

# Solid state coordination chemistry of the oxofluorovanadium–diphosphonate system in the presence of Cu(II)–tetrapyriddyprazine complex cations

## The crystal structures of $[\{\text{Cu}_2(\text{tpyprz})(\text{H}_2\text{O})_2\}\text{V}_4\text{FO}_8(\text{HO}_3\text{PCH}_2\text{PO}_3)_2]$ , $[\{\text{Cu}_2(\text{tpyprz})(\text{H}_2\text{O})_2\}\text{V}_4\text{F}_6\text{O}_6(\text{O}_3\text{PCH}_2\text{CH}_2\text{PO}_3)]$ , and $[\text{Cu}_2(\text{tpyprz})\{\text{HO}_3\text{P}(\text{CH}_2)_3\text{PO}_3\text{H}\}][\text{V}_2\text{F}_2\text{O}_5]$ (tpyprz = tetra-4-pyridylpyrazine)

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### Abstract

The hydrothermal reactions of  $\text{V}_2\text{O}_5$ ,  $\text{Cu}(\text{CH}_3\text{CO}_2)_2 \cdot \text{H}_2\text{O}$ , tetrapyriddyprazine (tpyprz), HF and the appropriate diphosphonic acid yielded a series of compounds of the  $\{\text{Cu}^2(\text{tpyprz})\}^{4+}/\text{V}_x\text{O}_y\text{F}_z^{n-}/\{\text{O}_3\text{P}(\text{CH}_2)_n\text{PO}_3\}^{4-}$  family of materials. The structure of  $[\{\text{Cu}_2(\text{tpyprz})(\text{H}_2\text{O})_2\}\text{V}_4\text{F}_6\text{O}_6(\text{HO}_3\text{PCH}_2\text{PO}_3)_2]$  (**1**) is one-dimensional, constructed from mixed valence  $\{\text{V}_3^{\text{V}}\text{V}^{\text{IV}}\text{FO}_8(\text{HO}_3\text{PCH}_2\text{PO}_3)_2\}^{4-}$  clusters linked through  $\{\text{Cu}_2(\text{tpyprz})(\text{H}_2\text{O})_2\}^{4+}$  rods. The two-dimensional  $[\{\text{Cu}_2(\text{tpyprz})(\text{H}_2\text{O})_2\}\text{V}_4\text{F}_6\text{O}_6(\text{O}_3\text{PCH}_2\text{CH}_2\text{PO}_3)]$  (**2**) is constructed from  $\{\text{V}_4\text{F}_6\text{O}_6(\text{O}_3\text{PCH}_2\text{CH}_2\text{PO}_3)\}_n^{4n-}$  chains crosslinked by  $\{\text{Cu}_2(\text{tpyprz})(\text{H}_2\text{O})_2\}^{4+}$  rods; mixed valence  $\{\text{V}_2^{\text{V}}\text{V}_2^{\text{IV}}\text{F}_6\text{O}_6(\text{O}_3\text{PCH}_2\text{CH}_2\text{PO}_3)\}^{4-}$  clusters are embedded in the network. Compound **3**,  $[\text{Cu}_2(\text{tpyprz})\{\text{HO}_3\text{P}(\text{CH}_2)_3\text{PO}_3\text{H}\}][\text{V}_2\text{F}_2\text{O}_5]$ , consists of  $[\text{Cu}_2(\text{tpyprz})\{\text{HO}_3\text{P}(\text{CH}_2)_3\text{PO}_3\text{H}\}]_n^{2n+}$  chains and isolated  $\{\text{V}_2\text{F}_2\text{O}_5\}^{2-}$  anions. Structures **1**–**3** are compared to the structures of the analogous series  $\{\text{Cu}_2(\text{bisterpy})\}^{4+}/\text{V}_x\text{O}_y\text{F}_z^{n-}/\{\text{O}_3\text{P}(\text{CH}_2)_n\text{PO}_3\}^{4-}$ , where bisterpy is 2,2':4':2'':2'''-quaterpyridine, 6',6''-di-2-pyridinyl. The temperature-dependent magnetic susceptibilities of **2** and **3** are also discussed.

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### 1. Introduction

Complex structures [1–6], based on a molecular scale composite of inorganic and organic components, provide the potential for the design of novel functional materials for technological applications [7]. An inorganic material may provide useful magnetic, dielectric or optical proper-

ties, mechanical hardness, and thermal stability, while organic compounds offer processability, structural diversity, a range of polarizabilities and luminescent properties [8]. Consequently, the combination of the characteristics of the organic and inorganic components offers an opportunity to conflate useful properties within a single composite, providing access to a vast area of complex, multifunctional materials [9–16].

Inorganic–organic hybrid materials [17–20] are extended arrays of metal atoms or clusters bridged by polyfunctional

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organic molecules. An important subclass of this family of materials is the hybrid metal oxides, which contain metal–oxygen–metal ( $M-O-M$ ) arrays as part of their structures. In such materials, the inorganic oxide contributes to the increased complexity, and hence functionality, through incorporation as one component in a multilevel structural material where there is a synergistic interaction between organic and inorganic components.

Metal organophosphonates are prototypical composite materials, which can exhibit a range of structures, including molecular clusters, chains, layers and three-dimensional frameworks [21–23]. An important subclass of these materials are the oxovanadium organophosphonates [24,25], whose structures are often characterized by a two-dimensional network of V–P–O layers separated by hydrophobic organic domains. However, the detailed structural chemistry may be exceedingly complex, reflecting a variety of structural determinants [26–48]. In developing the structural systematics of these materials, we have investigated the oxovanadium organodiphosphonate system, focusing on a number of variables, specifically: (i) the length and identity of the organic tether of the diphosphonates [47], (ii) the introduction of organic or metal complex cations [26,47], and (iii) the incorporation of fluoride anions into the V–P–O substructure [48,49].

Comparison of the structures of the three component oxyfluorovanadates of the  $\{Cu_2(\text{bisterpy})\}^{4+}/V_xO_yF_z^{n-}/\{O_3P(CH_2)_nPO_3\}^{4-}$  family (bisterpy = 2,2':4',4'':2'':2'''-quaterpyridyl-6,6''-di-2-pyridine) [48] to those of the non-fluorinated materials of the type  $\{Cu_2(\text{bisterpy})\}^{4+}/V_xO_y^{n-}/\{O_3P(CH_2)_nPO_3\}^{4-}$  reveals the profound structural consequences of fluoride incorporation. While both families exhibit anionic  $\{V_xO_yF_z^{n-}\}_n$  or  $\{V_xO_y^{n-}\}_n$  substructures and charge compensating complex coordination cations, the fluorinated phases manifest a considerably expanded range of V/P/O/F building blocks, including embedded clusters, chains and networks and three-dimensional frameworks. The fluorinated species also exhibited structures with V–O–V bonds in encapsulated binuclear and/or tetranuclear oxovanadium clusters, subunits which were absent in the structural chemistry of the  $\{Cu_2(\text{bisterpy})\}^{4+}/V_xO_y^{n-}/\text{diphosphonate}$  family of materials.

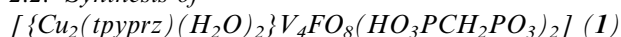
Encouraged by these observations, we have studied the introduction of fluoride into oxovanadate–diphosphonate phases with coordination complex cation subunits other than  $\{Cu_2(\text{bisterpy})\}^{4+}$ , such as the closely related, but more compact,  $\{Cu_2(\text{tpyprz})\}^{4+}$  (tpyprz = tetra-4-pyridylpyrazine). Three members of the  $\{Cu_2(\text{tpyprz})\}^{4+}/V_xO_yF_z^{n-}/\{O_3P(CH_2)_nPO_3\}^{4-}$  family, whose structures are unrelated to those observed for the  $\{Cu_2(\text{bisterpy})\}^{4+}/V_xO_yF_z^{n-}/\{O_3P(CH_2)_nPO_3\}^{4-}$  materials, were isolated:  $[\{Cu_2(\text{tpyprz})(H_2O)_2\}V_4FO_8(HO_3PCH_2PO_3)_2]$  (**1**),  $[\{Cu_2(\text{tpyprz})(H_2O)_2\}V_4F_6O_6(O_3PCH_2CH_2PO_3)]$  (**2**), and  $[Cu_2(\text{tpyprz})\{HO_3P(CH_2)_3PO_3\}][V_2F_2O_5]$  (**3**).

## 2. Experimental section

### 2.1. General considerations

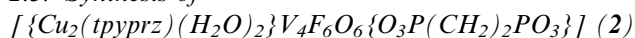
All chemicals were used as obtained without further purification: copper(II) acetate monohydrate, vanadium(V) oxide, tetra-2-pyridinylpyrazine, and hydrofluoric acid (48–51%) were purchased from Aldrich; methylenediphosphonic acid was purchased from Alfa Aesar. The diphosphonate ligands 1,2-ethylenediphosphonic acid and 1,3-propylenediphosphonic acid were prepared as previously reported [50,51]. All syntheses were carried out in 23 ml poly(tetrafluoroethylene)-lined stainless steel containers under autogenous pressure. The reactants were stirred briefly, and the initial pH measured before heating. Water was distilled above 3.0 M $\Omega$  in-house using a Barnstead Model 525 Biopure Distilled Water Center. The initial and final pH of the reactions were measured using Hydriion pH sticks.

### 2.2. Synthesis of



A mixture of  $V_2O_5$  (0.162 g, 0.891 mmol),  $Cu(CH_3CO_2)_2 \cdot H_2O$  (0.091 g, 0.456 mmol), tpyprz (0.087 g, 0.224 mmol), methylenediphosphonic acid (0.090 g, 0.511 mmol),  $H_2O$  (10.07 g, 559.4 mmol), and HF (0.314 g, 7.85 mmol) in the mole ratio 3.98:2.04:1.00:2.28:2497:35.04 was stirred briefly before heating to 150 °C for 168 h. Initial and final pH values of 1.5 and 1.5, respectively, were recorded. Black crystals of **1** suitable for X-ray diffraction were isolated in 15% yield. IR (KBr pellet,  $cm^{-1}$ ): 3096(w), 2950(w), 1607(m), 1562(m), 1478(m), 1405(m), 1248(w), 1192(m), 1125(m), 1080(m), 996(s), 789(m), and 744(m).

### 2.3. Synthesis of



A solution of  $V_2O_5$  (0.082 g, 0.451 mmol),  $Cu(CH_3CO_2)_2 \cdot H_2O$  (0.089 g, 0.446 mmol), tpyprz (0.086 g, 0.221 mmol), 1,2-ethylenediphosphonic acid (0.064 g, 0.337 mmol)  $H_2O$  (10.01 g, 556.1 mmol), and HF (0.555 g, 13.88 mmol) in the mole ratio 2.04:2.02:1.00:1.52:2516:62.81 was stirred briefly before heating to 150 °C for 72 h (initial and final pH values were 1.0 and 1.0, respectively). Black crystals of **2** suitable for X-ray diffraction were isolated in 90% yield. IR (KBr pellet,  $cm^{-1}$ ): 3068(w), 1597(m), 1476(m), 1411(m), 1296(w), 1261(w), 1191(m), 1111(s), 1045(m), 965(s), 785(m), and 760(m).

### 2.4. Synthesis of



A solution of  $V_2O_5$  (0.082 g, 0.451 mmol),  $Cu(CH_3CO_2)_2 \cdot H_2O$  (0.090 g, 0.451 mmol), tpyprz (0.086 g, 0.221 mmol), 1,3-propylenediphosphonic acid (0.093 g, 0.456 mmol),  $H_2O$  (10.02 g, 556.7 mmol) and HF (0.150 g, 3.75 mmol)

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