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Temperature dependence of the crystal chemistry of the oxovanadium–ethylenediphosphonate/copper(II)-2,2′-bipyridine system. Crystal structures of the two-dimensional $[Cu(bpy)VO_2(O_3PCH_2CH_2PO_3H)]{\bullet}1.5H_2O$ and of the one-dimensional $[Cu(bpy)VO_2(O_3PCH_2CH_2PO_3H)]$

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Abstract

Three different materials of the oxovanadium–ethylenediphosphonate/copper(II)-bipyridine system $[V/O/\{(CH_2)_2(PO_3H_x)_2\}^{(4-x)-}/Cu(II)(bpy)]$ were isolated via hydrothermal synthesis from identical starting solutions with temperatures as the only variable. The phases isolated at 120 and 230 °C are both two-dimensional networks, $[Cu(bpy)VO_2(O_3PCH_2CH_2PO_3H)]{\bullet}1.5H_2O$ (**1**$\bullet 1.5H_2O$) and $[Cu(bpy)VO(O_3PCH_2CH_2PO_3)]$ (**3**), respectively, while the phase produced at the intermediate temperature of 180 °C is the one-dimensional $[Cu(bpy)VO_2(O_3PCH_2CH_2PO_5H)]$ (**2**). Despite the unexpected absence of correlation between temperature and dimensionality, the number of Cu(II) atoms per 1000 Å^3 increases in the order 2.31:2.57:2.62 for **1**:**2**:**3**, as expected.

Keywords: Vanadophosphonates; Organic–inorganic hybrid; Hydrothermal synthesis; Bimetallic oxides

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The contemporary interest in organic/inorganic hybrid materials [1–3] reflects potential applications in areas such as gas storage [4], catalysis [5] and molecular electronics [3]. Metal organophosphonate phases are representative hybrid materials which have been extensively studied with respect to the structural consequences of steric demands of the organic subunit, spacer length modifications and additional functionality [6–8]. Oxovanadium organophosphonate structural chemistry is remarkably rich and includes solid phase materials with 1D, 2D and 3D structures incorporating either single valence V(IV) or V(V) sites or mixed valence V(IV)/V(V) sites [8], as well as molecular species exhibiting unusual structural diversity [9].

In the course of our investigations of the chemistry of the oxovanadium–organodiphosphonate system, we noted that structural determinants included not only the length of the organic spaces, but also the identity of organic cations introduced as charge compensating and space-filling components of the composite material. Furthermore, the chemistry of the cationic component could be elaborated by replacing simple organic charge compensations groups with a transition metal complex cation, allowing exploitation of the coordination preferences of this secondary metal site and the geometric variability possible at the associated ligand center. This building block approach to organic–inorganic materials was exploited in the preparation of three component materials of the type VO/organophosphonate/Cu(II)-ligand where the ligand is 2,2-bipyridine or *o*-phenanthroline [10–12].

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The structural determinants in this bimetallic oxide system included the identity of the organic component of the phosphonate ligand component which introduces steric constraints associated with ligand bulk or tether length in the case of diphosphonates, the coordination preferences of the secondary metal Cu(II), as well as the electronic and steric demands of the organoimine ligand. In addition, it was noted that factors associated with the hydrothermal domain, such as fill volume, pH, stoichiometry and temperature also influence the ultimate product. In particular, the temperature dependence of the structures is expected to be pronounced, since the density of (M–O–M) arrays is expected to increase with temperature. In this regard, it has been recently demonstrated that cobalt succinates exhibit increasing condensation and density at higher synthesis temperature under hydrothermal conditions [13]. These observations encouraged us to reexamine the oxovanadium–ethylenediphosphonate/Cu(II)-2,2′-bipyridine system using identical starting mixtures with temperature as the only variable. Two new phases have been identified $[Cu(bpy)VO_2(O_3PCH_2CH_2PO_3H)]\bullet 1.5H_2O$ (**1**$\bullet 1.5H_2O$) and $[Cu(bpy)VO_2(O_3PCH_2CH_2PO_3H)]$ (**2**). These structures are compared to that of the previously reported $[Cu(bpy)VO(O_3PCH_2CH_2PO_3)]$ (**3**), for which an improved synthesis is reported.

1. Experimental

Reagents were purchased from Aldrich Chemicals and Lancaster Chemicals (ethylenediphosphonic acid) and used without further purification. Syntheses were carried out in 23 ml polytetrafluoroethylene-lined stainless steel containers under autogenous pressure. Water was distilled about 3.0 Ω in-housing using a Barnstead model 525 Biopure distilled water center.

1.1. Synthesis of $[Cu(2,2'\text{-bipyridine})VO_2(O_3PCH_2CH_2PO_3H)]\bullet 1.5(H_2O)]$ (1)

A mixture of $CuSO_4 \cdot 5H_2O$ (0.129 g, 0.52 mmol), ethylenediphosphonic acid (0.136 g, 0.72 mmol), Na_3VO_4 (0.060 g, 0.33 mmol), 2,2′-bipyridine (0.079 g, 0.50 mmol) and H_2O (10.010 g, 556 mmol) was heated for 48 h at 120 °C. The mixture was cooled to room temperature and washed with water and acetone to give light blue crystals in 20% yield. IR (KBr pellet, cm^{-1}): 3503(s), 2916(m), 1685(m), 1654(m), 1636(m), 1566(m), 1495(m), 1314(m), 1069(s), 942(s), 837(m), 770(m), 718(m), 650(m).

1.2. Synthesis of $[Cu(2,2'\text{-bipyridine})VO_2(O_3PCH_2CH_2PO_3H)]$ (2)

A mixture of $CuSO_4 \cdot 5H_2O$ (0.129 g, 0.052 mmol), ethylenediphosphonic acid (0.136 g, 0.72 mmol), Na_3VO_4 (0.060 g, 0.3 mmol), 2,2′-bipyridine (0.079 g, 0.50 mmol) and H_2O (10.160 g, 564 mmol) was heated for 48 h at 180 °C. The mixture was then allowed to cool to room temperature. After extensive washing with water and acetone, turquoise crystals were isolated in 80% yield. IR (KBr pellet, cm^{-1}): 3119(m), 1686(m), 1654(m), 1577(m), 1499(m), 1448(m), 1413(m), 1316(m), 1258(m), 1089(s), 926(s), 860(m), 782(m), 721(m), 652(m).

Table 1
Summary of crystallographic data for the structures of $[Cu(2,2'\text{-bipyridine})VO_2(HO_3PCH_2CH_2PO_3)]\bullet 1.5(H_2O)]$ (**1**$\bullet$**1.5H₂O**) and $[Cu(2,2'\text{-bipyridine})VO_2(HO_3PCH_2CH_2PO_3)]$ (**2**)

	1$\bullet$1.5H$_2$O	**2**
Empirical formula	$C_{12}H_{16}CuN_2O_{9.50}P_2V$	$C_{12}H_{13}CuN_2O_8P_2V$
Fw	516.69	489.66
Space group	$C2/c$	P-1
a (Å)	18.038(1)	7.7137(3)
b (Å)	13.1953(9)	9.0088(3)
c (Å)	15.234(1)	11.6670(4)
α (deg)	90°	83.723(1)°
β (deg)	106.928(1)°	75.661(1)°
γ (deg)	90°	82.876(1)°
V (Å^3)	3468.7(4)	776.82(5)
Z	8	2
D_{calcd} (g cm^{-3})	1.979	2.093
μ (mm^{-1})	2.006	2.226
T (K)	90(2)	90(2)
λ (Å)	0.71073	0.71073
$R1$[a]	0.0312	0.0254
$wR2$[b]	0.0780	0.0687

[a] $R1 = \sum ||F_0| - |F_c|| / \sum |F_0|$.
[b] $wR2 = [\sum w(F_0^2 - F_c^2)^2 / \sum w(F_0^2)^2]^{1/2}$.

1.3. Synthesis of $[Cu(2,2'\text{-bipyridine})VO(O_3PCH_2CH_2PO_3)]$ (3)

A mixture of $CuSO_4 \cdot 5H_2O$ (0.129 g, 0.52 mmol), ethylenediphosphonic acid (0.136 g, 0.72 mmol), Na_3VO_4 (0.060 g, 0.33 mmol), 2,2′-bipyridine (0.079 g, 0.50 mmol) and H_2O (10.010 g, 556 mmol) was heated for 48 h at 230 °C. After cooling to room temperature and washing with water and acetone, light blue crystals of **3** were isolated in quantitative yield.

1.4. X-ray crystallography

Crystallographic data for all compounds were collected with a Brüker P4 diffractometer equipped with a SMART CCD system [14] and using Mo-α radiation ($\lambda = 0.71073$ Å). The data were collected at 90 K and corrected for Lorentz and polarization effects [15]. Absorption corrections were made using SADABS [16]. The structure solutions and refinements were carried out using the SHELXTL [17] crystallographic software package. The structures were solved using direct methods, and all of the nonhydrogen atoms were located from the initial solution. After locating all of the nonhydrogen atoms in each structure, the model was refined against F^2, initially using isotropic then anisotropic thermal