



Study on Novel Structure of $(\text{NH}_4)_3(\text{PV}_{15}\text{O}_{43})\text{Cl}_4(\text{H}_2\text{O})_{12}$

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The title compound, $(\text{NH}_4)_3(\text{PV}_{15}\text{O}_{43})\text{Cl}_4(\text{H}_2\text{O})_{12}$, prepared by a single solution reaction and crystal structure has been determined by means of single-crystal X-ray diffraction. The compound crystallize in cubic, system with space group and cell parameters, Fm-3m, $a = b = c = 22.12 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$, $V = 10823.2(8) \text{ \AA}^3$. The crystal packing is stabilized by O-H...O, O-H...Cl and O-H...N hydrogen bonding interaction.

Keywords: $(\text{NH}_4)_3(\text{PV}_{15}\text{O}_{43})\text{Cl}_4(\text{H}_2\text{O})_{12}$, Structure analysis, Hydrogen bonding, Polyoxometalates.

INTRODUCTION

Polyoxometalates (POMs), as anionic early transition metal oxide clusters, have received much attention, not only because of their potential applications in catalysis, sorption, biology, optical and electromagnetic functional materials, but also for their intriguing variety of architectures and topologies. An intriguing area in this field is the combination of metal cations with polyoxometalates to construct new low dimensional polyoxometalate architectures with particular topologies by self-assembly¹⁻⁵. Several successful strategies have been developed to design polyoxometalate-based architectures⁶. The polyoxometalates basic octahedral MO_6 and square pyramidal MO_5 units share either vertices or edges and, under the influence or not of some templating species, condense and grow larger clusters. With the exception of some few, almost all the elements have been incorporated either in the polyoxometalate structure itself or encapsulated within. This rather simplistic definition holds, however, for an enormous variety of structures ranging from small molecules to supramolecular nanosized aggregates displaying high symmetry in most cases. Polyoxometalates are unique from several viewpoints and their chemical and structural possibilities have still unseen limits. Regular shapes resembling balls, cylinders and wheels, as well as displaying channels or cavities have been reported⁷⁻¹⁰. The size and shape of a polyoxometalate can be purposely designed depending on the pH and the temperature conditions, the ionic strength or the presence of additional ligands during the synthesis, among other variables^{11,12}. Polyoxometalates is more

suitable as guest unit in the metal-organic host because they lead to larger pores, channels and cavities¹³. Thereby, one of the significant preparation hybrid material is to establish the possible connections between organic and/or inorganic molecular fragments on the basis of strong and directional interactions, weak interactions such as hydrogen-bonding, π - π stacking, C... π interaction, weak coordination interaction, *etc.*^{14,15}. In this paper, the new $(\text{NH}_4)_3(\text{PV}_{15}\text{O}_{43})\text{Cl}_4(\text{H}_2\text{O})_{12}$ complex is reported.

EXPERIMENTAL

All commercially obtained reagent-grade chemicals were used without further purification. A mixture of CuCl_2 (0.1 mmol, 0.014 g), diphenylamine (0.1 mmol, 0.017 g), NH_4VO_3 (0.1 mmol, 0.012 g) and Na_2HPO_4 (0.1 mmol, 0.015 g) were added into 20 mL water with 20 % methanol and heated for 6 h at 344 K. The solution was obtained by filtration after cooling the reaction to room temperature. Red block single crystals suitable for X-ray measurements were obtained after a few weeks.

RESULTS AND DISCUSSION

The title crystal structure (Fig. 1) is built up of heteropolyacid cluster, ammonium cation, chloride anion and water molecules. The packing diagram is shown in Fig. 2.

The crystal data and structure refinement is shown in Table-1. In the heteropolyacid cluster, the P1 atom is coordinated by four O1 atoms to form a tetrahedron. There are three

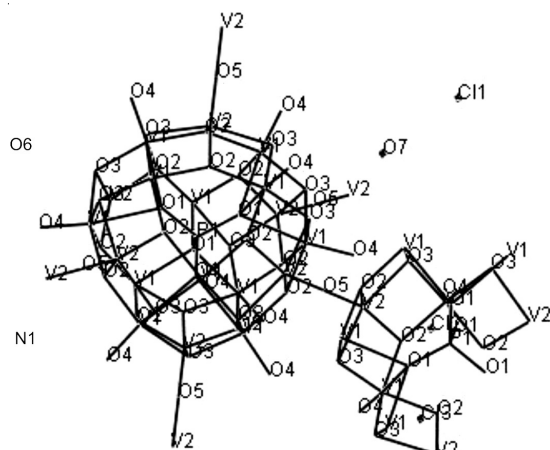


Fig. 1. Molecular structure of H36Cl4N3O55PV15

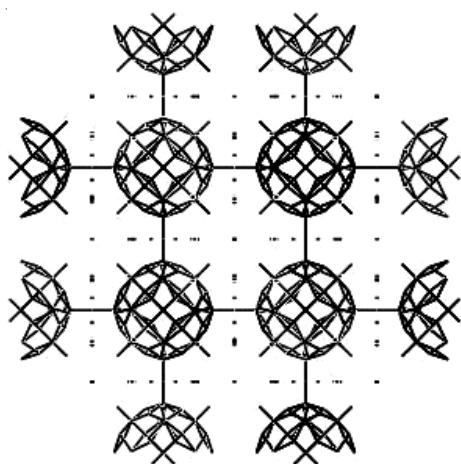


Fig. 2. Packing structure of H36Cl4N3O55PV15

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT
FOR THE TITLE COMPLEX

Empirical formula	H ₃₆ Cl ₄ N ₃ O ₅₅ PV ₁₅
Formula weight	1895.19
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Cubic, Fm-3m
Unit cell dimensions	a = 22.1200(10) Å α = 90° b = 22.1200(10) Å β = 90° c = 22.1200(10) Å γ = 90°
Volume	10823.2(8) Å ³
Z, Calculated density	8, 2.326 Mg/m ³
Absorption coefficient	2.808 mm ⁻¹
F(000)	7400
Crystal size	0.40 × 0.38 × 0.35 mm
Theta range for data collection	1.59 to 25.00°
Limiting indices	-26 ≤ h ≤ 26, -24 ≤ k ≤ 26, -24 ≤ l ≤ 26
Reflections collected / unique	15600/543 [R(int) = 0.0826]
Completeness to theta = 25.00	100 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.4398 and 0.3996
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	543/0/53
Goodness-of-fit on F ²	1.112
Final R indices [I > 2σ(I)]	R1 = 0.0777, wR2 = 0.2484
R indices (all data)	R1 = 0.0947, wR2 = 0.2761
Largest diff. peak and hole	2.027 and -3.252 e. Å ⁻³

μ_3 -O atoms, one μ_2 -O atom and one terminal O atom. The μ_3 -O1 bridges P1 and two V1, while μ_3 -O2 and μ_3 -O3 bridges two V1 and V2. The μ_2 -O5 bridges two V2. The distance d(P-O) is 1.532 Å. The distance d(V-O) are in the range of 1.601-2.371 Å. The angles of O-V-O are in the range of 74.1-171.2°. The angle of V2-O5-V2 is 180°. Selected bond lengths and bond angles are shown in Table-2.

TABLE-2
SELECT BOND LENGTHS [Å] AND ANGLES [°]
FOR THE TITLE COMPLEX

V(1)-O(4)	1.601(7)
V(1)-O(3)	1.894(4)
V(1)-O(2)	1.915(2)
V(1)-O(1)	2.371(7)
V(1)-V(2)	2.818(3)
V(2)-O(5)	1.711(7)
V(2)-O(2)	1.806(7)
V(2)-O(3)#4	2.105(8)
V(2)-V(1)#4	2.818(3)
P(1)-O(1)	1.532(11)
N(1)-H(1C)	0.9001
O(1)-V(1)#5	2.371(7)
O(2)-V(1)#6	1.915(2)
O(3)-V(1)#8	1.894(4)
O(5)-V(2)#9	1.711(7)
O(4)-V(1)-O(3)	99.8(3)
O(3)#1-V(1)-O(3)	90.6(5)
O(4)-V(1)-O(2)#1	99.8(3)
O(3)-V(1)-O(2)#1	87.6(3)
O(4)-V(1)-O(2)	99.8(3)
O(3)#1-V(1)-O(2)	87.6(3)
O(3)-V(1)-O(2)	160.3(3)
O(2)#1-V(1)-O(2)	87.6(4)
O(4)-V(1)-O(1)	171.2(4)
O(3)#1-V(1)-O(1)	74.1(2)
O(3)-V(1)-O(1)	74.1(2)
O(2)#1-V(1)-O(1)	86.5(3)
O(2)-V(1)-O(1)	86.5(3)
O(3)-V(1)-V(2)#2	48.3(2)
O(3)#1-V(1)-V(2)	48.3(2)
O(3)-V(1)-V(2)	134.2(2)
O(2)-V(1)-V(2)	39.3(2)
O(5)-V(2)-O(2)#3	116.3(3)
O(5)-V(2)-O(2)	116.3(3)
O(2)#3-V(2)-O(2)	127.4(6)
O(5)-V(2)-O(3)#1	102.7(3)
O(5)-V(2)-O(3)#4	102.7(3)
O(2)-V(2)-V(1)#4	108.5(3)
O(2)-V(2)-V(1)#5	108.5(3)
O(2)#3-V(2)-V(1)	108.5(3)
O(2)-V(2)-V(1)	42.25(9)
O(3)#4-V(2)-V(1)	122.0(3)
V(1)#4-V(2)-V(1)	122.9(3)
O(2)-V(2)-V(1)#6	42.25(9)
O(1)#4-P(1)-O(1)	109.471(1)
H(1C)-N(1)-H(1A)	106.8
P(1)-O(1)-V(1)	126.0(2)
P(1)-O(1)-V(1)#5	126.0(2)
V(1)-O(1)-V(1)#5	88.9(3)
P(1)-O(1)-V(1)#8	126.0(2)
V(2)-O(2)-V(1)	98.4(2)
V(1)-O(2)-V(1)#6	146.8(4)
V(1)#8-O(3)-V(1)	122.6(4)
V(1)-O(3)-V(2)#2	89.4(3)
V(2)-O(5)-V(2)#9	180.0

The crystal packing is stabilized by O-H...O, O-H...Cl and O-H...N hydrogen bonding interaction.

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