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The role of inorganic acidity on templated vanadate composition and dimensionality

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ABSTRACT

Compositional and structural differences in two organically templated vanadate compounds are directly ascribed to the acidity of the primary building units from which they are constructed. $[C_6H_{16}N_2][(VO)_2(HPO_3)_3]$ and $[C_6H_{16}N_2][VO(SeO_3)(HSeO_3)]_2$ were synthesized under analogous conditions with either phosphorous or selenous acid. The acidities of these primary building units are reflected in both their relative protonation states and the compositions of the resulting solids. Differences in intermolecular interactions cause deviations in dimensionality of the resulting $[(VO)_2(HPO_3)_3]_n{}^{2n-}$ layers and $[VO(SeO_3)(HSeO_3)]_n{}^{n-}$ chains, as identified and visualized using non-covalent interaction index calculations. Steric repulsions between adjacent $[VO(SeO_3)(HSeO_3)]_n{}^{n-}$ chains preclude the formation of two-dimensional layers, such repulsions are absent in $[C_6H_{16}N_2][(VO)_2(HPO_3)_3]$, as visualized using non-covalent interaction index calculations.

1. Introduction

Exploratory reactions play a pivotal role in solid state chemistry, enabling the formation of a host of new compounds and compositions. The 'endless wonder' [1] of exploratory reactions in solid state chemistry stems from the vast amounts of unexplored phase space and the discovery of unanticipated structure types. Organically templated metal oxides [2–5] constitute an extended family of compounds for which exploratory reactions have been critically important to their development. This system is particularly well suited to exploratory reactions given its exceptionally wide range of compositional flexibility, both within the organic and inorganic components [6]. Several challenges to exploratory syntheses of organically templated metal oxides exist. These include the absence of design capabilities in many chemical systems [7], the inability to calculate structures from a set of reactants [8–11], the need to re-optimize reaction conditions as compositional targets change, and the vast amount of phase space that exists to be explored [6]. Moreover, unpredictability in connectivity can mean that structure determination often requires single crystal diffraction quality samples.

A common strategy for deriving chemical insight from exploratory reactions is to isolate reaction variables. A series of reactions in which a single variable is present generally allows for one to directly ascribe the differences in composition, structure or property to the variable being studied. Such variables include pH [12], amine structure [13,14], reactant concentration [15,16], chemical hardness [17], and framework acidity [18], to name a few. To most efficiently synthesize new materials, insight into the mechanisms by which they are formed is critical. A generalized mechanism for organically templated metal oxide formation has been proposed by Ferey et al. [4,19] in which component speciation is dictated by reaction conditions and the development of secondary building units (SBUs) arises from inter-component interactions. Structuring new exploratory reactions so that both new compounds can be formed and additional understanding gained of the mechanisms by which they form is especially valuable.

This study involves the use of structurally similar primary building units, phosphorous acid and selenous acid, in the formation of new organically templated vanadium oxides. Differences in acidity between phosphorous and selenous acids are manifested in both the composition and connectivity of the resulting compounds. Non-covalent interaction (NCI) [20,21] indices were calculated to locate and visualize non-covalent interactions and to attribute dimensionality differences to these interactions. The structure of one new compound, $[C_6H_{16}N_2][(VO)_2(HPO_3)_3]$, is

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reported, as is its characterization using a series of analytical tools including single crystal X-ray diffraction.

2. Experimental

2.1. Materials

V_2O_5 ($\geq 98\%$), 1,4-dimethylpiperazine (1,4-dmpip, 98%), and H_3PO_3 (99%) were purchased from Sigma-Aldrich. All reagents were used as received. Deionized water was used in this synthesis.

2.2. Synthesis

A 23 mL poly(fluoro-ethylene-propylene) lined pressure vessel was used. Initial reaction pH was controlled by the addition of 4 M HCl and 4 M NaOH. The reaction was heated to 110 °C and allowed to soak for 24 h. The reaction was then cooled to room temperature at a rate of 6 °C h^{-1} to promote the growth of large single crystals. The autoclave was opened in air, and products were recovered through filtration. No additional crystalline or amorphous reaction products were observed.

$[C_6H_{16}N_2][(VO)_2(HPO_3)_3]$ was synthesized as square aquamarine crystals through the reaction of 0.0299 g (1.64×10^{-4} mol) V_2O_5, 0.6564 g (80.0×10^{-4} mol) H_3PO_3, 0.5207 g (45.6×10^{-4} mol) 1,4-dmpip, and 8.0 g H_2O. IR data (cm^{-1}): N–H, 1477, 1544, 1580; C–H, 3025; V=O, 982; P=O, 1000; P–H, 948, 2349. EA obsd (calc): C 14.88% (14.70%); H 3.46% (3.90%); N 4.17% (5.70%); P 18.79% (19.0%); V 21.00% (20.80%).

2.3. Single crystal X-ray diffraction

Data were collected using a Bruker AXS Smart Apex CCD diffractometer with Mo-Kα radiation ($\lambda = 0.71073$ Å). A single crystal was mounted on a Mitegen micromesh mount using a trace of mineral oil and cooled *in-situ* to 100(2) K for data collection. Frames were collected, reflections were indexed and processed, and the files scaled and corrected for absorption using APEX2 [22]. The heavy atom positions were determined using SIR92 [23]. All other non-hydrogen sites were located from Fourier difference maps. All non-hydrogen sites were refined using anisotropic thermal parameters using full matrix least squares procedures on F_o^2 with $I > 3\sigma(I)$. Hydrogen atoms were placed in geometrically idealized positions. All calculations were performed using crystals *v*. 14.23*c* [24]. Relevant crystallographic data are listed in Table 1.

2.4. Powder X-ray diffraction

Powder diffraction patterns were recorded on a GBC-Difftech MMA powder diffractometer. Dry powdered samples were packed into sample holders. Samples were mounted on glass plates. Calculated powder patterns were generated from single crystal data using ATOMS *v.* 6.0. [25] A powder X-ray diffraction pattern was consistent with a pattern predicted from the refined structure of $[C_6H_{16}N_2][(VO)_2(HPO_3)_3]$. No evidence of additional phases was observed.

2.5. Elemental analyses

All elemental analyses were performed by Micro Analysis. Carbon, nitrogen and hydrogen analyses were performed on a Perkin Elmer 2400 II Elemental Analyzer. Vanadium and phosphorous analyses were performed using ICP.

Table 1
Crystallographic data for compound $[C_6H_{16}N_2][(VO)_2(HPO_3)_3]$.

Compound	$[1,4\text{-dmpipH}_2][(VO)_2(HPO_3)_3]$
Formula	$C_6H_{19}N_2O_{11}P_3V_2$
fw	490.03
Space-group	*P*-1 (No. 2)
a (Å)	8.548(3)
b (Å)	9.168(3)
c (Å)	12.580(5)
α (°)	89.467(10)
β (°)	72.849(10)
γ (°)	65.478(14)
V (Å^3)	849.8(6)
Z	2
ρ_{calc} (g cm^{-3})	1.915
λ (Å)	0.71073
T (K)	100
μ (mm^{-1})	1.437
R_1,[a]	0.0266
wR_2[b]	0.0702

[a] $R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$.

[b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]^{1/2}$.

2.6. Infrared spectroscopy

Infrared measurements were obtained using a Perkin Elmer FT-IR Spectrum 1000 spectrophotometer. Samples were diluted with spectroscopic grade KBr and pressed into pellets. Scans were collected over the range of 400–4000 cm^{-1}.

2.7. Bond valence sums

Bond valence sums [26] calculations were performed using parameters compiled by Brese and O'Keeffe [27]. A complete table of bond valence sums for $[C_6H_{16}N_2][(VO)_2(HPO_3)_3]$ is available in the Supplementary data.

2.8. Electronic structure calculations

Solid-state electronic structure calculations were performed using ABINIT *v*6.4.1 [28,29]. ABINIT calculations used the Perdew–Burke–Ernzerhof generalized gradient approximation (PBE-GGA) exchange-correlation functional, norm-conserving Troullier–Martins pseudopotentials, a planewave basis set with energy cutoff of 25 Hartrees, a $6 \times 6 \times 6$ Monkhorst–Pack k-point sampling grid, and experimental crystal structures. Electron localization functions (ELFs) were calculated from the self-consistent valence electron densities and visualized using Vesta *v*3.2.1 [30].

2.9. Surface area calculations

Surface areas for the inorganic components in $[C_6H_{16}N_2][(VO)_2(HPO_3)_3]$ and $[C_6H_{16}N_2][VO(SeO_3)(HSeO_3)]_2$ were calculated using a rolling-sphere algorithm by Richards [31] (using the DMS program [32]) the molecular surface, and a geometric decomposition method that we reported earlier [33,34]. Lone pair positions were defined as local maxima in the ELF isosurfaces, with radii of 1.5 Å, based upon Galy's work [35,36]. Calculated surface areas are listed in Table 2.

2.10. Iterative-Hirshfeld charges

Iterative Hirshfeld (Hirshfeld-I) [37,38] atomic partial charge determinations were performed on the self-consistent valence electron density in conjunction with all-electron atomic charge densities generated using the HF96 atomic Hartree-Fock code [39],