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The Elusive Vanadate $(V_3O_9)^{3-}$: Isolation, Crystal Structure, and Nonaqueous Solution Behavior

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Abstract: The isolation, crystal structure, and nonaqueous solution characteristics of the first trinuclear vanadate are presented. The crystal structure reveals a six-membered cyclic arrangement of alternating vanadium and oxygen atoms for the anion of $[(C_4H_9)_4N]_3(V_3O_9)$. The ^{51}V NMR spectrum of this compound in CD_3CN exhibits multiple peaks. The relative intensities of each resonance can be altered by concentration and temperature changes, the later of which are reversible. Addition of $[(C_4H_9)_4N]Br$ and $NaClO_4$ also perturbs the equilibria between species observed. Conductivity data for $[(C_4H_9)_4N]_3(V_3O_9)$ in CH_3CN as a function of concentration display pronounced curvature and indicate formation of a neutral species in solution at the highest concentrations studied. Stoichiometric mixtures of $[(C_4H_9)_4N]_3(V_3O_9)$ with the known vanadates $[(C_4H_9)_4N]_3(HV_4O_{12})$, $[(C_4H_9)_4N]_3(V_5O_{14})$, and $[(C_4H_9)_4N]_3(H_3V_{10}O_{28})$ are prepared and examined by ^{51}V NMR. Equilibration between the various vanadates is observed and characterized. Resonances for these known vanadates, however, cannot be used to identify the peaks found for $[(C_4H_9)_4N]_3(V_3O_9)$, alone, in solution. The existence of ion pairs in acetonitrile is the only interpretation for the solution behavior of $[(C_4H_9)_4N]_3(V_3O_9)$ consistent with all data. As such, we can directly observe each possible ion pairing state by ^{51}V NMR: $(V_3O_9)^{3-}$ at −555 ppm, $\{[(C_4H_9)_4N](V_3O_9)\}^{2-}$ at −569 ppm, $\{[(C_4H_9)_4N]_2(V_3O_9)\}^{-}$ at −576 ppm, and $[(C_4H_9)_4N]_3(V_3O_9)$ at −628 ppm. To the best of our knowledge, $[(C_4H_9)_4N]_3(V_3O_9)$ presents the first case in which every possible ion paired state can be observed directly from a parent polyion. Isolation and characterization of this simple metal oxo moiety may now facilitate efforts to design functional polyoxometalates.

Introduction

Polyoxometalates impact a wide array of fields including catalysis, coatings, pigments, and electrochemical cells.[1] In particular, vanadates find applications in the areas of biochemistry, medicine, and catalysis.[2−4] The chemistry of vanadates is widely studied and quite complex.[5,6] For example, aqueous solutions of vanadium salts often contain multiple species such as mono-, di-, tetra-, and pentanuclear compounds.[7−10] This complexity arises, in part, from facile interconversions between different vanadium compounds and reactions with hydroxide and protons. Formation of macroscopic vanadium oxides depends on proper organization of smaller metal oxo units. For the most part, however, predicted or controlled synthesis of specific vanadate species is problematic.[5]

A host of discrete vanadates have been isolated and include $(HV_4O_{12})^{3-}$,[11] $(V_5O_{14})^{3-}$,[12] $(H_3V_{10}O_{28})^{3-}$,[13] $(V_{12}O_{32})^{4-}$,[14] $(V_{13}O_{34})^{3-}$,[15] and $(V_{15}O_{42})^{9-}$.[16] Surprisingly, the synthesis of a trinuclear analogue has remained elusive. Debate over the very existence of any $(V_3O_x)^{y-}$ species in aqueous solution has persisted in vanadate literature for decades. Supporting the presence of these V^{5+} oxos, cyclic $(V_3O_9)^{3-}$ or linear $(V_3O_{10})^{5-}$, are numerous potentiometric and ^{51}V NMR experiments.[10,17−24]

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Figure 1. Single crystal of $[(C_4H_9)_4N]_3(V_3O_9)\cdot 0.5H_2O$ shown with a dime for scale.

However, similar techniques have also led to conclusions that trinuclear vanadate is not present.[9,25,26] Despite these contradictions, a consensus has now been reached that a *linear* form of trinuclear vanadate, $(V_3O_{10})^{5-}$, does exist in aqueous solution.[17] As of yet, neither the linear nor cyclic forms of trinuclear vanadate have been isolated.

Clearly, we are in need of insights upon the fundamental nature of such metal oxo compounds in order to both understand the chemistry of catalysts already in use and tailor like compounds for future applications. Toward this goal, we present the synthesis, crystal structure, and nonaqueous solution behavior of the trinuclear vanadate $[(C_4H_9)_4N]_3(V_3O_9)$. We find the $(V_3O_9)^{3-}$ core remains free from equilibration to other vanadates in acetonitrile. Additionally, this trianion exhibits rare solution speciation in which all possible ion paired states are observed directly.

Experimental Section

General Procedures. The solvents CH_3CN and CD_3CN were dried, distilled according to standard procedures,[27] and stored under argon. The compounds $[(C_4H_9)_4N]_3(V_5O_{14})$[12] and $[(C_4H_9)_4N]_3(H_3V_{10}O_{28})$[28] were synthesized according to literature procedures. Satisfactory elemental analyses were obtained for both: Anal. Calcd for $C_{48}H_{108}N_3O_{14}V_5$: C, 47.80; H, 9.03; N, 3.48. Found: C, 47.62; H, 8.90; N, 3.49. Anal. Calcd for $C_{48}H_{111}N_3O_{28}V_{10}$: C, 34.16; H, 6.63; N, 2.49. Found: C, 34.18; H, 6.56; N, 2.55.

Preparation of $[(C_4H_9)_4N]_3(V_3O_9)\cdot 0.5H_2O$. Our preparation of this trinuclear vanadate is derived from a procedure to obtain $[(C_4H_9)_4N](H_2VO_4)$.[29] To a stirred solution of $[(C_4H_9)_4N]Br$ (17.9 g, 55.5 mmol) in dichloromethane (275 mL) was added water (27.5 mL) and $AgVO_3$ (11.4 g, 55.3 mmol). After stirring in darkness (4 h), a beige solid was removed by filtration. The organic layer of the filtrate was dried over Na_2SO_4 followed by solvent removal in vacuo to yield 14.2 g of an off-white solid. Dissolution of this crude product in anhydrous DMF (30 mL) followed by vapor diffusion of diethyl ether (150 mL) in the dark for 6 weeks yielded colorless crystals. Large, irregular crystals (average dimensions: 7.2 mm × 3.8 mm × 2.6 mm, Figure 1) were shown to be the unprecedented trinuclear vanadate $[(C_4H_9)_4N]_3(V_3O_9)$ by single-crystal X-ray diffraction methods. Formation of this new compound was accompanied by smaller, blocklike crystals (average dimensions: 2.5 mm × 2.1 mm × 1.1 mm) of a byproduct identified as the known[11] tetranuclear $[(C_4H_9)_4N]_3(HV_4O_{12})$ by X-ray crystallography (see Supporting Information). The two crystal forms were easily distinguishable by eye, allowing facile separation of this new vanadate (5.38 g, 28.1% yield) from the tetranuclear species (1.44 g, 9.3% yield) with forceps. Anal. Calcd for $C_{48}H_{109}N_3O_{9.5}V_3$: C, 55.80; H, 10.63; N, 4.07. Found: C, 55.58; H, 10.72; N, 3.89. Anal. Calcd for $C_{48}H_{109}N_3O_{12}V_4$: C, 51.28; H, 9.77; N, 3.74. Found: C, 51.55; H, 9.93; N, 3.58.

X-ray Crystal Structure. Single-crystal X-ray defraction data were acquired through Purdue University in-house facilities. The experimental procedures for the X-ray diffraction studies can be found in the Supporting Information. Crystal data for $[(C_4H_9)_4N]_3(V_3O_9)\cdot 0.5H_2O$: colorless cube; orthorhombic, space group $P2_12_12_1$ (No. 19); $a = 22.0495(5)$ Å; $b = 22.2453(5)$ Å; $c = 24.1378(3)$ Å; $V = 11839.5(7)$ Å^3; $Z = 8$; $T = 173$ K; $R(F_o) = 0.059$; GOF = 1.022.

^{51}V NMR Spectroscopy. NMR spectra were recorded on a Varian INOVA 300 spectrometer at 78.9 MHz for ^{51}V. All NMR samples were prepared in CD_3CN and flushed with argon. Spectra were collected at 25 ± 1 °C, unless noted otherwise. Chemical shift values were referenced to an external standard of neat $VOCl_3$ ($\delta = 0$ ppm). For variable-temperature experiments, a coaxial insert containing the $VOCl_3$ standard was used. Typical ^{51}V NMR parameters included 0.65 s acquisition time, 30−55 kHz spectral width, 13 μs pulse width, and 10−35 Hz line broadening. Variable-temperature experiments began at 25 °C. The probe temperature was changed by 5 or 10 °C increments, first moving below room temperature and then above. Samples were allowed to equilibrate at a given temperature for 20 min prior to data collection.

Conductivity. Conductivity measurements were recorded on an Oakton CON 100 Series Model 35607-10 conductivity/temperature meter equipped with a glass platinum electrode. The instrument was calibrated with NIST conductivity calibration standards of KCl. All solutions were maintained at a temperature of 25 ± 1 °C by use of a water bath and kept under a stream of argon. The initial solutions of 250 mM $[(C_4H_9)_4N]_3(V_3O_9)$ and $[(C_4H_9)_4N]PF_6$ were diluted with appropriate volumes of CH_3CN to obtain the desired series of concentrations.

Results

Synthesis. During vapor diffusion of ether into the DMF solution containing the crude vanadate, we observed that crystallization of $[(C_4H_9)_4N]_3(HV_4O_{12})$ preceded that of $[(C_4H_9)_4N]_3(V_3O_9)$. Perhaps depleting the solution of $(HV_4O_{12})^{3-}$ provided a lower vanadate concentration enabling $[(C_4H_9)_4N]_3(V_3O_9)$ formation. Although this vapor diffusion yielded two types of crystals, they were separated easily by hand. As can be seen in Figure 1, crystals of the trinuclear vanadate are quite large. We found that the color of the final $[(C_4H_9)_4N]_3(V_3O_9)$ crystals was dependent upon the vendor from which we obtained the starting materials. With $AgVO_3$ purchased from the Aldrich Chemical Co., the $[(C_4H_9)_4N]_3(V_3O_9)$ product was colorless. Slightly yellow crystals resulted when $AgVO_3$ was supplied by Acros Organics. In both cases, the compound was deemed pure by elemental analysis.

Crystal Structure. Figure 2 shows an ORTEP diagram of the $(V_3O_9)^{3-}$ trianion. Each of the three nearly tetrahedral vanadium atoms is bound by two bridging and two terminal oxygens. The three vanadium and three bridging oxygen atoms form a six-membered ring, contrary to proposals of a linear structure for trinuclear vanadate.[8,10,17,23,30,31] The six-membered ring has a distorted boat conformation in which one vanadium and one oxygen rise above the central, four-atom plane by

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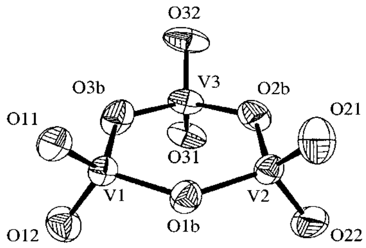

Figure 2. ORTEP representation of the $(V_3O_9)^{3-}$ anion with thermal ellipsoids drawn at the 50% probability level.

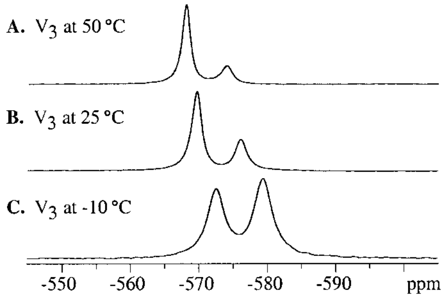

Figure 3. ^{51}V NMR spectra of 50 mM $[(C_4H_9)_4N]_3(V_3O_9)$, "V3", in CD_3CN at different temperatures.

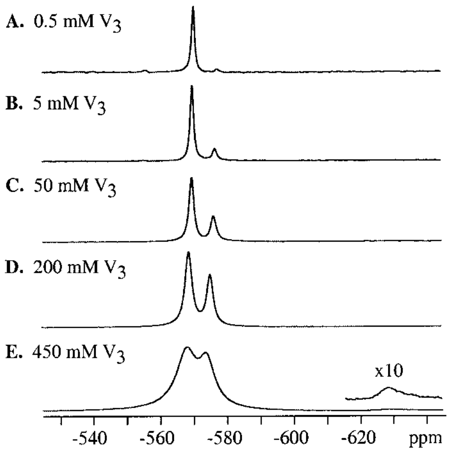

Figure 4. ^{51}V NMR spectra of $[(C_4H_9)_4N]_3(V_3O_9)$, "V3", in CD_3CN at different concentrations.

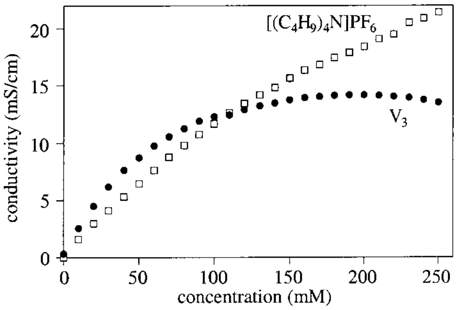

Figure 5. Conductivity versus concentration plot of $[(C_4H_9)_4N]_3(V_3O_9)$, "V3", and $[(C_4H_9)_4N]PF_6$ in acetonitrile.

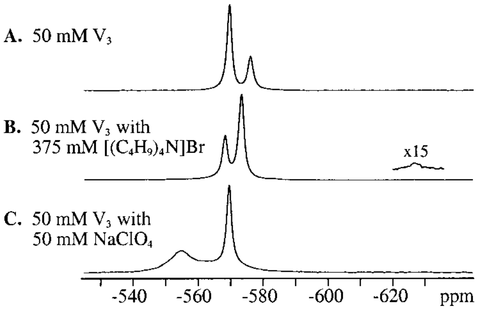

Figure 6. ^{51}V NMR spectra of $[(C_4H_9)_4N]_3(V_3O_9)$, "V3", in CD_3CN under various conditions: (A) 50 mM, (B) 50 mM with 375 mM $[(C_2H_5)_4N]Br$, and (C) 50 mM with 50 mM $NaClO_4$.

varying distances (Figure S1, Supporting Information). A water molecule hydrogen bonds to one of two $(V_3O_9)^{3-}$ anions in the asymmetric unit, but bears no significant influence upon V−O bond lengths. On average, the terminal V−O bonds are 1.63 Å and the bridging V−O bonds are 1.80 Å. The discreet $(V_3O_9)^{3-}$ anions are surrounded completely by $[(C_4H_9)_4N]^+$ cations (Figure S2, Supporting Information).

^{51}V NMR. A 50 mM solution of $[(C_4H_9)_4N]_3(V_3O_9)$ in CD_3CN exhibited a ^{51}V NMR spectrum with two resonances at −569 and −576 ppm (Figure 3B). Perusal of the $[(C_4H_9)_4N]_3(V_3O_9)$ crystal structure (Figure 2) suggests only one peak to be expected, owing to the similar environments of all vanadium atoms. Cooling of the sample to −10 °C both increased the line width of each resonance and changed the ratio of peaks, favoring the upfield −576 ppm species (Figure 3C). Heating of the −10 °C sample back to 25 °C returned the original spectrum (Figure 3B). Further heating of the sample to 50 °C sharpened both peaks somewhat and provided further bias toward the −569 ppm peak (Figure 3A). These data indicate that two species are present and in equilibrium with each other. Concentration also had a profound influence upon the $[(C_4H_9)_4N]_3(V_3O_9)$ ^{51}V NMR spectrum (Figure 4): A 450 mM solution still favored the species identified by a resonance at −569 ppm slightly (Figure 4E), although significantly less than at 50 mM. At 0.5 mM, the −576 ppm peak had disappeared almost completely, in favor of the −569 ppm species (Figure 4A). A weak signal at −555 ppm was also observable.

Conductivity. We examined the conductivity of this vanadate in acetonitrile as a function of concentration (Figure 5). The pronounced curvature in this plot indicated that $[(C_4H_9)_4N]_3(V_3O_9)$ does not behave as an ideal 3:1 electrolyte. Even the control salt $[(C_4H_9)_4N]PF_6$ deviated from ideal behavior at the high concentrations of this study, indicating ion pairing.

Salt Additions. Addition of $[(C_4H_9)_4N]Br$ to a 50 mM solution of $[(C_4H_9)_4N]_3(V_3O_9)$ increased the line widths of both peaks in the ^{51}V NMR spectrum (Figure S3, Supporting Information). A strong bias toward the upfield −576 ppm species was found by addition of excess $[(C_2H_5)_4N]Br$ (Figure 6B). The peak line widths were smaller for added $[(C_2H_5)_4N]Br$ compared to $[(C_4H_9)_4N]Br$. Ammonium deficiency was brought about by adding 1 equiv of $NaClO_4$ to a 50 mM solution of $[(C_4H_9)_4N]_3(V_3O_9)$ in CD_3CN. The resulting, insoluble $[(C_4H_9)_4N](ClO_4)$ was removed by centrifugation. As can be seen in the ^{51}V NMR spectrum (Figure 6C), the −576 ppm resonance was no longer visible, the −569 ppm peak persisted, and the presence of a new species at −555 ppm appeared.

Solutions of Mixed Vanadates. Figure 7 shows the ^{51}V NMR spectrum of $[(C_4H_9)_4N]_3(V_3O_9)$ compared to those of the known, organic-soluble vanadates $[(C_4H_9)_4N]_3(HV_4O_{12})$, $[(C_4H_9)_4N]_3(V_5O_{14})$, and $[(C_4H_9)_4N]_3(H_3V_{10}O_{28})$. Spectra for the stoichiometric mixtures of $[(C_4H_9)_4N]_3(V_3O_9)$ with each vanadate are also presented in Figure 7. As can be seen, both the higher nuclearity vanadates and mixtures with $(V_3O_9)^{3-}$ yielded many resonances not found in the $[(C_4H_9)_4N]_3(V_3O_9)$ spectra alone.

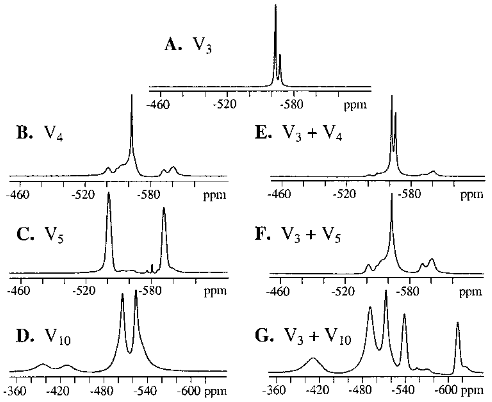

Figure 7. ^{51}V NMR spectra for solutions of different vanadates in CD_3CN: (A) $[(C_4H_9)_4N]_3(V_3O_9)$, "V3", (B) $[(C_4H_9)_4N]_3(HV_4O_{12})$, "V4", (C) $[(C_4H_9)_4N]_3(V_5O_{14})$, "V5", (D) $[(C_4H_9)_4N]_3(H_3V_{10}O_{28})$, "V10", (E) $[(C_4H_9)_4N]_3(V_3O_9)$ + $[(C_4H_9)_4N]_3(HV_4O_{12})$, (F) $[(C_4H_9)_4N]_3(V_3O_9)$ + $[(C_4H_9)_4N]_3(V_5O_{14})$, and (G) $[(C_4H_9)_4N]_3(V_3O_9)$ + $[(C_4H_9)_4N]_3(H_3V_{10}O_{28})$. The starting concentration of each compound was 50 mM.

Discussion

Vanadate ^{51}V NMR Spectra. To explain the multiple resonances present in the ^{51}V NMR spectra of $[(C_4H_9)_4N]_3(V_3O_9)$, it is tempting to turn to the aqueous chemical shift assignments already made for literature vanadates. However, aqueous and organic ^{51}V NMR shifts seldom correlate well.[32] For example, the aqueous assignment for monomeric $(VO_4)^{3-}$ is -538 ppm,[9,10,33,34] whereas in organic solvents (e. g., CD_3CN) this shift value is one of two ascribed to the pentanuclear species $(V_5O_{14})^{3-}$.[12] Additionally, literature reports show a discrepancy between the $(H_3V_{10}O_{28})^{3-}$ resonances in aqueous solutions[9,34] ($\delta = -427, -515, -534$ ppm) and in acetonitrile solutions[13] ($\delta = -396, -427, -506, -525$ ppm). These differences of chemical shifts are of similar variability to the different peaks we find for $[(C_4H_9)_4N]_3(V_3O_9)$. Thus, we restrict our comparisons to vanadates in organic solvents only.

The ^{51}V NMR spectrum for $[(C_4H_9)_4N]_3(HV_4O_{12})$ has not been reported previously in organic solvents. We interpret the spectrum of this compound (Figure 7B) to be, essentially, that of $[(C_4H_9)_4N]_3(V_3O_9)$ (vide infra) with a small component of $[(C_4H_9)_4N]_3(V_5O_{14})$. Thus, in acetonitrile solution, this tetranuclear compound equilibrates into tri- and pentanuclear species. The ^{51}V NMR spectrum of $[(C_4H_9)_4N]_3(V_5O_{14})$ (Figure 7C) shows resonances at -538 and -613 ppm in the expected 3:2 ratio along with some minor peaks (-556, -569, -590, -597, -628 ppm). The -556 and -569 ppm peaks are likely due to formation of $(V_3O_9)^{3-}$ (vide infra). The spectrum for $[(C_4H_9)_4N]_3(H_3V_{10}O_{28})$ (Figure 7D) has been reported previously[13] and our results correlate well with the literature. To determine the chemical shifts of the fully deprotonated decavanadate $(V_{10}O_{28})^{6-}$ in acetonitrile, we added 6 equiv of *N*,*N*-diisopropylethylamine to a 30 mM solution of $[(C_4H_9)_4N]_3(H_3V_{10}O_{28})$ (Figure S4, Supporting Information). The two peaks at -396 and -429 ppm in the $[(C_4H_9)_4N]_3(H_3V_{10}O_{28})$ spectrum coalesced into a single peak at -413 ppm. The resonances at -507 and -525 ppm moved downfield to -492 and -513 ppm, respectively, as predicted for increasing negative charge.[26]

A 1:1 mixture of $[(C_4H_9)_4N]_3(V_3O_9)$ and $[(C_4H_9)_4N]_3(HV_4O_{12})$ yields a spectrum equivalent to a superposition of the two individual compounds (Figure 7E). The 1:1 combination of $[(C_4H_9)_4N]_3(V_3O_9)$ with $[(C_4H_9)_4N]_3(V_5O_{14})$ results in a spectrum (Figure 7F) containing resonances for $(V_5O_{14})^{3-}$ (-538 and -613 ppm) and $(V_3O_9)^{3-}$ (-555 and -569 ppm). Determination of the fully deprotonated $(V_{10}O_{28})^{6-}$ chemical shifts allows us to assign the peaks present in the ^{51}V NMR spectrum of a 1:1 mixture of $[(C_4H_9)_4N]_3(V_3O_9)$ and $[(C_4H_9)_4N]_3(H_3V_{10}O_{28})$ (Figure 7G). The major peaks correspond to $(V_3O_9)^{3-}$ (-556 and -571 ppm, vide infra), $(V_5O_{14})^{3-}$ (-538 and -613 ppm), and $(V_{10}O_{28})^{6-}$ (-411, -491, and -513 ppm). At this time, we are unable to assign the resonances at -626 to -628 ppm found in the spectra of $[(C_4H_9)_4N]_3(HV_4O_{12})$, $[(C_4H_9)_4N]_3(V_5O_{14})$, $[(C_4H_9)_4N]_3(V_3O_9)$ + $[(C_4H_9)_4N]_3(HV_4O_{12})$, $[(C_4H_9)_4N]_3(V_3O_9)$ + $[(C_4H_9)_4N]_3(V_5O_{14})$, and $[(C_4H_9)_4N]_3(V_3O_9)$ + $[(C_4H_9)_4N]_3(H_3V_{10}O_{28})$. Most important for this study is the fact that the resonances observed for $[(C_4H_9)_4N]_3(V_3O_9)$, alone, cannot be attributed to equilibration with any of the above-mentioned vanadates.

Ion Pairing. Although equilibration with other vanadates is not consistent with all the NMR and conductivity data presented, the existence of solution ion pairs between $[(C_4H_9)_4N]^+$ and $(V_3O_9)^{3-}$ is. Indeed, ion pairing of vanadates in organic solvents has been reported previously.[13,18] Additionally, ion pairing has been proposed as a means of stabilizing smaller, cyclic vanadates.[19]

Both the conductivity and ^{51}V NMR data exhibit strong concentration dependencies. Added $[(C_4H_9)_4N]^+$ and $[(C_2H_5)_4N]^+$ salts have an effect on the ^{51}V NMR data similar to higher concentrations of $[(C_4H_9)_4N]_3(V_3O_9)$ alone. Line widths of the peaks in the ^{51}V NMR spectra for $[(C_2H_5)_4N]^+$ experiments are narrower than those observed for the addition of $[(C_4H_9)_4N]^+$ salts. Such a result is expected for ion pairing given the size difference between these cations: Higher charge density of the $[(C_2H_5)_4N]^+$ cation permits a more discrete interaction with the $(V_3O_9)^{3-}$ anion resulting in narrower resonances. Further supporting the presence of solution ion pairs is the observation that removal of $[(C_4H_9)_4N]^+$ from the solution by ClO_4^- precipitation shows an effect similar to lower concentrations. We conclude that the species at -576 ppm exhibits a higher degree of ion pairing than that at -569 ppm.

Highly charged species are more favored in dilute solution as evidenced by the conductivity data. At the lowest concentration examined (0.5 mM), the ion paired species at -576 ppm is almost unobservable by ^{51}V NMR whereas the peak at -569 ppm is strong and a small resonance appears at -555 ppm. We interpret this resonance at -555 ppm, observed at low concentrations and with $[(C_4H_9)_4N]^+$ removed from the system by ClO_4^-, to be from the $(V_3O_9)^{3-}$ anion, free of any ion pairing. Thus, the -569 ppm peak, predominant at intermediate concentrations and present with added salt, is the first ion pair, $\{[(C_4H_9)_4N](V_3O_9)\}^{2-}$. Further ion pairing brings about the third resonance at -576 ppm for the doubly ion paired $\{[(C_4H_9)_4N]_2(V_3O_9)\}^{1-}$. Higher temperatures are expected to dissociate ion pairs. In accord with this prediction, the ^{51}V NMR spectrum favors the single ion pair more at 50 °C than at lower temperatures (Figure 3).

The conductivity curve (Figure 5) shows decreasing values at high concentrations (e.g., >200 mM), indicating loss of

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charged species and formation of a neutral complex. Careful inspection of the $[(C_4H_9)_4N]_3(V_3O_9)$ ^{51}V NMR spectra at high concentrations (e.g., 450 mM, Figure 4E) reveals the presence of a weak resonance at −628 ppm. Decreased conductivity values and appearance of a ^{51}V NMR peak at −628 ppm at high concentrations (e.g., >200 mM) are subtle but reproducible. This −628 ppm peak is slightly more pronounced with added ammonium salts (Figure S5, Supporting Information). We assign this −628 ppm resonance to the neutral, completely ion paired species $[(C_4H_9)_4N]_3(V_3O_9)$. These assignments are consistent with the expectation of higher charged, anionic species appearing at downfield chemical shift values relative to similar compounds of lower negative charge.[26]

Appearance of the $[(C_4H_9)_4N]_3(V_3O_9)$ resonance at −628 ppm is likely to be coincidental with observations of −626 to −628 ppm peaks for $[(C_4H_9)_4N]_3(HV_4O_{12})$, $[(C_4H_9)_4N]_3(V_5O_{14})$, $[(C_4H_9)_4N]_3(V_3O_9) + [(C_4H_9)_4N]_3(HV_4O_{12})$, $[(C_4H_9)_4N]_3(V_3O_9) + [(C_4H_9)_4N]_3(V_5O_{14})$, and $[(C_4H_9)_4N]_3(V_3O_9) + [(C_4H_9)_4N]_3(H_3V_{10}O_{28})$. For solutions of $[(C_4H_9)_4N]_3(V_3O_9)$ alone, this resonance is detected only under conditions of added salts or extremely high concentration, consistent with a drop in conductivity values. The presence of a −626 to −628 ppm resonance in the other samples is found at lower concentrations and may indicate the presence of a species yet to be identified.

Collectively, the conductivity and ^{51}V NMR data provide a consistent description of the $[(C_4H_9)_4N]_3(V_3O_9)$ solution behavior. We are able to observe the entire complement of ion pairing possibilities available to this new vanadate trianion: $(V_3O_9)^{3-}$ at −555 ppm, $\{[(C_4H_9)_4N](V_3O_9)\}^{2-}$ at −569 ppm, $\{[(C_4H_9)_4N]_2(V_3O_9)\}^{1-}$ at −576 ppm, and $[(C_4H_9)_4N]_3(V_3O_9)$ at −628 ppm. Recent work with solution characterization of larger polyoxometalate clusters has also demonstrated the presence of ion pairing.[35,36] Increased degrees of ion pairing were reported at higher concentrations of the starting metal complex.[35] Solution ion pairs were also favored by addition of excess salts containing the counterion.[35,36] Our data and analysis provide similar conclusions with respect to the solution behavior of $[(C_4H_9)_4N]_3(V_3O_9)$. To the best of our knowledge, $[(C_4H_9)_4N]_3(V_3O_9)$ presents the first case in which all potential states of ion pairing can be observed directly from a parent polyion.

Conclusions

We present the first isolation of a trinuclear vanadate, the existence of which has been extensively debated.[9,10,17−26] Solution studies in acetonitrile indicate that the $(V_3O_9)^{3-}$ core remains stable in solution, free from common equilibria between multiple metal oxos. This simple building block now opens the door to construction of more elaborate and functional polyoxometalates.

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Supporting Information Available: Complete crystal structure data for $[(C_4H_9)_4N]_3(V_3O_9)\cdot 0.5H_2O$ and $[(C_4H_9)_4N]_3(HV_4O_{12})\cdot CH_2Cl_2$ as well as ^{51}V NMR data for $[(C_4H_9)_4N]_3(V_3O_9)$ and $[(C_4H_9)_4N]_3(H_3V_{10}O_{28})$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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