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

The crystal structures of [{Cu_2(tpyprz)$(H_2O)_2$}$V_4FO_8(HO_3PCH_2PO_3)_2$], [{Cu_2(tpyprz)$(H_2O)_2$}$V_4F_6O_6(O_3PCH_2CH_2PO_3)$], and [$Cu_2$(tpyprz){$HO_3P(CH_2)_3PO_3H$}][$V_2F_2O_5$] (tpyprz = tetra-4-pyridylpyrazine)

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Abstract

The hydrothermal reactions of V_2O_5, $Cu(CH_3CO_2)_2 \cdot H_2O$, tetrapyridylpyrazine (tpyprz), HF and the appropriate diphosphonic acid yielded a series of compounds of the $\{Cu^2(\text{tpyprz})\}^{4+}/V_xO_yF_z^{n-}/\{O_3P(CH_2)_nPO_3\}^{4-}$ family of materials. The structure of $[\{Cu_2(\text{tpyprz})(H_2O)_2\}V_4F_6O_6(HO_3PCH_2PO_3)_2]$ (**1**) is one-dimensional, constructed from mixed valence $\{V_3^{V}V^{IV}FO_8(HO_3PCH_2PO_3)_2\}^{4-}$ clusters linked through $\{Cu_2(\text{tpyprz})(H_2O)_2\}^{4+}$ rods. The two-dimensional $[\{Cu_2(\text{tpyprz})(H_2O)_2\}V_4F_6O_6(O_3PCH_2CH_2PO_3)]$ (**2**) is constructed from $\{V_4F_6O_6(O_3PCH_2CH_2PO_3)\}_n^{4n-}$ chains crosslinked by $\{Cu_2(\text{tpyprz}))(H_2O)_2\}^{4+}$ rods; mixed valence $\{V_2^{V}V_2^{IV}F_6O_6(O_3PCH_2CH_2PO_3)\}^{4-}$ clusters are embedded in the network. Compound **3**, $[Cu_2(\text{tpyprz})\{HO_3P(CH_2)_3PO_3H\}][V_2F_2O_5]$, consists of $[Cu_2(\text{tpyprz})\{HO_3P(CH_2)_3PO_3H\}]_n^{2n+}$ chains and isolated $\{V_2F_2O_5\}^{2-}$ anions. Structures **1**–**3** are compared to the structures of the analogous series $\{Cu_2(\text{bisterpy})\}^{4+}/V_xO_yF_z^{n-}/\{O_3P(CH_2)_nPO_3\}^{4-}$, where bisterpy is 2,2′:4′:4″:2″,2‴-quaterpyridine, 6′,6″-di-2-pyridinyl. The temperature-dependent magnetic susceptibilities of **2** and **3** are also discussed.

Keywords: Bimetallic oxides; Organic–inorganic hybrid materials; Vanadium organophosphonates; Copper–tetrapyridylpyridine components; Oxyfluorovanadates

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 properties, 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 $\{Cu_2(bisterpy)\}^{4+}/V_xO_yF_z^{n-}/\{O_3P(CH_2)_nPO_3\}^{4-}$ 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 $\{Cu_2(bisterpy)\}^{4+}/V_xO_y^{n-}/\{O_3P(CH_2)_nPO_3\}^{4-}$ 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 $\{Cu_2(bisterpy)\}^{4+}/V_xO_y^{n-}$/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 $\{Cu_2(bisterpy)\}^{4+}$, such as the closely related, but more compact, $\{Cu_2(tpyprz)\}^{4+}$ (tpyprz = tetra-4-pyridylpyrazine). Three members of the $\{Cu_2(tpyprz)\}^{4+}/V_xO_yF_z^{n-}/\{O_3P(CH_2)_nPO_3\}^{4-}$ family, whose structures are unrelated to those observed for the $\{Cu_2(bisterpy)\}^{4+}/V_xO_yF_z^{n-}/\{O_3P(CH_2)_nPO_3\}^{4-}$ materials, were isolated: $[\{Cu_2(tpyprz)(H_2O)_2\}V_4FO_8(HO_3PCH_2PO_3)_2]$ (**1**), $[\{Cu_2(tpyprz)(H_2O)_2\}V_4F_6O_6(O_3PCH_2CH_2PO_3)]$ (**2**), and $[Cu_2(tpyprz)\{HO_3P(CH_2)_3PO_3\}][V_2F_2O_5]$ (**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 MΩ in-house using a Barnstead Model 525 Biopure Distilled Water Center. The initial and final pH of the reactions were measured using Hydrion pH sticks.

2.2. Synthesis of $[\{Cu_2(tpyprz)(H_2O)_2\}V_4FO_8(HO_3PCH_2PO_3)_2]$ (1)

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), tpytrz (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 $[\{Cu_2(tpyprz)(H_2O)_2\}V_4F_6O_6\{O_3P(CH_2)_2PO_3\}]$ (2)

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), tpytrz (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 $[\{Cu_2(tpyprz)\}\{HO_3P(CH_2)_3PO_3H\}][V_2F_2O_5]$ (3)

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), tpytrz (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)