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Synthesis and O$_2$ Reactivity of a Titanium(III) Metal–Organic Framework

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ABSTRACT: Metal–organic frameworks featuring pores lined with exposed metal cations have received attention for a wide range of adsorption-related applications. While many frameworks with coordinatively unsaturated M$^\text{II}$ centers have been reported, there are relatively few examples of porous materials with coordinatively unsaturated M$^\text{III}$ centers. Here, we report the synthesis and characterization of Ti$_3$O(OEt)-(bdc)$_3$(solv)$_2$ (Ti-MIL-101; bdc$^{2-}$ = 1,4-benzenedicarboxylate; solv = N,N-dimethylformamide, tetrahydrofuran), the first metal–organic framework containing exclusively Ti$^{3+}$ centers. Through a combination of gas adsorption, X-ray diffraction, magnetic susceptibility, and electronic and vibrational spectroscopy measurements, this high-surface-area framework is shown to contain five-coordinate Ti$^{3+}$ centers upon desolvation, which irreversibly bind O$_2$ to form titanium(IV) superoxo and peroxo species. Electronic absorption spectra suggest that the five-coordinate Ti$^{3+}$ sites adopt a distorted trigonal-bipyramidal geometry that effectively shields nuclear charge and inhibits strong adsorption of nonredox-active gases.

INTRODUCTION

Metal–organic frameworks featuring both high surface areas and high densities of coordinatively unsaturated metal (M) centers have shown promise as new adsorbents for storing and separating gases.$^1$ When constrained by the framework to an appropriate geometry, low-coordinate metal cations can function as exposed positive charges on the pore surface that strongly polarize specific gas molecules, leading to increased gas uptake and highly selective adsorption.$^3$ In the context of H$_2$ storage for mobile applications, metal–organic frameworks with exposed divalent metal cations have demonstrated some of the highest H$_2$ storage densities to date as a direct result of strong M$^{2+}$–H$_2$ interactions.$^{3,5}$ While the strength of these interactions, which is typically in the range of −10 to −13 kJ/mol, is ideal for low-temperature storage applications, it is too weak for storage at ambient temperature. Frameworks with more strongly adsorbing sites are therefore required to achieve the higher H$_2$ capacities at ambient temperature that would allow for a commercially viable H$_2$ storage system.$^5$

The affinity of exposed metal cations for H$_2$ can be increased by increasing the charge density at the M center.$^{3,5,6}$ Synthesizing metal–organic frameworks with exposed trivalent or tetravalent cations thus represents a promising path to reaching the −15 to −20 kJ/mol binding enthalpies that are optimal for ambient-temperature H$_2$ storage.$^{6,7}$ While many families of metal–organic frameworks have been synthesized with exposed divalent metal cations,$^{3,6,8}$ there are comparatively few examples of frameworks with exposed trivalent metal cations.$^{3k,8,9}$ In several analogues of the M$_2$OX(bdc)$_3$ (M-MIL-101; bdc$^{2-}$ = 1,4-benzenedicarboxylate; X = F, Cl, OH; M = Cr,$^{10}$ Fe,$^{11}$ V,$^{12}$ Al,$^{13}$) and M$_3$OX(btc)$_2$ (M-MIL-100; btc$^{3-}$ = 1,3,5-benzenetricarboxylate; M = Cr,$^{14}$ Fe,$^{15}$ V,$^{12b}$ Al,$^{16}$ Sc,$^{17}$) series of frameworks, however, metal-bound solvent molecules can be partially, or in some cases, fully removed by heating under vacuum to generate five-coordinate M$^{3+}$ cations.$^{5,9}$ The M-MIL-101 and M-MIL-100 compounds are composed of triangular M$_3$O(COO)$_6$ clusters, wherein each metal is octahedrally coordinated and bound to bridging carboxylates at the equatorial positions, a μ$_3$O$^{2-}$ anion at one axial position, and either a solvent molecule or a charge-balancing anion at the other axial position. While exposed Cr$^{3+}$ sites in Cr-MIL-100 have led to CO$_2$ binding enthalpies exceeding −60 kJ/mol,$^{18}$ none of these frameworks have displayed the H$_2$ adsorption properties that might be expected for a material with a high density of exposed M$^{3+}$ cations.$^{19}$ Nonetheless, these frameworks represent a promising platform for studying H$_2$ adsorption on exposed M$^{3+}$ centers. Indeed, there is preliminary evidence for strong M$^{3+}$–H$_2$ interactions in Sc-MIL-100 based on IR spectroscopy, but this has not yet been confirmed by adsorption measurements.$^{20}$

Although there is significant interest in developing new titanium-based metal–organic frameworks, titanium analogues of MIL-100 and MIL-101 have not yet been realized. In
addition to the potential for characterizing the H₃ adsorption properties of five-coordinate TiIII centers, new titanium-based porous materials are of general interest because titanium has low toxicity, high natural abundance, and potentially useful redox and photocatalytic properties. Even though over 20000 metal–organic frameworks have been reported, there are currently just five examples of titanium-based frameworks that demonstrate permanent porosity: Ti₇O₄(OH)₂(bdc)₆ (MIL-125), Ti₃O₃(OH)(NH₂-bdc)₆ (MIL-125-NH₂), and TiO₂(OH)(tetrakis(4-carboxyphenyl)porphyrin) (PCN-22), which contain exclusively TiIV centers, and Ti₃O₂(OH)(bdc)₆ (Ti₃O₂-Uio-66) and Zn₆Ti₉O₉(bdc)₃ (TiIII-MOF-S), which are synthesized by partial postsynthetic metal exchange of ZrIV and ZnII, respectively, in the parent frameworks. Recognizing that TiIII-MOF-S contains just 2% titanium and 98% zinc, there are, to our best of knowledge, no examples of porous frameworks based solely upon titanium(III). Herein, we report the synthesis and characterization of the first such compound, Ti₅O(OEt)(bdc)₃(solvent)₂ (1; solvent = DMF, THF), representing a titanium(III) analogue of MIL-101.

**EXPERIMENTAL SECTION**

**General Information.** All reactions and subsequent manipulations were performed under anerobic and anhydrous conditions in an N₂-atmosphere glovebox or on an N₂-atmosphere Schlenk line. N,N-Dimethylformamide (DMF) and tetrahydrofuran (THF) were dried by passage over activated molecular sieves using a JC Meyer solvent system. Anhydrous ethanol (EtOH; 99.5%) was purchased from Sigma-Aldrich and used as received. All other reagents were obtained from commercial vendors and used without further purification. Ultra-high-purity grade (99.999% purity) He, N₂, O₂, and H₂ and research-grade CO (99.999% purity) and CO₂ (99.998% purity) were used for all adsorption measurements. IR spectra were obtained on a PerkinElmer Spectrum 100 Optica Fourier transform infrared spectrometer furnished with an attenuated total reflectance accessory. The instrument was placed inside an N₂-filled glovebag for air-sensitive samples. Elemental analysis for Cl was performed at Galbraith Laboratories.

**Synthesis of Ti₅O(OEt)(bdc)₃(DMF)₂ (1, Ti-MIL-101).** In a glovebox under an N₂ atmosphere, a 500 mL Schlenk flask was charged with 1,4-benzenedicarboxylic acid (H₂bdc; 0.675 g, 4.06 mmol), TiCl₃ (0.769 g, 4.99 mmol), and a small stir bar and then sealed with a rubber septum. The flask was transferred to a Schlenk line, and 300 mL of anhydrous DMF and 30 mL of anhydrous EtOH were added via cannula transfer. The solution was heated at 120 °C for 24 h, and then THF was decanted and replaced with fresh THF. This THF exchange was repeated two additional times. THF was then evaporated under reduced pressure, and the dark-purple solid was activated by heating at 150 °C for 24 h. The activated material was then placed inside a Kaption tube that was sealed on both ends with epoxy.

**NMR Digestion Experiments.** To determine the identity and amount of bound solvent and charge-balancing anions, NMR digestion experiments were performed for the DMF-solvated material after activation at 75 and 150 °C and for the THF-exchanged material after activation at 150 °C. Note that two independently synthesized batches of 1 were used for these experiments. For each digestion, 5–10 mg of a metal–organic framework was combined with 1 mL of d₄ methanol and 10 mL of 35 wt % DCl in D₂O in a 4 mL glass vial. The capillaries were attached to a Schlenk line, and the solution was allowed to slowly oxidize in air overnight. The NMR digestion results are summarized in Tables S1–S3 and are discussed in detail in the Supporting Information.

**Adsorption Measurements.** Gas adsorption isotherms for pressures in the range 0–1.1 bar were measured using a Micromeritics ASAP 2020 instrument. For standard measurements, activated samples were transferred under an N₂ atmosphere to a preweighed glass analysis tube, which was capped with a Transel. The sample was evacuated on the ASAP 2020 until the outgas rate was less than 3 mbar/min. The evacuated analysis tube containing a degassed sample was then carefully transferred to an electronic balance and weighed to determine the mass of the sample (typically 50–150 mg). The tube was fitted with an isothermal jacket and transferred back to the analysis port of the gas adsorption instrument. The outgas rate was again confirmed to be less than 3 mbar/min.

Langmuir surface areas and pore volumes were determined by measuring N₂ adsorption isotherms in a 77 K liquid-N₂ bath and calculated using the Micromeritics software, assuming a value of 162 Å² for the molecular cross-sectional area of N₂. A pore-size distribution was calculated using the density functional theory method with a QSDFT adsorption branch model of N₂ at 77 K adsorbed in carbon slit/cylindrical pores, as implemented in the Quadrachrome VersaWin software (Figures S27 and S28). Measurements at ~78 °C were performed using a dry ice/isopropyl alcohol bath, while measurements at 25 °C were performed using a recirculating dewar connected to an isothermal bath.

**Adsorption Isotherm Fitting.** The 77 and 87 K H₂ adsorption isotherms of 1 were independently fit with a dual-site Langmuir–Freundlich model (eq 1), where n is the amount adsorbed in mmol/g, P is the pressure in bar, nₛₑₘ is the saturation capacity in mmol/g, νᵢ is the Freundlich parameter, and bᵢ is the Langmuir parameter in bar⁻¹. For the two sites 1 and 2, the fitted parameters for each adsorption isotherm can be found in Table S4.

\[ n = \frac{nₛₑₘ νᵢ P^{νᵢ}}{1 + bᵢ P^{νᵢ}} + \frac{nₛₑₘ νᵢ P^{νᵢ}}{1 + bᵢ P^{νᵢ}} \]  

(1)\]

The Clausius–Clapeyron equation (eq 2) was used to calculate the isosteric heats of adsorption, hₑₘ, for each compound using the dual-site Langmuir–Freundlich fits at 77 and 87 K.

\[ \ln P = \frac{hₑₘ}{R T} \left( \frac{1}{T} \right) + C \]  

(2)\]

Here, P is the pressure, hₑₘ is the differential enthalpy of adsorption, n is the amount adsorbed, T is the temperature, R is the universal gas constant, and C is a constant. The isosteric heats of adsorption were obtained from the slope of plots of (ln P)ₓ versus 1/T.

**Powder X-ray Diffraction.** Microcrystalline powder samples of 1 (~5 mg) were loaded into 1.0 mm boron-rich glass capillaries inside a glovebox under an N₂ atmosphere. The capillaries were attached to a gas cell, which was connected to the analysis port of a Micromeritics ASAP 2020 gas adsorption instrument. The capillaries were fully evacuated at room temperature for 15 min and then flame-sealed and placed inside a Kaption tube that was sealed on both ends with epoxy.

High-resolution synchrotron powder X-ray diffraction data were subsequently collected at Beamline 11-BM at the Advanced Photon Source (APS) at Argonne National Laboratory. Diffraction patterns were collected at 100 K with a wavelength of 0.4137 Å. Discrete detectors covering an angular range from ~6 to 16° in 2θ were scanned over a 34° 2θ range, with data points collected every 0.001° in 2θ and a scan speed of 0.01°/s. Note that, because of the large number of collected data points, all diffraction patterns were rebinned to a step size of 0.005° in 2θ.
A standard peak search, followed by indexing via the single value decomposition approach, as implemented in TOPAS-Academic, allowed the determination of approximate unit cell dimensions. Precise unit cell dimensions were determined by performing a structureless Le Bail refinement in TOPAS-Academic (Figures S13 and S14).28

**UV–Vis–Near-IR (NIR) Diffuse-Reflectance Spectra.** UV–vis–NIR diffuse-reflectance spectra were collected using a CARY 5000 spectrophotometer interfaced with Varian Win UV software. The samples were held in a Praying Mantis air-free diffuse-reflectance cell. Poly(vinylidene fluoride) (PVDF) powder was used as a nonabsorbing matrix. The Kubelka–Munk conversion \( F(R) \) of the raw diffuse-reflectance spectrum (\( R \) vs wavenumber) was obtained by applying the formula \( F(R) = (1 - R)^2/2R \). This transform creates a linear relationship for the spectral intensity relative to the sample concentration and assumes that the sample is infinitely diluted in the nonabsorbing matrix, that the sample layer is infinitely thick, and that the sample has a constant scattering coefficient. Note that data above 12500 cm\(^{-1}\) were offset by a small, constant amount on the \( y \) axis to remove an artifact of the spectrometer after the detector and grating were changed for the higher-energy region of the scans.

### Magnetic Measurements

Samples were prepared by adding crystalline powder of \( 1 \) (16.7 mg) to a 5-mm-i.d. quartz tube containing a raised quartz platform. Solid eicosane was added to cover the sample to prevent crystalline toquing and provide good thermal contact between the sample and cryostat. The tubes were fitted with Teflon-sealable adapters, evacuated on a Schlenk line, and flame-sealed under static vacuum. Following flame sealing, the solid eicosane was melted in a water bath held at 40 °C. Magnetic susceptibility measurements were performed using a Quantum Design MPMS2 SQUID magnetometer. Direct-current (dc) magnetic susceptibility measurements were collected from 2 to 300 K under an applied field of 0.1 T. Diamagnetic corrections were applied to the data using Pascal's constants to give \( \chi_M = -0.0003324 \text{ emu/mol (1)} \) and \( \chi_M = -0.00024306 \text{ emu/mol (eicosane)} \). Data in the temperature range of 60–300 K were simulated using the software program PHI.29

**Electron Paramagnetic Resonance (EPR) Measurements.** EPR spectra were obtained at room temperature with a Varian E-12 spectrometer equipped with liquid-He cryostat, an EIP-547 microwave frequency counter, and a Varian E-500 gaussmeter, which was calibrated using 2,2-diphenyl-1-picrylhydrazyl (2,2-DPH) (g = 2.0036). The spectrum was fit using a version of the code ABGY modified to fit spectra using the downhill simplex method.31 The code was modified to use the Pilbrow line shape.32 The sample was sealed inside a 4-mm-o.d. quartz tube.

The areas of the EPR signals were determined by double integration (Figure S24). The first derivative spectrum was integrated using Simpson’s rule to give the absorption correction.32 The baseline was corrected empirically using a second-order polynomial, and the absorption spectrum was integrated by using Simpson’s rule again.

### RESULTS AND DISCUSSION

**Synthesis.** Heating TiCl\(_3\) and H\(_2\)bdic in a 10:1 mixture of anhydrous DMF and EtOH at 120 °C for 18 h afforded the solvated form of compound 1 (or Ti-MIL-101) as a dark-purple powder. The powder X-ray diffraction pattern of 1 is nearly identical with the simulated diffraction pattern of Cr-MIL-101,10 demonstrating that the two materials are isosstructural (Figure 1). A structureless Le Bail refinement further confirmed that 1 has a face-centered-cubic unit cell with \( a = 89.78(2) \) Å and \( V = 723600(500) \) Å\(^3\), which is slightly larger than that previously determined for Cr-MIL-101 \( [a = 88.869(1) \] Å; \( V = 701860.3(1) \) Å\(^3\)]. Moreover, elemental analysis and NMR digestion experiments confirmed that the molecular formula of 1 is indeed \( \text{Ti}_3\text{O}({\text{OEt}})(bdc)_2(DMF)_2 \), indicating that the framework contains six-coordinate Ti\(^{III}\) centers wherein \( 1/3 \) are ligated by a charge-balancing ethoxide anion and \( 2/3 \) are ligated by a DMF solvent molecule (see the detailed discussion in the Supporting Information). Despite the extensive literature on carboxylate-bridged titanium oxo clusters,33 it is interesting to note that there are surprisingly no reports of a titanium analogue of the triangular \( \text{M}_3\text{O}([\text{COO}])_3 \) clusters of the type found in basic iron acetate. Efforts to synthesize a titanium(III) analogue of MIL-100 using a similar procedure with \( \text{H}_2\text{bdic} \) instead of \( \text{H}_2\text{bdic} \) were unsuccessful, resulting only in amorphous powders.

**Gas Adsorption.** A 77 K \( \text{N}_2 \) adsorption isotherm was measured for 1 after heating to 150 °C under vacuum, and the resulting isotherm shape is characteristic of a material with a combination of micro- and mesopores (Figure S1), as expected for the MIL-101 structure type. On the basis of the saturation uptake, the compound has a Langmuir surface area of 3890 m\(^2\)/g and a total pore volume of 1.34 cm\(^3\)/g, which is consistent with, but slightly lower than, other MIL-101 analogues. In an effort to improve the surface area of 1, the as-synthesized framework was washed repeatedly with THF at 120 °C in order to exchange all DMF molecules for the more volatile THF and to fully remove any unreacted \( \text{H}_2\text{bdic} \) ligand from the framework pores. As expected, the Langmuir and BET surface areas of 1 were increased substantially after THF washing to 4440 and 2970 m\(^2\)/g, respectively, with a total pore volume of 1.50 cm\(^3\)/g (Figure 2a). To the best of our knowledge, these are by far the highest surface areas yet reported for any titanium-based porous material.

To probe for exposed Ti\(^{III}\) cations in activated 1, H\(_2\) adsorption isotherms were measured at 77 and 87 K (Figure 2b). Many metal–organic frameworks with square-pyramidal divalent metal cations exhibit steep 77 K \( \text{H}_2 \) adsorption isotherms at low pressures, and a similar shaped isotherm might reasonably be expected for a material with a high density of exposed Ti\(^{III}\) cations. In 1, however, the isotherms are relatively shallow with a low-coverage \( \text{H}_2 \) binding enthalpy of just ~6.4 kJ/mol, which is characteristic of weak physisorption. In addition, the \( \text{CO}_2 \) and \( \text{CO} \) adsorption isotherms at 25 °C are similar to those of other high-surface-area materials that have relatively nonpolar pore surfaces (Figures S8–S10), further indicating that there are no accessible exposed Ti\(^{III}\) cations in 1. Speculating that THF might still be bound to most of the Ti\(^{III}\) centers, we attempted to activate the framework at higher temperatures. While activation at 200 °C did not affect

![Figure 1. Powder X-ray diffraction pattern for 1 (purple) compared with a simulated diffraction pattern of Cr-MIL101 (\( \lambda = 0.41397 \) Å).](10.1021/acs.inorgchem.5b02056)
the surface area or H2 adsorption properties of I, activation at 225 °C led to a decrease in both the surface area and H2 uptake (Figure S6). These initial adsorption results suggest either that all TiIII centers in the framework remain six-coordinate upon activation or that any five-coordinate centers generated are for some reason unable to interact with and polarize adsorbing gas molecules.

Because O2 can undergo charge-transfer reactions with titanium(III) complexes to generate titanium(IV) superoxo and peroxo species, we predicted that any coordinatively unsaturated TiIII centers would react strongly with O2, even if these sites were unable to strongly polarize other small gas molecules. In sharp contrast to the other gases investigated, the O2 isotherm of I at 25 °C is very steep at low pressures, reaching a capacity of 0.85 mmol/g (2.6 wt %) at just 0.9 mbar, and is characteristic of a chemisorption process (Figure 3a). The capacity at 0.9 mbar corresponds to an average of 0.65 O2 molecules bound to each Ti3O cluster; however, we noticed that the Langmuir surface area of I had decreased to just 2640 m2/g after O2 adsorption. Because the reaction between TiIII and O2 is expected to be exothermic, we suspected that some framework decomposition could have occurred because of intense local heating in the sample during the isotherm measurement. To confirm this, we measured low-temperature O2 adsorption isotherms (Figure 3b). At −78 °C, I also exhibits a very steep O2 isotherm, but now, the steep portion of the isotherm reaches a loading of 1.1 mmol/g (3.4 wt %), which is just below that expected for the adsorption of one O2 per Ti3O cluster (1.3 mmol/g). Moreover, the Langmuir surface area was only slightly reduced to 3880 m2/g after the isotherm measurement. To evaluate the reversibility of O2 adsorption in I, a second O2 isotherm was measured at −78 °C after evacuation at room temperature (Figure 3b). The complete disappearance of the steep region of the adsorption isotherm demonstrates that the initial O2 binding is irreversible under these conditions. Moreover, we were unable to find any conditions suitable for regenerating the bare framework, even with heating to as high as 150 °C under dynamic vacuum.

**Powder X-ray Diffraction.** High-resolution powder X-ray diffraction patterns collected before and after O2 dosing demonstrate that I maintains the same structure type after O2 adsorption but with a significant volume contraction of 14.1(1)% as the unit cell length decreases from 89.78(2) to 85.35(2) Å (Figure S14). This large unit cell contraction, along with the increased molecular weight of the framework, likely accounts for most of the observed decrease in the surface area after O2 binding. Still, the large volume change and stoichiometry of one O2 reacting for every three TiIII centers...
are somewhat surprising, and the exact composition of the oxidized framework is not obvious. While it is possible that O$_2$ reacts with the framework through an outer-sphere electron transfer or by displacement of a metal-bound solvent molecule, it seems more likely that at least 1/3 of the Ti$^{III}$ centers in the activated framework must be five-coordinate in order for the O$_2$ adsorption isotherm to be so steep at low pressures. If this were the case, each Ti$_3$O cluster could bind one O$_2$ to generate a six-coordinate titanium(IV) superoxide with the other two metals remaining as Ti$^{III}$, or an additional intracluster electron transfer could potentially occur to generate a six-coordinate titanium(IV) peroxide with two Ti$^{IV}$ centers and one Ti$^{III}$ center per cluster (Figure 4). Owing to the large size of the cubic unit cell and the expected disorder in the location of Ti$^{III}$/IV species, it was not possible to solve the structure of 1 either before or after O$_2$ adsorption from the powder diffraction data, and attempts to synthesize single crystals of the framework were unsuccessful. As a result, we turned to spectroscopic techniques in order to determine the mechanism for O$_2$ adsorption in 1.

**EPR Spectroscopy.** While 1 is EPR-silent at room temperature, two clear signals are observed in the EPR spectrum at low and high fields upon O$_2$ dosing (Figure 5). Both segments of the spectrum were simulated separately to determine the relevant $g$ values for each feature, which are given in Table 1. On the basis of the similarity of the $g$ values to superoxide adsorbed on TiO$_2$ and other titanium oxo clusters,$^{35,36}$ the low-field signal is assigned to a superoxide radical anion coordinated to a Ti$^{IV}$ center. Likewise, the $g$ values for the broad signal at higher field are consistent with those reported for octahedral Ti$^{III}$ centers in molecular titanium oxo clusters,$^{35c}$ and the high-field signal is thus assigned to Ti$^{III}$.

Because both superoxide and titanium(III) are $S = 1/2$ species, the areas of the two EPR signals should be directly proportional to the relative populations of these two spin states. The observed signal areas were used to calculate the fractional populations of Ti$^{III}$/IV superoxide and Ti$^{III}$ peroxide, respectively.

**Table 1. EPR g Values for Oxidized 1 Compared to Literature Values**

<table>
<thead>
<tr>
<th></th>
<th>low-field signal (1)</th>
<th>superoxide on rutile$^{35a}$</th>
<th>high-field signal (1)</th>
<th>Ti$^{III}$ in a Ti$_3$O$_4$ cluster</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g_1$</td>
<td>2.021</td>
<td>2.0235</td>
<td>1.952</td>
<td>1.968</td>
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<td>2.0088</td>
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<td>1.943</td>
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<td>$g_3$</td>
<td>2.002</td>
<td>2.0026</td>
<td>1.923</td>
<td>1.923</td>
</tr>
</tbody>
</table>

Figure 4. Illustration of the proposed composition of the Ti$_3$O clusters in 1 after (a) heating at 150 °C vacuum, (b) reacting with O$_2$ to form titanium(IV) superoxide, and (c) reacting with O$_2$ to form titanium(IV) peroxide. Note that the cluster likely distorts upon desolvation of a metal site to accommodate a trigonal-bipyramidal, rather than square-pyramidal, coordination geometry at the five-coordinate Ti$^{III}$ center.

Figure 5. EPR spectrum for oxidized 1. The experimental spectrum is shown in black, and simulations of the low- and high-field signals are shown in blue and red, respectively.
proportional to their relative concentrations in the oxidized framework. If there are not any titanium(IV) peroxy species present, then each TiIII cluster would contain two TiIII centers and one titanium(IV) superoxide (Figure 4b). As discussed below, the TiIII centers should be strongly antiferromagnetically coupled and would therefore not be expected to display an EPR signal. Because the activated framework with all TiIII centers is also EPR-silent (Figure 4a), the observed TiIII signal can be assigned entirely to clusters containing titanium(IV) peroxy that have only a single TiIII center (Figure 4c).

By double-integrating the EPR spectrum (Figure S24), we estimate that there is roughly 12 times the amount of EPR-active titanium(III) as superoxide in the sample. Although integration performed in this manner is not particularly accurate, we can calculate that approximately 8% of the oxidized TiIII clusters should have a bound superoxide, while 92% should have a bound peroxy. We note, however, that the sample used for the EPR experiment was stored at ambient temperature for several days prior to measurement of the spectrum. It is possible that the second electron transfer to convert the superoxide to a peroxy is much slower than the initial electron transfer, and as a result, the exact distribution of superoxo and peroxy species may depend on both the storage time and temperature. Indeed, the color of the oxidized framework slowly changes from light purple to light pink over several weeks, even when stored under an N2 atmosphere. Regardless, the presence of titanium(IV) superoxo and/or peroxy species should also be observable by IR spectroscopy.

**IR Spectroscopy.** IR spectra were collected for 1 in a solvated state, after activation at 150 °C, after dosing with 16O2 at −78 °C, and after dosing with 18O2 at −78 °C (Figures S15–S21). Typically, the O−O stretching frequencies of superoxo and peroxy complexes are observed between 1200 and 800 cm−1.37,38 In the IR spectra of both solvated and activated 1, several overlapping framework vibrational modes, which are likely associated with the bridging carboxylates and charge-balancing ethoxide anions,39 occur in this region and make the identification of new bands after O2 adsorption difficult. Nonetheless, a new band is visible in the 18O2-dosed sample at 1042 cm−1 and can be tentatively assigned to the ν(18O−18O) stretch of a superoxide species (Figure S14). Using a simple harmonic oscillator model, the predicted ν(18O−18O) stretch is 1105 cm−1, which is at the same energy as those of several strong framework vibrations. In addition, a new weak band is observed at 907 cm−1 in the 16O2-dosed framework and can be assigned to the O−O stretch of a titanium(IV) peroxy (Figure S16).34b,37b,40 Consistent with this assignment, a new shoulder is observed in the 18O2-dosed spectrum at the expected frequency of 855 cm−1.

In all IR spectra, a strong band is also present near 740 cm−1 and can be assigned to the asymmetric TiO vibrational mode. As expected for stronger Ti−O bonds, this band occurs at higher frequencies than is observed in the molecular chromium(III) (660 cm−1) and iron(III) (600 cm−1) acetate clusters of the type M(O(CO)2)L3.41 After O2 binding, νasym(Ti2O) is blue-shifted from 740 to 747 cm−1 (Figure S17), which is consistent with stronger binding to the μ2−O2−anion after a portion of the TiIII portion of the TiIII−O2−anion is oxidized to TiIV.

**UV−Vis−NIR Spectroscopy.** To gain additional insight into exactly how O2 reacts with the Ti sites of 1, electronic absorption spectra were measured for all compounds (Figure 6). The solvated framework is dark-purple and exhibits three overlapping peaks in the visible region with maxima at approximately 20370, 18080, and 16260 cm−1. While octahedral titanium(III) complexes should have a single d→d transition (τ2g ← e′), two transitions are often observed when distortion of the octahedral ligand field splits the e′ levels.42 Because the octahedral TiIII centers in solvated 1 likely experience a tetragonal ligand field and exist in two different chemical environments, depending on whether there is a bound solvent molecule or anion in the axial position, the three observed peaks are likely the result of four overlapping d→d transitions. The relevant transitions appear to be separated by 1500−2000 cm−1, which is typical for the e′ splitting of titanium(III) complexes in a distorted octahedral coordination geometry.42

After activation, the framework has a gray-blue color, and the position of the highest-energy band is relatively unchanged, while the two lower-energy bands are shifted to 16980 and 15850 cm−1. More significantly, a new intense feature, which is diagnostic of five-coordinate TiIV,43 is observed in the NIR region of the spectrum at 6390 cm−1, along with a small shoulder at 8830 cm−1. While it is not possible to definitively assign the geometry of the five-coordinate TiIV centers based on this spectrum, trigonal-bipyramidal titanium(III) complexes are known to exhibit two electronic transitions at 7500−5000 cm−1 (e′′ → e′) and 16400−14000 cm−1 (e′ → a′1), which is consistent with the positions of the new bands observed here.44 There are also several examples of trinuclear titanium clusters with μ1−O bridges that contain one five-coordinate and two six-coordinate M centers, and in all cases, the five-coordinate sites adopt a slightly distorted trigonal-bipyramidal coordination geometry.45 The new electronic transitions in activated 1 can thus be assigned to a five-coordinate TiIV center, potentially in a distorted trigonal-bipyramidal geometry. Such a coordination geometry would indeed explain the lack of strong adsorption for nonredox-active gases in 1 because the TiIV charge would be effectively shielded after desorption.

As discussed in detail in the Supporting Information, NMR digestion experiments also support a molecular formula of Ti3O(OEt)(bdc)(solv) with one metal-bound solvent molecule per Ti3O cluster after activation at 150 °C. We note that a similar result was observed for Al-MIL-100 by solid-state NMR spectroscopy, where it was hypothesized that water was
removed from $\frac{1}{3}$ of the Al$^{3+}$ cations in the framework to generate five-coordinate Al$^{3+}$ cations.9

After O$_2$ adsorption, the framework appears light-purple in color. The NIR peak associated with five-coordinate Ti$^{III}$ disappears, as expected, and there is just one broad peak remaining in the visible region of the spectrum centered at 21690 cm$^{-1}$. This band is associated with d–d transitions from the remaining six-coordinate Ti$^{III}$ centers in the framework. The lower relative intensity of this peak could be attributed to the fact that less than half of the Ti centers are in a 3+ oxidation state after O$_2$ adsorption. It is also possible that the Ti$^{III}$ sites adopt a less distorted octahedral geometry, which might explain the absence of any obvious doublet peaks in this region. Additionally, there is significant absorption in the near-UV region after oxidation, which is likely associated with ligand or Ti$^{III}$ to Ti$^{IV}$ charge transfer.

Magnetic Susceptibility. The high percentage of titanium(IV) peroxo species present in oxidized 1 implies that the barrier to intercalation charge transfer through the oxo bridge in each Ti$_3$O unit is relatively low. To further probe the electronic structure of the material, dc magnetic susceptibility measurements were performed for activated 1 under an applied magnetic field of 0.1 T (Figure 7). The $\chi_M T$ value of 1 at 300 K and 0.1 T is 0.919 emu·K/mol, well below the value of 1.125 emu·K/mol expected for three noninteracting $S = \frac{1}{2}$ spins with $g = 2$. This low value suggests strong intracluster antiferromagnetic coupling, which is consistent with the lack of an EPR signal for 1 at room temperature. For comparison, the magnetism of dinuclear oxo-bridged Ti$^{III}$ molecules has been studied extensively, with special emphasis placed on the type and magnitude of magnetic coupling in relation to the Ti–O–Ti angle.46 When this angle is close to 120°, strong antiferromagnetic coupling is observed, supporting the assignment of strong antiferromagnetic coupling within the Ti$_3$O clusters in 1, which is expected to exhibit Ti–O–Ti angles near 120°.6

As expected for a Ti$_3$O cluster with one five-coordinate and two six-coordinate Ti$^{III}$ centers, efforts to simulate the data using an equilateral triangle model with a single coupling parameter were unsuccessful. The magnitude of the intracluster magnetic coupling was instead estimated by simulating the magnetic susceptibility data of 1 using the Hamiltonian $\hat{H} = -2J(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_1 \cdot \hat{S}_3) - 2\gamma(\hat{S}_1 \cdot \hat{S}_2)$, where $J$ represents the coupling of the five-coordinate Ti$^{III}$ to each of the six-coordinate Ti$^{III}$ sites and $\gamma$ represents the coupling between the two six-coordinate Ti$^{III}$ sites. A manual correction for temperature-independent paramagnetism was also included, with $\chi_{TIP} = 0.001$ emu/mol. The value of $\chi_{TIP}$ was determined from the decrease in the magnetic susceptibility of 1 under increased applied magnetic fields (Figure S25). Using the parameters $J = -68$ cm$^{-1}$, $\gamma = -128$ cm$^{-1}$, $g_1 = 1.73$, and $g_2 = g_3 = 2.00$, this model is in good agreement with the magnetic data above 60 K but less so at lower temperatures (Figure S26).

The value of $\chi_M T$ observed for 1 exhibits a discontinuity at 55 K and 0.352 emu·K/mol, which is close to the 0.375 emu·K/mol expected for a spin of $S = \frac{1}{2}$. This is consistent with antiferromagnetic coupling between two of the three Ti$^{III}$ centers to give an $S = \frac{1}{2}$ ground state. As the temperature decreases further, $\chi_M T$ trends toward zero, presumably because of antiferromagnetic interactions between neighboring Ti$_3$O clusters within the framework. These low-temperature features could be more successfully modeled using a simulation that included an intercluster coupling constant $\gamma'$. In this case, the magnetic data was best described by the parameters $J = -52$ cm$^{-1}$, $\gamma' = -137$ cm$^{-1}$, $J' = -3.9$ cm$^{-1}$, $g_1 = 1.85$, and $g_2 = g_3 = 2.00$ (Figure 7).

Importantly, the parameters in the $\chi_M T$ simulations are consistent with the proposed structural model of activated 1. For instance, a low $g$ value for the five-coordinate Ti$^{III}$ centers is consistent with the distortion expected to occur during generation of these sites. Additionally, stronger antiferromagnetic exchange between the two six-coordinate sites compared to that between the five- and six-coordinate sites is expected because the six-coordinate sites have more similar coordination geometries, which should lead to better orbital overlap and stronger magnetic coupling.

CONCLUSIONS AND OUTLOOK

Through a combination of gas adsorption, X-ray diffraction, spectroscopy, and magnetic susceptibility measurements, the new metal–organic framework Ti-MIL-101 was shown to feature five-coordinate Ti$^{III}$ centers that react with O$_2$ to form titanium(IV) superoxo and peroxo species. This compound is the highest-surface-area titanium-based porous material to date and represents the first all-titanium(III) metal–organic framework with permanent porosity. Perhaps more importantly, we have shown that, although there are coordinatively unsaturated Ti$^{III}$ centers in the framework, these sites do not function as exposed metal cations. In order to realize trivalent and tetravalent exposed metal cations capable of polarizing H$_2$ and other gas molecules, more rigid frameworks are needed to prevent the coordination geometry of the metal from distorting to shield exposed charge after desolvation. While this has been accomplished for divalent metals, it represents an ongoing challenge for the design and synthesis of higher-valent metal–organic frameworks.

Figure 7. Variable-temperature magnetic susceptibility data collected under $H_{ext} = 0.1$ T for 1 activated at 150 °C (circles). The solid line represents a simulation of the data using the Hamiltonian and parameters described in the text.
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.5b02046.

Additional experimental details, adsorption data, iso-therm fit parameters, powder X-ray diffraction data, IR spectra, UV−vis−NIR spectra, EPR spectrum integration results, and magnetic susceptibility data (PDF)

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ASSOCIATED CONTENT

Supporting Information

REFERENCES

AUTHOR INFORMATION

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(21) Furukawa, H.; Cordova, K. E.; O’Keeffe, M.; Yagi, O. M. *Science* 2013, 341, 1230444.


