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Protonation sites in a heteropolyvanadate of phosphorus: X-ray crystal structure of $(Me_3NH)_4(NH_4)[H_4PV_{14}O_{42}]$

M. Ishaque Khan, Jon Zubieta*
Department of Chemistry, Syracuse University, Center for Science and Technology, Syracuse, NY 13244-4100 (USA)

and Paul Toscano*
Department of Chemistry, SUNY at Albany, Albany, NY 12222 (USA)

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Abstract

The reaction of $(NH_4)_2HPO_4$ with $(NH_4)_2Na_2K_2V_{10}O_{28}$, followed by addition of Me_3NHCl, yields dark crystals of the phosphovanadate cluster $(Me_3NH)_4(NH_4)[H_4PV_{14}O_{42}]$. The structure consists of an α-Keggin framework capped by two [VO] subunits. The protonation sites were identified as the doubly-bridging oxygens, O10. Crystal data: orthorhombic space group *Fddd*, $a=10.706(2)$, $b=23.581(4)$, $c=37.271(8)$ Å, $V=9409.3(22)$ Å^3, $Z=8$. X-ray data were collected on a Siemens R3m/V diffractometer using a $\theta/2\theta$ scan technique with graphite monochromated MoKα radiation. A total of 2733 reflections was collected (to $2\theta=55°$), of which 1850 were used in subsequent structure solution and refinement ($I>3\sigma(I)$). The structure was solved by direct methods, and least-squares refinement converged at $R=0.033$.

Introduction

While the structural chemistry of heteropolyvanadates of arsenic has been extensively studied in recent years [1, 2], the chemistry of heteropolyvanadates of phosphorus remains relatively undeveloped [3]. The existence of the vanadophosphate anion $[PV_{14}O_{42}]^{9-}$ has been demonstrated and a Keggin-based structure was determined [3]. In common with other polyvanadate clusters such as $[H_nV_{10}O_{28}]^{(6-n)-}$, $[PV_{14}O_{42}]^{9-}$ may exist in variably protonated forms $[H_nPV_{14}O_{42}]^{(9-n)-}$. For the decavanadate species $[H_2V_{10}O_{28}]^{4-}$ and $[H_3V_{10}O_{28}]^{3-}$, the protonation sites have been shown to be bridging oxo groups [5, 6]. In the course of our investigations of the chemistry of polyvanadates, we have isolated the $[H_4PV_{14}O_{42}]^{5-}$ cluster and have unambiguously identified doubly bridging oxo groups as the protonation sites.

Experimental

Synthesis of $(Me_3NH)_4(NH_4)[H_4PV_{14}O_{42}]$

A solution of $(NH_4)_2HPO_4$ (2.64 g, 20 mmol) and $(NH_4)_2NA_2K_2[V_{10}O_{28}]$ (11.18 g, 10 mmol) in 250 ml of H_2O was heated to 70 °C for 2 h. After addition of Me_3NHCl (5 g), the solution was allowed to stand at room temperature overnight. Dark red–brown crystals of $(Me_3NH)_4(NH_4)[H_4PV_{14}O_{42}]$ were collected in 36% yield. *Anal.* Calc. for $C_{12}H_{48}N_5O_{42}PV_{14}$: C, 8.58; H, 2.86; N, 4.17. Found: C, 8.33; H, 2.99; N, 3.86%. Selected IR bands (KBr pellet, cm^{-1}): 1052(s), 975(s), 941(m), 870(m), 801(m), 752(m).

X-ray diffraction study

The crystal parameters and experimental conditions for the structural study are summarized in Table 1. Atomic positional parameters are listed in Table 2, while Table 3 and Table 4 list bond lengths and bond angles, respectively.

The position of the hydroxyl proton, H(10), was located on the final difference Fourier map. The assignment was confirmed by successful refinement of the positional and isotropic temperature factors of H(10).

Discussion

The reaction of $(NH_4)_2HPO_4$ with $NaVO_3$, followed by the addition of Me_3NHCl, yielded dark red–brown crystals of $(Me_3NH)_4(NH_4)[H_4PV_{14}O_{42}]$. The IR spectrum is characterized by a strong band at 1052 cm^{-1},

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*Authors to whom correspondence should be addressed.

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TABLE 1. Crystallographic data for $(Me_3NH)_4(NH_4)[H_4PV_{14}O_{42}]$

Temperature (K)	298
Crystal system	orthorhombic
Space group	*Fddd* (dark red–brown needles)
a (Å)	10.706(2)
b (Å)	23.581(4)
c (Å)	37.271(8)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	9409(2)
Molecular weight	1678.7
Z	8
D_{calc} (g cm^{-3})	2.37
$F(000)$	6624
Crystal dimensions (mm)	$0.15 \times 0.15 \times 0.60$
Scan rate (° min^{-1})	3 to 20
Scan type	$\theta/2\theta$
Scan width (°)	$2\theta(K_{\alpha1}) - 1.0$ to $2\theta(K_{\alpha2}) + 1.0$
2θ range (°)	3 to 55
Background measurement	stationary crystal, stationary counter, at the beginning and end of each scan each for 25% the time taken for the scan
Independent reflections collected	2733
Observed reflections	1850 ($I \geqslant 3\sigma I$)
Absorption coefficient (cm^{-1})	27.1
Reduction of intensity data and summary of structure solution and refinement[a]	
Absorption correction	not applied
Atom scattering factors[b]	neutral atomic scattering factors were used throughout the analysis
Anomalous dispersion[c]	applied to all non-hydrogen atoms[b]
R[d]	0.0328
R_w[d]	0.0332
Goodness of fit[e]	1.56

[a] Data were corrected for background, attenuators, Lorentz, and polarization effects in the usual fashion [7]. [b] Ref. 8. [c] Ref. 9. [d] $R = \Sigma[|F_o| - |F_c|/\Sigma|F_o|]$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(F_o) + g^*(F_o)^2$; $g = 0.0003$. [e] $GOF = [\Sigma w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$, where NO is the number of observations and NV is the number of variables. [f] The positional parameters and isotropic temperature factor of H(10) were refined. All other H positions are calculated.

assigned to ν(P–O), and features at 941 and 975 cm^{-1}, associated with ν(V–O, terminal). Three bands of medium intensity at 752, 801 and 870 cm^{-1} confirm the presence of several distinct V–O–V bridging modes.

The structure contains a crystallographically independent trimethylammonium cation, an ammonium cation situated at site 8a with 222 symmetry and hence with disordered H atoms, and the polyanion which is located such that the P atom occupies site 8b of 222 symmetry and V1 and O1 rest on a two-fold axis. Figure 1 shows the structure of the $[H_4PV_{14}O_{42}]^{5-}$ anion, which consists of a central PO_4 tetrahedron which shares its oxygen atoms with four V_3O_{13} groups, each of which is constructed from three edge-sharing VO_6 octahedra. The V_3O_{13} subunits are joined to each other by corner-sharing. This assembly produces a slightly distorted α-Keggin framework, capped by two [VO] subunits. The structure is completed by capping two oppositely disposed cavities of the Keggin surface. An unusual feature of the structure is the presence of a number of relatively short V···V distances: V1···V2 at 2.976(1) Å and V2···V3 at 2.933(2) Å. However, both potentiometric titration and valence sum calculations [10, 11] confirm that all vanadium sites are in the +5 oxidation state, such that these short distances are not ascribed to the presence of coupled reduced sites.

The hydrogen atom positions were directly located from difference electron density maps and shown to be bonded to the doubly-bridging sites O10. It is noteworthy that the average V–O distance for this doubly-bridging O10 is 1.972 Å, while the average of all other V–O distances for doubly-bridging oxo groups is 1.824 Å. These values may be compared to V–O distances of 1.944 Å for protonated doubly-bridging oxygen and 1.844 Å for all other doubly-bridging oxo groups in the $[H_2V_{10}O_{28}]^{4-}$ structure and distances of 1.973 and 1.828 Å, respectively, for $[H_3V_{10}O_{28}]^{3-}$.

Bond length–bond number calculations on the oxo groups of $[H_4PV_{14}O_{42}]^{5-}$ confirm these observations [10, 11]. Thus, in the absence of H(10) the calculated bond number for O10 is 1.23 valence units, while the valence sum with the H atom is 1.96 valence units.

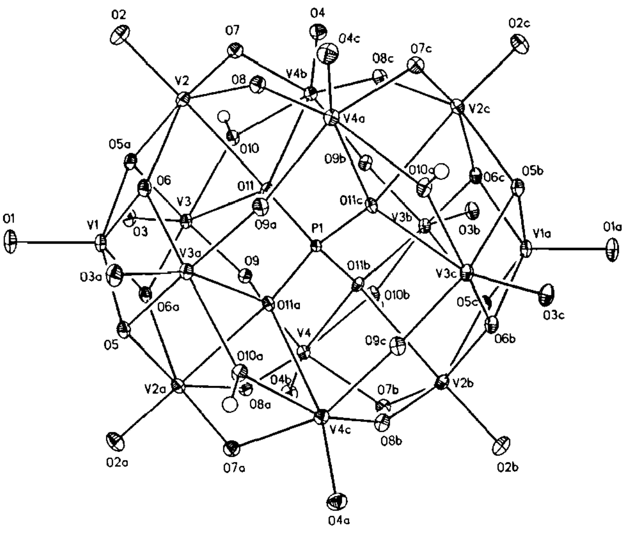

Fig. 1. Perspective view of the structure of $[H_4PV_{14}O_{42}]^{5-}$. Selected bond lengths (Å) and angles (°): V–O (terminal) 1.607(7), av.; V–O7, 2.376(6), av.; V1–O5, 1.892(3); V1–O6, 1.829(3); V2–O6, 2.058(3); V2–O7, 1.741(3); V2–O8, 1.898(3); V2–O5a, 1.919(3); V3–O9, 1.706(3); V3–O10, 1.923(3); V3–O5a, 2.089(3); V3–O6a, 1.964(3); V(4)–O9, 1.924(3); V4–O7b, 1.939(3); V4–O8a, 1.729(3); V4–O7b, 1.939(3); P1–O11, 1.539(3). V3–O10–V4b, 122.4(2); V2–O7–V4b, 123.6(2); V2–O8–V4a, 153.8(2); V3–O9–V4, 145.5(2).

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$)[a]

	x	y	z	U_{eq}
V(1)	1250	4615(1)	1250	16(1)
V(2)	−1144(1)	5215(1)	1195(1)	16(1)
V(3)	1238(1)	5258(1)	563(1)	15(1)
V(4)	3615(1)	6252(1)	621(1)	15(1)
P(1)	1250	6250	1250	10(1)
O(1)	1250	3937(2)	1250	27(1)
O(2)	−2187(3)	4739(1)	1267(1)	25(1)
O(3)	1363(3)	4779(1)	256(1)	22(1)
O(4)	−2154(3)	6328(1)	319(1)	24(1)
O(5)	2464(3)	4813(1)	1597(1)	17(1)
O(6)	161(3)	4948(1)	1564(1)	17(1)
O(7)	−1891(3)	5616(1)	867(1)	18(1)
O(8)	−1510(3)	5750(1)	1561(1)	19(1)
O(9)	2319(3)	5757(1)	448(1)	17(1)
O(10)	−194(3)	5633(1)	361(1)	17(1)
O(11)	425(3)	5878(1)	1007(1)	14(1)
N(1)	3764(4)	5577(2)	−584(1)	36(1)
C(1)	4925(5)	5919(3)	−528(2)	46(2)
C(2)	2632(5)	5903(3)	−487(1)	41(2)
C(3)	3832(7)	5042(2)	−383(2)	60(2)
N(2)	1250	1250	1250	20(2)
H(10)	−518(47)	5560(21)	186(13)	29(9)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3. Bond lengths and intermetallic distances (Å)

V(1)–O(1)	1.598(4)	V(1)–O(5)	1.892(3)
V(1)–O(6)	1.829(3)	V(2)–O(2)	1.605(3)
V(2)–O(6)	2.058(3)	V(2)–O(7)	1.741(3)
V(2)–O(8)	1.898(3)	V(2)–O(11)	2.400(3)
V(2)–O(5A)	1.919(3)	V(3)–O(3)	1.610(3)
V(3)–O(9)	1.706(3)	V(3)–O(10)	1.923(3)
V(3)–O(11)	2.375(3)	V(3)–O(5A)	2.089(3)
V(3)–O(6A)	1.964(3)	V(4)–O(9)	1.924(3)
V(4)–O(4B)	1.594(3)	V(4)–O(7B)	1.939(3)
V(4)–O(8A)	1.729(3)	V(4)–O(10B)	2.004(3)
V(4)–O(11B)	2.356(3)	P(1)–O(11)	1.539(3)
O(10)–H(10)	0.756(52)	N(1)–C(1)	1.495(8)
N(1)–C(2)	1.480(7)	N(1)–C(3)	1.472(7)
V(1)–V(2)	2.934(1)	V(1)–V(3)	2.977(1)
V(2)–V(3)	3.475(1)	V(2)–V(4A)	3.244(1)
V(3)–V(4)	3.441(1)	V(2)–P(1)	3.546(3)
V(3)–P(1)	3.469(3)	V(4)–P(1)	3.451(3)

TABLE 4. Bond angles (°)

O(1)–V(1)–O(5)	104.3(1)	O(1)–V(1)–O(6)	115.4(1)
O(5)–V(1)–O(6)	83.9(1)	O(5)–V(1)–I(5A)	151.5(2)
O(6)–V(1)–O(6A)	129.1(2)	O(2)–V(2)–O(6)	98.5(1)
O(2)–)–V(2)–O(7)	100.2(1)	O(6)–V(2)–O(7)	161.2(1)
O(2)–V(2)–O(8)	101.6(1)	O(6)–V(2)–O(8)	82.2(1)
O(7)–V(2)–O(8)	92.7(1)	O(2)–V(2)–O(11)	172.3(1)
O(6)–V(2)–O(11)	85.3(1)	O(7)–V(2)–O(11)	76.2(1)
O(8)–V(2)–O(11)	85.5(1)	O(2)–V(2)–O(5A)	102.0(1)
O(6)–V(2)–O(5A)	77.4(1)	O(7)–V(2)–O(5A)	99.9(1)
O(8)–V(2)–O(5A)	150.7(1)	O(11)–V(2)–O(5A)	72.2(1)
O(3)–V(3)–O(9)	104.4(1)	O(3)–V(3)–O(10)	96.4(1)
O(9)–V(3)–O(10)	97.2(1)	O(3)–V(3)–O(11)	163.0(1)
O(9)–V(3)–O(11)	89.9(1)	O(10)–V(3)–O(11)	72.4(1)
O(3)–V(3)–O(5A)	97.5(1)	O(9)–V(3)–O(5A)	156.5(1)
O(10)–V(3)–O(5A)	88.7(1)	O(11)–V(3)–O(5A)	70.1(1)
O(3)–V(3)–O(6A)	101.0(1)	O(9)–V(3)–O(6A)	91.5(1)
O(10)–V(3)–O(6A)	157.9(1)	O(11)–V(3)–O(6A)	87.4(1)
O(5A)–V(3)–O(6A)	75.7(1)	O(9)–V(4)–O(4B)	101.2(1)
O(9)–V(4)–O(7B)	159.1(1)	O(4A)–V(4)–O(7A)	97.3(1)
O(9)–V(4)–O(8A)	89.5(1)	O(4B)–V(4)–O(8A)	103.5(1)
O(7B)–V(4)–O(8A)	95.6(1)	O(9)–V(4)–O(10B)	85.5(1)
O(4B)–V(4)–O(10B)	95.0(1)	O(7B)–V(4)–O(10B)	83.3(1)
O(8A)–V(4)–O(10B)	161.5(1)	O(9)–V(4)–O(11B)	85.7(1)
O(4B)–V(4)–O(11B)	164.5(1)	O(7B)–V(4)–O(11B)	74.1(1)
O(8A)–V(4)–O(11B)	90.3(1)	O(10B)–V(4)–O(11B)	71.5(1)
O(11)–P(1)–O(11B)	108.0(2)	O(11)–P(1)–O(11A)	110.5(2)
O(11)–P(1)–O(11C)	110.0(2)	V(1)–O(5)–V(2A)	100.7(1)
V(1)–O(5)–V(3A)	96.6(1)	V(2A)–O(5)–V(3A)	120.2(1)
V(1)–O(6)–V(2)	97.9(1)	V(1)–O(6)–V(3A)	103.3(1)
V(2)–O(6)–V(3A)	140.1(2)	V(2)–O(7)–V(4B)	123.6(2)
V(2)–O(8)–V(4A)	153.8(2)	V(3)–O(9)–V(4)	145.5(2)
V(3)–O(10)–H(10)	126.8(37)	V(3)–O(10)–V(4B)	122.4(2)
H(10)–O(10)–V(4B)	110.7(37)	V(2)–O(11)–V(3)	93.4(1)
V(2)–O(11)–P(1)	127.0(1)	V(3)–O(11)–P(1)	123.4(1)
V(2)–O(11)–V(4B)	86.0(1)	V(3)–O(11)–V(4B)	93.3(1)
P(1)–O(11)–V(4B)	123.4(1)	C(1)–N(1)–C(2)	111.5(4)
C(1)–N(1)–C(3)	110.4(4)	C(2)–N(1)–C(3)	111.2(4)

The involvement of O7 in hydrogen bonding to the Na_4^+ protons is also apparent from valence sum calculations. While the bond number for O7 in the absence of hydrogen bonding is 1.81, a value of 1.96 is calculated with hydrogen contributions included.

It is clear that the oxovanadium ions $[H_nV_{10}O_{28}]^{3-}$ [6] and $[H_nPV_{14}O_{42}]^{(9-n)-}$ can exist in various protonation forms. In the case of $[H_3V_{10}O_{28}]^{3-}$ [6], the most basic surface oxygen could not be determined from protonation sites since two non-equivalent types of bridging oxygens are protonated. In contrast, both $[H_2V_{10}O_{28}]^{4-}$ [5] and $[H_4PV_{14}O_{42}]^{5-}$ exhibit a clear preference for the doubly-bridging oxygen sites. Analogous patterns of behavior have been established for $[Nb_2W_4O_{19}]^{4-}$ [12], $[V_2W_4O_{19}]^{4-}$ [13], $[SiV_3W_9O_{40}]^{7-}$ [14] and $[Mo_{12}PO_{40}]^{2-}$ [15] where doubly-bridging oxo groups are more nucleophilic/basic than terminal oxo groups.

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