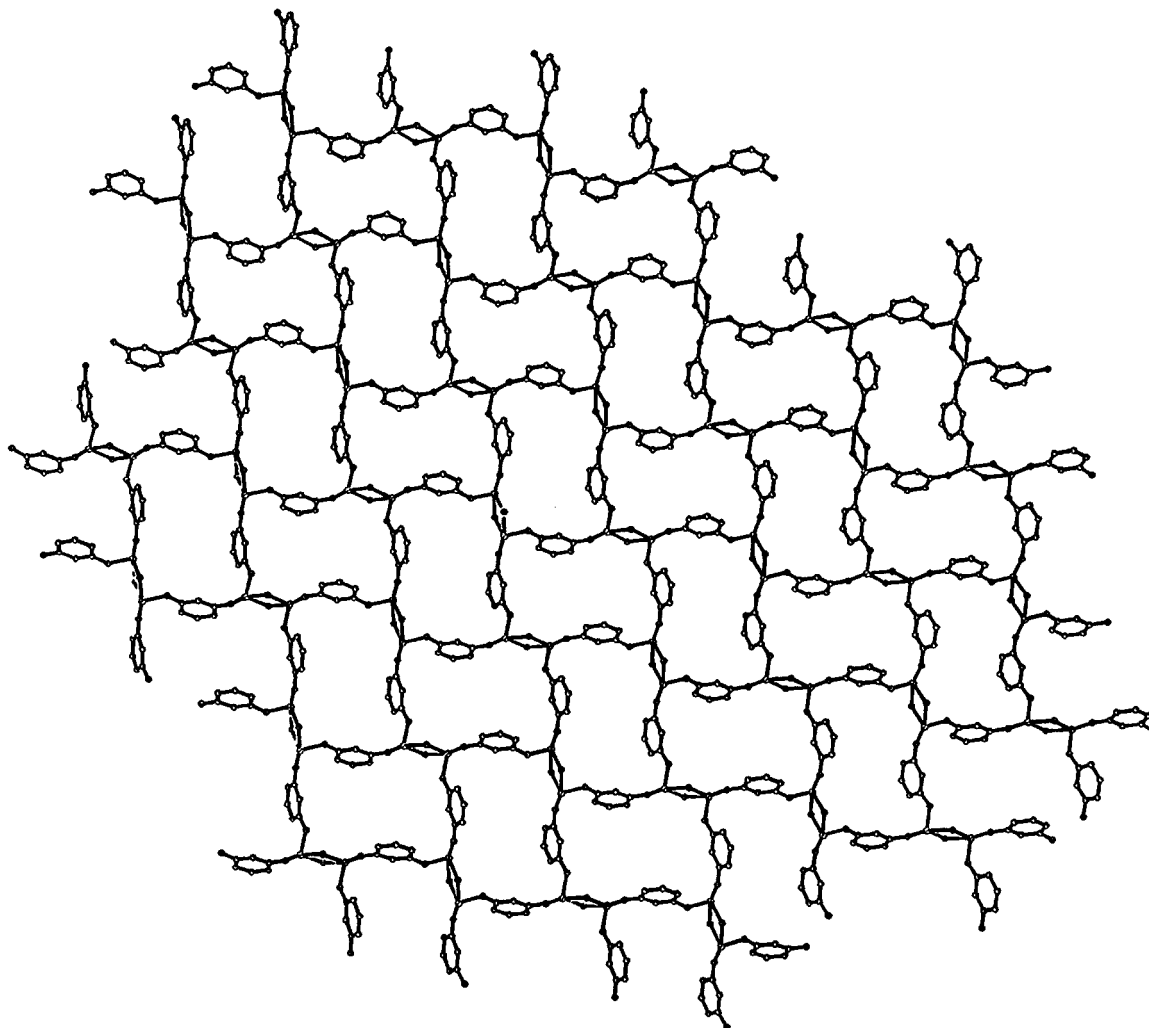


FIG. 5. Two-dimensional lattice of $\{[\text{Ti}(\mu_{1,3}\text{-}1,3\text{-OC}_6\text{H}_4\text{O})(\mu\text{-}1,3\text{-OC}_6\text{H}_4\text{OH})(1,3\text{-OC}_6\text{H}_4\text{OH})(\text{HO}^i\text{Pr})_2]_n\}$ (2) featuring the equatorial-O1, axial-O2, 1,3-diphenoxide connections. All nonconnecting ligands have been removed for clarity.

DISCUSSION

As in previous syntheses of CMON in solvents of relatively low binding ability (9), the dititanium building block dictates the connectivity of the three-dimensional net in $\{[\text{Ti}(\mu_{1,6}:\eta^2,\eta^1\text{-}4,4'\text{-OC}_{12}\text{H}_8\text{O})_{0.5}(\mu_{1,6}:\eta^2,\eta^1\text{-}4,4'\text{-OC}_{12}\text{H}_8\text{O})(\text{O}^i\text{Pr})(\text{HO}^i\text{Pr})_2 \cdot \text{THF}]_n\}$ (1). Each bioctahedron is held together by bridging aryloxy ligands, and hydrogen bonding between an axial aryloxy and an axial hydrogen donor from the adjacent titanium. The bioctahedron has 10 sites that can be used to link with neighboring dititanium units: four terminal equatorial, two bridging equatorial, and four axial. In 1, two axial positions are assumed by isopropanols and two equatorial sites are effectively removed by coordination to isopropoxide, leaving only six plausible connections. Note the contrast with

$[\text{Ti}_2(\mu_{1,4}\text{-OC}_6\text{H}_4\text{O})_2(\mu_{1,4}\text{-OC}_6\text{H}_4\text{OH})_2(\mu\text{-OC}_6\text{H}_4\text{OH})_2]_n$ and $[\text{Ti}_2(\mu_{2,7}\text{-O-C}_{10}\text{H}_6\text{O})_2(\mu_{2,7}:\eta^2,\eta^1\text{-OC}_{10}\text{H}_6\text{OH})_2(\text{O}^i\text{Pr})_2]_n$, whose eight connections generated body-centered structural motifs, and $[\text{Ti}_2(\mu_{1,4}\text{-OC}_6\text{H}_4\text{O})_2(\mu_{1,4}:\eta^2,\eta^1\text{-OC}_6\text{H}_4\text{O})_2 \cdot (\text{OH}_2)_2 \cdot (\text{H}_2\text{O})_2 \cdot (\text{HOC}_6\text{H}_4\text{OH}) \cdot (\text{MeCN})]_n$, whose eight linkages yielded a hexagonal connectivity (9). The three-dimensional motif in 1 is limited to frameworks of six connections: primitive, base-centered, or face-centered. The twisted bridge/axial connectivity in 1 affords a face-centered network that connects to adjacent layers via the equatorial 4,4'-biphenoxide, producing a overall base-centered three-dimensional network, or a primitive one if orientations of Ti_2O_2 cores are not distinguished.

The bioctahedral core of $\{[\text{Ti}(\mu_{1,3}\text{-}1,3\text{-OC}_6\text{H}_4\text{O})(\mu\text{-}1,3\text{-OC}_6\text{H}_4\text{OH})(1,3\text{-OC}_6\text{H}_4\text{OH})(\text{HO}^i\text{Pr})_2]_n\}$ (2) processes

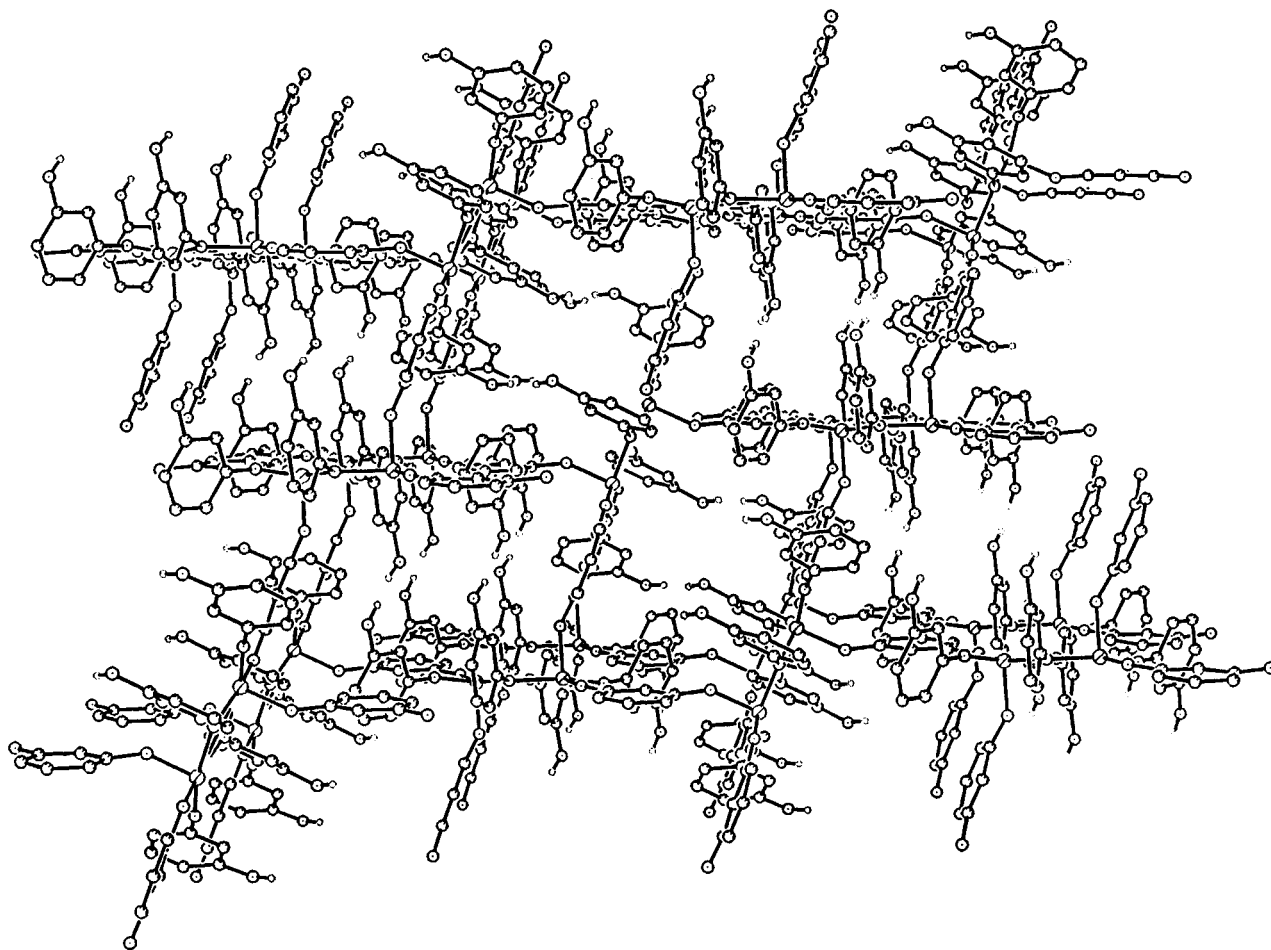


FIG. 6. Two layers of the two-dimensional covalent network of $\{[\text{Ti}(\mu_{1,3}\text{-1,3-OC}_6\text{H}_4\text{O})(\mu\text{-1,3-OC}_6\text{H}_4\text{OH})(1,3\text{-OC}_6\text{H}_4\text{OH})(\text{HO}^i\text{Pr})_2]\}_n$ (2), viewed perpendicular to the layers. The isopropanol ligands have been removed for clarity.

8 sites of potential connectivity, having 2 of the 10 occupied by isopropanols. Instead of forming the expected three-dimensional network, the 1,3-disposition of the aryloxy or phenolic linkages on the resorcinol-based ligands severely restricts their ability to bridge dititanium cores. A single, dense, face-centered two-dimensional net is created, but the four remaining resorcinol connectors fail to condense into neighboring dititanium cores, and instead form a subtly interpenetrating two-dimensional structure. Interfacial interactions between the layers are difficult to discern and may derive from hydrogen bonding or perhaps from elements of aromatic stacking and the accompanying dipolar attractions between phenolic residues. The simple substitution of resorcinol for hydroquinone (cf. $[\text{Ti}_2(\mu_{1,4}\text{-OC}_6\text{H}_4\text{O})_2(\mu_{1,4}\text{-OC}_6\text{H}_4\text{OH})_2(\mu\text{-OC}_6\text{H}_4\text{OH})_2]_n$) as the organic spacer has lowered the dimensionality of the network as a consequence of the more constrained environment of the 1,3-benzene vs 1,4-benzene regiochemistry.

CONCLUSIONS

CMON solids can be synthesized by a modified sol-gel procedure employing titanium(IV)-alkoxides and a variety of dihydroxy-functionalized aromatics. Control of the topology and dimensionality of the material was previously shown to depend on the donating ability of the solvent or coligand (9, 10). As observed in this study, if the number of sites available on connecting points—in this case the dititanium building blocks—is restricted, another control element is realized. In addition, structural requirements of the linkages can be tuned to dramatically effect the ultimate dimensionality, and presumably the topology, of the material synthesized. The serendipitous discovery of the networks herein, and the relationship between structural elements and final geometry, have provided two additional means to the ultimate goal: the preparation of CMON by design. The scope of these materials continues to be probed, and struc-

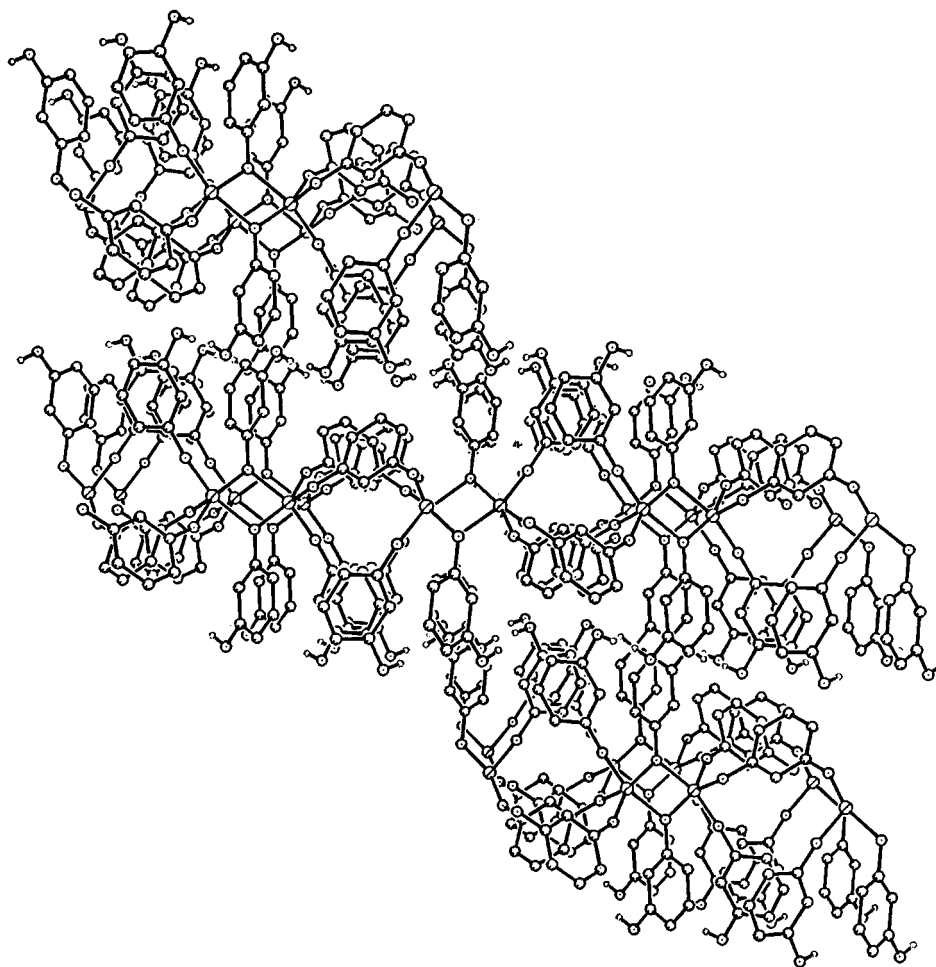


FIG. 7. Three layers of the two-dimensional covalent network of $\{[\text{Ti}(\mu_{1,3}\text{-}1,3\text{-OC}_6\text{H}_4\text{O})(\mu\text{-}1,3\text{-OC}_6\text{H}_4\text{OH})(1,3\text{-OC}_6\text{H}_4\text{OH})(\text{HO}^i\text{Pr})]_2\}_n$ (**2**), viewed parallel to the layers. The isopropanol ligands have been removed for clarity.

ture/property relationships are currently under investigation.

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