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BRIEF COMMUNICATIONS

Hydrothermal Synthesis and Single-Crystal Structural Characterization of $VO(VO_3)_6(VO(C_{10}H_8N_2)_2)_2$

GUOHE HUAN, JACK W. JOHNSON, AND ALLAN J. JACOBSON

Corporate Research Laboratories, Exxon Research & Engineering Company, Annandale, New Jersey 08801

AND JOSEPH S. MEROLA

Department of Chemistry, Virginia Polytechnic and State University, Blacksburg, Virginia 24061

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$VO(VO_3)_6(VO(C_{10}H_8N_2)_2)_2$ has been synthesized by the hydrothermal reaction of V_2O_3 with 2,2′-bipyridine. The compound is monoclinic, space group $P2_1/n$ (No. 14), a = 7.579 (2) Å, b = 26.713 (8) Å, c = 12.776 (3) Å, β = 94.97 (2)°, Z = 2. Its structure consists of $(VO_3)_n$ chains of corner-sharing pentavalent vanadium tetrahedra joined by V^{4+} square pyramids, with octahedral $VO(C_{10}H_8N_2)_2$ groups arrayed on the periphery of the chains. The V^{4+} sites are isolated magnetically, with the compound exhibiting Curie–Weiss behavior in the temperature range 10–300 K. The calculated μ_{eff} is 1.68 μ_B/V^{4+}, close to the spin-only value. © 1991 Academic Press, Inc.

Introduction

In the course of a program of exploratory hydrothermal synthesis of new vanadium phases containing organic molecules or anions as structural components (*1–3*), a new compound containing vanadium, oxygen, and 2,2′-bipyridine was isolated. Its structure combines elements of the solid state chain compounds AVO_3 with those of typical molecular V^{4+} species.

Synthesis

V_2O_3 (0.150 g; 0.001 mole, Alfa) and 0.156 g 2,2′-bipyridine (0.001 mole) were placed in a 23-ml Teflon-lined steel autoclave (Parr Instruments). The filling was adjusted to ~60% with distilled water and the mixture was heated at 200°C and autogeneous pressure for 2 days. The product (black prisms, 0.21 g, 66% yield based on vanadium) was separated by filtration, washed several times with distilled water, and dried in air. Chemical analysis: observed, C 33.93%, H 2.18%, N 7.94%, V 31.86%; Calculated for $C_{40}H_{32}N_8V_9O_{21}$, C 33.85%, H 2.27%, N 7.90%, V 32.31%.

The inverse magnetic susceptibility as a function of temperature showed Curie–Weiss behavior in the temperature range

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TABLE I

ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC DISPLACEMENT COEFFICIENTS ($\text{Å}^2 \times 10^3$) FOR $VO(VO_3)_6(VO(C_{10}H_8N_2)_2)_2$

	x	*y*	*z*	*U*
V(1)	2419(1)	1049(1)	3890(1)	27(1)
V(2)	506(1)	1578(1)	1557(1)	25(1)
V(3)	−2717(1)	1016(1)	171(1)	24(1)
V(4)	2694(1)	1059(1)	−248(1)	26(1)
V(5)	144(1)	−32(1)	389(1)	25(1)
O(1A)	1140(1)	649(1)	4363(1)	42(1)
O(2A)	580(1)	2135(1)	2013(1)	44(1)
O(2B)	−1752(1)	1427(1)	1171(1)	34(1)
O(2C)	1353(1)	1170(1)	2492(1)	38(1)
O(3A)	−2285(1)	1247(1)	−929(1)	47(1)
O(3B)	−5053(1)	993(1)	238(1)	49(1)
O(3C)	−1824(1)	445(1)	295(1)	43(1)
O(4A)	2524(1)	1182(1)	−1475(1)	51(1)
O(4B)	1766(1)	1568(1)	444(1)	33(1)
O(4C)	1597(1)	532(1)	−14(1)	41(1)
O(5A)	630(1)	−105(1)	1612(1)	42(1)
N(1)	4412(1)	992(1)	5155(1)	31(1)
N(2)	4329(1)	581(1)	3298(1)	28(1)
C(1)	4363(1)	1216(1)	6107(1)	44(1)
C(2)	5664(1)	1150(1)	6910(1)	48(1)
C(3)	7058(1)	839(1)	6765(1)	47(1)
C(4)	7114(1)	592(1)	5810(1)	40(1)
C(5)	5792(1)	686(1)	5020(1)	30(1)
C(6)	5750(1)	457(1)	3960(1)	29(1)
C(7)	7062(1)	147(1)	3644(1)	43(1)
C(8)	6893(1)	−48(1)	2629(1)	51(1)
C(9)	5442(1)	71(1)	1982(1)	46(1)
C(10)	4171(1)	385(1)	2330(1)	38(1)
N(3)	1173(1)	1674(1)	4529(1)	31(1)
N(4)	4097(1)	1739(1)	3560(1)	28(1)
C(11)	−333(1)	1617(1)	5004(1)	48(1)
C(12)	−1191(1)	2012(1)	5427(1)	58(1)
C(13)	−533(1)	2482(1)	5338(1)	57(1)
C(14)	1000(1)	2548(1)	4847(1)	51(1)
C(15)	1832(1)	2136(1)	4451(1)	31(1)
C(16)	3481(1)	2176(1)	3910(1)	32(1)
C(17)	4331(1)	2624(1)	3761(1)	45(1)
C(18)	5836(1)	2626(1)	3228(1)	51(1)
C(19)	6431(1)	2187(1)	2846(1)	47(1)
C(20)	5540(1)	1749(1)	3025(1)	38(1)

Note. Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor. Oxygen atoms labeled A are coordinated to only one vanadium atom, while oxygen atoms labeled B and C are shared between two vanadium atoms.

10–300 K, with $C_g = 7.48 \times 10^{-4}$ cm^3/g and $\theta = -4$ K. The calculated μ_{eff} is 1.68 μ_B/V^{4+}, close to the spin-only value.

X-Ray Crystallography

Crystal data for $VO(VO_3)_6(VO(C_{10}H_8N_2)_2)_2$: Monoclinic, $P2_1/n$ (No. 14) $a = 7.579$ (2) Å, $b = 26.713$ (8) Å, $c = 12.776$ (3) Å, $\beta = 94.97$ (2)°, $Z = 2$, D(calc) $= 1.829$ g/cm^3. A Nicolet $R3m$/V diffractometer with Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) and a graphite monochrometer were used to collect 5012 diffraction maxima ($2\theta \leq 50°$) by ω scans from a black flat needle of dimensions $0.1 \times 0.2 \times 0.6$ mm at 298 K. Of these, 4520 were unique, $R_{\text{int}} = 0.017$, and 3633 observed ($F \geq 3\sigma(F)$). No absorption correction was applied to the data ($\mu = 1.587$ mm^{-1}). The structure was solved by direct methods and refined by full-matrix least-squares methods, minimizing $\Sigma w(F_o - F_c)^2$, where $w = (\sigma^2(F) + 0.0004 F^2)^{-1}$. During the refinement, disorder was detected in the vicinity of V(5) and modeled by giving weights of 0.5 to V(5) and O(5A). Nonhydrogen atoms were refined anisotropically to $R = 0.0393$, $R_w = 0.0432$, GOF $= 1.23$. An extinction correction $\chi = 0.00056$ (6) was included where $F_{\text{corr}} = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$. Hydrogen atoms were located in a difference map and included in the refinement as riding on the carbon atoms to which they were attached. The highest peak on the final difference Fourier map was 0.36 e$^-$/Å^3 and the largest hole was -0.47 e$^-$/Å^3. All computations were performed using SHELXTL PLUS (Nicolet) on a MicroVAX II.

Structure Description

The atomic coordinates and important bond distances are listed in Table I and Table II. The structure consists of chains that extend along the crystallographic *a* direction, centered at the origin and at *x, 1/2, 1/2*, as shown in Fig. 1. A view of the bonding within chains is depicted in Fig. 2, with the hydrogen atoms of the bipyridyl ligand omitted. Each chain contains two smaller chains of corner-sharing VO_4 tetrahedra composed of V(2), V(3), and V(4). Each tet-

TABLE II

Selected Bond Distances (Å) for $VO(VO_3)_6(VO(C_{10}H_8N_2)_2)_2$

V(1)–O(1A)	1.597 (1)	V(5)–O(5A)	1.586 (1)		
V(1)–O(2C)	1.923 (1)	V(5)–O(3C)	1.958 (1)		
V(1)–N(1)	2.120 (1)	V(5)–O(4C)	1.962 (1)		
V(1)–N(2)	2.102 (1)	V(5)–O(3C)′	1.947 (1)		
V(1)–N(3)	2.116 (1)	V(5)–O(4C)′	1.908 (1)		
V(1)–N(4)	2.298 (1)				
V(2)–O(2A)	1.596 (1)	V(3)–O(3A)	1.594 (1)	V(4)–O(4A)	1.595 (1)
V(2)–O(2B)	1.785 (1)	V(3)–O(3B)	1.781 (1)	V(4)–O(4B)	1.798 (1)
V(2)–O(4B)	1.780 (1)	V(3)–O(2B)	1.790 (1)	V(4)–O(3B)	1.775 (1)
V(2)–O(2C)	1.702 (1)	V(3)–O(3C)	1.673 (1)	V(4)–O(4C)	1.675 (1)

Note. Oxygen atoms labeled A are coordinated to only one vanadium atom, while oxygen atoms labeled B and C are shared between two vanadium atoms. Atoms marked with a prime are related to the unprimed atoms by a center of symmetry.

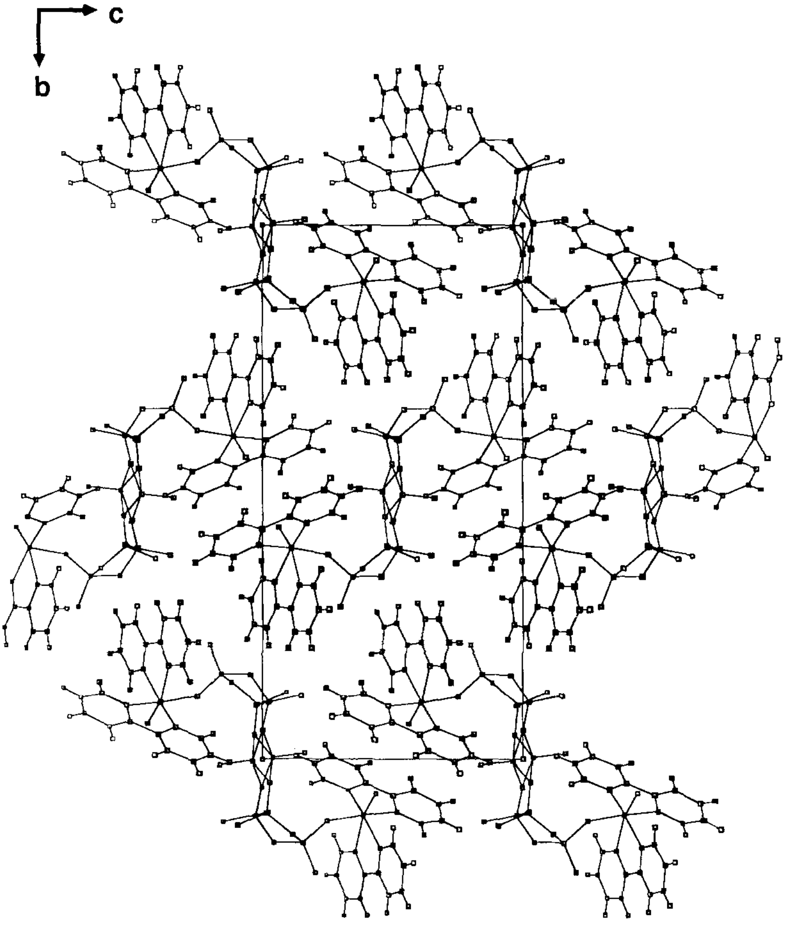

Fig. 1. View of an *a* axis projection of the structure of $VO(VO_3)_6(VO(C_{10}H_8N_2)_2)_2$, looking down the chains.

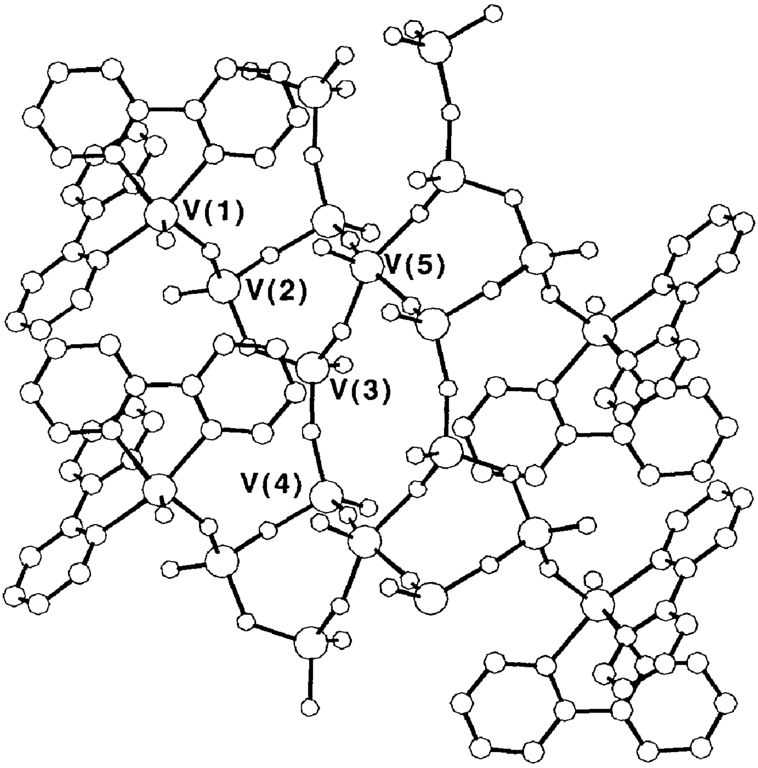

FIG. 2. View of the structure within a chain. Only one orientation of the disordered V(5) and O(5A) is shown, and the hydrogen atoms of the bipyridyl group are omitted for clarity.

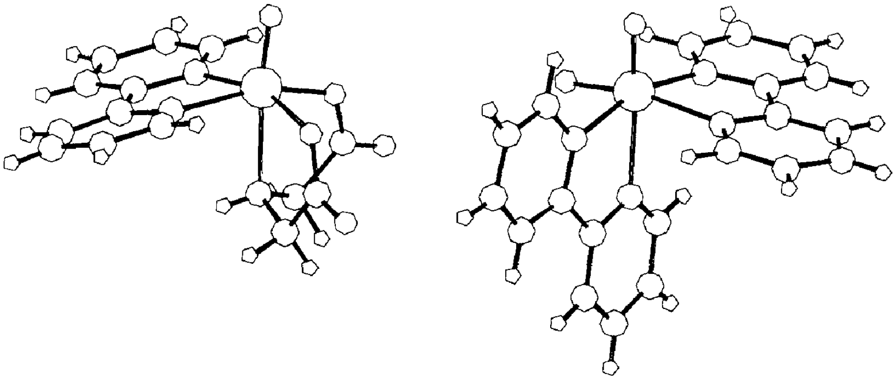

FIG. 3. Comparison of the coordination environment of the tetravalent vanadium atom in $VO(bpy)(HN(CH_2CO_2)_2 \cdot H_2O$ (left) with that of V(1) in $VO(VO_3)_6(VO(bpy)_2)_2$ (right).

rahedron in these chains share two oxygen atoms with other tetrahedra in the chain. One other oxygen atom in each tetrahedron is unshared, and the fourth oxygen atom of the V(2) tetrahedra is shared with V(1), while the V(3) and V(4) tetrahedra share their fourth vertex with V(5), linking the two tetrahedral chains together. The coordination geometry about V(5) is square pyramidal, and the terminal V=O group is disordered about the inversion center contained in the plane of the four basal oxygen atoms. Large octahedral $VO(bpy)_2$ groups are attached to the outer parts of the chains through an oxygen bridge to the V(2) tetrahedra.

Chains of corner-sharing V^{5+} tetrahedra are found in the metavanadates MVO_3 (M = NH_4, K, Rb, Cs) (*4*). The V–O distances in these compounds range from 1.803 to 1.806 Å for the shared oxygen atoms and 1.625–1.647 Å for the terminal oxygen atoms. In $VO(VO_3)_6(VO(bpy)_2)_2$ the V–O distances along the tetrahedral chains are in the range 1.775–1.798 Å. The distances from the vanadium atoms of the tetrahedral V^{5+} chain to the unshared oxygen atoms are 1.595 (1) Å, and the V–O distances that bridge to the tetravalent V(1) and V(5) are 1.702 (1) and 1.674 (1), respectively. The geometry of the tetrahedral chain is different from that of the chains in the metavanadates, since both square pyramidal and distorted octahedral V^{4+} atoms have to be accommodated in $VO(VO_3)_6(VO(bpy)_2)_2$. Bond valence calculations confirm the assignment of the tetrahedrally coordinated V(2), V(3), and V(4) as pentavalent and V(1) and V(5) as tetravalent (*5*). The magnetic susceptibility data support this assignment, indicating three isolated V^{4+} species per formula unit with an average magnetic moment of 1.68 μ_B.

The coordination environment around V(1) is similar to that found in the molecular complex $VO(bpy)(HN(CH_2CO_2)_2 \cdot H_2O$ (*6*), as is shown in Fig. 3. The equatorial V–N bond distances in the latter compound are 2.102 (2) and 2.110 (2) Å, while in $VO(VO_3)_6(VO(bpy)_2)_2$ they range from 2.102 (1) to 2.116 (1) Å. The V–N bond that is *trans* to the vanadyl oxygen is longer than the equatorial V–N bond in both the molecular complex and the extended lattice compound; the distances are 2.328 (3) and 2.298 (1) Å, respectively.

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