Inorg. Chem. **2003**, *42*, 4250–4252

Inorganic Chemistry
Communication

Synthesis and Properties of $V_6O_{16}Cu(C_4H_4N_2)_2{\cdot}(H_2O)_{0.22(1)}$: Charge Density Matching of a Metal-Segregated Layer Structure

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Received March 11, 2003

A metal-segregated layered compound, containing square nets of $Cu(pyz)_2^{2+}$ and buckled $V_6O_{16}^{2-}$ layers, has been synthesized using hydrothermal techniques to have the composition $V_6O_{16}Cu(C_4H_4N_2)_2{\cdot}(H_2O)_{0.22(1)}$ ($C_4H_4N_2$ = pyrazine, pyz). The Cu(II) square nets are nearly regular and undergo an antiferromagnetic transition at 8 K. In contrast to the plethora of recently synthesized metal–oxide clusters, chains, and networks in the VO_x/M/L (M = late transition element; L = organonitrogen ligand) system, this compound is a relatively rare example that contains two different metals distributed into distinct layers. An application of charge density matching to form layered structures is postulated.

Many recent papers and reviews have highlighted the abundance of rich and subtle chemistry found in the hydrothermal synthesis of polyoxovanadate/metal−ligand compounds.[1] Demonstrations of the great flexibility of polyoxovanadates to adopt a wide range of different cluster, chain, and network frameworks have been made, which illustrate the ability of vanadium to adopt varied coordination environments (octahedral, square pyramidal, tetrahedral) and oxidation states (5+ and 4+). Examples include the cluster species $\{V_4O_{12}\}^{4-}$,[2] $\{V_{10}O_{28}\}^{6-}$,[3] the chain species $\{V_2O_6\}^{2-}$,[4] $\{V_4O_{12}\}^{4-}$,[5] and the layered species $\{V_{12}O_{32}\}^{2-}$,[6] and $\{V_6O_{17}\}^{2-}$.[7] As has been stated previously,[1] the diversity of polyoxovanadate species makes an accurate prediction of their structures an extremely daunting task. However, the number of accessible structures (>50 and growing) and vanadium species proves a fertile testing ground for examining synthesis−structure−property relationships. One important question is how to additively combine substructures, such as layers, of different metal−oxides to generate a composite that possesses a combination of their individual properties, such as catalytic, optical, or magnetic. Our synthetic efforts to combine copper and vanadium oxide layers have uncovered the unexpected and new compound $V_6O_{16}Cu(pyz)_2{\cdot}(H_2O)_{0.22(1)}$, displaying a segregated metal distribution into layers.

The title compound was synthesized via typical hydrothermal procedures[8] and was characterized by single-crystal X-ray diffraction methods,[9] infrared spectroscopy,[10] and magnetic susceptibility measurements to have the structure shown in Figure 1. The compound contains alternating layers of $Cu(pyz)_2^{2+}$ and $V_6O_{16}^{2-}$ chemical species, blue and red polyhedra, respectively. The buckled $V_6O_{16}^{2-}$ layers are composed of three symmetry-unique vanadium polyhedra. V2 and V3 display what has previously been described[1c,11] as a “3 + 2” trigonal bipyramidal geometry, each with two

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[8] After single-crystal identification of the $V_6O_{16}Cu(pyz)_2{\cdot}(H_2O)_{0.22(1)}$ compound, the best synthetic conditions were found by adding 7.88×10^{-2} g (3.26×10^{-4} mol) of $Cu(NO_3)_2$, 1.78×10^{-1} g (9.79×10^{-4} mol) of V_2O_5, 5.23×10^{-2} g (6.53×10^{-4} mol) of pyrazine, 1.62×10^{-2} g (3.26×10^{-4} mol) of 49% HNO_3, and 1.17 g (6.53×10^{-2} mol) of H_2O to an FEP Teflon pouch. The pouch (3 in. × 3 in.) was heat sealed, placed inside a 150 mL Teflon-lined reaction vessel, and $\sim{}^1/_3$ backfilled with H_2O before closing. The bomb was heated to 115 °C for 24 h and slowly cooled to room temperature at 6 °C/h. Transparent dark green blocks were recovered by filtration in ∼45% yield based on Cu.

[9] A single-crystal X-ray analysis was performed on an Enraf-Nonius CAD4-MACH diffractometer. Crystal data for $V_6O_{16}Cu(pyz)_2{\cdot}(H_2O)_{0.22(1)}$: monoclinic, space group $C2/c$ (No. 14) with $a = 22.121(6)$ Å, $b = 9.309(2)$ Å, $c = 10.014(3)$ Å, $V = 1899.6(8)$ Å^3, and $Z = 4$ at 221 K. Final anisotropic structure refinement on F^2 gave R_f/R_w (all data) = 0.045/0.044 and GOF = 1.50. All hydrogen atoms were allowed to ride on the parent carbon or oxygen atoms. To verify the presence of H_2O in the compound, IR data were taken and show a relatively weak O−H signal at 3419 cm^{-1}, as expected for the very large ratio of V−O to O−H bonds.

[10] IR (KBr, cm^{-1}): 3419w, 3101w, 3050w, 1485w, 1416m, 1229m, 1161s, 1115s, 1070s, 968s, 926m, 891w, 813m, 719m, 568s, 456m.

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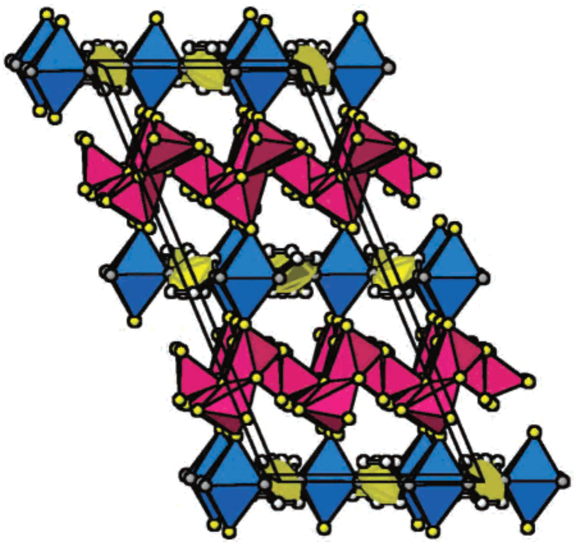

Figure 1. A polyhedral drawing of the unit cell of $V_6O_{16}Cu(pyz)_2\cdot(H_2O)_{0.22(1)}$. The buckled $V_6O_{16}^{2-}$ layer is highlighted by the vanadium-centered red polyhedra, while the blue polyedra are $Cu(pyz)_4O_2$ and the yellow hexagons are pyrazine.

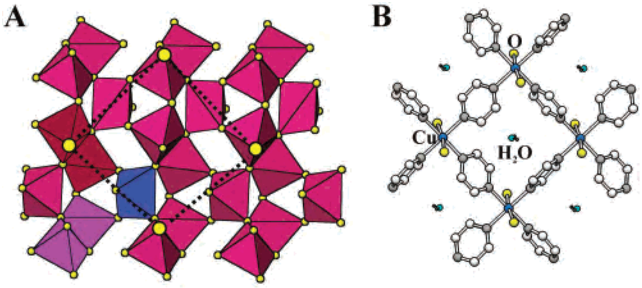

Figure 2. An ~[010] view of the $V_6O_{16}^{2-}$ (A) and $Cu(pyz)_2^{2+}$ (B) layers. Red and purple polyhedra are edge-bridged V2 and V3 trigonal bipyramids, and blue indicates the distorted V1 octahedron.

short vanadyl (V═O) bonds (1.601(3) and 1.710(3) Å for V2, and 1.689(3) and 1.625(3) Å for V3) and three intermediate V−O distances at 1.852(3)−1.998(3) Å. V1 exhibits a "4 + 1 + 1" geometry, with four equatorial bonds ranging from 1.832(3) to 2.016 Å, one short vanadyl bond, 1.587(3) Å, and one longer axial bond, 2.306(3) Å. These polyhedra share edges and vertices to from the $V_6O_{16}^{2-}$ layer, Figure 2A. Briefly, two V2 and two V3 centered polyhedra share a common edge to form binuclear V_2O_8 units, red and purple polyhedra, respectively. These binuclear species share a common vertex and alternate down the *b*-axis to form a chain, i.e., $V_2O_4O^{a}_{2/2}O^{b}_{2/2}$ (a = shared edge; b = shared vertice). Also, the V1 (blue polyhedron) connects adjacent chains by bonding to oxygen atoms on the shared edges of the binuclear units of one chain (1.832(3) and 1.843(3) Å), and also to the unshared oxygens of two binuclear units on the adjacent chain (1.958(3) and 2.016(3) Å). Bond valence calculations[12] were performed for each vanadium environment ($e^{[(R_0 - R)]/B}$; $B = 0.375$; $R_0 = 1.803$), and sum to +5.09, +5.08, and +5.05 for V1, V2, and V3, respectively.

$Cu(pyz)_2^{2+}$ square nets, shown in Figure 2B, are located both above and below each $V_6O_{16}^{2-}$ layer. The octahedral coordination around each copper is Jahn−Teller distorted, with equatorial bonds to four pyrazine ligands, 2.026(4) Å (×2) and 2.031(4) Å (×2), and longer axial bonds to two oxygen atoms, 2.362(3) Å (×2). The equatorial Cu−N bonds form the square net, which is also slightly distorted, with Cu−Cu edge lengths of 6.82 and 6.85 Å and Cu−Cu−Cu angles of 94.5° and 85.8°, that alternate around the edges and vertices, respectively. Magnetic susceptibility data, Figure 3, show a behavior expected for an antiferromagnetic ordering in a square lattice of Cu^{2+} ions, with a χ_{max} at ~8 K. The enlarged oxygen atoms (yellow) and dashed lines in Figure 2A show the bonding sites of the Cu^{2+} ions, and the position of the pyrazine groups, relative to the $V_6O_{16}^{2-}$ layer. H_2O molecules partially occupy (22(1)%) the center position of the square net, and also hydrogen bond to oxygen atoms in the $V_6O_{16}^{2-}$ layer at 1.661(3) Å (×2).

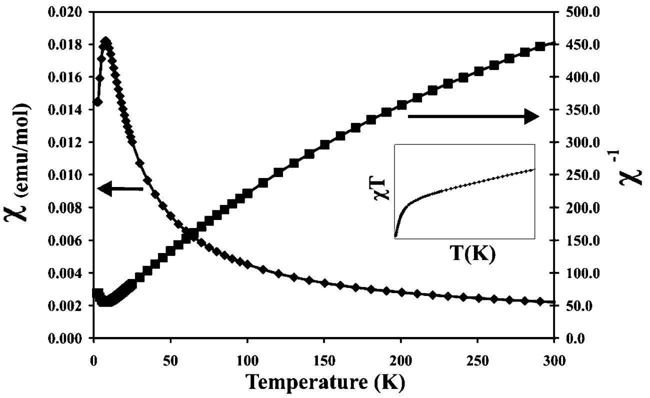

Figure 3. Magnetic susceptibility data for the title compound: χ (emu/mol), χ^{-1}, and χT (inset) vs temperature.

In the large family of polyoxovanadate/metal−ligand (VO_x/M/L) systems, the $V_6O_{16}^{2-}$ and $Cu(pyz)_2^{2+}$ layers are unique thus far. The closest relative found has been the $[\{M(bpy)\}_2V_{12}O_{32}]$ (M = Ni, Co, Cu) series of compounds,[6] with an identical V/O ratio. However, the chelating 2,2′-bipyridyl ligand, in place of pyrazine, leads to mixed Cu/V layers in the structure. Also recently reported is the $[Cu_2(pyrazine)V_4O_{12}]$ compound,[13] which contains pyrazine as well. However, $[Cu_2(pyrazine)V_4O_{12}]$ has a three-dimensional structure containing cyclic $V_4O_{12}^{4-}$ clusters and square pyramidal copper, which results from the slightly smaller V/O ratio (3:9, vs 3:8 here) and the smaller pyrazine/Cu ratio (1:2, vs 2:1 here). The fact that these systems respond to such small changes in reaction conditions by significantly altering their structural topologies again demonstrates the large degrees of freedom available, but this is difficult to control.

As ordered metal−oxide layers are sought after for various types of physical properties, such as in high-temperature superconductors,[19] we were led to examine the chemical conditions that might be necessary for the formation of multilayered compounds. One useful tool to control and predict the formation of silica/surfactant layered composite structures has been the concept of charge density matching

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Table 1. Layered $V_xO_y^{n-}$/CuL_x^{m+} Species and Charge Densities (±/Å^2)

$V_xO_y^{n-}$ [a]	charge density[b]	CuL_z^{m+} [c]	charge density[b]
$V_3O_7^-$ [14]	−0.0362	Cu(4,4′-bpy)$_2^{2+}$ [15]	+0.0159
$V_6O_{14}^{2-}$ [16]	−0.0400		
$V_6O_{16}^{2-}$	−0.0429	Cu(pyz)$_2^{2+}$	+0.0429
$V_8O_{21}^{4-}$ [17]	−0.0446		
$V_2O_5^-$ [18]	−0.0493		

[a] Except for $V_6O_{16}^{2-}$, the counterions are molecular species: tetramethylammonium,[14] 1,4-diazabicyclo[2.2.2]octane,[16] Cu(2,2′-bpy)$^{2+}$,[17] and 4-aminopyridinium.[18] [b] Units are formal charge per area, i.e., (n^- or m^+)/Å^2. [c] For Cu(4,4′-bpy)$_2^{2+}$, the counterions are molecular species: either $Cr_2O_7^{2-}$ or $MoO_2F_4^{2-}$.[15]

at their surface interface.[20,21] The concept is that two different materials will self-organize to have similar charge densities at their surfaces and, therefore, achieve local electroneutrality.

The same concept has a practical utility to help guide the hydrothermal synthesis of multilayered structures. For example, one might incorrectly visualize the metal oxide layer as having an overall "average" charge associated with it, such as one might envision each V_6O_{16} layer here to have a 2− charge. To understand why this is an incomplete (or incorrect) description, consider the following series: $V_{12}O_{32}^{4-}$, $V_{18}O_{48}^{6-}$, $V_{24}O_{64}^{8-}$, which is the $V_6O_{16}^{2-}$ layer extended out to 2, 3, and 4 unit cells. Thus, the actual charge balance (n^-) of a $V_xO_y^{n-}$ layer depends on the total area, as implied only vaguely in the formula.

To determine if charges will balance in a composite structure of multiple layers, one needs to carefully consider the charge per unit area. The charge densities of some selected $V_xO_y^{n-}$ and CuL_z^{m+} layers were calculated and are shown in Table 1. Each of these entries was calculated by dividing the formal charge on each layer, as determined by the counterions, by the area in Å^2 per unit cell. The italicized V and Cu entries are those for the title compound here and are matched at a charge density of ±0.0429. All of the remaining $V_xO_y^{n-}$/CuL_z^{m+} layers exist in different compounds with molecular species as the charge balance. The listed range of $V_xO_y^{n-}$ charge densities is from −0.036 to −0.05/Å^2, well within the same range as that calculated from copper−pyrazine compounds (e.g., Cu(pyz)(NO$_3$)$_2$; +0.044),[22] and the title compound may have been predicted to exist. Similarly, it is also predicted that Co(pyz)$_2^{2+}$ and Fe(pyz)$_2^{2+}$ square nets, known in M(pyz)$_2$Cl$_2$ (M = Fe, Co)[23,24] with charge densities of ∼+0.038, can be layered with $V_3O_7^-$ or $V_6O_{14}^{2-}$.

Square nets made of the longer 4,4′-bipyridine ligand (∼7.1 vs ∼2.8 Å for pyrazine) have a smaller charge density, and a simple 1:1 layered compound would not be predicted to form between it and the vanadium oxides listed in Table 1 without breaking the rule of electroneutrality. At least two examples of a Cu(4,4′-bpy)$_2^{2+}$ square net are known,[15] and these exhibit self-interpenetrating nets and contain only molecular anions as well. According to a hypothetical calculation, the Cu(4,4′-bpy)$_2^{2+}$ layer would require an extra 3+ charge per formula to bring its charge density to ∼0.04, close to that for $V_6O_{14}^{2-}$.[2] The larger cavities within the Cu(4,4′-bpy)$_2^{2+}$ square net might provide an extra site for an extra 3+ ion to fill (and prevent self-interpenetration), with bonding sites both above and below to the oxide groups of the vanadium oxide layers. Alternatively, one could seek other suitable metal−oxide layers with smaller negative charge densites.

Charge density matching helps to understand the $V_6O_{16}Cu(C_4H_4N_2)_2\cdot(H_2O)_{0.22(1)}$ compound and is proposed as a way to calculate "allowed" compositions of new multilayered materials. In contrast to the many known metal−oxide/ligand hybrid compounds, this features a relatively rare example of a segregated metal atom distribution. Further synthetic results of Co(pyz)$_2^{2+}$ and Fe(pyz)$_2^{2+}$ in combination with $V_xO_y^{n-}$ layers will be reported in an upcoming full paper.

Acknowledgment. P.M. thanks Dave Schultz for the use of a SQUID magnetometer, Brent Gunnoe for the use of an infrared spectrometer, and Mike Whangbo for helpful discussions. P.D.B. gratefully acknowledges support from the National Science Foundation (NSF) for the funding of the X-ray diffractometer (Award 9509532).

Supporting Information Available: Tables of crystallographic data, atomic parameters, and nearest neighbor distances. Infrared data of $V_6O_{16}Cu(pyz)_2\cdot H_2O_{0.22(1)}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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