

Synthesis, Magnetism, and X-ray Molecular Structure of the Mixed-Valence Vanadium(IV/V)–Oxygen Cluster $[\text{VO}_4\text{C}(\text{V}_{18}\text{O}_{45})]^{9-}$

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Within the transition metal oxide systems, vanadium presents a unique chemistry due to its capacity to form a great number of mixed-valence oxo clusters which often have the peculiarity to incorporate species that function, for size, shape, and charge, as templates. Prismatic, lustrous dark brown crystals of $[(n\text{-C}_4\text{H}_9\text{NH}_3)_9[\text{V}_{19}\text{O}_{49}]\cdot 7\text{H}_2\text{O}]$ are obtained by reacting $(n\text{-C}_4\text{H}_9\text{NH}_3)\text{VO}_3$, VOSO_4 , and $(n\text{-C}_4\text{H}_9\text{NH}_2)$ in H_2O . The X-ray crystal structure shows an ellipsoidal metal–oxo cluster formed by 15 VO_5 and 3 VO_4 polyhedra surrounding an almost regular VO_4 tetrahedron located on the 3-fold axis of a trigonal cell of dimensions $a = 19.113(5)$ Å and $c = 13.743(5)$ Å with space group $P\bar{3}$ and $Z = 2$. Exponentially weighted bond valence sum calculations, manganometric titration of the V^{IV} centers, and magnetic measurements are consistent with the presence of three localized and three delocalized electrons. Variable-temperature solid-state susceptibility studies indicate antiferromagnetic coupling between V^{IV} centers. Cyclic voltammetry in acetonitrile shows a irreversible reduction at -1.24 V and a reversible oxidation at $+0.17$ V (vs Ag/AgCl). The title compound converts quantitatively to the metal oxide $\text{K}_2\text{V}_3\text{O}_8$ with an extended layered structure as soon as a potassium salt is added to a neutral aqueous solution of the polyoxoanion.

Introduction

Several authors evidenced that polyoxoanions often resemble molecular fragments of metal oxide extended structures.¹ Klemperer, Müller, and co-workers, in recent years, discovered that many metal–oxo clusters (behaving as carcerands similarly to the organic molecules) have the remarkable capacity to inglobe species charged or neutral that function as templates in the self-organization process of formation of the metal oxide cage. Subsequently an analogous effect was supposed in the formation of extended metal oxide structures (whereas now the templating agent is on the surface).² However the laws governing these processes are still unknown: the control of the linkage of fragments of inorganic complexes or molecules to form macromolecules or extended structures would be of enormous importance for the understanding of prebiotic processes and for the molecular engineering of materials.

Molecular metal oxides find nowadays application in many fields other than in catalysis, e.g. in solid-state chemistry, as electron acceptor components of charge-transfer salts,^{3,4} as electronic conductors in oxide lattices,⁵ etc., and in bio-medicine, for their antitumoral, antiviral and antiretroviral activity.⁶

In recent years, there has been an increasing interest, among transition metals, in the chemistry of vanadium, due to its capacity to form a great number of mixed-valence oxo clusters encapsulating neutral or charged molecules functioning as templates.^{7–10}

Here we report on the synthesis and chemical and magnetic characterization (including manganometric titration of the V^{IV} content) and single-crystal X-ray structure of the new mixed-valence $[(n\text{-C}_4\text{H}_9\text{NH}_3)_9(\text{V}_{19}\text{O}_{49})\cdot 7\text{H}_2\text{O}]$ (1) oxo cluster in which the central VO_4^{3-} anion functions as a template. Further we evidence the resembling of the metal oxide cluster, when flattened out, with the extended layered structure of $\text{K}_2\text{V}_3\text{O}_8$, obtained by reaction of 1 with a potassium salt in a neutral aqueous solution. One example of a similar cage is noted in the literature: Johnson disserted about the metal–oxo cluster $\text{K}_8[\text{V}_{19}\text{O}_{48}(\text{OH})]$;¹¹ however, the number of protons and the $\text{V}^{\text{IV}}/\text{V}^{\text{V}}$ ratio in his anion were not unambiguously determined and, moreover, there was no explanation for additional electron density found in the proximity of the central V atom.¹²

Experimental Section

General Methods. Reagent grade chemicals were used as received. Elemental analyses (C, H, N) were performed by Servizio Microanalisi, Area della Ricerca di Roma, CNR, and by H. Malissa Analytische Laboratorien, Lindlar, Germany (other elements). Infrared spectra were obtained on a Perkin-Elmer 16F PC FT-IR spectrophotometer. DC susceptibility measurements were performed by a commercial SQUID magnetometer in the temperature range 2–330 K by applying a field of 500 Oe. The experimental data were corrected for diamagnetic contributions using standard Pascal constants. Cyclic voltammograms were recorded in a single-compartment cell with 0.1 M Bu_4NBF_4 by using a 0.03-in. Pt-disk working electrode; a 0.03-in. wire served as auxiliary electrode.

Preparation. $(n\text{-C}_4\text{H}_9\text{NH}_3)\text{VO}_3$ was prepared by adding 1.4 mol L^{-1} of butylamine to a 0.66 mol L^{-1} suspension of V_2O_5 in H_2O . The

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Table 1. Crystallographic Data

chem formula: C ₃₆ H ₁₂₂ N ₉ O ₅₆ V ₁₉	fw = 2545.3
space group: P $\bar{3}$ (No. 147)	Z = 2
a = 19.113(3) Å	d(calcd) = 1.944 Mg/m ³
c = 13.743(5) Å	μ(Mo Kα) = 2.037 mm ⁻¹
V = 4348(2) Å ³	λ = 0.710 69 Å
R ^a = 0.0374	T = 20 °C
R _w ^b = 0.0577	

$${}^a R = \sum |F_o - F_c| / \sum F_o, {}^b R_w = \sum (|F_o - F_c| \sqrt{w}) / \sum F_o \sqrt{w}.$$

mixture was heated 3 h at reflux, the opaque solution was filtered off, and the filtrate was concentrated in a rotavapor until the white crystalline product began to precipitate.

(*n*-C₄H₉NH₃)₉V₁₉O₄₉·7H₂O (1). A solution of (*n*-C₄H₉)NH₃VO₃ (375 mg, 2.16 mmol), VOSO₄·5H₂O (253 mg, 1.1 mmol), *n*-C₄H₉NH₂ (0.2 mL, 2.02 mmol), and H₂O (5 mL) in a Erlenmeyer flask was heated at reflux for 3 h. Then the mixture was left slowly cooling overnight. The prismatic lustrous dark-brown crystals were filtered off, washed with cold water, and dried. Yield: 230 mg (62% referred to (*n*-C₄H₉)NH₃VO₃). Anal. Calcd for C₃₆H₁₀₈N₉O₄₉V₁₉·7H₂O: C, 16.99; H, 4.83; N, 4.95; V, 38.03. Found: C, 16.75; H, 4.72; N, 4.77; V, 37.95. IR (KBr, main absorptions bands): 998 (m, ν(V^{IV}=O_{term})), 983 (vs, ν(V^V=O_{term})), 957, 930, 791 (s), 722 (m), 668 (m).

(*n*-C₃H₇NH₃)₉V₁₉O₄₉·7H₂O (2). The preparation is analogous as for **1**. The elemental analyses were correct. IR (KBr, main absorptions bands): 988 (m, ν(V^{IV}=O_{term})), 974 (vs, ν(V^V=O_{term})), 949, 798 (s), 722 (m), 678 (m). The powder X-ray diffraction pattern data indicate a crystal system trigonal with a = 18.893(2) Å and c = 12.298(3) Å.

X-ray Structure analysis of 1. A well-grown crystal was fixed inside a Lindemann capillary in nitrogen atmosphere. Data were collected on a Huber/Ital Structure automated diffractometer fitted with a molybdenum source and a graphite monochromator and corrected for Lorentz-polarization effects. Selected crystal data are given in Table 1. The structure was solved by direct methods by using the SIR92 program.¹³ Carbon atoms C(15), C(25), and C(35) were found to occupy regions of diffuse maxima in difference Fourier maps so that it was impossible to determine their exact atomic positions. Therefore for the *n*-butylammonium molecules it was necessary to use rigid-body least-squares refinement, using standard distances and angles with resulting high thermal parameters; refinement of all non-hydrogen atoms with anisotropic vibrational amplitude was performed. The hydrogen atoms, except those bound to N(3) and those of the methyl groups, were found by difference Fourier syntheses, and their positions were assigned in idealized locations. By the same method the water molecules were localized, except the hydrogen atoms. Atomic coordinates and equivalent isotropic thermal parameters are given in Table 2.

Results and Discussion

As pointed out by Klemperer et al., many polyoxoanion cages, when flattened out, become fragments of extended metal oxide structures; e.g. the [V₃₀O₇₄]¹⁰⁻ cage is reduced to the V₂O₅ sheet fragment after cleaving 15 V-O bonds.¹⁴ In spite of such close similarity the process of formation of a polyoxometalate, known as self-assembly, is yet unknown. From the synthetic point of view, is it possible to address the reaction toward the polymerization in order to obtain the metal oxide extended structure or toward the formation of a molecular fragment (in the form of a polyoxometalate)? In the attempt to reply to this question we considered the K₂V₃O₈ mixed-valence metal oxide,¹⁵ constituted of sheets of vanadium oxide intercalated by potassium cations, and tried to isolate its molecular building block.

Table 2. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients (Å² × 10³)

	x	y	z	U(eq) ^a
V(1)	7429(1)	2139(1)	8517(1)	39(1)
V(2)	6003(1)	2228(1)	9640(1)	40(1)
V(3)	8177(1)	2640(1)	6306(1)	34(1)
V(4)	8509(1)	4507(1)	5515(1)	31(1)
V(5)	7422(1)	2874(1)	4523(1)	31(1)
V(6)	8763(1)	4097(1)	7787(1)	36(1)
V(7)	6667	3333	7319(1)	29(1)
O(1)	7625(2)	1618(2)	9263(3)	53(2)
O(2)	5588(2)	1474(2)	10386(3)	51(2)
O(3)	8592(2)	2192(2)	5804(3)	46(2)
O(4)	9221(2)	5078(2)	4779(2)	36(1)
O(5)	7712(2)	2585(2)	3595(2)	41(2)
O(6)	9637(2)	4577(2)	8302(3)	46(2)
O(12)	6352(2)	1771(2)	8559(2)	39(2)
O(13)	7612(2)	1925(2)	7381(3)	43(2)
O(16)	8117(2)	3212(2)	8701(2)	39(2)
O(22)	7049(2)	2764(2)	10115(3)	55(2)
O(27)	6667	3333	8589(4)	38(2)
O(34)	8393(2)	3463(2)	5303(2)	32(1)
O(35)	7125(2)	2139(2)	5578(2)	37(1)
O(36)	8939(2)	3356(2)	7043(2)	36(1)
O(45)	7588(2)	3908(2)	4382(3)	44(2)
O(46)	8985(2)	4756(2)	6618(2)	35(1)
O(67)	7560(2)	3442(2)	6924(2)	37(1)
O(W1)	13333	6667	7806(6)	79(3)
O(W2)	11505(3)	5753(3)	7583(3)	76(3)
O(W3)	11908(5)	4414(4)	8516(5)	146(5)
N(11)	10507(3)	6114(3)	6373(3)	53(2)
C(12)	10352	6734	6819	113(5)
C(13)	9974	7046	6068	243(15)
C(14)	9823	7684	6554	694(53)
C(15)	9446	7997	5803	1605(80)
N(21)	10682(3)	4031(3)	7010(4)	65(3)
C(22)	10647	3360	6418	128(6)
C(23)	10361	2597	7046	215(13)
C(24)	10333	1920	6410	565(41)
C(25)	10047	1157	7038	893(46)
N(31)	10113(5)	4202(7)	10134(6)	155(7)
C(32)	9744	3339	10430	464(30)
C(33)	9822	2836	9606	885(64)
C(34)	9436	1950	9938	776(61)
C(35)	9514	1447	9115	1625(70)

^a Equivalent isotropic *U* is defined as one-third of the trace of the orthogonalized *U*_{ij} tensor.

Following the preparation of K₂V₃O₈,¹⁶ if we substitute the potassium ions with RNH₃⁺ cations (R = *n*-C₃H₇, *n*-C₄H₉) (i.e. using RNH₃VO₃ instead of KVO₃), prismatic dark brown crystals of the (RNH₃)₉V₁₉O₄₉ polyoxometalates **1** and **2** are isolated. It is sufficient to add a potassium salt to a neutral aqueous solution of the (RNH₃)₉V₁₉O₄₉ polyoxometalate to precipitate quantitatively the microcrystalline brown powder of K₂V₃O₈. Similarly to the [V₃₀O₇₄]¹⁰⁻ cage, we therefore suggest that by cleaving appropriate bonds of the cage of [V₁₈O₄₅]⁶⁻, the polyoxoanion becomes a fragment of the extended structure of [V₃O₈]²⁻ preserving the same ratio 1:2 of the V^{IV}/V^V ions (see below).

In the effort to further substantiate this hypothesis, we tried also to isolate the K₉V₁₉O₄₉ polyoxometalate from the following reaction: KVO₃ + VOSO₄ + KOH → K₂V₃O₈. In fact by addition of ethanol to the blue solution of the above reactants, a blue powder is filtered out which has an IR spectrum (main IR bands: 971 (vs), 950 (sh, m), 814 (s), 722 (s), 668 (m)) different from that of a superposition of the vanadium reactants (main IR bands: KVO₃, 964 (m), 919 (s), 894 (m), 854 (m), 668 (m); VOSO₄, 1134 (vs), 1048 (vs), 988 (s), 800 (m), 600

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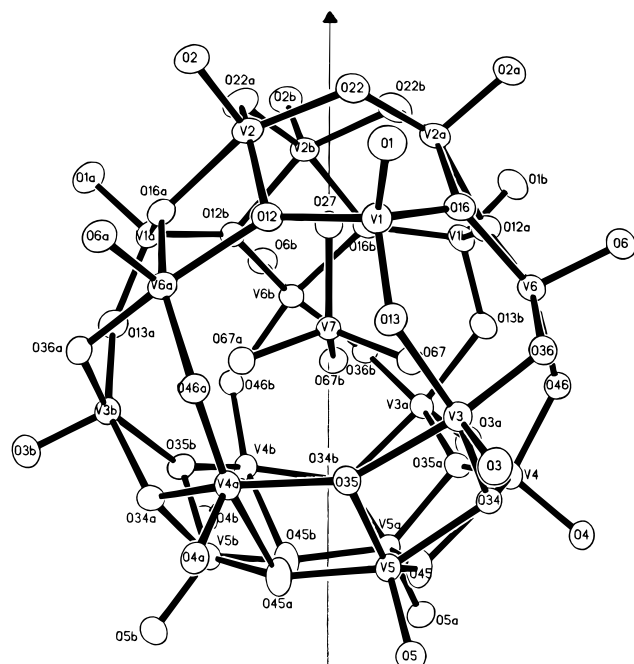


Figure 1. View of the structure of the $[\text{VO}_4\text{C}(\text{V}_{18}\text{O}_{45})]^{9-}$ anion with the 3-fold axis.

(m)) and very similar to the IR spectra of **1** and **2**. Unfortunately the low quality of the X-ray powder data prevented a comparison with the corresponding X-ray spectra of **1** and **2**. However the polyoxometalate is a fleeting intermediate in the formation of the extended structure of $\text{K}_2\text{V}_3\text{O}_8$; in fact, if not well dried, the powder turns from blue to olive green to brown in a few hours forming $\text{K}_2\text{V}_3\text{O}_8$. The bigger RNH_3^+ counterions in **1** and **2** probably constitute a barrier to the agglomerations of the polyoxoanions units whereas the small K^+ cations cannot screen sufficiently the polyoxoanions units, and the extended structure essentially governed by the weak $\text{O}=\text{V} \cdots \text{O}=\text{V}$ interactions can be formed.

The anion $[\text{V}_{19}\text{O}_{49}]^{9-}$ (see Figure 1) has the shape of an ellipsoid of C_3 symmetry with the 3-fold axis passing through the atoms V(7) and O(27). The metal-oxo cluster is formed by 18 VO_n ($n = 4$ or 5) polyhedra surrounding an almost regular VO_4 tetrahedron. The coordination of the three symmetry-related V(1) and the central V(7) ions is tetrahedral; the three symmetry-related V(5) show a square pyramidal coordination whereas all other vanadium centers form distorted octahedra with oxygen atoms, including those of the central VO_4 .

To determine the influence of the VO_4 central unit on the shape of the cage, it is useful (lacking the structure of the analogous "empty" cage) the comparison with the Müller's anion $[(\text{VO}_4)\text{V}_{18}\text{O}_{37}(\text{OH})_9]^{8-}$.¹² In fact the two anions present a similar shape (an ellipsoid of C_3 symmetry) formed by 12 VO_6 octahedra and 6 VO_4 tetrahedra in Müller's anion and 12 VO_6 octahedra, 3 VO_5 square pyramids, and 3 VO_4 tetrahedra in our case. In the first case the total charge of -8 is accomplished through protonation of 9 oxygen atoms; all the V^{IV} atoms are in an octahedral environment whereas all the V^{V} atoms are in a tetrahedral one and the central VO_4 unit is disordered over two sites in the ratio 1:1. In our case the total charge is -9 , no protonation is needed (due to the lower number of V^{IV} compared with the Müller's anion), the central VO_4 is univocally located, and the V^{V} atoms are, other than octahedral, also tetrahedral coordinated. It is important to note that the templating effect is due to a mutual action of both the template and the templated units. In fact, the same VO_4 central unit, other than in an ellipsoid of C_3 symmetry, is also observed in

Table 3. Shortest Intermolecular Distances (\AA)^a

Between the Anions and <i>n</i> -Butylammonium			
N(11)···O(46)	2.79(1)	N(21)···O(4) ^{VII}	2.94(1)
N(11)···O(34) ^{VII}	2.94(1)	N(31)···O(6)	2.89(2)
N(21)···O(36)	2.91(1)		
Between <i>n</i> -Butylammonium and the Water Molecules			
N(11)···O(W2)	2.86(1)	N(21)···O(W3)	2.93(1)
N(21)···O(W2)	2.96(1)		
Between the Anion and the Water Molecules			
O(2) ^{VIII} ···O(W2)	2.81(1)	O(22) ^{VIII} ···O(W3)	2.89(1)
Between the Water Molecules			
O(W1)···O(W2)	3.04(1)		

^a Symmetry code: (VII) $2 - x, 1 - y, 1 - z$; (VIII) $1 + y, 1 - x + y, 2 - z$.

Table 4. Selected Bond Lengths (\AA)

V(2)–O(12)	1.998(4)	V(2)–O(22)	1.851(4)
V(2)–O(16A)	1.991(3)	V(2)–O(22A)	1.844(2)
V(3)–O(13)	1.934(3)	V(3)–O(34)	1.973(3)
V(3)–O(35)	2.008(3)	V(3)–O(36)	1.740(3)
V(4)–O(34)	1.915(4)	V(4)–O(45)	2.196(4)
V(4)–O(46)	1.708(3)	V(4)–O(35A)	1.876(5)
V(5)–O(34)	1.942(3)	V(5)–O(35)	1.898(3)
V(5)–O(45)	1.849(4)	V(5)–O(45A)	1.842(3)
V(6)–O(16)	1.968(3)	V(6)–O(36)	1.907(4)
V(6)–O(46)	1.952(3)	V(6)–O(12A)	1.992(5)

a completed reduced cage ($[\text{V}_{18}\text{O}_{42}\text{H}_9]^{6-}$) with a tetrahedral T_d symmetry,⁷ the same one accomplished by the SO_4 tetrahedral template but with the mixed-valence $[\text{V}_{18}\text{O}_{42}]^{8-}$ cage.⁷ The subtle balance of geometrical and electronic factors leading to the observed different cages does not allow at the moment any systematic rationalization of the problem.

The crystal structure consists of an arrangement of molecules of polyoxoanions and *n*-butylammonium molecules linked each other by means of a net of hydrogen bonds between the nitrogen atoms and the oxygen atoms of the anions (see Figure 2). Interstitial spaces are occupied by water molecules, which are also linked by means of hydrogen bonds to the oxygen atoms of the anions [except the O(W1) which lies on the 3-fold axis] and to the nitrogen atoms of the *n*-butylammonium molecules. The most interesting contacts are reported in Table 3.

Cyclic voltammetry in acetonitrile showed an irreversible reduction at -1.24 V and a reversible oxidation wave at $+0.17$ V (vs Ag/AgCl). At more positive potentials, a number of irreversible oxidations were observed.

Manganometric titration of the vanadium atoms evidences the presence of formally six V^{IV} centers in agreement with charge compensation considerations.

A summation of the exponentially weighted V–O bond lengths for each V atom¹⁷ enables one to distinguish the V^{V} from the V^{IV} ions (Table 4). Surely V(1) and V(7) are V^{V} ions (they are also in a tetrahedral environment, and till now no example was known in the literature of V^{IV} atoms in such environment). The summation of the exponentially weighted V–O bond lengths indicates the V(6) ions as V^{IV} centers whereas the V(2) and V(4) centers are intermediate between the V^{V} and the V^{IV} ions. All the V(6), V(2), and V(4) atoms are in octahedral or in square pyramidal environments that, as differs from tetrahedral coordination, are compatible both for V^{IV} and V^{V} ions. Further we note that the V(6) ions are bonded to V(2) and V(4) through two ($\mu_3\text{-O}$)–V bonds and one

(17) The formulas applied for the bond valence summation are $s = s_i$, where s = valence of the vanadium ion, and $s_i = (R/R_1)^{-N}$, where N and R_1 are empirical values equal to 5.1 and 1.791 for V^{V} ions and 5.2 and 1.770 for V^{IV} ions, respectively, and R = cation–oxygen bond length; see: Brown, I. D.; Wu, K. K. *Acta Crystallogr.* **1976**, *B32*, 1957.

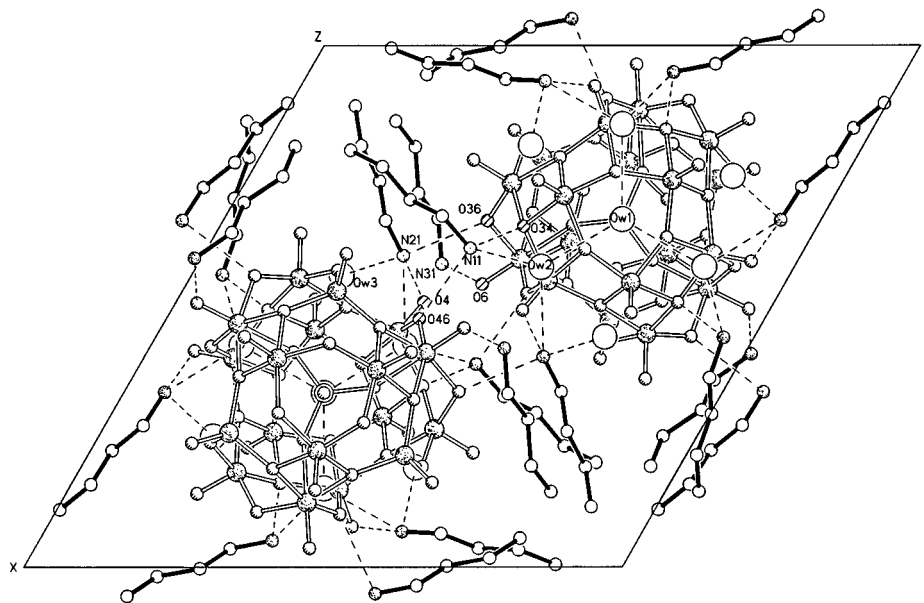


Figure 2. Crystal structure of **1** with projection along [001] showing the net of hydrogen bonds linking the polyoxo-anions with the n-butylammonium and the water molecules.

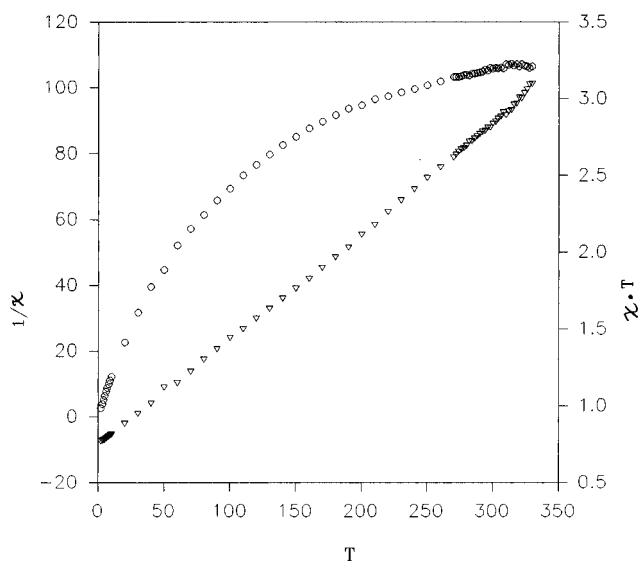


Figure 3. χ^{-1} vs T (○) and χT vs T (▽) of **1** in the 2–330 K temperature range.

(μ_2 -O)–V oxygen bond, respectively, and the V(2) atoms are bonded together by three (μ_2 -O)–V oxygen bonds. The V(2)–V(6), V(4)–V(6), and V(2)–V(2) distances vary between 3.05 [V(2)–V(6)] and 3.31 Å [V(4)–V(6)] values, considered in the literature as acceptable for charge delocalization among the vanadium centers. According to the summation of the exponentially weighted V–O bond lengths the V(3) and V(5) ions are among the 98.8% V^V centers even though both geometrical coordination as V–V distance considerations could enable charge delocalization between these centers.

Magnetic Properties. Variable-temperature solid-state magnetic susceptibility studies were performed on powdered samples of **1** in the range 2–330 K (Figure 3). The lack of a Curie or Curie–Weiss law (i.e. linear χ^{-1} vs T dependence, implying a temperature-independent magnetic moment which should be expected in case of uncoupled spins) suggests the presence of relevant magnetic interactions. In this case the χT value can be used just for an estimation of the magnetic moment and its temperature variation. At $T = 292$ K, $\chi T = 2.78$ emu mol⁻¹ K. As there are nine vanadium centers among which the six electrons are distributed, this value should correspond to a formal

moment of $1.57 \mu_B$ for each vanadium center ($= \mu/\sqrt{n}$). With decreasing temperature the χT value decreases continuously (Figure 3), clearly indicating the presence of antiferromagnetic interactions between the vanadium centers, as observed in other mixed-valence oxo clusters.^{18–22} This behavior is well consistent both with structural data and bond valence summation (see above), where the magnetic interactions occur within the three groups V(2)/V(6)/V(4) (with two electrons for each group) interconnected by the three V(2) ions (no direct V(4)–O–V(4) interconnection is instead observed through the V(4) centers; see Figure 1). Antiferromagnetic interactions are transmitted through oxygen bonds between localized spins on V(6) and delocalized spins on V(2)^{IV–V} and V(4)^{IV–V} ions. This allows an efficient electron transfer between localized spins too.

At $T = 2$ K, χT is = 0.77 emu mol⁻¹ K, which should correspond to a magnetic moment of $0.83 \mu_B$ /vanadium center, a value still much lower than the spin only value for one unpaired electron ($1.73 \mu_B$), denoting the presence of antiferromagnetic interactions (also if the six electrons were considered localized on formally six V^{IV} ions, the magnetic moment per V^{IV} center of $1.01 \mu_B$ would be too low for one unpaired electron).

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Supporting Information Available: Tables providing a full summary of crystal data and the structure determination, complete bond lengths, complete bond angles, anisotropic displacement coefficients, and H atom coordinates and a figure providing a view of the formula unit with atomic numbering (8 pages). Ordering information is given on any current masthead page.

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