

A new member of Mo₃₆- polyoxoanion's family: synthesis, crystal structure, and physico-chemical properties of K₁₀[Mo₃₆O₁₁₀(OH)₆(H₂O)₁₂].38 H₂O

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Abstract: The new giant Mo₃₆ polyoxomolybdate formulated as K₁₀[Mo₃₆O₁₁₀(OH)₆(H₂O)₁₂].38 H₂O (1) was isolated by conventional solution method by the reaction of K₂MoO₄ and KNO₃ in aqueous solution (pH = 1.8), at room temperature, and structurally characterized by single-crystal X-ray diffraction methods. The title compound crystallized in the monoclinic system, space group P2₁/n with unit a = 16.5180 (0) Å, b = 18.4485 (0) Å, c = 24.2424 (0) Å, α = 90.00°, β = 99.51°, γ = 90.00°, V = 7285.79 (0) Å³, and Z = 2. The refinement of the structure led to a residual factor R = 0.061 for 15,676 reflections.

Key words: Giant polyoxomolybdates, synthesis and crystal structure, X-ray diffraction, infrared spectroscopy, UV-VIS, TG analysis

1. Introduction

Polyoxometalates (POMs), as one kind of significant metal oxide cluster with several topologies and nanosizes, have been attracting interest in different fields such as catalysis, electrochemistry, medicine, and magnetism.^{1–5} The evolution of POM chemistry is dependent upon the synthesis of new solids possessing various structures and properties. Although synthesis of the materials remains a challenge, a large number of novel poly-oxoanions with unexpected shapes and sizes are still being discovered.^{6–10} Thus, the self-assembly process of nanoscale polyoxometalates has attracted the attentions of many groups, and a series of novel POMs possessing unique structures and properties has been reported.^{11–13} As nano-sized anions, giant high-core POMs clusters are attracting the attention of researchers more and more.^{14–16} In particular, Mo_x clusters (x = 12, 16, 18, 36, 57, 126, 132, 154, 248, 256, 328) have been isolated successfully.^{17–21}

They exhibit different and fascinating conformations, such as bowl-like, basket-like, and tire. One of the features is that all those big clusters are composed of the primary units: MoO_y (y = 4, 5, 6, 7) polyhedral linked through corner- or edge-sharing modes. In this family, the {Mo₃₆} cluster can then be considered as the genetic material to assemble bigger clusters.^{22–26}

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2. Results and discussion

2.1. Crystal data

X-ray intensity data were collected on an Enraf-Nonius CAD-4 diffractometer with Mo K_{α} monochromatic radiation ($k = 0.71073 \text{ \AA}$). The structure was solved by the Patterson method, using SIR2011,²⁷ which allows the location of molybdenum atoms. The remaining nonhydrogen atoms were found by the successive difference Fourier maps using the SHELXL-2014²⁸ and Crystal²⁹ programs. A summary of the crystallographic data and structure refinements of (1) is given in Table 1 and final values of the atomic coordinates and displacement parameters are given in Table 2.

Table 1. Crystal structure data for compound.

Crystal data	
Empirical formula	$K_{10} [Mo_{36}O_{110} (OH)_6 (H_2O)_{12}] \cdot 38H_2O$
Formula weight (g mol^{-1})	6607.68
Crystal system	Monoclinic
Space group	$P2_1/n$
Z	2
Lattice parameters a (\AA) b (\AA) c (\AA) α ($^{\circ}$) β ($^{\circ}$) γ ($^{\circ}$)	16.5180 (0) 18.4485 (0) 24.2424 (0) 90.00 99.51 90.00
Cell volume (\AA^3)	7285.79 (3) 7285.79 (0)
Calculated density (g/cm^3)	3.012
F_{000}	6272
Intensity measurement	
Diffractometer	Enraf-Nonius CAD4
Monochromator	Graphite
Wavelength [K_{α} (Mo)]	$\lambda = 0.71073 \text{ \AA}$
Temperature	293 K
Theta range	$2.0^{\circ}/27.0^{\circ}$
h, k, l range	$-21/2, -1/23, -30/30$
Number of measured reflections	19,422
Number of independent reflections	15,676
Structure determination	
Unique reflection included ($I > 2\sigma(I)$)	8293
Number of refined parameters	966
Absorption correction	Ψ -scan
T_{min}, T_{max}	0.8703, 0.9993
$R[F^2 > 2\sigma(F^2)], wR(F^2)$	0.06, 0.167
Weights	$w = 1/[\sigma^2(F_o^2) + (0.0744P)^2 + 9.9737P]$, where $P = (F_o^2 + 2F_c^2)/3$
Extinction coefficient	0.00000 (2)
Goof S	1.00
$\delta\rho_{min}/\delta\rho_{max}$ ($e/\text{\AA}^3$)	$-1.97 / 2.13$

2.2. Structure description of compound (1)

The crystal structure consists of an arrangement of discrete $[Mo_{36} O_{110} (OH)_6 (H_2O)_{12}]^{10-}$ macro isopolyanions separated by a system of hydrated K^+ ions and additional H_2O molecules (Figure 1). The polyoxoanion consists of two subunits related to each other by a center of inversion. Each subunit is composed by 18 molyb-

Table 2. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2) for compound.

	<i>x</i>	<i>y</i>	<i>z</i>
Mo1	0.22140 (6)	0.16831 (6)	0.01508 (5)
Mo2	0.26347 (6)	0.12417 (6)	-0.10876 (5)
Mo3	0.36455 (6)	0.03695 (6)	-0.00052 (5)
Mo4	0.21439 (6)	0.21372 (6)	0.14630 (5)
Mo5	0.35482 (6)	0.29227 (6)	0.08661 (5)
Mo6	0.04966 (6)	-0.08246 (6)	-0.23977 (5)
Mo7	0.37997 (6)	0.24738 (6)	-0.03748 (5)
Mo8	0.34168 (6)	0.08110 (6)	0.12467 (5)
Mo9	0.12439 (7)	0.05590 (7)	0.15505 (5)
Mo10	0.17536 (7)	-0.03478 (7)	-0.09718 (5)
Mo11	0.02267 (7)	0.24118 (7)	0.16806 (5)
Mo12	0.31893 (7)	0.44481 (7)	-0.09158 (5)
Mo13	0.26779 (7)	-0.15509 (7)	0.01836 (6)
Mo14	0.28905 (7)	0.48970 (7)	0.03365 (5)
Mo15	0.09392 (7)	0.10960 (7)	-0.20326 (5)
Mo16	0.24229 (7)	-0.11087 (7)	0.14286 (6)
Mo17	0.19838 (8)	0.28891 (7)	-0.15584 (6)
Mo18	0.14452 (8)	0.37773 (7)	0.10048 (7)
K1	0.4857 (3)	0.4422 (2)	0.15157 (19)
K2	0.5703 (5)	0.2196 (4)	0.1743 (3)
K3	0.5211 (5)	0.1019 (6)	-0.1271 (5)
K4	0.0403 (4)	0.1549 (4)	0.3999 (3)
K5	-0.0192 (12)	0.1000 (11)	-0.0268 (10)
O1	0.0833 (6)	0.0509 (6)	0.0865 (4)
O2	0.2724 (5)	0.0311 (5)	-0.0636 (4)
O3	0.2912 (5)	0.2301 (5)	-0.1015 (4)
O4	0.1249 (5)	0.2874 (5)	0.1451 (4)
O5	0.2598 (5)	0.0778 (5)	0.0416 (4)
O6	0.1827 (5)	0.0551 (5)	-0.1458 (4)
O7	0.2359 (5)	0.1054 (5)	0.1496 (4)
O8	0.3463 (6)	-0.1990 (6)	-0.0045 (5)
O9	0.1492 (5)	0.1886 (5)	0.0568 (4)
O10	0.0694 (6)	0.0212 (5)	-0.2385 (4)
O11	0.3260 (5)	-0.0089 (5)	0.1345 (4)
O12	-0.0236 (5)	0.1753 (5)	0.2102 (4)
O13	0.3302 (5)	0.1419 (5)	-0.0312 (4)
O14	0.1808 (5)	0.1793 (5)	-0.1625 (4)
O15	0.3537 (5)	0.3802 (5)	0.0625 (4)
O16	0.4129 (5)	0.0777 (5)	0.0702 (4)
O17	0.3079 (5)	0.1895 (5)	0.1027 (4)

Table 2. Continued.

	x	y	z
O18	0.3643 (6)	0.4838 (5)	-0.0193 (4)
O19	0.2708 (5)	0.2567 (5)	0.0083 (4)
O20	0.4222 (5)	0.2467 (5)	0.0405 (4)
O21	0.1682 (5)	0.1503 (5)	-0.0505 (4)
O22	0.1796 (6)	-0.0307 (5)	0.1654 (5)
O23	0.1076 (7)	0.2530 (6)	0.2591 (5)
O24	0.2626 (6)	0.3707 (6)	-0.1392 (4)
O25	0.1166 (5)	0.1646 (5)	0.1651 (4)
O26	0.2209 (6)	-0.1066 (5)	-0.0514 (4)
O27	0.3785 (6)	0.3383 (5)	-0.0521 (4)
O28	0.3141 (6)	-0.1554 (6)	0.0962 (4)
O29	0.4200 (5)	0.2930 (5)	0.1483 (4)
O30	0.2476 (6)	0.3046 (5)	0.1116 (4)
O31	0.2100 (6)	0.4469 (6)	0.0744 (5)
O32	0.2128 (8)	0.4145 (7)	0.1835 (5)
O33	0.1942 (5)	-0.0749 (5)	0.0567 (4)
O34	0.3382 (5)	0.1054 (5)	-0.1446 (4)
O35	0.5576 (7)	0.3300 (6)	0.2463 (5)
O36	0.0232 (6)	0.1149 (6)	-0.1605 (5)
O37	0.2347 (5)	0.4162 (5)	-0.0351 (4)
O38	0.4443 (5)	0.0376 (6)	-0.0353 (4)
O39	0.2680 (6)	0.2295 (6)	0.2089 (4)
O40	0.2831 (7)	-0.0720 (6)	-0.1440 (5)
O41	0.3497 (5)	-0.0513 (5)	0.0187 (4)
O42	0.3069 (7)	-0.1242 (7)	0.2056 (5)
O43	0.4638 (6)	0.2148 (6)	-0.0615 (4)
O44	-0.0260 (6)	-0.0819 (6)	-0.2979 (4)
O45	0.4062 (7)	0.4538 (6)	-0.1177 (5)
O46	0.1342 (6)	-0.1091 (6)	-0.2645 (5)
O47	-0.0136 (7)	0.3217 (6)	0.1890 (6)
O48	0.2320 (6)	0.5630 (6)	0.0068 (5)
O49	0.2627 (7)	0.5168 (6)	-0.1184 (5)
O50	0.4112 (6)	0.1076 (6)	0.1799 (5)
O51	0.1710 (7)	-0.1770 (6)	0.1420 (6)
O52	0.0406 (6)	0.0435 (5)	0.1878 (4)
O53	-0.0301 (6)	0.2274 (7)	0.1037 (5)
O54	0.2909 (8)	0.2552 (8)	-0.2138 (5)
O55	0.3546 (7)	0.5248 (5)	0.0873 (4)
O56	0.1000 (8)	0.3407 (7)	0.0345 (5)
O57	0.1325 (6)	0.2988 (6)	-0.1070 (5)

Table 2. Continued.

	<i>x</i>	<i>y</i>	<i>z</i>
O58	0.1177 (6)	-0.0772 (6)	-0.1548 (4)
O59	0.1941 (7)	-0.2197 (7)	0.0176 (5)
O60	0.2045 (7)	0.1022 (7)	-0.2575 (5)
O61	0.1872 (8)	0.0703 (8)	0.2533 (5)
O62	0.1372 (8)	0.3092 (6)	-0.2155 (5)
O63	0.1042 (6)	-0.0032 (6)	-0.0607 (5)
O64	0.0641 (7)	0.4235 (7)	0.1148 (6)
O65	0.4638 (8)	0.2361 (8)	-0.1804 (6)
O66	0.6070 (15)	0.3539 (15)	0.1202 (11)
O67	0.2429 (15)	-0.2219 (10)	-0.1697 (8)
O68	0.5743 (6)	0.1296 (7)	0.0834 (5)
O69	0.1213 (8)	-0.0932 (10)	0.2724 (7)
O70	0.5277 (9)	0.4035 (10)	0.0152 (9)
O71	0.1934 (18)	0.1858 (15)	0.3663 (13)
O72	0.507 (3)	0.0472 (15)	-0.2416 (12)
O73	-0.1102 (12)	0.4137 (16)	0.1055 (13)
O74	-0.0885 (7)	0.3318 (6)	0.0179 (5)
O75	-0.0719 (10)	0.5426 (14)	0.0787 (9)
O76	-0.0049 (13)	0.2437 (11)	-0.0588 (14)
O77	-0.226 (3)	0.320 (3)	0.088 (2)
O78	0.343 (2)	0.062 (2)	0.307 (3)
O79	-0.0720 (13)	0.250 (2)	-0.2193 (11)
O80	0.2932 (10)	-0.0251 (9)	-0.2516 (6)
O81	0.1426 (5)	0.3653 (6)	-0.0420 (5)
O82	-0.090 (5)	0.420 (5)	-0.053 (5)
O83	0.546 (7)	-0.121 (6)	-0.326 (4)
O84	0.429 (3)	-0.040 (4)	-0.299 (2)

dates and connected via four common O atoms O(12), O(52), O(10), and O(58) to constitute an elongated ‘ring’ around the b axis. In Figure 2 the complete $[\text{Mo}_{36} \text{O}_{110} (\text{OH})_6 (\text{H}_2\text{O})_{12}]^{10-}$ ion is shown.

There are seven types of oxygen atoms according to the number of bonded atoms. The Mo–O bond distances for the different kinds of O atoms vary in quite wide limits (Table 3): from 1.652 Å to 1.783 Å (average 1.717 Å) for Mo–O (terminal) bonds, from 1.702 Å to 2.364 Å (av. 2.033 Å) for Mo–O bonds with oxygen connected to two Mo, from 1.842 Å to 2.277 Å (av. 2.059 Å) for Mo–O (triply bridging), from 2.059 Å to 2.388 Å (av. 2.223 Å) for Mo–O (quadruply bridging) bonds, from 2.320 Å to 2.402 Å (av. 2.361 Å) for Mo–OH₂ (terminal), and from 2.214 Å to 2.333 Å (av. 2.273 Å) for Mo–OH (doubly bridging: O27 and O33), and 1.970 Å for the Mo–OH (triply bridging: O25). Bond-order sums estimated according to different models (Pauling,³⁰ Donnay & Allmann,³¹ and Schröder³²) lead to a consistent set of values 6.0 + 0.2 for Mo and 2.0 + 0.2 for O.

Table 3. The Mo–O bond distances.

Mo1—O21	1.718 (9)
Mo1—O9	1.726 (8)
Mo1—O19	1.842 (9)
Mo1—O5	1.863 (9)
Mo1—O13	2.323 (8)
Mo1—O17	2.388 (9)
Mo2—O34	1.659 (9)
Mo2—O6	1.953 (9)
Mo2—O14	2.002 (9)
Mo2—O3	2.008 (9)
Mo2—O2	2.028 (9)
Mo2—O13	2.041 (9)
Mo2—O21	2.331 (9)
Mo3—O38	1.678 (9)
Mo3—O41	1.722 (9)
Mo3—O16	1.920 (9)
Mo3—O2	1.974 (8)
Mo3—O13	2.118 (9)
Mo3—O5	2.277 (9)
Mo4—O39	1.652 (10)
Mo4—O25	1.970 (9)
Mo4—O30	1.993 (8)
Mo4—O4	2.005 (9)
Mo4—O7	2.028 (9)
Mo4—O17	2.059 (8)
Mo4—O9	2.305 (9)
Mo5—O29	1.691 (9)
Mo5—O15	1.723 (9)
Mo5—O20	1.899 (9)
Mo5—O30	1.976 (9)
Mo5—O17	2.109 (9)
Mo5—O19	2.256 (9)
Mo6—O46	1.682 (9)
Mo6—O44	1.721 (10)
Mo6—O12 ⁱ	1.933 (9)
Mo6—O10	1.940 (9)
Mo6—O58	2.180 (9)
Mo6—O52 ⁱ	2.224 (9)
Mo7—O43	1.698 (9)
Mo7—O27	1.715 (10)
Mo7—O20	1.905 (9)
Mo7—O3	1.978 (9)
Mo7—O13	2.128 (8)
Mo7—O19	2.274 (8)
Mo8—O50	1.686 (11)
Mo8—O11	1.702 (9)
Mo8—O16	1.910 (9)
Mo8—O7	1.993 (8)
Mo8—O17	2.120 (9)

Table 3. Continued.

Mo8—O5	2.233 (9)
Mo9—O1	1.691 (10)
Mo9—O52	1.721 (9)
Mo9—O22	1.836 (10)
Mo9—O25	2.027 (10)
Mo9—O7	2.079 (8)
Mo9—O61	2.449 (12)
Mo10—O63	1.687 (10)
Mo10—O58	1.741 (9)
Mo10—O26	1.811 (10)
Mo10—O6	2.049 (9)
Mo10—O2	2.068 (9)
Mo10—O40	2.365 (10)
Mo11—O53	1.675 (11)
Mo11—O47	1.710 (10)
Mo11—O12	1.833 (9)
Mo11—O4	2.050 (9)
Mo11—O25	2.108 (9)
Mo11—O23	2.421 (11)
Mo12—O45	1.676 (10)
Mo12—O49	1.689 (11)
Mo12—O24	1.926 (10)
Mo12—O18	1.928 (10)
Mo12—O37	2.172 (9)
Mo12—O27	2.330 (10)
Mo13—O8	1.697 (10)
Mo13—O59	1.701 (12)
Mo13—O28	1.916 (10)
Mo13—O26	1.955 (9)
Mo13—O33	2.214 (9)
Mo13—O41	2.344 (9)
Mo14—O55	1.679 (10)
Mo14—O48	1.715 (11)
Mo14—O18	1.931 (10)
Mo14—O31	1.932 (10)
Mo14—O37	2.220 (10)
Mo14—O15	2.337 (9)
Mo15—O36	1.688 (10)
Mo15—O35 ⁱⁱ	1.690 (10)
Mo15—O10	1.854 (10)
Mo15—O14	2.055 (9)

Table 3. Continued.

Mo15—O6	2.104 (9)
Mo15—O60	2.425 (11)
Mo16—O51	1.694 (10)
Mo16—O42	1.725 (11)
Mo16—O22	1.936 (10)
Mo16—O28	1.950 (10)
Mo16—O33	2.209 (10)
Mo16—O11	2.364 (9)
Mo17—O62	1.665 (11)
Mo17—O57	1.745 (12)
Mo17—O24	1.851 (10)
Mo17—O14	2.045 (9)
Mo17—O3	2.143 (9)
Mo17—O54	2.324 (13)
Mo18—O64	1.658 (10)
Mo18—O56	1.783 (13)
Mo18—O31	1.850 (10)
Mo18—O4	2.041 (10)
Mo18—O30	2.155 (9)
Mo18—O32	2.244 (13)

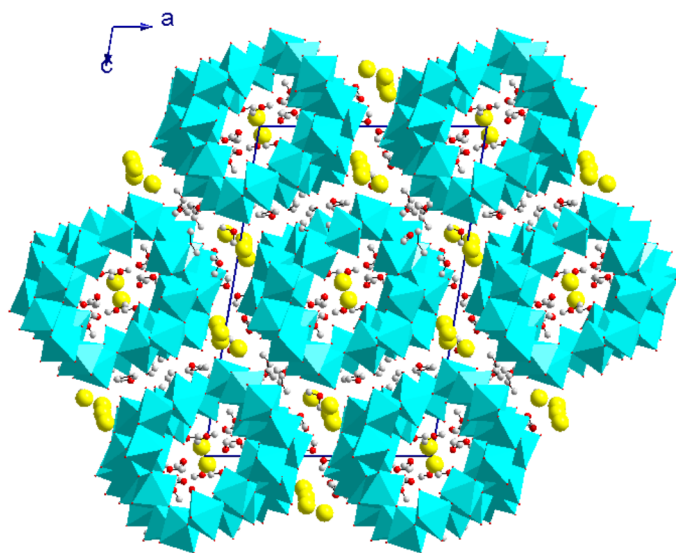


Figure 1. View along the b axis showing the channels filled by K^+ ions and water molecules.

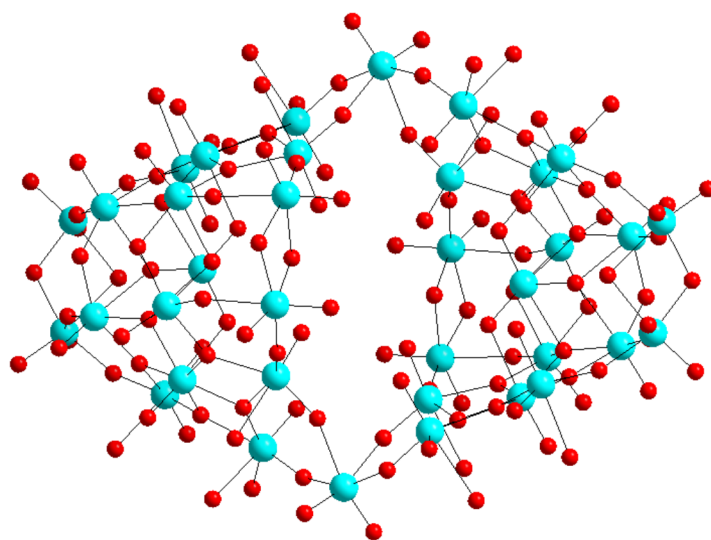


Figure 2. The complete $[Mo_{36} O_{110} (OH)_6 (H_2O)_{12}]^{10-}$ ion.

In fact, the 36-molybdate anions are separated in the crystal structure by the system of ten K^+ ions and 38 H_2O molecules per formula unit. The interatomic distances for the K^+ coordination and for the hydrate water molecules are given in Table 4. Parts of this system are poorly ordered, and partial occupancy factors had to be introduced for several atoms. In individual cells, different sets of these sites can be chosen to give consistent packing systems with the distances in Table 4. The coordinations of the K^+ are normal (Figure 3).

The geometry of the $H_2O...H_2O$ and $H_2O...O$ system (Table 5) indicates some degree of hydrogen bonding between the anions and the cation hydrate arrangement. Yet, as a whole, the packing of the hydrate water system appears quite loose and the bonding forces very weak, in accordance with the easy loss of water.

The most remarkable features of the structure, however, which as yet are unknown in the chemistry of isopolymolybdates and of compounds in the system MoO_3 -water, are the presence of MoO_7 polyhedra and of

Table 4. Distances for the K^+ coordinations and for the hydrate water molecules.

K1—O29	2.956 (10)
K1—O15	3.029 (10)
K1—O10	2.872 (10)
K1—O44	2.874 (12)
K1—O45	2.833 (10)
K1—O69	2.834 (17)
K1—O66	2.780 (2)
K1—O55	2.885 (12)
K1—O35	3.172 (12)
K2—O35	2.713 (12)
K2—O68	2.767 (14)
K2—O62 ^{vii}	2.768 (14)
K2—O29	2.807 (11)
K2—O66	2.910 (3)
K2—O67 ^{iv}	3.110 (3)
K2—O50	3.363 (15)
K3—O43	2.875 (15)
K3—O28 ^{iv}	2.876 (13)
K3—O65	2.881 (18)
K3—O72	2.930 (3)
K3—O34	2.982 (12)
K3—O38	2.983 (15)
K3—O11 ^{iv}	3.083 (12)
K3—O41 ^{iv}	3.236 (15)
K4—O44 ⁱ	2.790 (12)
K4—O71	2.840 (3)
K4—O65 ^{viii}	2.935 (17)
K4—O43 ^{viii}	2.941 (12)
K4—O55 ^{ix}	2.948 (11)
K4—O45 ^{viii}	2.966 (14)
K4—O70 ^{viii}	3.040 (2)
K4—O27 ^{viii}	3.089 (12)
K5—O76	2.780 (3)
K5—O33 ⁱ	2.900 (2)
K5—O63	3.000 (2)
K5—O1	3.110 (2)
K5—O1 ⁱ	3.230 (2)
K5—O63 ⁱ	3.260 (3)
K5—O21	3.370 (2)
O70—H170	0.855 (17)
O70—H270	0.850 (2)
O71—H171	0.870 (3)
O71—H271	0.850 (3)
O72—H172	0.840 (3)
O72—H272	0.920 (4)
O73—H173	0.860 (2)
O73—H273	0.870 (2)

Table 4. Continued.

O74—H174	0.854 (13)
O74—H274	0.848 (11)
O75—H175	0.830 (3)
O75—H275	0.874 (18)
O76—H176	0.850 (2)
O76—H276	0.850 (2)
O77—H177	0.930 (5)
O77—H277	0.870 (4)
O78—H178	0.810 (4)
O78—H278	0.870 (6)
O79—H179	0.880 (2)
O79—H279	0.862 (18)
O80—H180	0.864 (14)
O80—H280	0.857 (15)
O81—H181	0.850 (9)
O81—H281	0.777 (11)
O82—H182	1.040 (15)
O82—H282	0.840 (4)
O83—H183	1.250 (17)
O83—H283	0.90 (9)
O84—H184	0.83 (5)
O84—H284	0.89 (5)

Table 5. Hydrogen-bond^a geometry (Å, °). ^aSymmetry codes: (i) $-x, -y, -z$; (ii) $x-1/2, -y+1/2, z-1/2$; (iii) $x+1/2, -y+1/2, z-1/2$; (iv) $-x+1, -y, -z$; (v) $-x+1, -y+1, -z$; (vi) $-x+1/2, y+1/2, -z+1/2$; (vii) $x+1/2, -y+1/2, z+1/2$; (viii) $x-1/2, -y+1/2, z+1/2$; (ix) $-x+1/2, y-1/2, -z+1/2$.

D-H...A	D-H	D...A	H...A	D-H...A
O65-H165...O43	0.857	2.908	2.183	142.25
O65-H265...O54	0.848	2.858	2.014	173.77
O66-H266...O49	0.868	3.213	2.430	150.36
O66-H266...O77	0.868	3.049	2.459	125.78
O67-H167...O40	0.869	2.889	2.177	138.86
O67-H167...O58	0.869	3.431	2.635	152.86
O67-H267...O77	0.844	2.726	1.977	147.58
O68-H168...O8	0.853	2.802	2.030	150.11
O68-H168...O41	0.853	3.291	2.666	131.10
O68-H268...O40	0.849	2.773	1.996	151.55
O69-H169...O22	0.855	3.132	2.584	122.92
O69-H169...O52	0.855	3.382	2.550	164.83
O69-H169...O61	0.855	3.266	2.642	130.83
O69-H269...O79	0.853	3.218	2.673	123.01
O70-H170...O18	0.856	2.730	2.464	98.82
O70-H170...O66	0.856	2.820	2.619	94.56
O70-H270...O18	0.844	2.730	2.403	103.73
O71-H271...O61	0.850	3.461	2.686	152.24
O72-H172...O83	0.842	3.400	2.593	161.24
O72-H172...O84	0.842	2.366	1.655	140.58
O73-H173...O47	0.856	2.903	2.063	166.78
O73-H173...O64	0.856	2.854	2.543	102.54
O73-H273...O49	0.867	2.893	2.108	150.10
O73-H273...O77	0.867	2.561	2.217	103.41
O74-H174...O48	0.854	3.045	2.408	131.88
O74-H174...O73	0.854	2.677	1.985	137.36
O74-H174...O77	0.854	3.068	2.612	114.66
O74-H274...O53	0.849	2.884	2.090	155.63
O74-H274...O59	0.849	2.751	2.509	97.47
O75-H175...O73	0.835	2.580	1.825	149.50
O75-H275...O37	0.872	2.824	2.164	132.07
O75-H275...O57	0.872	3.200	2.545	132.56
O75-H275...O81	0.872	2.164	1.623	117.03
O76-H176...O74	0.847	2.975	2.176	157.22
O76-H276...O57	0.855	2.903	2.174	143.05
O76-H276...O81	0.855	3.287	2.476	158.83
O77-H177...O73	0.923	2.561	1.995	117.94
O77-H177...O74	0.923	3.068	2.220	152.61
O77-H277...O48	0.879	3.145	2.657	116.16

Table 5. Continued.

O77–H277···O49	0.879	3.177	2.336	159.95
O77–H277···O73	0.879	2.561	2.304	96.74
O78–H178···O61	0.797	2.679	1.943	153.20
O78–H278···O83	0.874	2.225	1.511	136.02
O79–H179···O51	0.877	3.004	2.193	153.65
O79–H279···O36	0.861	3.160	2.358	155.17
O80–H180···O40	0.864	2.778	1.967	155.97
O80–H180···O46	0.864	3.022	2.692	104.15
O80–H280···O60	0.857	2.758	1.976	151.20
O81–H181···O56	0.850	2.138	1.872	96.20
O81–H181···O76	0.850	3.287	2.664	131.27
O81–H281···O19	0.778	3.023	2.269	163.52
O82–H282···O75	0.839	2.945	2.223	144.26
O83–H283···O78	1.177	2.225	1.728	98.18
O84–H184···O80	0.825	2.693	1.915	156.69
O84–H284···O83	0.886	2.189	1.995	90.46
O23–H223···O12	0.858	2.702	2.311	108.00
O23–H223···O47	0.858	2.714	2.436	99.57
O32–H232···O4	0.854	2.832	2.568	99.14
O32–H232···O30	0.854	2.796	2.317	115.70
O33–H133···O5	0.850	3.063	2.294	150.57
O33–H133···O11	0.850	2.900	2.626	100.25
O33–H133···O26	0.850	2.791	2.606	93.53
O33–H133···O41	0.850	2.901	2.309	126.99
O40–H140···O67	1.059	2.889	2.271	115.39
O40–H140···O80	1.059	2.778	2.302	105.41
O40–H240···O26	0.926	2.696	2.418	97.21
O40–H240···O68	0.926	2.773	1.936	149.38
O54–H154···O3	0.815	2.758	2.586	93.50
O54–H154···O24	0.815	2.882	2.322	126.42
O54–H154···O65	0.815	2.858	2.578	101.82
O60–H160···O14	0.962	2.791	2.442	101.04
O60–H160···O34	0.962	3.221	2.673	116.66
O60–H160···O54	0.962	3.260	2.352	157.13
O61–H161···O7	0.874	2.836	2.157	134.21
O61–H161···O25	0.874	2.853	2.507	104.37
O61–H161···O39	0.874	3.471	2.685	150.23
O61–H261···O22	0.870	2.816	2.315	116.71
O61–H261···O78	0.870	2.679	2.486	93.14
O4–H1O4···O23	0.850	2.895	2.399	117.76
O4–H1O4···O32	0.850	2.832	2.302	120.74
O4–H1O4···O47	0.850	2.752	2.492	98.68

Table 5. Continued.

O4–H2O4···O47	0.850	2.752	2.256	117.26
O4–H2O4···O53	0.850	2.819	2.089	143.55
O4–H2O4···O56	0.850	2.821	2.623	94.56
O4–H2O4···O64	0.850	2.758	2.499	98.62
O83–H1O83···O50	0.850	3.290	2.660	131.99
O83–H1O83···O84	0.850	2.189	1.849	101.98

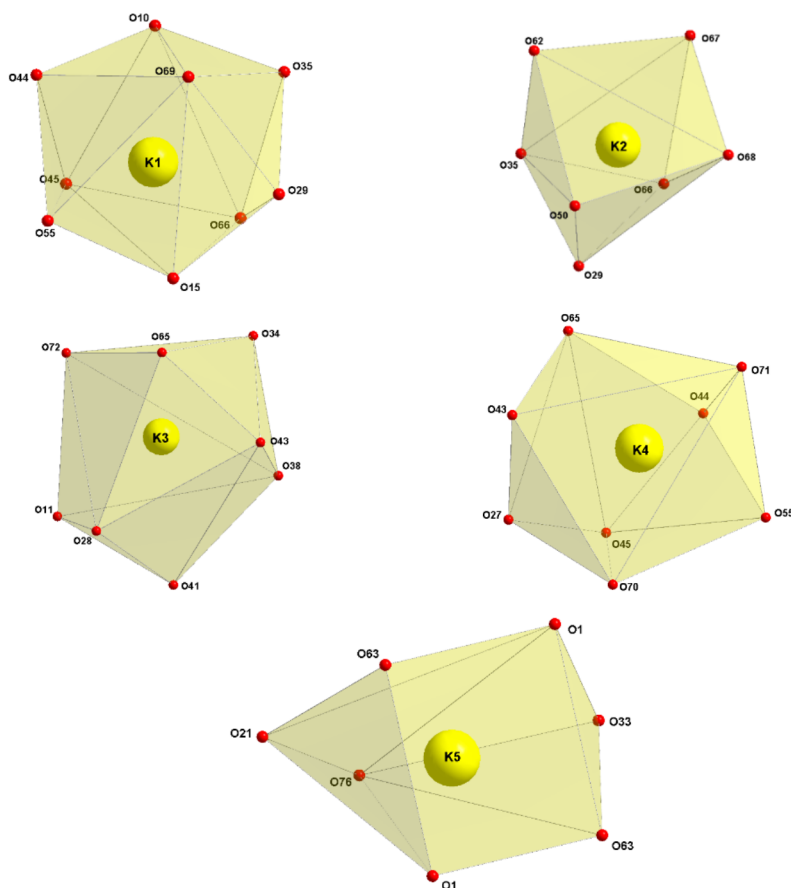


Figure 3. The potassium environments.

bridging (OH) molecules coordinated simultaneously to two molybdenum atoms (O27, O33), and in another case to three molybdenum (O25). The MoO_7 polyhedra [two in each half of the 36-molybdate, central atoms Mo (2) and Mo (4) can be viewed as pentagonal bipyramids.

They are linked to neighboring octahedral through the five equatorial edges, and both through a sixth edge to Mo (1). It is important to note that the groups of nine polyhedra forming each quarter of the 36-molybdate are very similar to the basic structural motifs in the oxides $\text{MO}_{17}\text{O}_{47}$ (Kihlberg)³³ and Mo_5O_{14} (Kihlberg),³⁴ in spite of the completely different conditions of formation. The direct coordination of H_2O molecules to the metal as in the present 36-molybdate is also a characteristic feature of all polymeric compounds

precipitating from highly acidic molybdate solutions. Examples are the decamolybdates, $\text{Ct-MoO}_3 \cdot \text{H}_2\text{O}$ ^{35,36} and $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$.³⁷

2.3. IR absorption spectrometry

The IR spectrum of $\text{K}_{10}[\text{Mo}_{36}\text{O}_{110}(\text{OH})_6(\text{H}_2\text{O})_{12}] \cdot 38\text{H}_2\text{O}$ is shown in Figure 4. The broad peak range from 500 to 960 cm^{-1} was assigned to characteristic asymmetric vibrations for $\{\text{Mo}_{36}\}$ polyanions. Strong vibrations with wavenumber ranging from 850 to 951 cm^{-1} are assigned to $\nu(\text{Mo-O}_t)$, $\nu(\text{Mo-OH})$, and $\nu(\text{Mo-OH}_2)$ vibrations (with O_t = terminal oxygen). The bonds ranging from 764 to 527 cm^{-1} are characteristic of $\nu(\text{Mo-O}_b\text{-Mo})$ and $\nu(\text{Mo-O}_c\text{-Mo})$ vibrations (with O_b = bridged oxygen of two octahedral sharing a corner, O_c = bridged oxygen of two octahedral sharing an edge).³⁸ The $\nu(\text{O-H})$ and $\delta(\text{H-O-H})$ of water molecules appear respectively at 3332 and 1617 cm^{-1} .³⁹

2.4. Thermogravimetric analysis

The TGA study was carried out from 40 to 800 °C. As shown in Figure 5, the thermal gravimetric curve shows a first step of weight loss in the temperature range 40–150 °C corresponding to one endothermic peak at 62 °C due to the dehydration of the compound (crystallization water molecules) (found: 5.97%; calc.: 10.35%). It appears impossible to determine the precise water content of our compound only depending on single crystal X-ray crystallography, because not only are most of the crystallization water molecules badly disordered, but also they rapidly lose part of the hydrate water when the crystals are isolated from the solution.⁴⁰

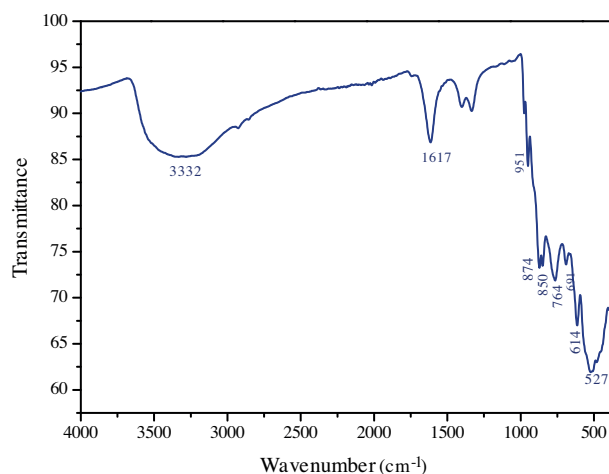


Figure 4. IR spectrum of the compound.

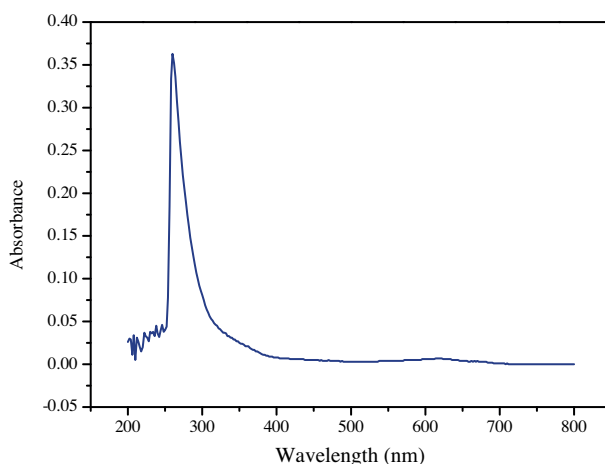


Figure 5. UV-Vis spectrum of the compound.

At 300 °C, the curve reveals another weight loss corresponding to the dehydration of the coordination water molecules (found: 2.68% ; calc: 3.64%).

Beyond 400 °C, there are some endothermic peaks probably due to the decomposition of the polyoxoanion framework.

2.5. UV-Vis absorption

The UV spectra of our compound measured in DMSO shows only one broad absorption peak, centered at 260 nm (Figure 6). This characteristic band is ascribed to ligand-to-metal charge transfers, from terminal oxygen

to molybdenum center, where electrons are promoted from the low energy electronic states, mainly composed of oxygen 2p orbitals, to the high-energy states, which are mainly composed of metal d orbitals.^{41–44}

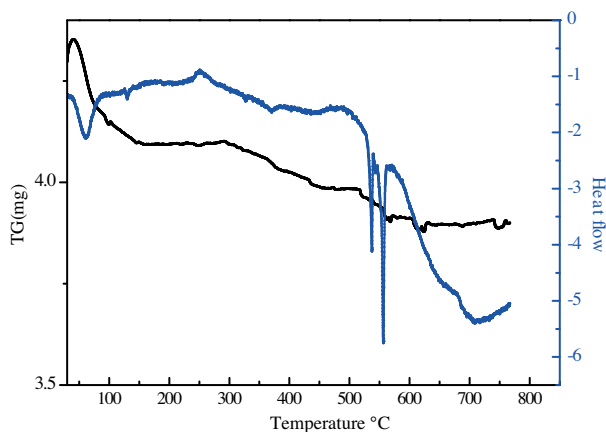


Figure 6. TGA–DSC thermograms of the compound.

3. Experimental

3.1. General procedures

All reagents and solvents for synthesis were purchased from commercial sources and used without further purification. Infrared spectrum was recorded at room temperature on a PerkinElmer Spectrum Two ATR-FTIR, over the wavenumber range between 4000 and 400 cm^{-1} . Thermogravimetric analysis (TG) was performed on a Setaram Labsys Evo TG/DSC (1600 °C) instrument with a heating rate of 10 °C min^{-1} . The UV-Vis spectrum was measured using a DR 5000 UV-Vis spectrophotometer (HACH) in the 180–800 nm range.

3.2. Synthesis of $\text{K}_{10}[\text{Mo}_{36}\text{O}_{110}(\text{OH})_6(\text{H}_2\text{O})_{12}]\cdot 38\text{H}_2\text{O}(1)$

K_2MoO_4 (3 mmol) was dissolved in H_2O (20 mL). Then KNO_3 (0.5 mmol) was dissolved and added to the mixture solution with stirring. The pH value of the mixture was carefully adjusted to approximately 1.8 with a HCl solution (2 M). Afterwards the solution was heated to 80 °C. After a few days, colorless block crystals were deposited from the filtrate by evaporation at room temperature.

4. Conclusion

In summary, we have successfully synthesized a new compound based on $[\text{Mo}_{36}\text{O}_{110}(\text{OH})_6(\text{H}_2\text{O})_{12}]^{10-}$ polyoxoanion. The physicochemical characterization using IR, TG, and DTA analyses and UV-Vis are reported. The studies of the title compound not only afford a preparation route concerning Mo_{36} polyoxanions, but also expand the family of giant polyoxomolybdates from a structural point of view.

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Supporting Data

CCDC 1534850 contains the supplementary crystallographic data for (1). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. Fax: 44 1223 336033.

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