Hydrothermal Synthesis of a Microporous Organic-Inorganic Hybrid Framework $[Fe_{0.28}V_{0.72}OH_{0.8}(NH_4)_{0.2}(C_8H_4O_4)] \cdot 0.53(C_8H_6O_4)$

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ABSTRACT

Single crystals of a novel organic-inorganic framework $[Fe_{0.28}V_{0.72}OH_{0.8}(NH_4)_{0.2}(C_8H_4O_4)]\cdot 0.53(C_8H_6O_4)$, **1**, have been prepared by hydrothermal synthesis in the presence of an oxidizing agent. The structure was solved by single crystal X-ray diffraction: space group Pnma, a = 17.6956 (19) Å, b = 6.8745 (7) Å, c = 11.9303(12) Å. The three dimensional framework is constructed from Fe/V-O chains that are cross-linked by 1,4-benzene dicarboxylate (BDC) anions forming large one-dimensional channels. As synthesized, the compound contains additional dicarboxylate groups occupying disordered positions in the channels that can be removed by heating. The chemical reactivity of **1** and its magnetic properties are reported. The new phase is closely related to analogous Cr (III) and V(III) phases recently reported by Férey and co-workers.

INTRODUCTION

Microporous compounds are of interest due to their potential for use as molecular sieves, ion exchangers, and catalysts [1-3]. Hybrid inorganic-organic materials have brought new and interesting properties to microporous materials not seen in pure inorganic systems. The use of functionalized organic molecules or secondary-building units (SBU) as linkers to various metals allows for a larger range of framework structures, magnetic and electronic properties, and catalytic capabilities [3,4]. It also allows a greater number of transition metals not normally present in zeolite structures to be incorporated into the compounds under mild synthetic conditions [5].

Many novel inorganic-organic hybrid compounds have been synthesized in the last decade Several of these compounds are assembled through the utilization of metal-oxo moieties in conjunction with organic groups to form framework structures [2-8]. Compounds such as Zn_4OBDC contain isolated metal-oxo clusters connected by dicarboxylate organic linkers [2]. We have reported novel chiral Co-V and Ni-V inorganic-organic hybrid compounds containing Co-O or Ni-O octahedra interconnected with 2-pyrazinecarboxylate anions to form tubular helical chains that are supported by chains of vanadium oxide tetrahedra [3].

Recently, Férey described several new transition-metal (V, Cr)- BDC frameworks, in which chains of *trans* corner-shared metal octahedra are cross-linked by dicarboxylate anions [4,5]. These compounds and other related hybrid structures demonstrate the formation of non-interpenetrated microporous frameworks with large surface areas [7]. We have attempted to extend this class of compounds by synthesizing a microporous compound with a structure analogous to that adopted by the (V, Cr)- BDC compounds, but that incorporates trivalent iron into the framework. Trivalent iron molecular structures with carboxylate bridged diiron centers are of particular interest due to their presence in metalloproteins that catalyze the oxidation of methane into methanol [8]. Solid-state analogs that contain similar functionality are consequently of interest but their synthesis is difficult to control because of Fe^{3+} hydrolysis into insoluble stable oxides and hydroxides that occurs over a broad pH range [9,10]. Here we report the first hybrid framework containing both Fe^{3+} and V^{3+} containing carboxylate bridged metal centers.

EXPERIMENTAL

Iron oxalate was purchased from Alfa Aesar. 1,4-benzene dicarboxylic acid and ammonium metavandate were purchased from Aldrich Chemicals. All materials were used as supplied. Infrared spectroscopy was performed on a Galaxy FTIR 5000 series spectrometer with pressed KBr pellets. The following reagents were added to the Teflon liner of a 23-ml Parr stainless steel autoclave; 0.5mmol of $Fe_2(C_2O_4)_3$ (0.2443 g), 1 mmol (0.1695 g) BDC, 1 mmol (0.1182 g) NH_4VO_3 and 556 mmol (10 ml) of deionized H_2O. The reactants were sealed in the autoclave and heated at 180 ºC for 2 d. The reaction was quenched and filtered revealing dark red-brown rectangular prisms of **1**, colorless crystals of BDC acid and black unidentified powder. The final pH was approximately 4-5. After multiple washings with DMF, the product (small prisms) was isolated. IR (KBR, cm^{-1}): 3612s, 3054w, 3002w, 2852w, 2653m, 2653m, 2532m, 2362w, 2341w, 1945m, 18791w, 1822w, 1702s, 1552s, 1506s, 1396s, 1276s, 1159s, 1132s, 1020s, 904m, 879s, 824s, 760m, 740s, 644m, 571s, 514m.

Numerous experiments were carried out to optimize the synthesis of **1** and to synthesize a pure iron(III) phase. The removal of NH_4VO_3 from the reaction resulted in the formation of iron oxides, iron oxalates and recrystallized terephthalic acid. Adjustments to the reaction ratios resulted in either the formation of a fourth phase of iron oxalate or the exclusion of **1**. The use of $Fe(NO_3)_3$ as a reactant always led to the formation of iron oxide and no **1**. Several other synthetic alterations and processes including the adjustment of pH and amine diffusion were attempted, but the formation of a single phase of **1** or of a pure iron phase was not successful under aqueous hydrothermal conditions.

RESULTS

Crystal structure

X-ray single crystal analysis was performed on a Siemens SMART platform diffractometer (SAINT version 4.05) outfitted with a 1K CCD area detector and monochromatized graphite Mo-Ka radiation (Siemens Analytical X-ray Instruments, Madison, WI). The $0.4 \times 0.1 \times 0.1$ mm crystal was mounted on a glass fiber and a hemisphere of data (1271 frames with a 5-cm detector distance) was collected using a narrow frame method with 0.30° in ω at 223 K with an exposure time of 30 s $frame^{-1}$. The first 50 frames were remeasured at the end of collection to ensure crystal stability. The structure was solved by direct methods using SHELXTL program [10]. Compound **1** crystallizes in the space group Pnma with unit cell dimensions of a = 17.6956(19) Å, b = 6.8745(7) Å, c = 11.9303(12) Å (Tables I and II). The metal is coordinated to six oxygen atoms in an octahedral geometry (Figure 1). The equatorial Fe,V-O bond lengths are 2.004(3) Å and 1.996(3) Å, and the shorter axial bond lengths are 1.934(3) Å. The bond valences of Fe^{3+} and V^{3+} were calculated to be 2.63 and 2.90, respectively [11]. The octahedral Fe/V-O centers are linked by sharing *trans* hydroxyl groups (evident O-H infrared band at 3612 cm^{-1}), forming M-OH-M chains.

Table I. Crystal Data and Selected Bond Lengths and Angle for 1

Formula sum		Unit cell dimensions	*a* = 17.696(2) Å
Formula weight	321.71		*b* = 6.8745(7) Å
Crystal system	Orthorhombic		*c* = 11.930(1) Å
Space group	Pnma (no. 62)	Cell volume	*V* = 451.3(3) $Å^3$
Z	4	R	0.076
ρ_{calc}	1.464 g/cm^3		
(V,Fe)—O1	1.934(3) Å	(V,Fe)—O2	2.004(3) Å
(V,Fe)—O3	1.996(3) Å	(V,Fe)-O1-(V,Fe)	125.4(1)

Table II. Atomic coordinates and isotropic displacement parameters ($Å^2$) for 1

Atom	x	y	z	Uiso	Occ.
Fe1	0.0000	0.0000	0.0000	0.025(1)	0.28
V1	0.0000	0.0000	0.0000	0.025(1)	0.72
O1	0.0741(2)	0.0864(5)	-0.1169(3)	0.030(1)	1
O2	0.0064(2)	0.2500	0.0738(5)	0.025(1)	1
O3	0.4115(2)	0.0859(5)	-0.4090(3)	0.030(1)	1
C1	0.1009(4)	0.2500	-0.1429(6)	0.025(2)	1
C2	0.1726(4)	0.2500	-0.2104(6)	0.030(2)	1
C3	0.2068(3)	0.0743(8)	-0.2394(6)	0.042(2)	1
C4	0.2743(3)	0.0743(9)	-0.2971(5)	0.040(2)	1
C5	0.3083(4)	0.2500	-0.3253(6)	0.026(2)	1
C6	0.3836(4)	0.2500	-0.3864(6)	0.026(2)	1
C,O1	0.3610(9)	0.001(2)	-0.024(1)	0.25(5)	0.25
C,O2	0.469(1)	0.2500	-0.150(2)	0.13(2)	0.25
C,O3	0.370(2)	0.2500	-0.035(2)	0.15(2)	0.25
C,O4	0.367(2)	-0.2500	-0.033(3)	0.17(3)	0.25
C,O5	0.4664(9)	0.000(2)	-0.136(1)	0.20(2)	0.25
C,O6	0.466(1)	-0.2500	-0.153(2)	0.15(2)	0.25
O,C1	0.3610(9)	0.001(2)	-0.024(1)	0.25(5)	0.25
O,C2	0.469(1)	0.2500	-0.150(2)	0.13(2)	0.25
O,C3	0.370(2)	0.2500	-0.035(2)	0.15(2)	0.25
O,C4	0.367(2)	-0.2500	-0.033(3)	0.17(3)	0.25
O,C5	0.4664(9)	0.000(2)	-0.136(1)	0.20(2)	0.25
O,C6	0.466(1)	-0.2500	-0.153(2)	0.15(2)	0.25
C7	0.4138(9)	0.126(5)	-0.084(2)	0.25(8)	0.50
C8	0.4133(9)	-0.124(5)	-0.085(2)	0.20(5)	0.50

The bent chains (the Fe/V-O2-Fe/V angle is 125.4º) are bridged by the oxygen atoms of the benzene dicarboxylate groups in the equatorial positions of the octahedra. The bridging by the BDC creates a three dimensional framework possessing large diamond shaped channels parallel to the *b* axis with dimensions of 17.696(2) x 11.930(1) Å (Figure 2) measured from iron atom to iron atom. The channels are occupied by highly disordered benzenedicarboxylic acid molecules that were modeled by partially occupied C,O positions as shown in Table II. Further understanding of this structure was gathered through elemental analysis, thermogravimetric analysis and magnetic susceptibility measurements. Compound **1** is structurally similar to vanadium and chromium compounds reported by Férey *et al.* [4,5].

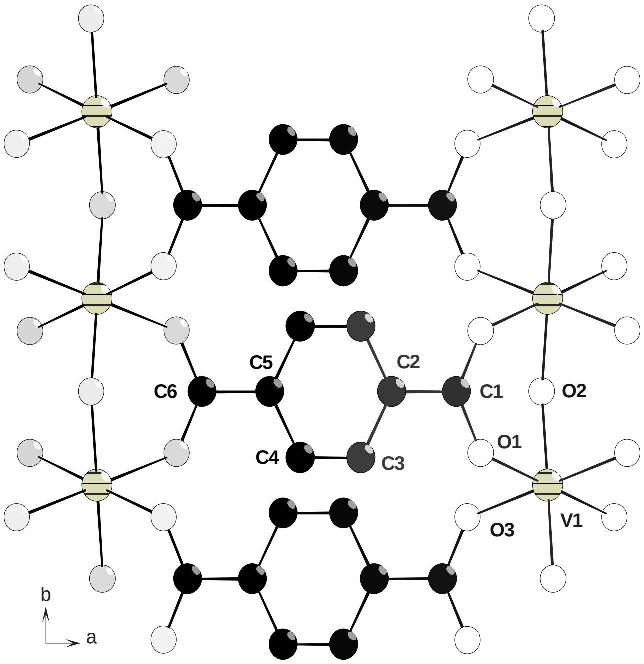

Figure 1. A view of the structure of **1** along (001), showing the Fe,V-O chains cross-linked by bezenedicarboxylate anions.

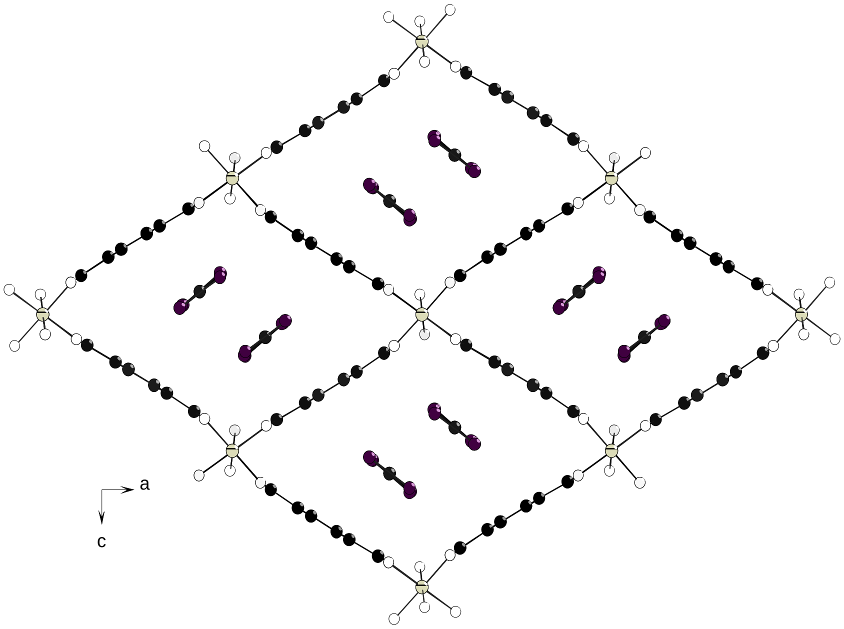

Figure 2. View of the structure of **1** along (010) showing the diamond shaped channels containing disordered benzene dicarboxylic acid molecules.

Analysis

Elemental analysis was performed by Gailbraith Laboratories (Knoxville, Tennessee). Elemental analysis of **1** gave the following percentages; 44.15 %C, 2.64 %H, 0.86 %N, 4.64 %Fe, 11.05 %V. The calculated values for the composition $[Fe_{0.28}V_{0.72}OH_{0.8}(NH_4)_{0.2}(C_8H_4O_4)]\cdot 0.53(C_8H_6O_4)$ of **1** are 45.25% C, 2.70% H, 0.86%N, 4.81 %Fe, 11.29%V. The Fe: V ratio is 1:2.38 or a 28% occupation of Fe in the metal sites. The analysis is consistent with ~0.5 moles of benzene dicarboxylic acid and a small concentration of ammonium cations presumably both present in the channels**.**

Thermogravimetric analysis was performed with a Dupont 2100 V5.1A TGA. The sample was analyzed with a heating rate of 1°C min^{-1} to 800°C in air. A small amount of surface water was lost below ~100°C. Beginning at ~200°C, some of the benzenedicarboxylic acid in the channels was removed (approx. 15.87 %). The removal of the channel BDC was not complete at 375 °C, the temperature at which the framework began to decompose with the loss of the coordinated BDC molecules. Complete elimination of framework BDC occurred at 436°C (51.87%, calc. 50.97%).

Magnetic measurements were performed on a Squid magnetometer in a temperature range of 2K to 300K at a magnetic field of 0.1T. The data are shown in Figure 3 in the form of $1/\chi$ versus the temperature (K). The data indicate antiferromagnetic coupling between the V^{3+} and Fe^{3+} ions along the chain and is similar to that previously reported for the linear chain compound $V_{1.23}(PO_4)(OH)_{0.69}(H_2O)_{0.31}\cdot 0.33H_2O$ [12]. A more detailed analysis of the magnetic susceptibility data will be presented elsewhere.

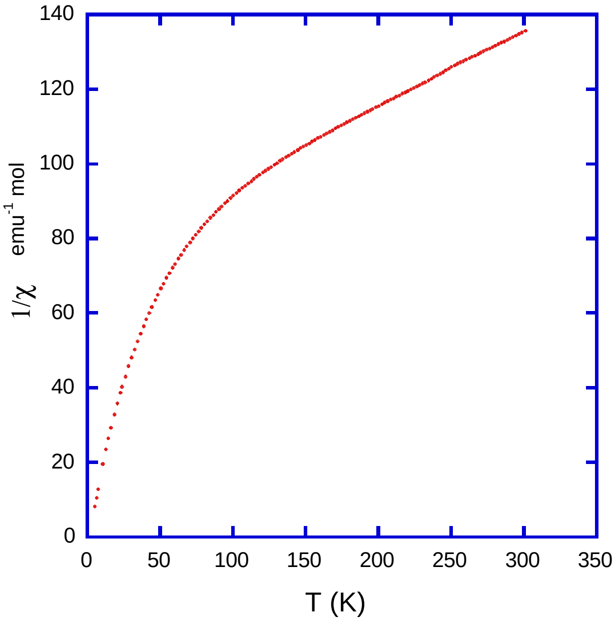

Figure 3. $1/\chi$ (mol emu^{-1})v. Temperature (K)

CONCLUSIONS

Compounds with the composition M(OH)($C_8H_4O_4$), M=Cr, V and (VO)($C_8H_4O_4$) with closely related structures have recently been reported [4,5]. Compound **1** is the first example of this structure type to contain Fe^{3+} on the metal sites together with V^{3+}. As observed in the other compounds, **1** contains highly disordered BDC molecules in the large diamond-shaped channels, which can be removed upon heating. On heating **1** in air, oxidation of the V^{3+} to V^{4+} occurs. The presence of V(IV) can be seen by analysis of X- single crystal data, which indicates the presence of a vanadyl (V=O) group. Because of the additional disorder that is introduced on oxidation, the exact structure of oxidized phase has not yet been determined. Solid proof of its existence is provided through elemental analysis. Most recently, using a different synthetic approach, we have successfully synthesized and characterized the pure Fe^{3+} phase Fe(OH)(BDC). The details of this work will be described in a future publication.

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REFERENCES

1. M.E. Davis, *Nature*, **417**, 813-821 (2002).
2. L. Halian, M. Eddaoudi, M. O'Keeffe, O.M. Yaghi, *Nature*, **402**, 276-279 (1999).
3. L. Zheng, T. Whitfield, X. Wang, A.J. Jacobson, *Angew. Chem.*, **39**, 4528-4531 (2000).
4. M. Riou-Cavallec, C. Albinet, C. Livage, N. Guillou, M. Noguès, J.M. Grenèche, G. Férey, *Solid State Sciences*, **4**, 267-270 (2002).
5. F.Millange, C. Serre, G. Férey, *Chem. Commun.*, **8**, 822-823 (2002).
6. K. Barthelet, J. Marrot, D. Riou, G. Férey, *Angew. Chem.*, **41**, 281-284 (2002).
7. N. L. Rosi, M. Eddaoudi, J. Kim, M. O'Keeffe, O.M. Yaghi, *Angew. Chem.*, **41**, 284-287 (2002).
8. M. Merkx, D. A. Kopp, M. Sazinsky, J. Blazyk, J. Müller, S. Lippard, *Angew. Chem.*, **40**, 2782-2807 (2001).
9. C. Baes, R.E. Mesmer, *The Hydrolysis of Cations*, (Krieger Publishing Company, 1986) pp. 226-237.
10. D.J. Vaughn, R.A.D. Pattrick editors, *The Mineralogical Society Series, Mineral Surfaces*, **5**, (Chapman & Hall, 1995).
11. G.M. Sheldrick, *SHELXTL, Program for Refinement of Crystal Structures*, (Siemens Analytical X-ray Instruments Inc., Madison, WI) (1994).
12. J.T. Vaughey, W.T. Harrison, A.J. Jacobson, D.P. Goshorn, J.W. Johnson, *Inorganic Chemistry*, **33**, 2481-2487 (1994).