NOTE

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: $(K_{12}P_4V_{72}O_{172}) \cdot 24Cl \cdot 24(OH) \cdot 14.4(H_2O)$, is prepared by the hydrothermal method. Cubic, Fm-3m. $a = b = c = 21.866(2) \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$. $V = 10454.6(17) \text{ \AA}^3$. $Z = 2$. $R_1 = 0.0479$, $wR_2 = 0.1191$. $T = 291(2) \text{ K}$. 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 medicine¹. 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 stacking². 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 reported⁵⁻⁷.

All commercially obtained reagent-grade chemicals were used without further purification. 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 measurements 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 connects 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 μ_2 -O atoms and a terminal O1w atom. The μ_2 -O4 atom bridges V1 and K1 atom, while μ_2 -O5 atom bridges two V2 atoms, while μ_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	$\text{Cl}_{24}\text{H}_{52.80}\text{K}_{12}\text{O}_{210.40}\text{P}_4\text{V}_{72}$
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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REFERENCES

1. A. Müller, R. Sessoli, E. Krickemeyer, H. Bögge, J. Meyer, D. Gatteschi, L. Pardi, J. Westphal, K. Hovemeier, R. Rohlfing, J. Döring, F. Hellweg, C. Beugholt and M. Schmidtman, *Inorg. Chem.*, **36**, 5239 (1997).
2. A. Dolbecq, P. Mialane, L. Lisnard, J. Marrot and F. Secheresse, *Chem. Eur. J.*, **9**, 2914 (2003).
3. D. Drewes, E.M. Limanski and B. Krebs, *J. Chem. Soc. Dalton. Trans.*, **21**, 2087 (2004).
4. H.X. Liu, F.F. Jian and J. Wang, *J. Chem. Crystallogr.*, **40**, 306 (2010).
5. H.-X. Liu, *Z. Kristallogr. NCS*, **226**, 441 (2011).
6. H.X. Liu, J. Wang, Y.F. Li and F.F. Jian, *J. Chem. Crystallogr.*, **41**, 1254 (2011).
7. H.-X. Liu, *Z. Kristallogr. NCS*, **225**, 243 (2010).