

A two-dimensional organic–inorganic material constructed from copper-dipyridylamine and vanadate chains: $[\text{Cu}(\text{dpa})\text{VO}_3]^\dagger$

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The hydrothermal reaction of a mixture of CuCl_2 , NaVO_3 , 4,4'-dipyridylamine (dpa) and Et_4NOH in water yields $[\text{Cu}(\text{dpa})\text{VO}_3]$, a material constructed from one-dimensional $\{\text{VO}_2\text{O}_{2/2}\}_n^{2-}$ chains and $\{\text{Cu}(\text{dpa})\}_n^{2+}$ chains linked into a two-dimensional framework.

The inorganic oxides are characterized by diverse physical properties, resulting in applications to areas as diverse as heavy construction and microelectronics.¹ The widespread interest in inorganic oxide/organic hybrid materials reflects the potential exploitation of these phases for tailoring the structures and properties of oxides. The dramatic influence of organic components on oxide structures has been demonstrated for materials as diverse as biomineralized systems,² zeolites,³ mesoporous compounds of the MCM-41 class,⁴ organically templated oxometal phosphates and phosphonates,^{5,6} and molybdenum oxides.⁷

Layered inorganic oxides constitute a diverse subclass of the oxides and include clays, layered double hydroxides,⁸ and transition metal phosphates and phosphonates.^{9,10} As an extension of our investigations of organically templated metal oxides,⁷ we recently described a new class of materials which contain amine-templated transition or post-transition metal cations situated between or decorating the surface of vanadium oxide layers, the VOXI class of materials.^{11,12} In elaborating this chemistry, the role of polymeric cations constructed from geometrically constrained organonitrogen ligands bridging first row transition metal centers on the structures of vanadium oxides has been addressed. The versatility of such polymeric coordination complex cations in providing one-, two-, or three-dimensional substructures suggested that these structural motifs could be exploited as scaffolding for directing the architecture of the vanadium oxide anion component. This expectation has been realized in the preparation of $[\text{Cu}(\text{dpa})\text{VO}_3]$ (**1**), a two-dimensional material composed of linked $\{\text{Cu}(\text{dpa})\}_n^{2+}$ and $\{\text{VO}_2\text{O}_{2/2}\}_n^{2-}$ one-dimensional chains.

Compound **1** is formed as orange needles in 25% yield[‡] in the hydrothermal reaction of CuCl_2 , NaVO_3 , 4,4'-dipyridylamine, Et_4NOH , and H_2O in the mole ratio 1:2:2:1:1500 at 160 °C for 72 h. Hydrothermal techniques are now well established for the preparation of materials from relatively insoluble and unreactive precursors. Advantages include enhanced rates of solvent extraction of solids and crystal growth from solution and the ability to overcome differential solubilities of organic and inorganic components. The judicious choice of reaction conditions and precursors 'directs' the self-assembly of metastable phases which are not accessible by other synthetic routes.

The infrared spectrum of **1** exhibits a strong band at 910 cm^{-1} associated with $\nu(\text{V}=\text{O})$ and a series of bands in the 1050–1450 cm^{-1} range attributed to the ligand. Thermogravimetric analysis exhibits a weight loss of ca. 50% in the range 350–420 °C corresponding to loss of the ligand.

As shown in Fig. 1, the structure of **1**§ consists of a two-dimensional covalent network constructed from the linking of

$\{\text{Cu}(\text{dpa})\}_n^{2+}$ and $\{\text{VO}_2\text{O}_{2/2}\}_n^{2-}$ chains. The anionic component consists of a buckled chain of corner-sharing $\{\text{VO}_4\}$ tetrahedra. Three distinct $\{\text{Cu}(\text{dpa})\}_n^{2+}$ chain types provide charge balance and serve to decorate the periphery of the vanadate chains or to bridge the chains into the network structure.

The first polymeric cation chain type (A), shown in Fig. 2, runs parallel to the vanadate chains with the Cu(I) sites bonded to a vanadate oxygen at every fifth vanadium site of the anionic chain, forming a ladderlike double chain motif with the side rails provided by the $\{\text{V}-\text{O}-\text{V}-\}$ and $\{\text{Cu}-\text{dpa}-\text{Cu}-\}$ chains and the rungs by the $\{\text{Cu}-\text{O}-\text{V}-\}$ linkages. This architecture also results in an unusual twenty-two membered ring motif of approximate dimensions 11.5×3.3 Å. The copper site exhibits $\{\text{CuN}_2\text{O}\}$ distorted trigonal planar geometry.

These mixed metal double chains are interconnected into a network structure through parallel $\{\text{Cu}(\text{dpa})\}_n^{2+}$ chains running at 73° to the axes of the vanadate chains. There are two types of these parallel chains. The first (B) consists of pairs of adjacent $\{\text{Cu}(\text{dpa})\}_n^{2+}$ chains which exhibit tetrahedral $\{\text{CuN}_2\text{O}_2\}$ sites. These cationic chains are orientated with respect to the vanadate

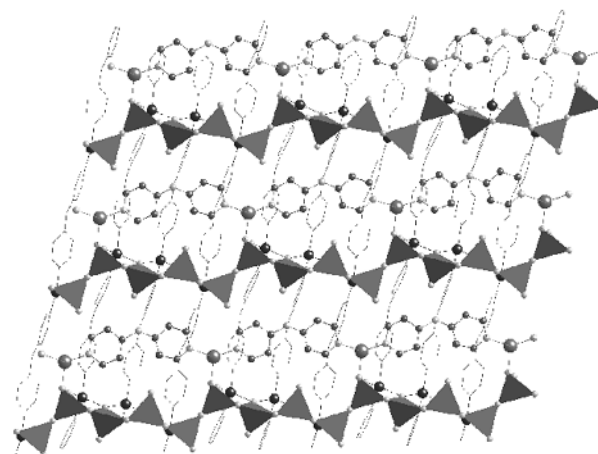


Fig. 1 A view of a single layer of $[\text{Cu}(\text{dpa})\text{VO}_3]$ (**1**) parallel to the crystallographic a axis, showing the crisscross network motif. The vanadium sites are illustrated in polyhedral representation. Copper sites of the (A) chains are grey spheres while the copper atoms of the (B) double chains are black spheres. The copper centers of the (C) chains are masked by the vanadate tetrahedra. Selected bond lengths (Å): chain (A): Cu1–O2, 2.106(4); Cu1–N21, 1.925(5); Cu1–N23, 1.933(5); chain (B): Cu2–N11, 1.931(5); Cu2–N13, 1.936(5); Cu2–O4, 2.122(4); Cu2–O9, 2.357(4); Cu3–N3, 1.975(5); Cu3–N1, 1.988; Cu3–O10, 2.204(4); Cu3–O9, 2.223; chain (C): Cu4–N33, 1.906(5); Cu4–N31, 1.927(5); Cu4–O11, 2.054(4).

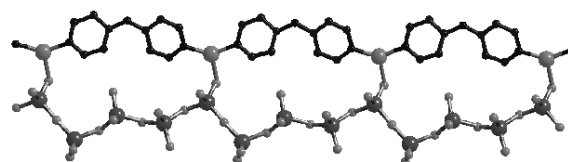


Fig. 2 A view of the double chain formed by fused $\{\text{VO}_3\}_n^{2-}$ and parallel $\{\text{Cu}(\text{dpa})\}_n^{2+}$ chains.

[‡] Electronic Supplementary Information (ESI): Colour versions of Figs. 1 and 4, see: <http://www.rsc.org/suppdata/cc/1999/1669/>

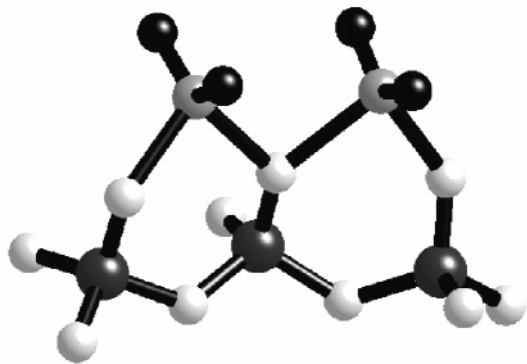


Fig. 3 The $\{V_3Cu_2O_{12}N_4\}$ cluster formed by the interaction of the vanadate chain and the $\{Cu(dpa)_n\}^{n+}$ double chains in the crisscross network.

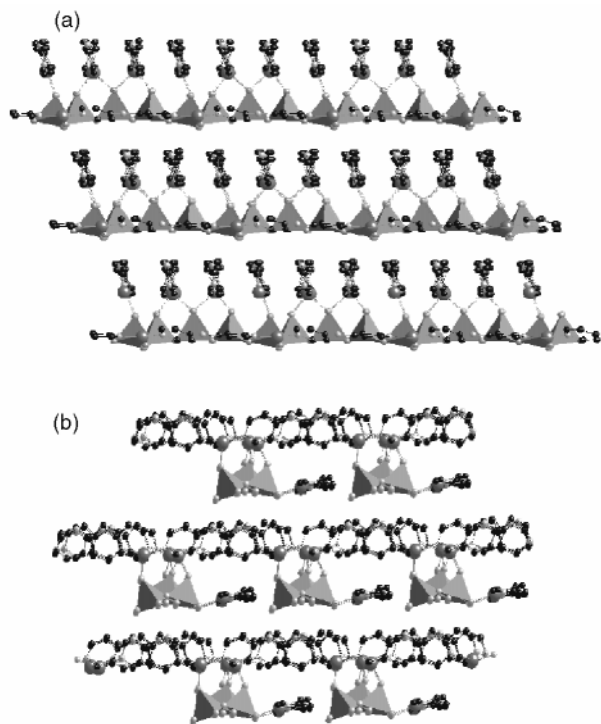


Fig. 4 (a) A view of the structure parallel to the (B) type double chains, showing the alternation of (B) double chains and (C) chains. (b) A view of the stacking of layers parallel to the crystallographic c axis, showing the location of (A) chains within the slots formed by vanadate chains and the (B) and (C) chains of neighboring layers. The amine of the (A) chain exhibits hydrogen bonding to an oxo group of the adjacent intralamellar vanadium oxide chain: $N32 \cdots O7$, 2.71 Å. The amines associated with the (B) and (C) chains exhibit interlamellar hydrogen bonding to the adjacent layer: $N2 \cdots O5$, 2.89 Å; $N12 \cdots O3$, 2.85 Å; $N22 \cdots O1$, 2.76 Å.

chains so as to bridge Cu sites on adjacent chains through the oxo group of one vanadate tetrahedron of the anionic chain. The consequence of this arrangement of submotifs is the unusual pentanuclear $\{Cu_2V_3\}$ oxo-bridged cluster shown in Fig. 3.

The buckling of vanadate chain results in a translation by one polyhedral edge length of $\{Cu(dpa)_n\}^{n+}$ chains adjacent to the oxo-bridged pairs, as shown in Figs. 1 and 4. When viewed parallel to this third chain motif (C), the alternation of $\{Cu(dpa)_n\}^{n+}$ paired chains and single chains is apparent. The Cu site of this chain type exhibits distorted $\{CuN_2O\}$ trigonal planar geometry.

The interconnection of these one-dimensional substructures results in the crisscross network pattern shown in Fig. 1. When viewed parallel to the vanadate chain, as in Fig. 4(b), the distinctiveness of the $\{Cu(dpa)_n\}^{n+}$ chain types is highlighted, as well as the unusual architecture of the layer repeat pattern. The $\{Cu(dpa)_n\}^{n+}$ chains designated (A) occupy cavities bordered by adjacent $\{VO_3\}_n^{n-}$ parallel chains, the (B) and (C) type $\{Cu(dpa)_n\}^{n+}$ chains of the same layer and those of an adjacent layer. The folding of the (A) chains into the intralamellar slots results in strong hydrogen bonding between the amine group and the oxo groups of the adjacent vanadate chain.

The preparation of compound **1** emphasizes the power of hydrothermal techniques in the isolation of organic–inorganic oxide materials. Furthermore, the structure of the resulting hybrid solid illustrates the observation that both metal and ligand have significant structure-directing influences on the vanadium oxide substructure which adapts to maximize covalent and noncovalent interactions with the coordination complex cation. In this respect, it is noteworthy that previously described examples of vanadium oxide–inorganic complex hybrid materials which exploited mononuclear coordination complex subunits exhibit two-dimensional vanadate substructures exclusively. In contrast, the coordination complex polymer of **1** directs the vanadate substructure into a one-dimensional type. Thus, while the structure-directing role of the polymeric cation is evident, the chemistry of the organic–inorganic interface is complex and remains largely unmapped, rendering predictability of structures a goal yet to be achieved.

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Notes and references

‡ The crystals coprecipitate with an amorphous powder. Compound **1** is readily separated from the powder by exploiting its greater density in water. Satisfactory elementary analyses were obtained.

§ *Crystal data*: $C_{40}H_{36}Cu_4O_{12}N_{12}V_4$, $M_w = 1334.73$, triclinic $P1$, $a = 11.0353(3)$, $b = 11.2938(3)$, $c = 11.4311(4)$ Å, $\alpha = 81.612(1)$, $\beta = 65.755(1)$, $\gamma = 61.907(1)^\circ$, $V = 1143.96(6)$ Å³, $Z = 1$, $D_{\text{calc}} = 1.937$ g cm⁻³, $T = 160$ K; structure solution and refinement based on 6010 reflections converged at $R1 = 0.0434$, $wR2 = 0.0828$. CCDC 182/1335.

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