

were incubated at various concentrations (0.1–2.5 µg per well) on polystyrene microtiter plates in phosphate-buffered saline, and VVA-HRP was used to detect the direct binding properties. As shown in Figure 4, hexadecavalent glyco-

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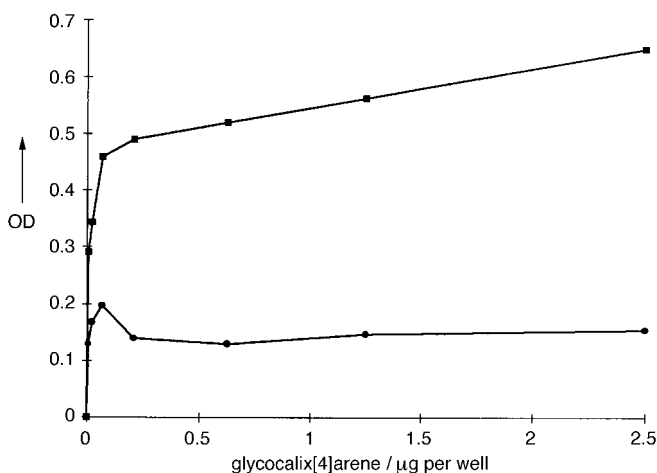


Figure 4. Enzyme-linked lectin assay (VVA-HRP) showing the hydrophobic adsorption of glyco-calix[4]arenes onto the surface of a polystyrene microtiter plate. ■: **14** (16-mer), ●: **8** (4-mer). OD = optical density measured at 410 nm.

calix[4]arene **14** was hydrophobically adsorbed onto the microtiter plate surface with as little as 0.2 µg of material

per well. Moreover, the interaction could be again inhibited by adding excess allyl  $\alpha$ -D-GalNAc monomer (data not shown).

Amphiphilic  $\alpha$ -GalNAc-containing *p*-tert-butylcalix[4]arenes with up to 16 carbohydrate units were efficiently synthesized by a novel double N-alkylation strategy. In these novel biomaterials the carbohydrate residues are well exposed to aqueous environments as shown by their lectin-binding properties. Moreover, the materials can be directly adsorbed onto the lipophilic surface of polystyrene microtiter plates and thus should be useful in bioanalytical devices.

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### Organically Templated Mixed-Valent Ti<sup>III</sup>/Ti<sup>IV</sup> Phosphate with an Octahedral–Tetrahedral Open Framework\*\*

Sambandan Ekambaram and Slavi C. Sevov\*

The zeolitic aluminum silicates and the more recently discovered microporous aluminum phosphates have attracted tremendous interest due to their application as catalysts, ion-exchangers, and molecular sieves in many technologically important processes. Nevertheless, due to the presence of main group elements only, these materials have no potential for redox reactions and redox catalysis. It is highly desirable, therefore, to build microporous compounds containing d-block metals as an integral part of the framework and in close proximity to the voids. Titanium has been of particular interest as a potential substitute for silicon owing to the available oxidation state of four and appropriate size. Substitutions of the tetrahedral silicon have been achieved at the doping level,<sup>[1]</sup> and despite the small amounts of titanium, the resulting materials have shown highly improved

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catalytic properties.<sup>[2]</sup> More recently, microporous titanium(IV) silicates such as ETS-4, ETS-10, and others with substantial fractions of titanium were discovered,<sup>[3]</sup> and had shown good catalytic activity as well.<sup>[4]</sup> These possess octahedral–tetrahedral frameworks comparable to those of some transition metal phosphates.<sup>[5]</sup> Titanium-based microporous compounds with trivalent or mixed-valent titanium would be of even greater interest. Such reduced metal compounds with open frameworks are known for molybdenum, vanadium, and iron, for example, but none is known for titanium. Here we report the synthesis and structure of the first mixed-valent titanium(III)/titanium(IV) phosphate with open-framework structure, named TPO-1. The new compound,  $\text{Ti}^{\text{III}}\text{Ti}^{\text{IV}}(\text{PO}_4)(\text{HPO}_4)_2(\text{H}_2\text{O})_2 \cdot 0.5\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ , is made hydrothermally by using a quite unconventional source for the titanium, the element itself.

The compound was initially obtained in an attempt to hydrothermally synthesize organically templated titanium borophosphate in an approach analogous to that employed for other transition metal borophosphates,<sup>[6]</sup> and therefore the starting materials included boric acid. Later, the reaction conditions were optimized for high yield, and consisted of only titanium metal, phosphoric acid, and 1,3-diaminopropane. Interestingly, successful synthesis can be carried out only when elemental titanium is used. Our attempts to use  $\text{TiF}_3$  or  $\text{Ti}_2\text{O}_3$  as the source for titanium failed. TPO-1 crystallizes as square prisms and cubes with deep blue-purple color; the latter is the first indication of the presence of  $\text{Ti}^{\text{III}}$  centers.

The structure of TPO-1 was determined by single-crystal X-ray diffraction. It is built of octahedrally coordinated titanium and tetrahedrally coordinated phosphorus centers (Figures 1 and 2). Although the compound is phosphorus-rich

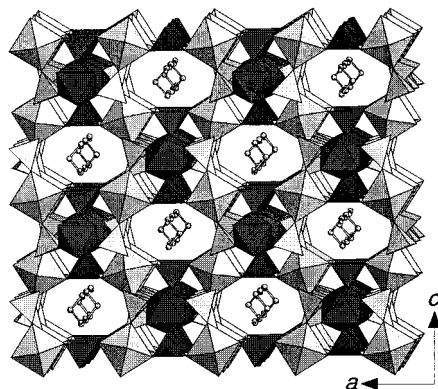


Figure 1. Polyhedral representation of the structure of TPO-1. The  $\text{Ti}^{\text{IV}}\text{O}_6$  and  $\text{PO}_4$  polyhedra are shown as darker polyhedra, and  $\text{Ti}^{\text{III}}\text{O}_4(\text{H}_2\text{O})_2$  and  $\text{PO}_3(\text{OH})$  as lighter polyhedra. The 1,3-diaminopropane molecules in the channels are shown as a ball-and-stick representation.

( $\text{Ti}:\text{P}=2:3$ ) there is no P–O–P bonding. Also, unlike the titanosilicates that contain titanium in an octahedral environment,<sup>[3]</sup> there is no Ti–O–Ti bonding either. The two types of titanium,  $\text{Ti}^{\text{III}}$  and  $\text{Ti}^{\text{IV}}$ , are in equimolar ratio. The  $\text{Ti}^{\text{III}}$  center is at an inversion center and has two water molecules (O7) in *trans* position. The distances around it are slightly longer than those around  $\text{Ti}^{\text{IV}}$  (Figure 3) as might be expected. The

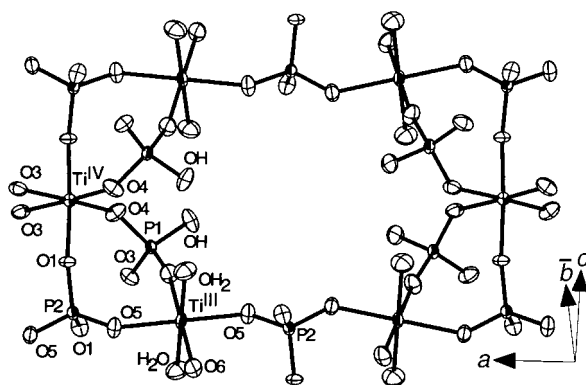


Figure 2. An ORTEP view (thermal ellipsoids at the 50% level) of the “real” cross-section of the channels (see text for more details). The view is approximately along the [011] direction of the orthorhombic cell. All hydroxyl groups and water molecules point towards the center of the channel.

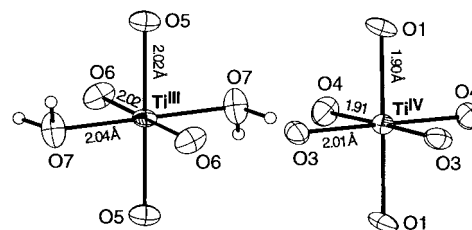


Figure 3. The coordination around  $\text{Ti}^{\text{III}}$  (left) and  $\text{Ti}^{\text{IV}}$  (right) with the distances to the nearest neighbors. All non-hydrogen atoms are drawn with thermal ellipsoids of 70% probability.

calculated valence sums for the two atoms are 3.17 and 4.32 for  $\text{Ti}^{\text{III}}$  and  $\text{Ti}^{\text{IV}}$ , respectively.<sup>[7]</sup> The distance to the water molecules, 2.039(6) Å, is very similar to Ti–OH<sub>2</sub> distances in other  $\text{Ti}^{\text{III}}$  compounds; in the hexaaquatitanium(III) trication this distance lies between 2.018(5) and 2.046(6) Å,<sup>[8]</sup> in a cesium titanium alum this distance is 2.028(5) Å.<sup>[9]</sup> The structure has channels along the *b* axis, and the diaminopropane molecules are positioned inside them. The latter are disordered among two positions, and seem to be free of hydrogen bonding. The shortest N–O distance is 3.003 Å, and is to the OH group at P1 (Figure 2). The amount of the amine present, half of a molecule per formula unit, was additionally confirmed by elemental analysis. The channels are not exactly straight but rather zigzag within the *bc* plane (up and down in Figure 1). Thus, Figure 1 depicts only the “projection” of the opening. Figure 2, which is a view approximately along the [011] direction, shows the real size of the cross-section. The dimensions of that opening are 6.0–6.2 by 6.4–6.5 Å for the horizontal (OH–OH) and vertical (O5–O5) distances on Figure 2, respectively.

The IR spectrum of TPO-1 contains the characteristic bands of a free amine. Thus, broad bands observed at 3508, 3436, and 3152  $\text{cm}^{-1}$  correspond to combination and overlapping of stretching vibrations of  $\text{H}_2\text{O}$ ,  $\text{NH}_2$ , and  $\text{CH}_2$  groups. Sharp bands at 1635 and 1508  $\text{cm}^{-1}$  (doublet) can be assigned to the bending vibrations of the  $\text{NH}_2$  and  $\text{CH}_2$  groups, respectively. At the same time the spectrum does not contain bands at around 3000–2800 and 2000  $\text{cm}^{-1}$  that are characteristic for protonated amines (the stretching and combination bands of  $\text{NH}_3^+$ , respectively). Multiple bands are observed in

the region 1100–900 cm<sup>-1</sup>, and they correspond to vibrations of the phosphate group. The compound absorbs in the yellow–orange region with absorption bands at around 550 and 575 nm, and appears deep blue–purple.

The temperature dependence of the molar magnetic susceptibility of two samples showed Curie behavior. The measured points were fitted with  $\chi_m = C_m/(T - \theta) + \text{TIP}$ , where  $C_m$  and  $\theta$  are the Curie and Weiss constants, respectively, and TIP is the temperature-independent paramagnetism resulting from mixing of low-lying empty states. The Weiss constant was approximately zero for both samples, –0.67 and –0.78 K, and indicates the lack of interactions between the Ti<sup>III</sup> (d<sup>1</sup>) atoms. The TIP values differed somewhat, 1.74 and  $3.91 \times 10^{-4}$  emu mol<sup>-1</sup>, perhaps due to the quite different amounts of sample used for the two measurements. The Curie constant, however, was virtually identical for the two samples, and indicated magnetic moments of 1.24 and 1.21  $\mu_B$ , respectively. This is clearly consistent with one spin per mole of TPO-1, and unequivocally confirms the presence of Ti<sup>III</sup> and Ti<sup>IV</sup> in equimolar ratio. Further proof for this assignment is the  $g$  value of 2.026 derived from the EPR spectrum of the sample.

Thermogravimetric analysis of the sample showed two steps, one in the range 100–235 °C and another one in the 330–355 °C range, with weight losses of 7.22 and 5.30 %, respectively. These were attributed to dehydration (calcd 7.95 %) and removal of the 1,3-diaminopropane (calcd 8.8 %), respectively. Some coke formation that occurs during the latter step may explain the discrepancy between the observed and calculated weight losses. After the first step, that is above ~260 °C, the compound loses color and becomes white, the structure collapses, and the resulting X-ray powder diffraction pattern indicates amorphous state. This is attributed to the instability of square-planar titanium resulting from the removal of the two *trans* water molecules around the Ti<sup>III</sup> center. This perhaps is followed by easy oxidation of the unsaturated titanium atoms and local geometrical rearrangement leading to the loss of crystallinity. According to the IR spectrum of the sample, the diaminopropane remains in the sample up to around 330 °C. Above 600 °C the compound recrystallizes into TiP<sub>2</sub>O<sub>7</sub>.<sup>[10]</sup> Attempts to photodecompose the organic template by using a medium-pressure mercury lamp as source were unsuccessful.

### Experimental Section

**Synthesis:** TPO-1 was initially synthesized from a mixture of elemental titanium, boric acid, phosphoric acid, 1,3-diaminopropane, HF, and water in a molar ratio of 1:6.54:13.65:2.21:3.36:600 in an attempt to make open-framework titanium borophosphate. Later it was found that boron and fluorine are not part of the structure, and the synthesis was optimized. The compound is synthesized hydrothermally as a single phase (according to the Guinier powder pattern) in 100 % yield with respect to Ti from a mixture of elemental titanium (Alfa-Aesar, powder, 325 mesh, 99 %), 1,3-diaminopropane (Acros, 99 %), H<sub>3</sub>PO<sub>4</sub>, and deionized water in molar ratio of 2:2.21:13.65:500 (pH 2). The mixture was heated in a teflon-lined stainless steel autoclave at 170 °C for one day under autogenous pressure. The product, aggregates of deep blue–purple square prisms, was consecutively washed with water, alcohol, and acetone. Elemental analysis performed by the Galbraith Laboratories: calcd: C 3.96, H 2.42, N 3.08; found: C 3.58, H 3.09, N 2.92.

**Magnetic, thermal, and spectroscopic measurements:** The magnetizations of two samples (38 and 94 mg) of two different reactions were measured at

a field of 3 T over the temperature range 10–270 K with a step of 10 °C on a Quantum Design MPMS SQUID magnetometer. An EPR spectrum of the compound was recorded at room temperature on a VARIAN spectrometer. Thermogravimetric analysis (TGA) was carried out in a flow of air (150 mL min<sup>-1</sup>) on 36 mg of sample on a CAHN TG-131 unit up to 600 °C with a heating rate of 10 K min<sup>-1</sup>. IR spectra (KBr disk) were taken before and after heat treatment on a Perkin-Elmer PARAGON-100. A spectrum in the visual region was recorded in reflection mode on a Varian Cary-3 from the sample contained in a thin-wall cuvet of fused silica.

**Crystal structure determination:** Data were collected from a single crystal with a cubic shape (0.20 × 0.20 × 0.20 mm) on a CAD4 single crystal diffractometer with monochromated MoK $\alpha$  radiation at 21 °C ( $\omega$ -2 $\theta$  scans,  $2\theta_{\text{max}} = 50^\circ$ , one octant). After corrections for Lorentz and polarization effects the data set was consistent with one space group only, *Pnma* (no. 52). Direct methods revealed the two titanium and three phosphorus atoms. Subsequent least-squares refinement on  $F^2$  followed by difference Fourier maps with the aid of the SHELXTL V5.0 package revealed the remaining oxygen atoms. The 1,3-diaminopropane molecule was found disordered on two sites, and therefore the corresponding carbon and nitrogen atoms were refined with fixed appropriate occupancies. All hydrogen atoms were located as required by geometry and refined as riding on the corresponding oxygen, nitrogen, and carbon atoms. The refinement of all nonhydrogen atoms with anisotropic thermal parameters converged with  $R1/wR2$  ( $I > 2\sigma I$ ) = 0.0667/0.1841 for 1104 reflections and 122 parameters. (crystal data: Ti<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>(HPO<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> · 0.5NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>, orthorhombic, *Pnna*,  $a = 12.702(5)$ ,  $b = 9.365(4)$ ,  $c = 11.253(8)$  Å,  $V = 1339(1)$  Å<sup>3</sup> from Guinier data with Si as an internal standard and CuK $\alpha$  radiation,  $Z = 4$ ,  $\rho_{\text{calcd}} = 2.262$  g cm<sup>-3</sup>,  $\mu = 16.28$  cm<sup>-1</sup>, residual electron density = +1.38/–0.70 e Å<sup>-3</sup> at 1.84/1.06 Å from O4/Ti<sup>IV</sup>.) A data set collected on a different crystal showed the same disorder of the 1,3-diaminopropane in the channels. Both crystals were carefully checked for superstructure but none was found. Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-410058.

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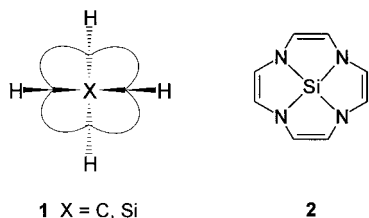
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## First Synthesis and Structure of a Tetraazasilafenestrane\*\*

Bangwei Ding, Reinhart Keese,\* and Helen Stoeckli-Evans

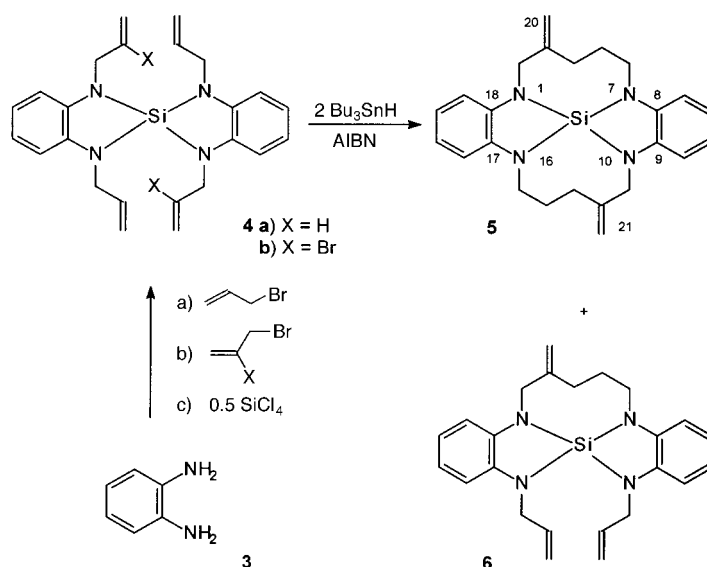
According to quantum-chemical calculations planar tetra-coordination should inherently be easier to achieve in silicon compounds than in the corresponding carbon compounds. These conclusions are based on results by Hoffmann, Alder, and Wilcox, who discussed the structural features of fenestranes of type **1** with X = C,<sup>[1]</sup> as well as our computational



results for silafenestranes of type **1** with X = Si.<sup>[2]</sup> Despite considerable computational efforts no structures with a planar-tetra-coordinate C(C)<sub>4</sub> substructure have been found.<sup>[3]</sup> Schleyer et al. have computationally explored the prerequisites for enhanced planarization in compounds such as **1** (X = Si), and proposed that planar-tetrasubstituted silicon should

be favored by electronegative, π-donor substituents.<sup>[4]</sup> In 1992 Boldyrev, Schleyer, and Keese reported computational results according to which **2** is planar and has a minimum energy at the ab initio HF/3-21G\* level.<sup>[5]</sup>

Whereas fenestranes have been prepared by a variety of methods,<sup>[7]</sup> neither silafenestranes nor tetraazasilafenestranes have hitherto been reported. In the course of our investigations of these structurally unusual molecules, we examined ring-closure reactions of appropriately functionalized spiro-tetraazasilanes. Although Si–N bonds are kinetically labile and sensitive to moisture, spiro-tetraazasilanes such as **4a** and **4b** could readily be prepared from *o*-phenylenediamine (**3**). Since ring-closure metathesis reactions of **4a** with Grubbs' catalyst<sup>[8]</sup> remained unsuccessful and radical-induced reactions with a dialkylborane led only to hydroboration of a double bond, we considered cyclization reactions of **4b**. Whereas Pd<sup>0</sup>- and Pd<sup>II</sup>-induced cyclizations remained unsuccessful as well, ring-forming radical reactions were observed when **4b** was treated with Bu<sub>3</sub>SnH and azobisisobutyronitrile (AIBN) under carefully controlled conditions (Scheme 1).<sup>[9]</sup>



Scheme 1. Synthesis of **5** and **6**.

The tetraazasilafenestrane **5**, formed by a double *8-endo* radical cyclization, was separated from the tricyclic compound **6** by chromatography and showed the expected number of NMR signals.<sup>[10]</sup> In comparison with **4a**, **4b** and **6** the <sup>29</sup>Si NMR signal of **5** is shifted downfield, indicating a different environment for the silicon atom. Definite proof of the tetracyclic structure was established by an X-ray structure analysis (Figure 1).<sup>[11]</sup> A salient feature of the SiN<sub>4</sub> core structure of **5** is the 84.7° angle between the planes of the diazasilacyclopentene rings. Since the planes of the two five-membered rings in tetraazasilaspiro[4.4]nonanes are almost perpendicular to each other, the distortion must be due to the alkylene chains bridging the spiro rings.<sup>[12]</sup> Three of the four nitrogen atoms are in a pyramidal environment, leading to a pseudo-envelope conformation for both diazasilacyclopentene rings.<sup>[13]</sup>

To realize planarization in the central SiN<sub>4</sub> core of tetraazasilafenestranes, smaller rings are required. Our efforts to

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