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Observation of a Novel Cyclic Tetrametavanadate Anion Isolated from Aqueous Solution

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Introduction

Interest in inorganic vanadium–oxygen cluster anions has received an increasing attention in recent years because of their topological versatility[1] and their successful use in several disciplines such as analytical and clinical chemistry, catalysis, biochemistry and medicine.[2]

The major constitutents of so-called "metavanadate" aqueous solutions (pH = 8–12; [V] = 10^{-3}–10^{-1} mol L^{-1}) are the cyclic tetramer, $[V_4O_{12}]^{4-}$, and the pentamer, $[V_5O_{15}]^{5-}$. The existence of these anions had been well-established in aqueous solution by potenciometric and ^{51}V NMR techniques.[3,4] But the only salts that had so far been crystallized from such solutions contain polymeric chains anions.[5] Our research on polyoxovanadates of protonated organic bases has led us to isolate a *cyclo*-tetrametavanadate salt of *tert*-butylammonium, $[(CH_3)_3CNH_3]_4[V_4O_{12}]$, containing a novel discrete anion based on a ring of four VO_4 tetrahedra. Although other crystal structures containing the $\{V_4O_{12}\}$ core have been described, this is the first time that the discrete unprotonated cyclic tetrametavanadate anion, $[V_4O_{12}]^{4-}$, has been reported in solid-state polyoxovanadate chemistry. Other particularly distinguishing features of this compound are that it was obtained from aqueous solution and that the discrete anion shows a new conformation of the tetravanadium core $\{V_4O_{12}\}$. A protonated cyclic tetrameric anion, $[HV_4O_{12}]^{3-}$, was structurally characterized in the compound $(n\text{-}Bu_4N)_3[HV_4O_{12}]$, which was prepared by dissolving V_2O_5 in alcoholic n-Bu_4NOH.[6] There have been described also two complex anions, $[(\eta\text{-}C_8H_{12})Ir(V_4O_{12})]^{3-}$ and $\{[(\eta\text{-}C_8H_{12})Ir]_2(V_4O_{12})\}^{2-}$, which were obtained as tetra-n-butylammonium salts from acetonitrile solutions.[7] In these latter compounds, the $[V_4O_{12}]^{4-}$ unit is not a discrete polyanion, and it is stabilized by coordinating of the oxygen atoms of polyanion to one or two $(\eta\text{-}C_8H_{12})Ir$ moieties.

Experimental Section

Vanadium pentoxide and *tert*-butylamine were purchased from Merck and were used without further purification. Elemental analyses were performed on a Perkin-Elmer 240 C-, H-, N-analyzer and vanadium was determined thermogravimetrically as V_2O_5 after thermal decomposition of the compound in an argon–oxygen atmosphere on a Setaram Tag 24 S 16 thermobalance. The density of the compound was measured by flotation in acetone/CCl_4.[8] Infrared spectrum was obtained from KBr pellets using a Nicolet 740 FT-IR spectrometer.

Synthesis of $[(CH_3)_3CNH_3]_4[V_4O_{12}]$. To a stirred aqueous suspension (50 mL) of V_2O_5 (0.57 g, 3.1 mmol) was added an excess of *tert*-butylamine (2.0 mL, 18.8 mmol) and the mixture heated under reflux for 3 h. The resulting colorless solution (pH = 10.4) was filtered off for removing any insoluble residues and then allowed to stand at room temperature. After 2 months, prismatic colorless crystals of $[(CH_3)_3CNH_3]_4[V_4O_{12}]$ were obtained (yield: 0.183 g, 17% of the theoretical referred to V). They were filtered off, washed with water and ethanol, and dried in air. Anal. Calcd for $C_{16}H_{48}V_4N_4O_{12}$: C, 27.76; H, 6.99; N, 8.09; V_2O_5, 52.54. Found: C, 27.81; H, 6.99; N, 8.02; V_2O_5, 51.80. $D_0 = 1.39$ (1) g cm^{-3}. Selected FT-IR bands (KBr, cm^{-1}): 935 (m, sh), 890 (vs, br) ($\nu_s(V(O_t)_2)$); 810 (vs, vbr), 735 (w, sh) ($\nu_{as}(V(O_t)_2)$); 660 (m) ($\nu_{as}(V–O_b–V)$); 500 (m), 455 (s) ($\nu_s(V–O_b–V)$); 375 (m), 350 (m) ($\delta(VO_2)$). Symbols: br, broad; vs, very strong; s, strong; m, medium; w, weak; sh, shoulder.

Table I. Summary of Crystallographic Data for $[(CH_3)_3CNH_3]_4[V_4O_{12}]$

formula	$C_{16}H_{48}V_4N_4O_{12}$	Z	2
fw	692.34	μ(Mo Kα), cm^{-1}	11.058
space group	$I4/m$	ρ(calcd), g cm^{-3}	1.38
a, Å	15.000(2)	ρ(obsd), g cm^{-3}	1.39(1)
b, Å	15.000(2)	T, K	295(1)
c, Å	7.379(2)	R,[a] %	4.4 (all data: 5.9)
V, Å^3	1660(1)	R_w,[b] %	4.3

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$.

Table II. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å^2 × 10^3; Å^2 × 10^4 for V atom) for $[(CH_3)_3CNH_3]_4[V_4O_{12}]$

	x	y	z	U_{eq}[a]
V(1)	0.12623(2)	0.10428(2)	0.00000	203(2)
O(1)	0.1800(1)	0.1476(2)	0.1744(3)	56(1)
O(2)	0.1374(2)	–0.0136(1)	0.0000	63(1)
N(1)	0.7607(1)	0.1745(1)	0.5000	30(1)
C(2)	0.7049(2)	0.0914(2)	0.5000	41(1)
C(3)	0.7665(3)	0.0120(2)	0.5000	60(1)
C(4)	0.6502(3)	0.0928(2)	0.3260(8)	94(2)

[a] Equivalent isotropic $U_{eq} = (1/3)\sum[U_{ij} \cdot a_i^* \cdot a_j^* \cdot a_i \cdot a_j \cos(a_i,a_j)]$.

Crystallographic Analysis. A colorless prismatic single crystal with the approximate dimensions 0.25 × 0.20 × 0.10 mm was mounted on an Enraf-Nonius CAD-4 diffractometer. X-ray data were collected with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å) at room temperature using the ω–2θ scan technique. Cell parameters and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $15 < 2\theta < 30°$. A total of 1941 independent reflections ($R_{int} = 0.029$) were measured in the range $2 \le \theta \le 35°$ (h = 0–24, k = –16 to 17, l = 0–11), 1384 of which, with $I > 3\sigma(I)$, were used in the development and refinement of the structure. No significant decay of intensity of two standard reflections recorded after every 100 reflections was observed. The intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction following the procedure DIFABS[9] with minimum and maximum correction coefficients 0.868 and 1.342, respectively, was applied. The atomic scattering factors and anomalous dispersion factors were taken from the literature.[10] The structure was solved by combination of Patterson and difference Fourier methods and refined by full-matrix least-squares methods. Non-hydrogen atoms were refined anisotropically. All hydrogen atoms were clearly visible in a difference-Fourier synthesis and were refined isotropically, except for the hydrogens of methyl groups for which the positional coordinates were refined but their isotropic thermal parameters were fixed (U = 0.07 Å^2). The highest peak in the final Fourier difference map was 0.76 e/Å^3 and is associated with O(1). Most calculations were carried out using the X-RAY76 System.[11] Crystal data and data collection parameters are summarized in Table I. Positional coordinates are included in Table II, while selected bond distances and angles are listed in Table III.

Results and Discussion

The crystal structure of the $[(CH_3)_3CNH_3]_4[V_4O_{12}]$ compound

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Table III. Selected Bond Lengths and Angles for $[(CH_3)_3CNH_3]_4[V_4O_{12}]^a$

	Distances (Å)		
V(1)–O(1)	1.652(2)	N(1)–C(2)	1.501(3)
V(1)–O(2)	1.776(2)	C(2)–C(3)	1.507(5)
V(1)–O(2)^i	1.761(3)	C(2)–C(4)	1.524(6)
V(1)···V(1)^{ii}	3.473(1)		
V(1)···V(1)^{iii}	4.912(2)		
	Angles (deg)		
O(1)–V(1)–O(1)^{iv}	102.3(1)	N(1)–C(2)–C(3)	108.4(2)
O(1)–V(1)–O(2)	110.2(1)	N(1)–C(2)–C(4)	106.8(2)
O(1)–V(1)–O(2)^i	110.9(1)	C(3)–C(2)–C(4)	109.9(2)
O(2)–V(1)–O(2)^i	111.7(1)		
V(1)–O(2)–V(1)^{ii}	158.2(2)		

^{a} Symmetry codes: (i) $-y, x, z$; (ii) $-y, x, -z$; (iii) $-x, -y, -z$; (iv) $x, y, -z$.

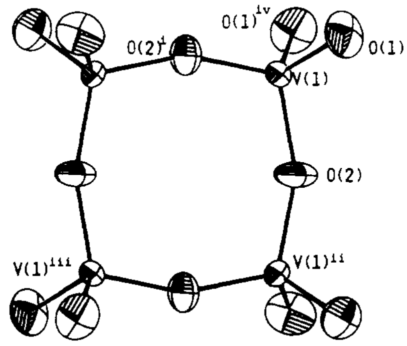

Figure 1. ORTEP plot (30% probability thermal ellipsoids) of the $[V_4O_{12}]^{4-}$ anion with the numbering scheme. Symbols on the figure correspond to the symmetry codes given in the footnote to Table III.

consists of discrete cyclic anions, $[V_4O_{12}]^{4-}$, and *tert*-butylammonium cations, $[(CH_3)_3CNH_3]^+$, linked together by means of electrostatic interactions and an extensive network of hydrogen bonds. The tetrameric anion possesses rigorous crystallographic C_{4h} symmetry, and it is made up of four corner-linked VO_4 tetrahedra forming a ring around the 4-fold axis. Figure 1 shows the ORTEP view of this discrete tetrametavanadate anion.

The vanadium and the bridging oxygen atoms are placed on the corners of two different squares rotated 45° one respect to the other forming a strictly planar V_4O_4 ring. The terminal oxygen atoms lay at 1.287(2) Å above and below the ring plane. This planar V_4O_4 unit is found neither in the $[HV_4O_{12}]^{3-}$ anion[6] nor in the complex anions.[7] Whereas the anion $[HV_4O_{12}]^{3-}$ has a bent structure in which the vanadium atoms are situated above and below the plane formed by the four bridging atoms (symmetry of the ring nearly D_{2d}), the rings in the complex anions assume a more planar configuration, each having all four vanadium atoms nearly in the same plane. Other nonplanar V_4O_4 moieties have been described earlier in vanadium(IV, V) carboxylates complexes.[12,13]

The $V-V_{trans}$ and $V-V_{cis}$ distances of 4.912(2) and 3.473(1) Å, respectively, are consistent with the absence of V–V interactions. The $V-O_t$ bond distance is 1.652(2) Å, and the $V-O_b$ bond lengths are 1.776(1) and 1.761(2) Å, which confirms that there is not a vertical plane passing through the vanadium atoms or through the bridging oxygen atoms. These distances are similar to those observed in other metavanadate anions.[5] All the O–V–O bond angles are within the range 102.3(1)–111.7(1)°, but only the O_t-V-O_t angle of 102.3(1)° is clearly smaller than the tetrahedral angle. The $V-O_b-V_{cis}$ angle of 158.2(2)° is similar to the Si–O–Si angle [162.4(5)°] in an analogous cyclic tetrasilicate anion,[14] but it is larger than those found in the $[HV_4O_{12}]^{3-}$ anion[6] and in the $\{[(\eta\text{-}C_8H_{12})Ir]_2(V_4O_{12})\}^{2-}$ complex anion[7] (125–146°) as well as in polymeric metavanadate anions[15,16] (130–145°), these facts are probably due to the high symmetry of the planar cyclic structure adopted. In the $[(\eta\text{-}C_8H_{12})Ir(V_4O_{12})]^{3-}$ anion[7] there are two V–O–V angles close to 131 and 141°, respectively, and another angle V–O–V of 155° with the oxygen atom shared by the two VO_4 tetrahedra which are not coordinated to the $(\eta\text{-}C_8H_{12})Ir$ moiety.

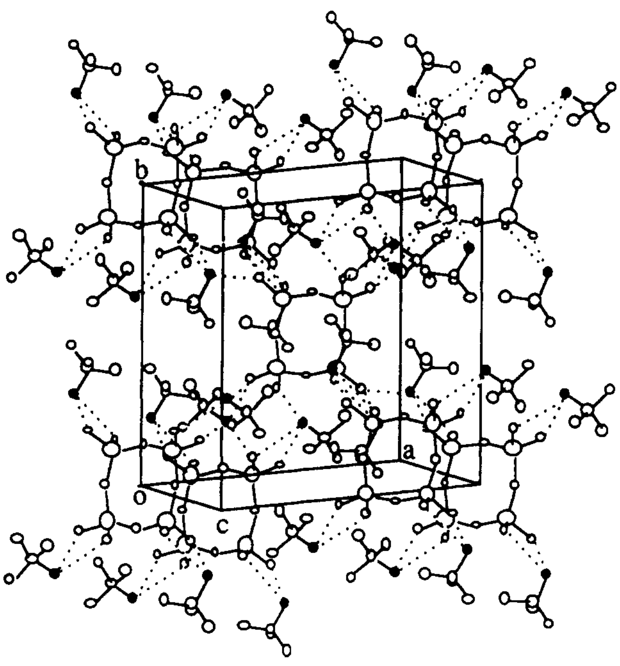

Figure 2. Cell packing of $[(CH_3)_3CNH_3]_4[V_4O_{12}]$, where dashed lines indicate hydrogen contacts.

The nitrogen and two carbon atoms of the cation are located on the anion plane, the third and fourth carbon atoms are in a general position at 1.284(6) Å above and below this plane. An extensive network of hydrogen contacts of the types N–H···O (N···O: 2.770–3.049 Å)[17] and C–H···O (C···O: 3.408–3.486 Å)[18] between *tert*-butylammonium cations and polyanion terminal oxygen atoms connect not only anions of the same *z* level but also anions on different *z* levels. A cell packing view of the compound including the network hydrogen contacts is shown in Figure 2 (hydrogen atoms were omitted for clarity).

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Supplementary Material Available: Tables giving anisotropic thermal parameters for non-hydrogen atoms, hydrogen atom locations, and complete bond lengths and angles and inter- and intramolecular contact distances including hydrogen contacts (7 pages). Ordering information is given on any current masthead page.

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