NOTE

Study on Novel Structure of Molybdenum Tungsten Imidazole Complex: $(\text{H}_{12}\text{MoW}_7\text{O}_{30})(\text{C}_3\text{H}_4\text{N}_2)_4(\text{H}_2\text{O})_3$

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A novel molybdenum tungsten imidazole complex $(\text{H}_{12}\text{MoW}_7\text{O}_{30})(\text{C}_3\text{H}_4\text{N}_2)_4(\text{H}_2\text{O})_3$ with the m.f. $\text{C}_{12}\text{H}_{34}\text{MoN}_8\text{O}_{33}\text{W}_7$ has been synthesized from a single solution reaction and the crystal structure has been determined by means of single-crystal X-ray diffraction. The Mo atom is coordinated by seven O atoms. There are two kinds coordinations mode for W atom. The crystal is stabilized by O-H...O and N-H...O hydrogen bonds interaction.

Key Words: Molybdenum tungsten complex, Imidazole, Structure analysis.

Supramolecular compounds based on polyoxometalates construct a small subset of the large family of polyoxometalates which have attracted considerable attention due to variety of their structures and potential application¹⁻³. The self-assembly of supramolecular structure performs *via* ligand-metal coordination bonds, hydrogen bonds, electrostatic force and π - π stacking interaction⁴. Recently, the strategy of self-assembly through intermolecular weak interactions is a focus of the design of new polyoxometalates based hybrids⁵, which have been intensively investigated in many important aspects such as catalysis, electrical conductivity, magnetic properties and biological chemistry⁶. In this paper, the novel molybdenum tungsten imidazole complex is reported.

All commercially obtained reagent-grade chemicals were used without further purification. A mixture of MnSO_4 (0.01 mmol, 0.002 g), $(\text{NH}_4)_2\text{WO}_4$ (0.1 mmol, 0.03 g), $(\text{NH}_4)_2\text{MoO}_4$ (0.1 mmol, 0.02 g), imidazole (0.1 mmol, 0.007 g), citric acid (0.1 mmol, 0.02 g) and dilute HCl were added into 20 mL water with 20 % (v/v) ethanol and heated for 5 h at 343 K. The solution was obtained by filtration after cooling the reaction to room temperature. Colourless block single crystals suitable for X-ray measurements were obtained after a few weeks.

The title crystal structure (Fig. 1) is built up of molybdenum tungsten acid, imidazole and water molecular. The 1D chain structure extending along b axis is shown in Fig. 2. The View of the three-fold interpenetration network along the b axis is shown in Fig. 3. The crystal data and structure refinement is

shown in Table-1. The Mo atom is coordinated by seven O atoms (one O1, two O1w, two O2w, two O3w). The W2 atom is coordinated by five O atoms and the others W atoms are coordinated by six O atoms. The μ_2 -O1 atom bridges Mo1 and W2. The μ_3 -O8 atom bridges W1, W3 and W4. The μ_4 -O7 atom bridges two W1, W2 and W4, while μ_4 -O13 atom bridges two W3, W4 and W5. The distances of d(Mo-O) and d(W-O) are in the range of 2.428-2.496 Å and 1.697-2.506 Å, respectively. The bond angles of Mo1-O1-W2 is 161.2°. Selected bond lengths and bond angles are shown in Table-2.

Fig. 1. Molecular structure of the title complex

Fig. 2. 1D chain structure extending along b axis

Fig. 3. Perspective view of the 3D packing diagram along the b axis

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

Empirical formula	C ₁₇ H ₃₄ MoN ₈ O ₃₃ W ₇
Formula weight	2201.36
Temperature	291(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, C ₂ /m
Unit cell dimensions	a = 15.6529(8) Å α = 90° b = 19.3356(8) Å β = 103.975(4)° c = 14.1045(5) Å γ = 90°
Volume	4142.5(3) Å ³
Z, Calculated density	4, 3.530 Mg/m ³
Absorption coefficient	19.755 mm ⁻¹
F(000)	3944
Crystal size	0.28 × 0.24 × 0.22 mm
Theta range for data collection	1.49 to 26.00°
Limiting indices	-8 ≤ h ≤ 19, -23 ≤ k ≤ 22, -17 ≤ l ≤ 17
Reflections collected/unique	12725/4205 [R(int) = 0.0141]
Completeness to θ = 26	99.8 %
Absorption correction	Semi-empirical from equivalents
Max and min transmission	0.02 and 0.01
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	4205/0/296
Goodness-of-fit on F ²	1.092
Final R indices [I > 2σ(I)]	R1 = 0.0210, wR2 = 0.0653
R indices (all data)	R1 = 0.0237, wR2 = 0.0676
Largest diff. peak and hole	0.618 and -1.868 e.Å ⁻³

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

C(1)-N(1)	1.310(8)	O(4W)-H(4X)	0.8500
C(1)-N(2)	1.366(7)	W(1)-W(2)	3.1993(3)
C(1)-H(1)	0.9300	N(1)-C(1)-N(2)	108.0(5)
C(2)-C(3)	1.307(9)	C(3)-C(2)-N(1)	107.8(5)
C(2)-N(1)	1.377(9)	C(2)-C(3)-N(2)	109.0(6)
C(2)-H(2)	0.9300	N(2)-C(3)-H(3)	125.5
C(3)-N(2)	1.343(8)	N(4)-C(6)-H(6)	123.9
C(4)-N(3)	1.290(7)	C(1)-N(1)-C(2)	107.8(5)
C(5)-N(3)	1.372(7)	C(4)-N(3)-C(5)	108.5(5)
C(6)-N(4)	1.286(8)	C(7)-N(4)-H(4A)	127.3
C(7)-N(4)	1.375(9)	W(2)-O(1)-Mo(1)	161.2(3)
Mo(1)-O(3W)	2.428(4)	W(4)-O(4)-W(2)	105.1(2)
Mo(1)-O(1)	2.470(5)	W(4)-O(9)-W(5)	108.9(2)
Mo(1)-O(1W)	2.470(4)	O(8)-W(1)-W(2)	87.34(8)
Mo(1)-O(2W)	2.496(4)	O(1)-W(2)-O(2)	105.5(2)
N(2)-H(2A)	0.8600	O(2)-W(2)-O(7)	150.6(2)
O(1)-W(2)	1.704(5)	O(2)-W(2)-W(1)	135.66(5)
O(2)-W(2)	1.756(5)	O(7)-W(2)-W(1)	42.25(3)
O(3)-W(1)	1.941(4)	O(4)-W(2)-W(1)	83.32(8)
O(4)-W(4)	1.732(5)	O(9)-W(4)-O(4)	105.9(2)
O(5)-W(1)	1.707(4)	O(4)-W(4)-O(13)	173.0(2)
O(6)-W(1)	1.697(4)	O(4)-W(4)-O(7)	83.6(2)
O(7)-W(2)	2.141(5)	O(15)-W(5)-O(16)	105.0(2)
O(8)-W(4)	1.894(3)	O(15)-W(5)-O(13)	106.1(2)
O(9)-W(4)	1.723(5)	O(15)-W(5)-O(9)	174.7(2)
O(1W)-H(1X)	0.9600	O(16)-W(5)-O(9)	80.3(2)

Crystal is stabilized by O-H...O and N-H...O hydrogen bonds interaction

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