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# Synthesis and Crystal Structure of Phosphorus Vanadium Heteropoly Acid Potassium Compound: $(K_{12}P_4V_{72}O_{172})\cdot 24Cl\cdot 24(OH)\cdot 14.4H_2O$

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Phosphorus vanadium heteropoly acid potassium: $(K_{12}P_4V_{72}O_{172})\cdot 24Cl\cdot 24(OH)\cdot 14.4(H2O)$, is prepared by the hydrothermal method. Cubic, Fm-3m. a = b = c = 21.866(2) Å α = β = γ = 90°. V = 10454.6(17) Å$^3$. Z = 2. $R_1$ = 0.0479, $wR_2$ = 0.1191. T = 291(2) K. The V atoms are linked with O atom bridge. It is striking that the structure of the phosphorus vanadium heteropoly acid potassium exhibits extensive hydrogen-bonding interactions.

**Key Words: Heteropoly acid, Structure analysis.**

Polyoxometalates, as early transition-metal oxide clusters, bear many properties that make them attractive for applications in catalysis, separation, imaging, materials science and medicine[1]. It should be noted that polyoxometalate, known as their wide applications in before-mentioned fields, is an outstanding class of inorganic components to build the interesting hybrid materials *via* two kinds of interactions, *i.e.* coordinate covalent bonds and weaker intermolecular forces. Furthermore, the construction of new polyoxometalate-based hybrid supramolecular frameworks with versatile organic ligands or metal complex moieties constitutes an emerging area, by means of weaker intermolecular forces such as hydrogen bond and π-π stacking[2]. It is well known that the Anderson-type polyoxoanions exhibit attractive planar structures. In addition, each Mo (or V) atom has two terminal oxygen atoms with high reactivity[3,4], which may facilitate the construction of novel hybrid compounds. Recently, some new polyoxometalates complex have been reported[5-7].

All commercially obtained reagent-grade chemicals were used without further purication. A mixture of $CdCO_3$ (0.1 mmol, 0.017 g), $NH_4VO_3$ (0.1 mmol, 0.012 g), KCl (0.1 mmol, 0.008 g), $Na_2HPO_4$ (0.1 mmol, 0.036 g), KOH (0.2 mmol, 0.012 g) and 1,2,3-benzotriazole (0.1 mmol, 0.012 g) were added into 20 mL water with 40 % (v/v) ethanol and heated for 12 h at 414 K. The solution was obtained by filtration after cooling the reaction to room temperature. Brown block single crystals suitable for X-ray measu-rements were obtained after a few weeks. 1,2,3,-Benzotriazole does not take part in the reaction.

The molecular structure of the complex is shown in Fig. 1. Packing diagram of three-dimensional structure of the complex is shown in Fig. 2.

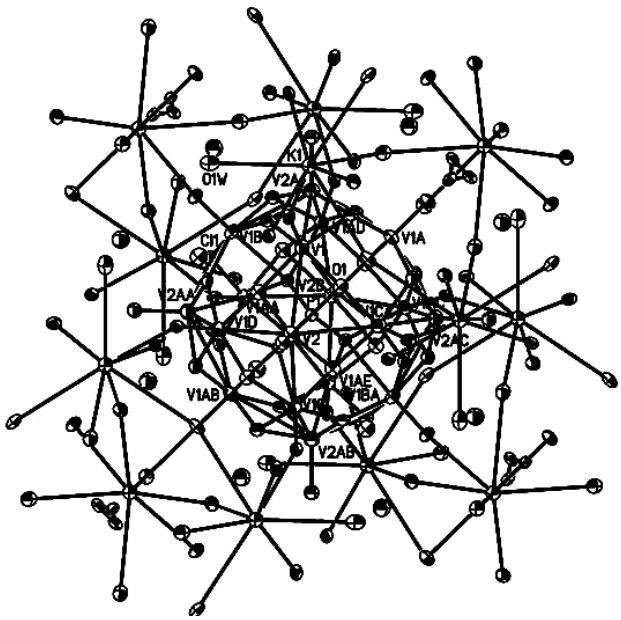


Fig. 1. Molecular structure of the title complex

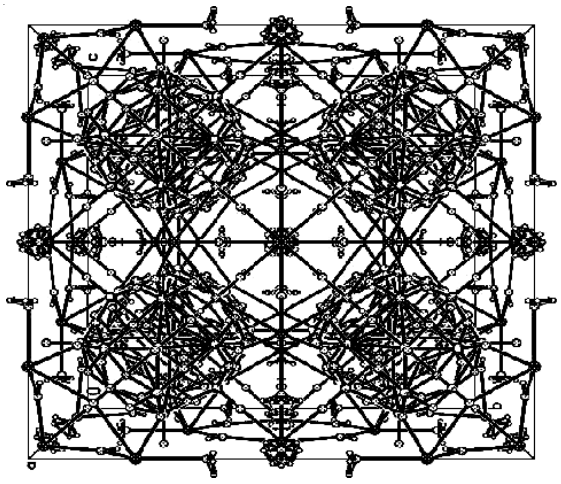

Fig. 2. Packing diagram of three-dimensional structure of the complex

The crystal data and structure refinement is shown in Table-1. The title crystal structure is built up P-V cluster, Cl anion, K cation and water molecules. A tetrahedral configuration is formed by a P1 atom and four O1 atoms. The O1 atom connectes three V1 atoms. The V1 atom is coordinated by six O atoms (O1, two O2, two O3, O4). The V2 atom is coordinated by five O atoms (two O2, two O3, O5). There are three $\mu_2$-O atoms and a terminal O1w atom. The $\mu_2$-O4 atom bridges V1 and K1 atom, while $\mu_2$-O5 atom bridges two V2 atoms, while $\mu_2$-O6 atom bridges two K1 atoms. The coplanar is formed of the atoms (K1, O5, O6, O1w). The coplanar is formed of the atoms (P1, V1, O1, O2, O4). The d (P-O) is 1.544 Å. The d (V-O) are in the range of 1.568-2.370 Å. The d (K-O) are in the range of 2.842-3.356 Å. Selected bond lengths and bond angles are shown in Table-2.

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

| | |
|---|---|
| Empirical formula | $Cl_{24}H_{52.80}K_{12}O_{210.40}P_4V_{72}$ |
| Formula weight | 8531.18 |
| Temperature | 291(2) K |
| Wavelength | 0.71073 Å |
| Crystal system, space group | Cubic, Fm-3m |
| Unit cell dimensions | a = 21.866(2)Å $\alpha = 90^\circ$ |
| | b = 21.866(2) Å $\beta = 90^\circ$ |
| | c = 21.866(2) Å $\gamma = 90^\circ$ |
| Volume | 10454.6 $Å^3$ |
| Z, Calculated density | 2, 2.710 $Mg/m^3$ |
| Absorption coefficient | 3.745 $mm^{-1}$ |
| F(000) | 8176 |
| Crystal size | 0.32 × 0.29 × 0.20 mm |
| Theta range for data collection | 2.64 to 26.92°. |
| Limiting indices | -26 <= h <= 20, -26 <= k <= 25, -26 <= l <= 26 |
| Reflections collected/unique | 13453/574 [R(int) = 0.0584] |
| Completeness to theta = 25.93 | 100 % |
| Absorption correction | Semi-empirical from equivalents |
| Max and min transmission | 0.5213 and 0.3803 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 574/0/53 |
| Goodness-of-fit on $F^2$ | 1.093 |
| Final R indices [I > 2σ(I)] | R1 = 0.0363, wR2 = 0.1191 |
| R indices (all data) | R1 = 0.0479, wR2 = 0.1338 |
| Largest diff. peak and hole | 0.981 and -0.907 e. $Å^3$ |

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

| | |
|---|---|
| K1-O4 | 2.842(4) |
| K1-O1W | 3.074(9) |
| K1-O6 | 3.356(4) |
| O1-P1 | 1.544(5) |
| O1-V1 | 2.370(3) |
| O2-V2 | 2.084(4) |
| O3-V2 | 1.801(4) |
| O3-V1 | 1.913(3) |
| O4-V1 | 1.568(4) |
| O5-V2 | 1.6480(15) |
| O4-K1-O4 | 83.67(4) |
| O4-K1-O6 | 137.78(4) |
| O1W-K1-O6 | 122.79(9) |
| O6-K1-O6 | 72.95(9) |
| O1W-K1-O2W | 175.1(4) |
| P1-O1-V1 | 125.51(9) |
| V1-O1-V1 | 89.65(13) |
| V1-O2-V2 | 90.01(13) |
| V2-O3-V1 | 98.67(12) |
| V1-O4-K1 | 152.29(16) |

It is striking that the structure of the title compound exhibits extensive hydrogen-bonding interactions

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