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A three-dimensional organic–inorganic composite material constructed from copper–triazolate networks linked through vanadium oxide chains: $[\{Cu_3(trz)_2\}V_4O_{12}]$

Pamela J. Hagrman,[a] **Craig Bridges,**[b] **John E. Greedan**[b] **and Jon Zubieta** *[a]

[a] *Department of Chemistry, Syracuse University, Syracuse, New York 13244, USA*
[b] *Department of Chemistry, McMaster University, 1280 Main Street West, Hamilton, Ontario, Canada L8S 4M1*

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The hydrothermal reaction of a mixture of V_2O_5, 1,2,4-triazole (trz), $Cu(NO_3)_2\cdot2.5H_2O$ and H_2O yields $[\{Cu_3(trz)_2\}V_4O_{12}]$, a material constructed from one-dimensional $\{V_4O_{12}\}_n^{4n-}$ chains linked to undulating $\{Cu_3(trz)_2\}_n^{4n+}$ networks.

The significant contemporary interest in inorganic oxide materials reflects their diverse physical properties, with applications to catalysis, sorption, clathration, electrical conductivity, magnetism and photochemistry.[1,2] Despite such widespread utility, the ability to modify the structures of such materials or to design new materials remains rather primitive.[3] One approach to altering the microstructures of inorganic oxides mimics nature's exploitation of organic manipulators as a component of a composite material.[4] Inspired by the structural role of organic molecules in the important families of materials such as zeolites,[5] mesoporous oxides of the MCM-41 class,[6] biomineralized materials[7] and oxometal phosphates,[8] we have recently begun to elaborate on the chemistry of organically templated molybdenum oxides.[9–14] As part of these studies, the role of polymeric cations constructed from geometrically constrained organonitrogen ligands bridging first row transition metal centers on the structures of entrained molybdenum oxide anions has been investigated.[15] While one-dimensional coordination cation polymers were common structural motifs, higher dimensionality cation substructures were only recently observed, requiring the use of a tripodal 1,2,4-triazolate (trz) ligand to expedite the formation of the three-dimensional $\{Cu_2(trz)_2(H_2O)_2\}_n^{2n+}$ cationic framework of $[\{Cu_2(trz)_2(H_2O)_2\}Mo_4O_{13}]$.[16]

This Cu–triazolate cationic framework appeared to provide a matrix for the entraining of a unique molybdenum oxide chain. As a natural extension of the structural chemistry of such composite oxide materials, the chemistry of the Cu–triazolate cationic subunit with vanadium oxides was initiated, on the naive assumption that one-dimensional, rather than the more common two-dimensional,[17] oxide substructures would be encapsulated within the cationic framework. However, it is apparent that the oxide subunit behaves not as a "ship-in-the-bottle" but rather as a synergistically active component of the composite, such that the product $[\{Cu_3(trz)_2\}V_4O_{12}]$ **1** consists of one-dimensional vanadate chains entrained within an unexpected Cu–triazolate two-dimensional network.

Compound **1** is formed in 20% yield as green plates in the hydrothermal reaction at 200 °C for 35 h of V_2O_5, 1,2,4-triazole, $Cu(NO_3)_2\cdot2.5H_2O$ and H_2O, in the mole ratio 1.0 : 1.2 : 0.95 : 2000 and adjusted to pH 5.5 by the addition of $(C_2H_5)_4NOH$.† The infrared spectrum of **1** exhibits a strong band at 920 cm^{-1} ascribed to ν(V=O) and a series of bands in the 1200–1490 cm^{-1} range associated with the ligand. Thermogravimetric analysis of **1** exhibits a weight loss of *ca.* 20% in the range 290–340 °C, corresponding to the loss of the ligand and yielding an amorphous light blue material.

As shown in Fig. 1, the structure of **1** ‡ consists of a three-dimensional covalent framework constructed from two-dimensional $\{Cu_3(trz)_2\}_n^{4n+}$ networks linked through one-dimensional $\{VO_3\}_n^{n-}$ chains. The cationic network when viewed parallel to [001] displays a pronounced sinusoidal ruffling with an amplitude of about 4.75 Å and a period of 8.87 Å. The layers are composed of Cu(II) sites diagonally coordinated through triazolate ligands, each of which bridges three copper sites. Within each layer, there are large rhombic rings, $\{Cu_6(trz)_6\}$, which form the distinctive lattice work motif with each ring sharing an edge with six adjacent rings, shown in Fig. 2a.

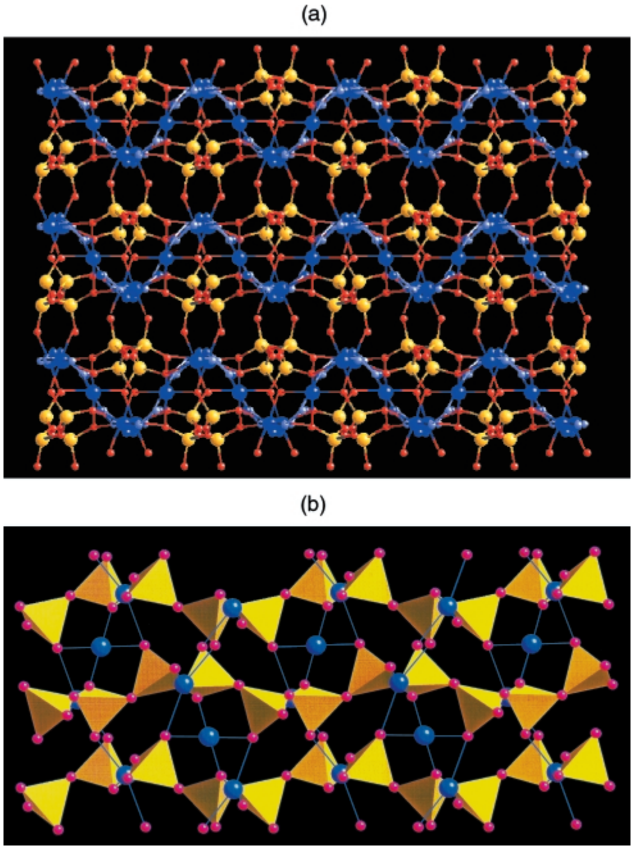

Fig. 1 (a) A view parallel to the [001] direction showing the structure of **1**. The $\{Cu_3(trz)_2\}_n^{4n+}$ layers are viewed edge-on and are represented by the blue spheres giving rise to the distinctive sinusoidal wave; the carbon and nitrogen atoms of the triazolate ligands are shown as smaller dark blue and light blue spheres, respectively. The view is parallel to the $\{VO_3\}_n^{n-}$ chains which are shown as large yellow spheres for the V(V) sites and red spheres for the oxygen atoms. (b) A view parallel to the crystallographic *a*-axis of the bimetallic oxide $\{Cu_3V_4O_{12}\}_n^{2n+}$ substructure. The tiazolate ligands have been omitted in order to highlight the three-dimensional metal oxide substructure. The vanadium sites are rendered as yellow tetrahedra and the Cu(II) sites as large dark blue spheres.

The $\{VO_3\}_n^{n-}$ linear chains nestle in the troughs formed by the ruffling of the layers. The copper sites of the network are covalently bound to the terminal oxo-group of the vanadate

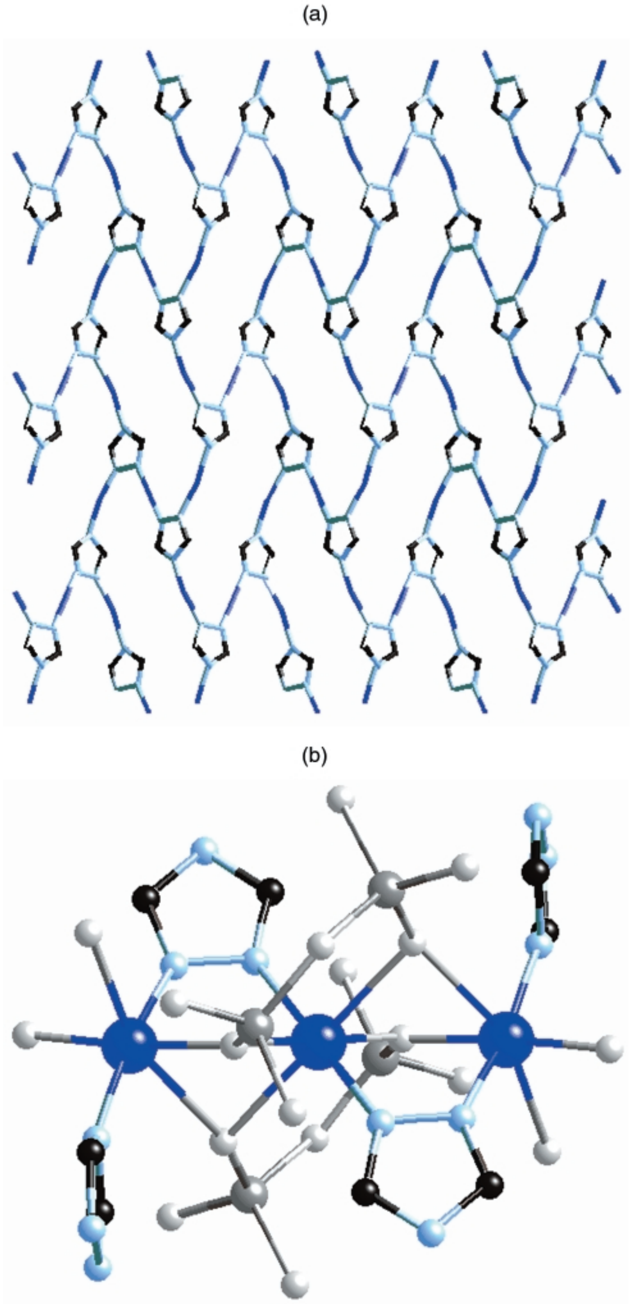

Fig. 2 (a) A stick representation of the two-dimensional network substructure adopted by the $\{Cu_3(trz)_2\}_n^{4n+}$ polymeric cation. (b) The trinuclear motif from which the network is constructed, showing also the coordination to the oxo-groups of the $\{V_2O_7\}^{4-}$ fragments of the vanadate chains. Large blue spheres represent the Cu sites, while large and small grey spheres are used to render the V and O atoms, respectively. Selected bond lengths (Å): central copper Cu1–N2 1.945(3)(×2), Cu1–O3 2.018(2)(×2), Cu1–O5 1.961(3)(×2); outer copper Cu2–N1 1.966(3), Cu2–N3 1.973(3), Cu2–O5 1.961(3), Cu2–O3 2.031, Cu2–O4 2.427(3), Cu2–O6 2.708(3).

chains so as to give distorted octahedral 4+2 $\{CuN_2O_4\}$ geometry at each copper site, as illustrated in Fig. 2b. This connectivity pattern results in oxo- and triazolato-bridged trinuclear Cu(II) units, each of which bridges through triazolate ligands to four adjacent trinuclear units in forming the two-dimensional network. The Cu(II) sites of this trinuclear unit may also be described as bridged by two $\{V_2O_7\}^{4-}$ fragments to form a bimetallic heptanuclear cluster motif. The folding of the copper–triazolate sheet is a consequence of the relative orientations of the triazolate ligands, which alternate in pairs with parallel and perpendicular ring planes. The vanadate chains which occupy the folds of the copper–triazolate layers consist of corner-sharing vanadium tetrahedra, shown in Fig. 1b. Each chain serves to link two adjacent copper–triazolate networks to produce the three-dimensional covalent framework of **1**.

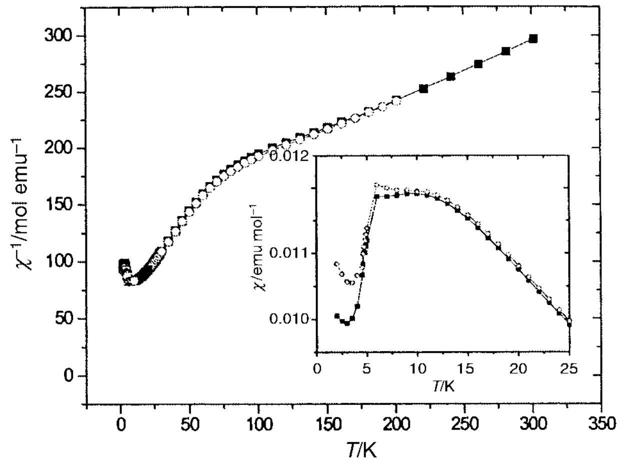

Fig. 3 Zero-field-cooled (ZFC) and field-cooled (FC) magnetic susceptibility data for **1**. The filled squares are the ZFC susceptibility data, and the empty squares are the FC susceptibility data. The solid lines are guides to the eye only.

Compound **1** exhibits complicated magnetic behavior. The shape of the susceptibility curve shown in Fig. 3 is qualitatively similar to that expected for an isolated linear trinuclear cluster, and the copper(II) geometries of the cluster are similar to those of trinuclear copper(II) compounds which have been modeled successfully.[18] However, attempts to fit the susceptibility data for **1** to the non-interacting $S = 1/2$ trimer model were unsuccessful except over narrow temperature ranges and with unrealistic fitting constants. This observation suggests that intertrimer interactions cannot be neglected for **1**. It is also noteworthy that the susceptibility exhibits a sharp drop below 6 K and an FC-ZFC divergence, suggesting long-range antiferromagnetic ordering.

It is instructive to compare the structure of **1** to that of the single other example of copper–triazolate templated metal oxide, $[\{Cu_2(trz)_2(H_2O)_2\}Mo_4O_{13}]$.[16] In contrast to the two-dimensional cationic motif adopted by **1**, the copper–triazolate substructure of $[\{Cu_2(trz)_2(H_2O)_2\}Mo_4O_{13}]$ consists of a three-dimensional framework, through which undulating molybdate chains are threaded. This observation belies the naive "ship-in-the-bottle" construct, wherein the engineered metal–triazolate substructure provides a rigid matrix for the isolation of the metal oxide motif, but rather suggests a synergism between the oxide and cationic coordination complex polymer at the organic–inorganic interface. While the approach of introducing the appropriate metal cation and ligand to accomplish the self-assembly of a polymeric cationic substructure has allowed a more or less predictable approach to the isolation of low dimensional oxide subunits, absolute synthetic control in the sense of crystal engineering remains elusive. Such composite materials are metastable phases, crystallizing under non-equilibrium conditions from a complex hydrothermal domain, an inherent dynamism which contributes to the structural complexity. We are currently exploring the use of preformed cationic networks and frameworks and of oxide clusters and the exploitation of non-hydrothermal conditions as synthetic approaches.

Acknowledgements

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Notes and references

† The other product is an amorphous gray powder. Calc. for $C_4H_4N_6O_{12}V_4Cu_3$: C, 6.64; H, 0.55; N, 11.6. Found: C, 6.26; H, 0.71; N, 11.4%.

‡ Crystal data for $C_4H_4N_6O_{12}V_4Cu_3$: $M = 722.51$, monoclinic, $P2_1/n$, $a = 8.9216(3)$, $b = 8.8643(3)$, $c = 11.4100(4)$ Å, $\beta = 111.799(1)°$, $V = 837.82(5)$ Å^3, $Z = 2$, $D_c = 2.864$ g cm^{-3}, $\mu = 5.943$ mm^{-1}, $T = 293(2)$ K; structure solution and refinement based on 1967 reflections converged at $R1 = 0.0463$, $wR2 = 0.1046$. CCDC reference number 186/1587.

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