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Hydrothermal synthesis and structural characterization of prototypical organic–inorganic hybrid materials: [{Cu(2,2′-bpy)(H$_2$O)}(VO)(O$_3$PCH$_2$PO$_3$)], [Cu(2,2′-bpy)(VO)(O$_3$PCH$_2$CH$_2$PO$_3$)], and [Cu(2,2′-bpy)(VO)(O$_3$PCH$_2$CH$_2$CH$_2$PO$_3$)]·H$_2$O. Bimetallic phosphonate networks with surface-modifying organic subunits

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Hydrothermal reactions of Cu$_2$O or CuCl$_2$ with Na$_3$VO$_4$, 2,2′-bipyridine and the appropriate organodiphosphonate yielded the bimetallic, two-dimensional phosphonate phases, [{Cu(2,2′-bpy)(H$_2$O)}(VO)(O$_3$PCH$_2$PO$_3$)], [Cu(2,2′-bpy)(VO)(O$_3$PCH$_2$CH$_2$PO$_3$)] and [Cu(2,2′-bpy)(VO)(O$_3$PCH$_2$CH$_2$CH$_2$PO$_3$)]·H$_2$O.

The ability of organic molecules to alter inorganic microstructures offers a powerful method for the synthesis of novel solid state materials.[1] Such organic–inorganic hybrid materials exploit the unique characteristics of organic and inorganic subunits in the complementary design of solid state structures with composite or even new properties. While the structure directing influence of organic cations has been documented in numerous oxide phases such as zeolites,[2] mesoporous materials of the MCM-41 class,[3] transition metal phosphates, phosphonates and oxides,[4–7] the introduction of the organic component as a ligand in a metal–organic subunit of the hybrid material has also been realized.[8–11] Metal organophosphonate phases are prototypical hybrid materials for which structural modification through incorporation of an organic subunit is effected through variations in the steric demands of the organic moiety, the tether length, and/or the presence of additional functional groups.[12] In the specific case of oxovanadium–organodiphosphonate phases, the structural chemistry was profoundly influenced not only by the length of the organic spacer, but also by the introduction of organic cations as charge compensating and space filling entities with multipoint hydrogen bonding interactions to the oxide component.[13] However, the structural consequences of introducing metal–organic subunits as potential structure-directing agents have not been explored for this family of materials. In this communication, we describe preliminary studies of the modification of oxometal–organodiphosphonate phases by metal–organic subunits, thus exploiting both the spatial transmission of structural information by the diphosphonate ligand and the surface modification of the oxide material by a multidentate organonitrogen ligand. The unusual bimetallic, two-dimensional phases [{Cu(2,2′-bpy)(H$_2$O)}(VO)(O$_3$PCH$_2$PO$_3$)] (**1**), [Cu(2,2′-bpy)(VO)(O$_3$PCH$_2$CH$_2$PO$_3$)] (**2**), and [Cu(2,2′-bpy)(VO)(O$_3$PCH$_2$CH$_2$CH$_2$PO$_3$)]·H$_2$O (**3**) represent the prototypical structures of this class of materials.

The hydrothermal reaction of Cu$_2$O, Na$_3$VO$_4$, 2,2′-bipyridine, methylenediphosphonate and H$_2$O in the mole ratio 1.0 : 1.1 : 1.0 : 2.1 : 2000 for 48.5 h at 200 °C yielded dark green rhombs of **1** in 60% yield. The analogous reactions with ethylenediphosphonate or propylenediphosphonate yield **2** or **3** in 45% and 30% yields, respectively.† The infrared spectrum of **1** displayed a strong band at 960 cm^{-1} attributed to ν(V=O) and two strong bands in the 1050–1160 cm^{-1} range assigned to the PO$_3^{2-}$ stretching modes.

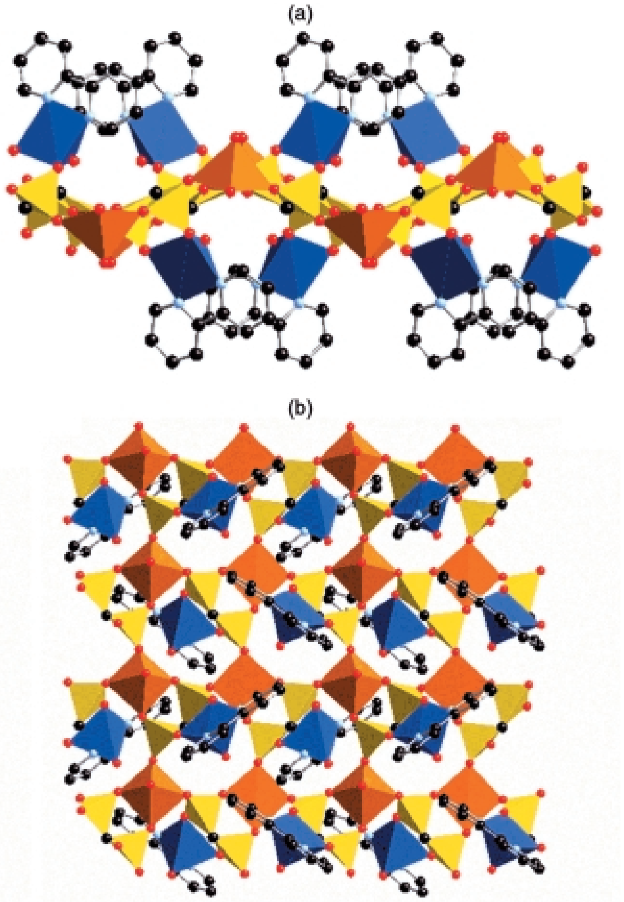

Fig. 1 (a) A view of the structure of [{Cu(2,2′-bpy)(H$_2$O)}(VO)(O$_3$PCH$_2$PO$_3$)] (**1**), parallel to the oxide plane. (b) A polyhedral representation of the layer structure of **1**. Selected bond lengths (Å): Cu–O$_{\text{aqua}}$, 2.216(3); Cu–O$_{\text{phosphonate}}$, 1.933(2), 1.954(3); Cu–N, 2.033(3), 2.216(3); V–O$_t$, 1.593(3); V–O$_{\text{phosphonate}}$, 1.987(5), ave. of 4 V–O bonds. Abbreviations: O$_t$ = terminal oxo-groups.

The structure of [{Cu(2,2′-bpy)(H$_2$O)}(VO)(O$_3$PCH$_2$PO$_3$)] (**1**),‡ shown in Fig. 1, consists of two-dimensional layers constructed from corner-sharing Cu(II) square pyramids, V(V) square pyramids and phosphorus tetrahedra. The coordination sphere of the Cu(II) site is defined by the nitrogen donors of a bipyridine ligand and two oxygen donors of a chelating methylenediphosphonate ligand in the basal plane, and an aqua ligand in the apical position. The basal plane of the vanadium center

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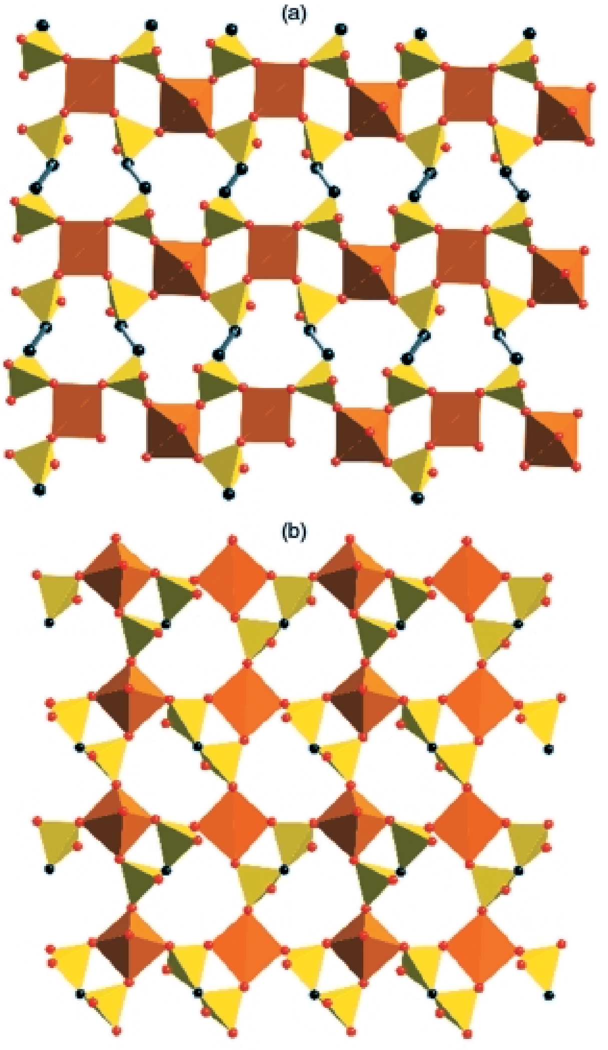

Fig. 2 Polyhedral representations of the (a) $\{(VO)(O_3PCH_2PO_3)\}^{2-}$ and (b) $\{(VO)(O_3PCH_2CH_2PO_3)\}^{2-}$ networks of **1** and **2**, respectively.

consists of two oxygen donors from a chelating methylenediphosphonate ligand and two oxygen donors from each of two monodentate methylenediphosphonate groups; the apical position is occupied by the terminal oxo-group. Each methylenediphosphonate ligand links one copper and three vanadium sites.

The layer structure of **1** may be described as undulating $\{(VO)(O_3PCH_2PO_3)\}^{2-}$ networks with a period of 11.8 Å and an amplitude of 2.8 Å, decorated with $\{Cu(bpy)(H_2O)\}^{2+}$ groups which project into the interlamellar regions. The $\{(VO)(O_3PCH_2PO_3)\}^{2-}$ network, shown in Fig. 2, is constructed from fourteen-membered $\{V_3P_4O_6C\}$ rings linked through corner-sharing interactions into a two-dimensional covalently linked layer. The $\{Cu(bpy)(H_2O)\}^{2+}$ groups are sited above and below the cyclic cavities.

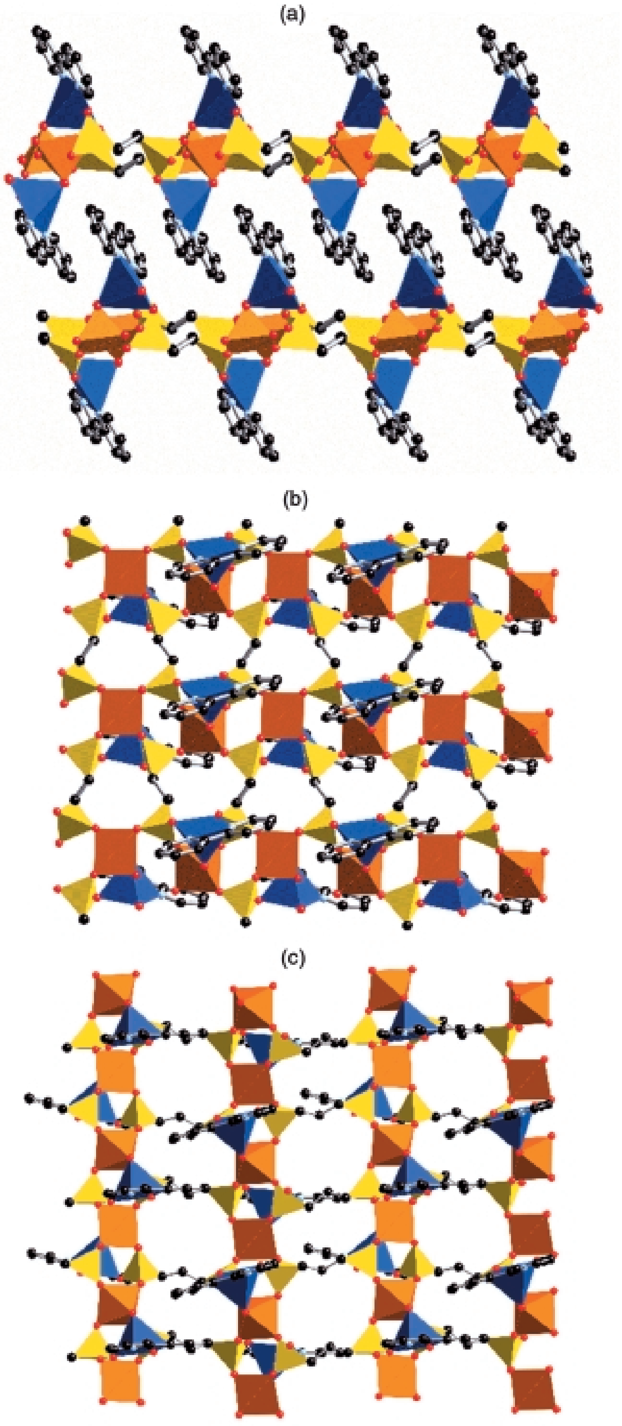

Fig. 3 (a) A view of the structure of [Cu(2,2′-bpy)(VO)($O_3PCH_2CH_2PO_3$)] (**2**), parallel to the oxide plane. (b) A polyhedral representation of the layer structure of **2**, showing the {Cu(2,2′-bpy)(VO)-($O_3PR)_2$} chains, linked through ethylene bridges into a covalent network. Selected bond lengths (Å): Cu–O_b(V), 2.394(2); Cu–$O_{phosphonate}$, 1.919(2), 1.942(2); Cu–N, 2.006(2), 2.030(2); V–O_b(Cu), 1.611(2); V–$O_{phosphonate}$, 1.962(4), ave of 4 V–O bonds. (c) A view of the structure of [Cu(2,2′-bpy)(VO)($O_3PCH_2CH_2CH_2PO_3$)]·H_2O (**3**), normal to the oxide plane. Selected bond lengths (Å), averages: Cu–O_b(V), 2.387(7); Cu–$O_{phosphonate}$, 1.920(8); Cu–N, 2.000(9); V–O_b(Cu), 1.605(7); V–$O_{phosphonate}$, 1.973(8). Abbreviations: O_b = bridging oxo-groups.

As shown in Fig. 3, the structure of **2**‡ consists of a two-dimensional network again constructed from corner-sharing vanadium $\{VO_5\}$ square pyramids, phosphate tetrahedra and copper $\{CuO_3N_2\}$ square pyramids. The vanadium(IV) site is defined by four oxygen donors from each of four phosphonate groups in the basal plane and an apical oxo-group which bridges to the copper(II) center. The copper geometry consists of the nitrogen donors of the bpy ligand and two oxygen donors from each of two phosphonate ligands in the basal plane and the bridging oxo-group in the apical position. The oxo-bridge is asymmetric with a V–O bond distance of 1.611(2) Å and a Cu–O distance of 2.394(2) Å. Each $\{PO_3\}$ terminus of the diphosphonate ligand bridges one copper and two vanadium sites. Consequently, the structure may be described as {Cu(bpy)(VO)($O_3PCH_2)_2$} chains, tethered through the ethylene bridges of the diphosphonate ligands into a two-dimensional covalently linked network. Within the one-dimensional oxide substructure, the common eight-membered cyclic motif $\{V_2P_2O_4\}$ of corner-sharing $\{VO_5\}$ square pyramids and $\{O_3PR\}$ tetrahedra is observed.[6] These rings are linked through the vanadium sites into a chain, which is decorated by the $\{Cu(bpy)\}^{2+}$ moieties, linked to the vanadium oxo-group and the oxygen donors of the diphosphonate ligands not involved in the $\{V_2P_2O_4\}$ ring formation. This results in the additional ring motifs $\{VCuP_2O_4\}$ and $\{VCuPO_3\}$. The connectivity gives rise to a distinctive partitioning of the layer structure of **2** into inorganic chain substructures and tethering organic domains. The $\{Cu(bpy)\}$ subunits project into the interlamellar regions above and below the plane.

The structural consequences of introducing an additional methylene group in **2** are significant. While structure **1** contains vanadium centers with terminal oxo-groups, the oxo-groups in **2** bridge to the copper sites. Consequently, although the copper geometries in both **1** and **2** are square pyramidal $\{CuN_2O_3\}$, one oxygen donor in **1** is provided by an aqua ligand, in contrast to the bridging oxo group in **2**. The $[(VO)\{O_3P(CH_2)_n\text{-}PO_3\}]^{2-}$ networks of **1** and **2**, shown in Fig. 2, are quite distinct, with the former displaying fourteen-membered $[V_3P_4O_6C]$ rings and the latter fourteen-membered $[V_2P_4O_4C_4]$ rings.

While the structure of the $\{(VO)(O_3PCH_2PO_3)\}^{2-}$ network of **1** is quite distinct from other examples of oxovanadium–methylenediphosphonate layered materials,[14,15] the $\{(VO)\text{-}(O_3PCH_2CH_2PO_3)\}^{2-}$ network of **2** is reminiscent of the oxovanadium–phosphonate layer of $[H_3NCH_2CH_2NH_3]\text{-}[(VO)(O_3PCH_2CH_2PO_3)]$.[13] The covalent connectivities of the oxovanadium–phosphonate network structures of **2** and this latter material are identical, and the terminal oxo-group and pendant P–O groups observed in $[H_3NCH_2CH_2NH_3][(VO)(O_3\text{-}PCH_2CH_2PO_3)]$ serve to anchor the $\{Cu(bpy)\}^{2+}$ moiety to the layer structure in **2**.

The structure of the propylenediphosphonate derivative **3**‡ is analogous to that of **2**, as shown in Fig. 3c. Compound **3** shares with **2** the common structural motifs of $\{Cu(bpy)\text{-}(VO)(O_3PCH_{2-})_2\}$ chains and cyclic $\{V_2P_2O_4\}$ rings within the chains. The propylene groups bridge chains into a two-dimensional network. However, the consequences of tether extension are apparent in the relative orientations of the $\{Cu(bpy)\}^{2+}$ moieties in **2** and **3**. In contrast to compound **2** in which the $\{Cu(bpy)\}^{2+}$ units link to phosphonate oxygen donors on the same edge of the oxovanadium phosphonate chain and consequently orient the bpy plane approximately parallel to the V–V vectors of the chain, the $\{Cu(bpy)\}^{2+}$ groups of **3** coordinate oxygen donors from phosphonate groups on opposite edges of the chain, with a concomitant orientation of the bpy plane perpendicular to the V–V vectors of the chain. It would appear that chain lengthening in **3** relieves the steric strain which would result from the perpendicular orientation of bpy units in a shorter tether system.

The compounds of this study illustrate the synergistic influences of diphosphonate tether lengths and the metal–organic subunit on the structures of hybrid materials. As noted previously,[13] the organic linker of the diphosphonate acts as a spacer between phosphate and oxovanadium polyhedra, consequently influencing the dimensionality of the hybrid phase. This characteristic is manifested in the structures of $[H_2N(CH_2CH_2)_2NH_2][(VO)(O_3PCH_2PO_3)]$, $[H_3N(CH_2)_2NH_3]\text{-}[(VO)\{O_3P(CH_2)_2PO_3\}]$, and $[H_3N(CH_2)_2NH_3][(VO)_4(OH)_2\text{-}(H_2O)_2\{O_3P(CH_2)_3PO_3\}_2]$ where the spacer length correlates with the dimensionality of the phase: 1-D, 2-D and 3-D, respectively. This trend reflects in part the tendency of V/P/O compositions to form two-dimensional networks. Short tether lengths prevent this segregation of the structure into discrete V/P/O inorganic layers, separated by organic spacers. Consequently, the 3-D or "pillared" layer structure can only be achieved in the propylene derivative $[H_3N(CH_2)_2NH_3]\text{-}[(VO)_4(OH)_2(H_2O)_2\{O_3P(CH_2)_3PO_3\}_2]$. In this light, the structural role of the metal–organic subunit $\{Cu(bpy)\}^{2+}$ may be appreciated as that of a covalent anchor to the oxovanadium–diphosphonate substructure, serving to "passivate" the oxide surface and prevent extension of the V/P/O skeleton in two dimensions. In contrast to "naked" oxovanadium organophosphonate phases which commonly exhibit two-dimensional V/P/O networks, the V/P/O substructures of **2** and **3** consist of chains, linked through the organic spacers of the diphosphonate. However, in structure **1**, the $\{Cu(bpy)\}^{2+}$ subunit bonds to a chelating $(O_3PCH_2PO_3)^{4-}$ ligand, thus precluding the in chain bis-bidentate coordination mode favored by the compact methylenediphosphonate ligand in forming oxovanadium–phosphonate chain structures. Consequently, the structural roles adopted by the metal–organic subunit and the diphosphonate geometry display a synergistic interaction.

It is also noteworthy that the metallorganic subunit exhibits the "4+1" coordination geometry common to the Jahn–Teller distorted Cu(II) site. Variations in the identity of this metal site will lead to coordination preferences necessitating structural reorganization of the bimetallic composite material. We are now developing families of oxovanadium diphosphonates incorporating Ni(II), which favors regular six coordination, and Zu(II), which exhibits four, five or six coordination, as the secondary metal sites. Similarly, systematic variations in ligand denticity, steric and electronic requirements and the hydrothermal reaction conditions are required if predictability and the control offered by supramolecular architecture[16,17] are to be achieved for this strategy for the design of solid state materials.

Acknowledgements

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Notes and references

† Reactions were carried out in Teflon-lined Parr acid digestion bombs at *ca.* 40% fill volume. Reaction conditions summary: **1,** Cu_2O (0.040 g, 0.28 mmol), Na_3VO_4 (0.055 g, 0.30 mmol) 2,2′ bipyridine (0.045 g, 0.29 mmol), methylenediphosphonate (0.100 g, 0.58 mmol), H_2O (10.2 ml, 563 mmol). **2**, Cu_2O (0.071 g, 0.50 mmol), Na_3VO_4 (0.085 g, 0.46 mmol), 2,2-bpy (0.090 g, 0.58 mmol), ethylenediphosphonate (0.192 g, 1.01 mmol), H_2O (10.0 ml, 557 mmol). **3**, $CuCl_2$ (0.120 g, 0.70 mmol), Na_3VO_4 (0.083 g, 0.45 mmol) 2,2-bpy (0.067 g, 0.43 mmol) propylenediphosphonate (0.060 g, 0.30 mmol), H_2O (10.00 ml, 557 mmol). Satisfactory C, H, N analyses were obtained in all cases.

‡ Crystal data: **1**, $C_{11}H_{10}CuN_2O_8P_2V$ (M, 474.63): orthorhombic $Pca2_1$, $a = 11.616(2)$, $b = 10.755(2)$, $c = 12.300(3)$ Å, $V = 1536.6(6)$ Å^3, $T = 90(2)$ K, $Z = 4$, μ(Mo-Kα) = 22.47 cm^{-1}, $R1 = 0.0418$; 3653 reflections, $R(\text{int}) = 0.0441$. **2**, $C_{12}H_{12}N_2O_7P_2CuV$ ($M = 945.31$): monoclinic $P2_1/n$, $a = 8.2003(3)$, $b = 9.4047(4)$, $c = 19.9483(7)$ Å, $\beta = 96.603(1)°$, $V = 1528.2(1)$ Å^3, $T = 293(2)$ K, $Z = 2$, μ(Mo-Kα) = 22.54 cm^{-1}, $R1 = 0.0266$; 3685 reflections, $R(\text{int}) = 0.0300$. **3**, $C_{13}H_{16}N_2O_8P_2CuV$ ($M = 1021.36$): monoclinic, $P2_1/c$, $a = 9.9137(9)$, $b = 17.648(1)$, $c = 20.876(1)$ Å, $\beta = 103.167(2)°$, $V = 3562.5(6)$ Å^3, $T = 293(2)$ K, $Z = 4$, μ(Mo-Kα) = 19.48 cm^{-1}, $R1 = 0.0692$, 8472 reflections; $R(\text{int}) = 0.0583$. CCDC reference number 186/1956.

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