Asian Journal of Chemistry; Vol. 25, No. 2 (2013), 1165-1166

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.12991

NOTE

Crystal Structure of $(NH_4)_9(P_2VW_{22}O_{78})(H_2O)_2$

HAI-XING LIU*, XIAO-YAN REN, LI-MEI WAN, YUN-CHEN ZHANG and XI-SHI TAI

College of Chemistry and Chemical Engineering, Weifang University, Weifang 261061, P.R. China

*Corresponding author: E-mail: haixingliu@tom.com

(*Received*: 2 November 2011; *Accepted*: 31 August 2012) AJC-12069

The title compound, $(NH_4)_9(P_2VW_{22}O_{78})(H_2O)_2$, is prepared by hydrothermal method. It contains PVW heteropolyacid anion, ammonium cations and water molecular. The crystal packing is stabilized by intermolecular N-H···O and N-H···N hydrogen bonds interaction.

Key Words: Hydrothermal, $(NH_4)_9(P_2VW_{22}O_{78})(H_2O)_2$.

Keggin-type polyoxometalates $[XM_{12}O_{40}]^{n-}$ (X = B, P, Si, *etc*.; M = Mo, W) and their derivatives have been investigated for over a century because of rich structural chemistry and diverse physicochemical properties[1]. Potential activities of Keggin anions as catalysts is shown by previous workers[2-5]. The polyoxometalates may provide structurally well-characterized surfaces formed by approximately coplanar. we sythesize the $(NH_4)_9(P_2VW_{22}O_{78})(H_2O)_2$ and report its crystal structure here.

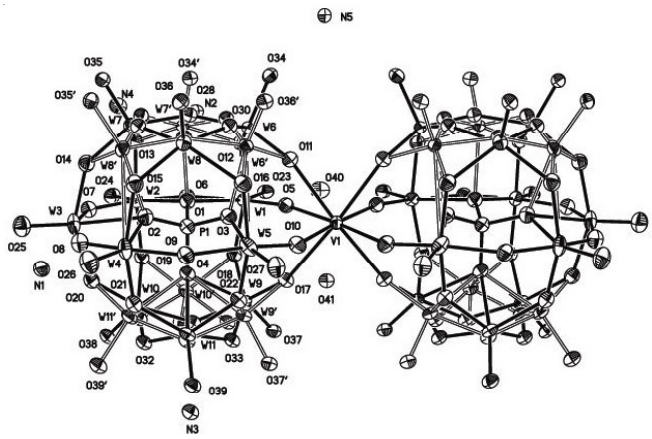

Fig. 1. Molecular structure of the title compound with atom-labling scheme

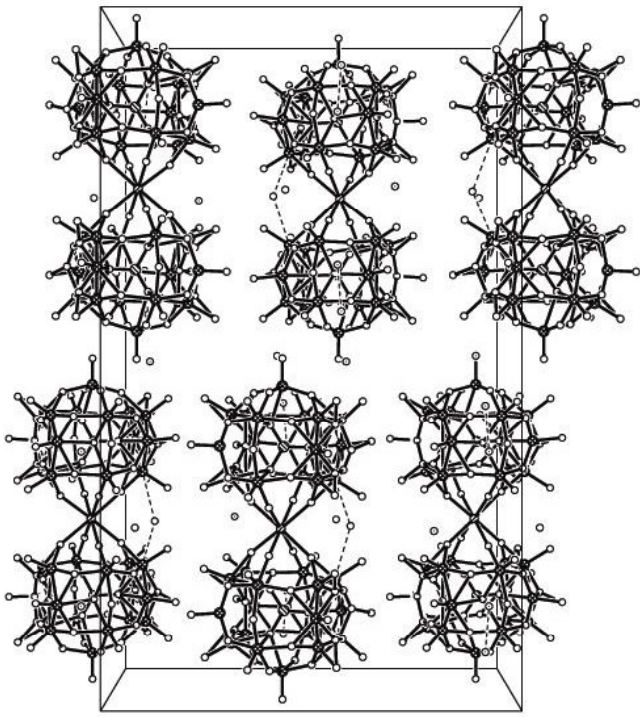

Fig. 2. Packing diagram of three-dimensional of the title complex

All commercially obtained reagent-grade chemicals were used without further purication. A mixture of $CdCO_3$ (0.1 mmol, 0.018 g), $(NH_4)_2WO_4$ (0.1 mmol, 0.029 g), NH_4VO_3 (0.1 mmol, 0.012 g), H_3PO_4 (0.2 mL) and triethylamine (1 mL) were added into 20 mL water with 20 % (v/v) ethanol and heated for 12 h at 140 ºC. The solution was obtained by filtration after cooling to room temperature. Colourless block single crystals suitable for X-ray measurements were obtained after a few weeks. Triethylamine and Cd^{2+} do not take part in the reaction.

The crystal structure of $(NH_4)_9(P_2VW_{22}O_{78})(H_2O)_2$ (Fig. 1) is built up of heteropolyacid cluster, ammonium cation and water molecules. The packing diagram of three-dimensional structure of the title complex is shown in Fig. 2. The crystal

data and structure refinement is shown in Table-1. In the heteropolyacid cluster, the P atom is coordinated by four O atoms(O1, O2, O3, O4) to form a tetrahedron. There are eleven terminal O atoms, twenty-four μ_2-O atoms, two μ_3-O atoms and one μ_4-O atom. The μ_2-O3 bridges P1 and W5, while μ_2-O5 bridges W1 and V1. The μ_2-O10 bridges W5 and V1, while μ_2-O17 bridges W9 and V1. The μ_3-O1 bridges P1, W1 and W2, while μ_3-O2 bridges P1, W3 and W4. The μ_4-O4 bridges P1, W9, W10 and W11. The five atoms (W1, W2, W4, W5, V1) are on the equatorial plane. The distance from O1 to the plane is 0.332 Å, while the distance from O2 (or O3) to the plane is 0.371 Å. The distance from O4 to the plane is 1.684 Å. The d (W-O) are in the range of 1.58-2.45 Å. The d (V-O) are in the range of 2.33-2.48 Å. Some bond lengths are shown in Table-2.

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR 100113 g

Identification code	100113g
Empirical formula	$H_{40}N_9O_{80}P_2VW_{22}$
Formula weight	5603.99
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, Pbcm
Unit cell dimensions	a = 12.9700(10) Å, α = 90° b = 23.120(2) Å, β = 90° c = 38.810(3) Å, γ = 90°
Volume	11637.8 (16) $Å^3$
Z, Calculated density	4, 3.198 Mg/m^3
Absorption coefficient	21.826 mm^{-1}
$F_{(000)}$	9696
Crystal size	0.31 mm × 0.18 mm x 0.16 mm
Theta range for data collection	1.57-25.02°
Limiting indices	-15 ⇐ h⇐13, -27⇐ k⇐ 21, -46 ⇐ l ⇐ 42
Reflections collected/unique	56934/10396 [R(int) = 0.2447]
Completeness to theta = 25.02	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.1279 and 0.0564
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	10396 / 0 / 684
Goodness-of-fit on F^2	1.018
Final R indices [I > 2σ(I)]	R1 = 0.1076, wR_2 = 0.2705
R indices (all data)	R1 = 0.2568, wR_2 = 0.3720
Largest diff. peak and hole	3.252 and -4.696 $eÅ^{-3}$

TABLE-2
BOND LENGTHS [Å] FOR 100113 g

V(1)-O(10)	2.33(3)
V(1)-O(5)	2.37(3)
V(1)-O(17)	2.46(3)
V(1)-O(11)	2.48(3)
W(1)-O(23)	1.70(3)
W(1)-O(1)	2.37(3)
W(2)-O(24)	1.67(3)
W(2)-O(1)	2.34(3)
W(3)-O(25)	1.58(4)
W(3)-O(2)	2.39(3)
W(4)-O(26)	1.61(3)
W(4)-O(2)	2.39(3)
W(5)-O(27)	1.71(3)
W(5)-O(3)	2.36(3)
W(6)-O(11)	1.82(3)
W(6)-O(12)	1.98(3)
P(1)-O(1)	1.54(3)
P(1)-O(4)	1.55(3)
N(1)-H(1C)	0.9002
N(2)-H(2C)	0.9002

The crystal packing is stabilized by intermolecular N-H···O and N-H···N hydrogen bonds interaction.

ACKNOWLEDGEMENTS

This study were supported by the Natural Science Foundation of Shandong Province (No. ZR2010BL025), State Key Laboratory of Inorganic Synthesis and Preparative Chemistry (Jilin University) (No. 2011-13) and MOE Key Laboratory of Analytical Chemistry for Life Science (Nanjing University) (No. KLACLS1002) and the National Science Foundation of China (No. 211771132).

REFERENCES

1. C.L. Hill, *Chem. Rev*., **98**, 1 (1998).
2. I.V. Kozhevnikov, *Chem. Rev*., **98**, 171 (1998).
3. H.-X. Wu, M. Zhou, Y.-X. Qu and H.-X. Li, *Chin. J. Chem. Eng*., **17**, 200 (2009).
4. M.-L. Xue, C. Wei and L. Yang, *Chin. Chem. Lett*., **20**, 344 (2009).
5. H.-H. Li, K.-W. Li and H. Wang, *Chin. J. Inorg. Chem*., **25**, 512 (2009).