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The crystal structure of potassium ammonium hexamolybdotellurate with telluric acid $K_5NH_4[TeMo_6O_{24}].Te(OH)_6.6H_2O$

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ABSTRACT

An inorganic compound formulated as $K_5NH_4[TeMo_6O_{24}].Te(OH)_6.6H_2O$ (**1**) has been isolated by conventional solution method and structurally characterized by single-crystal X-ray diffraction methods, scanning electron microscopy (SEM), IR, UV–vis spectra, and cyclic voltammetry measurements. This compound crystallizes in the monoclinic system, space group $C2/c$ with unit $a = 18.6841(1)\text{Å}$, $b = 10.0513(1)\text{Å}$, $c = 21.1065(1)\text{Å}$, $\beta = 116.495(1)^\circ$, $V = 3547.49(4)\text{Å}^3$, $Z = 4$, $R = 0.033$ and $wR(F^2) = 0.087$ for 3432 unique observed reflexions [$I > 2\sigma(I)$]. The crystal structure of (**1**) is built up from an Anderson clusters connected through hydrogen-bonding interactions into a three-dimensional supramolecular network.

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1. Introduction

The transition metals in group five and six, such as V, Mo and W, are well known to form isopolyoxometalates (isopolyanions) by dehydrative condensation of the monooxoanions and heteropolyoxometalates (heteropolyanions) by involving a third element e.g. P or Si. These materials have attracted increasing attention worldwide because of their particularly interesting nanosized structures and their potential applications in many fields such as catalysis, pharmacology, medicine, nanotechnology, and molecular electronics [1–5].

Due to these reasons, many works containing the Anderson–Evans anion $[TeMo_6O_{24}]^{6-}$ (Fig. 1) have been devoted to the study of mixed molybdotellurate. However, the literature gives few works and partial results of compounds containing at the same time $[TeMo_6O_{24}]^{6-}$ cluster and $(Te(OH)_6)$ units: $Rb_6(TeMo_6O_{24}).Te(OH)_6.6H_2O$ [6], $Cs_6(TeMo_6O_{24}).2Te(OH)_6.4H_2O$ [7], $(NH_4)_6(TeMo_6O_{24}).Te(OH)_6.7H_2O$ [8], $Li_6(TeMo_6O_{24}).Te(OH)_6.18H_2O$ [9]. As a continuation of these works, we report here, the results of

a structure refinement of $K_5(NH_4)(TeMo_6O_{24})(Te(OH)_6) \cdot 6(H_2O)$. The compound is built up of a $[TeMo_6O_{24}]^{6-}$ cluster and a $Te(OH)_6$ group linked to three potassium and ammonium cations which coordinated with six water molecules.

2. Experimental

2.1. Materials and measurements

KOH (98%), $(NH_4)_6Mo_7O_{24}.4H_2O$ (99%) and $Te(OH)_6$ (99%) were purchased from Sigma-Aldrich and used without further purification. The infrared spectra were recorded as KBr pellets, in the 4000–400 cm^{-1} range on a Nicolet 470 FTIR spectrophotometer (resolution: 0.125 cm^{-1}). The UV–visible absorption spectrum was recorded on a Perkin-Elmer Lambda 19 spectrophotometer. Cyclic voltammetry analyzes were carried out on a CHI 660B electrochemical station using a conventional three electrode single compartment cell. The working electrode was a glassy carbon, platinum gauze was used as counter electrode, and the Ag/AgCl (saturated KCl) was the reference electrode. The measurements were performed at room temperature and the cell was briefly deoxygenated with argon before each scan.

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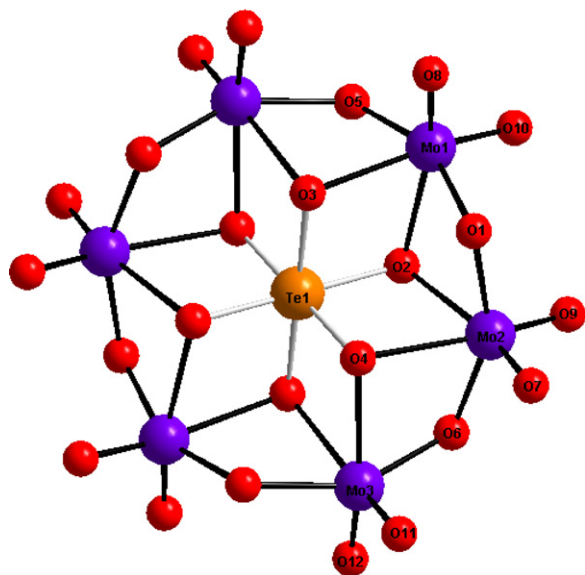


Fig. 1. A polyhedral representation of the Anderson-Evans anion $[\text{TeMo}_6\text{O}_{24}]^{6-}$ in 1.

2.2. Synthesis

Single crystals of $\text{K}_5\text{NH}_4[\text{TeMo}_6\text{O}_{24}]\cdot\text{Te}(\text{OH})_6\cdot 6\text{H}_2\text{O}$ were obtained from an aqueous solution of KOH, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ and $\text{Te}(\text{OH})_6$ with a K: Mo: Te molar ratio of 1:3:1. The resulting mixture was stirred and the pH was adjusted to 3.5 with acetic acid. The solution was kept for 2 weeks at ambient conditions, and then colorless block crystals suitable for X-ray crystallography were obtained. The semi-quantitative energy-dispersive spectroscopy (EDS) analysis of one of the colorless crystals obtained as mentioned above was performed with a JEOL-JSM 5400 scanning electron microscope; it revealed the presence of K, Te, Mo, N and O elements. Anal. calc. for $\text{K}_5\text{NH}_4[\text{TeMo}_6\text{O}_{24}]\cdot\text{Te}(\text{OH})_6\cdot 6\text{H}_2\text{O}$ (%): K, 11.93; Te, 15.57; Mo, 35.13 Found (%): K, 11.78; Te, 15.64; Mo, 35.21.

3. Results and discussion

3.1. X-ray data collection

A suitable crystal with dimensional (0.10 mm–0.10 mm–0.25 mm) was chosen for X-ray diffraction studies. The intensities of the diffraction data were measured using an Enraf-Nonius CAD-4 diffractometer with monochromated graphite Mo Ka radiation ($\lambda = 0.71069\text{\AA}$) [10] at 293 K [10]. The numbers of collected and independent reflections were, respectively, 4430 and 3854. Unit cell dimensions were obtained by least-square refinement of the angular settings in the $2.16 < \theta < 26.98^\circ$. The reflections were corrected for Lorentz and polarization effects; an empirical absorption correction was also applied using psi-scan data [11].

The structure was successfully developed in the centrosymmetric space group C2/c (No. 15), solved by the Patterson method using SHELXS-97 [12] and refined with anisotropic temperature factors for non-hydrogen

atoms, by full matrix least-squares based on F^2 using SHELXL-97 [13] program included in the WINGX software package [14]. Refinement of all atoms, except of nitrogen (N) led to $R = 0.066$ and $R_w = 0.167$. Moreover, the displacement parameters led us to consider that the four K3 atoms of the cell are spread randomly over eight positions. At the stage, the difference synthesis map shows residual peaks at 0.5, -0.289 , and 0.75 which are attributed to the nitrogen N. The refinement of the occupancy factors of the two N and K3 was then performed leading to 50% and 50% for N and K, respectively, and to an improvement of the agreement factors: $R = 0.033$ and $R_w = 0.087$ for 3432 unique observed reflexions [$I > 2\sigma(I)$], the corresponding formula is thus $\text{K}_5\text{NH}_4[\text{TeMo}_6\text{O}_{24}]\cdot\text{Te}(\text{OH})_6\cdot 6\text{H}_2\text{O}$.

Besides, the semi-quantitative energy-dispersive spectroscopy (EDS) analysis of one of colorless crystals obtained as mentioned above was performed with a JEOL-JSM 5400 scanning electron microscope; it revealed the presence of N, K, Te, Mo and O elements. The positions of the hydrogen atoms attached to oxygen water were determined from a difference Fourier map and were refined isotropically. The details of the data collection and structure refinements for $\text{K}_5\text{NH}_4[\text{TeMo}_6\text{O}_{24}]\cdot\text{Te}(\text{OH})_6\cdot 6\text{H}_2\text{O}$ are listed in Table 1. The final atomic coordinates are given in Table 2; for geometrical parameters see Table 3.

Table 1

Crystal structure data for $\text{K}_5\text{NH}_4[\text{TeMo}_6\text{O}_{24}]\cdot\text{Te}(\text{OH})_6\cdot 6\text{H}_2\text{O}$.

Crystal data	
Compound	CSD-number
Formula/formula weight	$\text{K}_5\text{NH}_4[\text{TeMo}_6\text{O}_{24}]\cdot\text{Te}(\text{OH})_6\cdot 6\text{H}_2\text{O}/1638.53$
Space group	C2/c
Crystal system	Monoclinic
Z	4
Lattice parameters	$a = 18.6841(1)\text{\AA}$ $b = 10.0513(1)\text{\AA}$; $\beta = 116.495(1)^\circ$ $c = 21.1065(1)\text{\AA}$ $3547.49(4)\text{\AA}^3$
Volume	3.068
Calculated density (g/cm^3)	4.372
Absorption coefficient, μ (mm^{-1})	3072
$F_0\ 0\ 0$	0.1 \times 0.1 \times 0.1/colorless
Crystal size (mm^3)/color	
Intensity measurement	
Diffractometer	Enraf-Nonius CAD4
Monochromator Graphite	Wavelength [Ka(Mo)] $l = 0.71073\text{\AA}$
Temperature	293(2) K
Theta range	$2.16^\circ/26.98^\circ$
h, k, l range	$-23/1, -1/12, -24/26$
Number of measured reflexions	4430
Number of independent reflexions [Rint =]	3854 [0,031]
Structure determination	
Unique reflexion included ($I > 2\sigma(I)$)	3432
Number of refined parameters	249
Absorption correction	Ψ -scan
Tmin, Tmax	0.510, 0.945
R, $R_w[F^2 > 2\sigma(F^2)]$	0.033, 0.088
Weights	$w = 1/[s^2(F_o^2) + (0.0398P)^2 + 25.3973P]$ where $P = (F_o^2 + 2F_c^2)/3$
Extinction coefficient	0.00195(7)
$\Delta\rho_{\text{min}}/\Delta\rho_{\text{max}}$ ($\text{e}/\text{\AA}^3$)	$-1.177/1.047$
Largest shift/error	0.001

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

Atomes	x	y	z	Occupancy	U_{eq}
Mo1	0.0471 (1)	0.1048 (1)	0.3750 (1)	1	0.0217 (1)
Mo2	0.1844 (1)	0.1002 (1)	0.5406 (1)	1	0.0206 (1)
Mo3	0.8624 (1)	0.0046 (1)	0.3325 (1)	1	0.0220 (1)
Te1	0	0	0.5	1	0.0141 (1)
Te2	0.5	0	0.5	1	0.0291 (1)
K1	0.3661 (1)	-0.1379 (2)	0.7245 (1)	1	0.0542 (4)
K2	0.2687 (1)	0.0039 (1)	0.3713 (2)	1	0.0663 (5)
K3	0.3419 (2)	0.7755 (1)	0.5312 (1)	0.5	0.0686 (11)
N	0.4746 (3)	-0.2882 (3)	0.7371 (3)	0.5	0.0493 (4)
O1	0.1177 (2)	0.2066 (3)	0.4588 (2)	1	0.0228 (7)
O2	0.0815 (3)	-0.0363 (2)	0.4695 (3)	1	0.0183 (6)
O3	-0.0419 (2)	0.1264 (2)	0.4227 (2)	1	0.0178 (6)
O4	-0.0770 (3)	-0.1237 (2)	0.4338 (2)	1	0.0185 (6)
O5	-0.0371 (4)	-0.0269 (3)	0.3273 (4)	1	0.0259 (7)
O6	0.8013 (3)	0.0313 (2)	0.3853 (3)	1	0.0253 (7)
O7	0.2367 (2)	0.2277 (3)	0.5954 (2)	1	0.0335 (9)
O8	0.0076 (4)	0.2413 (2)	0.3232 (4)	1	0.0343 (9)
O9	0.2467 (2)	0.0242 (2)	0.5123 (2)	1	0.0343 (9)
O10	0.1149 (3)	0.0403 (1)	0.3504 (3)	1	0.0381 (10)
O11	0.8107 (3)	-0.1277 (4)	0.2803 (2)	1	0.0363 (9)
O12	0.8284 (3)	0.1418 (2)	0.2794 (2)	1	0.0349 (9)
O13	0.5930 (2)	-0.0449 (2)	0.4884 (2)	1	0.0557 (14)
H1	0.5920	-0.1212	0.4591	1	0.2000
O14	0.4312 (2)	-0.1104 (3)	0.4228 (3)	1	0.0524 (13)
H2	0.4380	-0.0010	0.4211	1	0.2000
O15	0.4816 (4)	0.1389 (3)	0.4310 (2)	1	0.0512 (12)
H3	0.4572	0.2085	0.4415	1	0.2000
OW1	0.3540 (4)	-0.0904 (3)	0.7928 (3)	1	0.0667 (16)
H11	0.4065	-0.1244	0.8245	1	0.2000
H12	0.3245	-0.1591	0.7590	1	0.2000
OW2	0.7064 (3)	0.2522 (3)	0.3642 (2)	1	0.0898 (23)
H21	0.6613	0.2388	0.3182	1	0.2000
H22	0.7467	0.1859	0.3702	1	0.2000
OW3	0.4387 (3)	-0.0344 (2)	0.6690 (2)	1	0.1561 (5)
H31	0.4719	-0.0932	0.7073	1	0.2000
H32	0.4749	0.0191	0.6580	1	0.2000

Table 3
Selected bond lengths (\AA).

Bond lengths					
Mo1-O1	1.697 (4)	Te1-O2 ⁱⁱ	1.933 (3)	K1-O12 ^{ix}	2.731 (5)
Mo1-O8	1.704 (4)	Te1-O2	1.933 (3)	K1-OW3	2.763 (1)
Mo1-O5	1.957 (4)	Te1-O3 ⁱⁱ	1.936 (3)	K1-OW1	2.773 (6)
Mo1-O1	1.958 (4)	Te1-O3	1.936 (3)	K1-O8 ^{viii}	2.808 (5)
Mo1-O2	2.292 (3)	Te1-O4	1.942 (3)	K1-O7	2.864 (5)
Mo1-O3	2.308 (3)	Te1-O4 ⁱⁱ	1.942 (3)	K1-O8 ⁱ	3.190 (5)
				K1-O11 ⁱⁱⁱ	3.262 (5)
				K1-O6 ⁱⁱⁱ	3.403 (4)
Mo2-O9	1.707 (4)	Te2-O14 ⁱⁱⁱ	1.915 (5)	K2-O10	2.730 (4)
Mo2-O7	1.710 (4)	Te2-O14	1.915 (4)	K2-OW2 ^{iv}	2.760 (7)
Mo2-O1	1.939 (4)	Te2-O13 ⁱⁱⁱ	1.914 (4)	K2-O7 ⁱ	2.800 (5)
Mo2-O6 ⁱⁱⁱ	1.971 (4)	Te2-O13	1.914 (5)	K2-OW1 ^{xi}	2.897 (7)
Mo2-O2	2.294 (3)	Te2-O15 ⁱⁱⁱ	1.933 (5)	K2-O13 ⁱⁱⁱ	2.963 (6)
Mo2-O4 ⁱⁱ	2.309 (3)	Te2-O15	1.933 (5)	K2-O14	2.963 (5)
				K2-O11 ^v	3.188 (5)
				K2-O9	3.188 (5)
				K2-O12 ^v	3.191 (5)
Mo3-O12	1.711 (4)			K3-OW2 ^x	2.746 (1)
Mo3-O11	1.723 (4)			K3-O2 ^j	2.802 (5)
Mo3-O6	1.937 (4)			K3-O9 ^{vi}	2.989 (6)
Mo3-O5 ^{vii}	1.954 (4)			K3-O13 ^x	3.071 (7)
Mo3-O3 ^{vii}	2.297 (3)			K3-O15 ^x	3.146 (7)
Mo3-O4 ^{vii}	2.314 (3)			K3-OW3 ^{vi}	3.268 (13)
				K3-OW2 ^{xii}	3.306 (9)
				K3-O9 ^j	3.363 (6)

Symmetry codes: (i) $-x+1/2, -y+1/2, -z+1$; (ii) $-x, -y, -z+1$; (iii) $-x+1, -y, -z+1$; (iv) $x-1/2, y-1/2, z$; (v) $-x+1, y, -z+1/2$; (vi) $x, y+1, z$; (vii) $x+1, y, z$; (viii) $x+1/2, -y+1/2, z+1/2$; (ix) $x-1/2, -y+1/2, z+1/2$; (x) $-x+1, -y+1, -z+1$; (xi) $x, -y, z-1/2$; (xii) $x-1/2, y+1/2, z$.

3.2. Structure description

Single-crystal X-ray diffraction analysis reveals that compound **1** crystallizes in the monoclinic space group $C2/c$. In the basic structural unit of **1**, there is an Anderson anion clusters $(\text{TeMo}_6\text{O}_{24})^{6-}$ and $\text{Te}(\text{OH})_6$ group linked to three potassium and ammonium cations which coordinated with six water molecules. Bond valence sum calculations indicate [15] that all the molybdenum atoms and tellurium atoms are hexavalent, all potassium atoms are monovalent, O13, O14 and O15 are OH groups and OW1-OW3 are water molecules. All other oxygen atoms have values close to 2. A projection of the structure, showing the displacement ellipsoids, is presented in Fig. 2.

The $(\text{TeMo}_6\text{O}_{24})^{6-}$ cluster was characterized for the first time in 1948 [16], but its structure had been already predicted in 1937 [17]. The Anderson structure consists of a planar arrangement of six edge-sharing MoO_6 polyhedra around the central tellurium atom. The six molybdenum atoms form a regular hexagon. The central Te^{VI} atom is surrounded octahedrally by six oxygen atoms. The Te-O bond lengths and O-Te-O bond angles differ only slightly in the compounds and are in good agreement with those bond lengths and angles found in other compounds containing the $(\text{TeMo}_6\text{O}_{24})^{6-}$ anion [18,19].

The oxygen atoms of the anion can be divided into three groups: terminal oxygen atoms (O_t) with short Mo-O-bond lengths, molybdenum-bridging oxygen atoms (O_b) with middle Mo-O bond lengths and oxygen atoms bonded to one tellurium and two molybdenum atoms (O_c) bearing long Mo-O bond lengths. As expected, the terminal oxygen atoms show the shortest Mo-O bond lengths between 1.697 (3) and 1.722 (4) Å. The intermediate Mo-O bonds exhibit Mo-O distances between 1.937 (1) and 1.971 (1) Å. The two long Mo-O bonds are located trans to the short Mo-O bonds and show Mo-O distances between 2.292 (3) and 2.3147 (3) Å. The Mo-Mo distances lie in the 3.266 (2) - 3.353 (1) Å range and the Te-Mo distances are in the 3.279 (1) - 3.347 (3) Å range. Each $(\text{TeMo}_6\text{O}_{24})^{6-}$ cluster is joined to the telluric acid molecule $\text{Te}(\text{OH})_6$ through hydrogen bonds forming infinite chains and all oxygen atoms of the $\text{Te}(\text{OH})_6$ molecule are involved in the coordination of

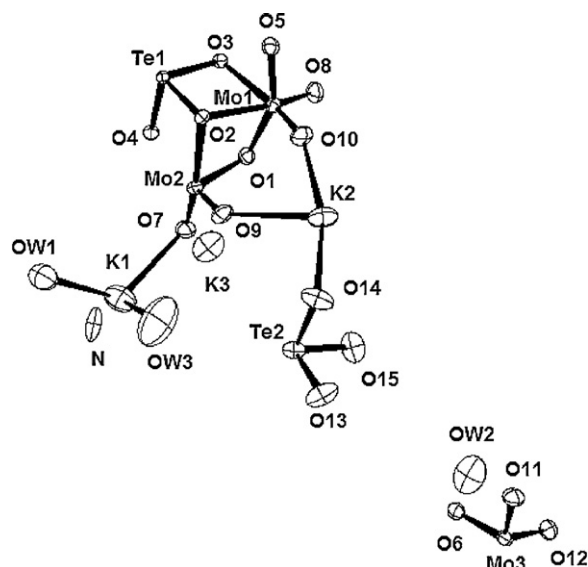


Fig. 2. Asymmetric unit of the title compound showing the 50% probability displacement ellipsoids.

potassium cations which is similar to the situation observed in $\text{Li}_6(\text{TeMo}_6\text{O}_{24})(\text{Te}(\text{OH})_6) \cdot 18\text{H}_2\text{O}$. However, the difference exists in the connectivity fashions between the anion $(\text{TeMo}_6\text{O}_{24})^{6-}$ and K^+ on the one hand, and between the anion and Li^+ on the other hand. In **1** the K^+ ions occupy a three distinct sites and shares all the O atoms of the anion $(\text{TeMo}_6\text{O}_{24})^{6-}$, except O1, O3, O4 and O5. Whereas, in $\text{Li}_6(\text{TeMo}_6\text{O}_{24})(\text{Te}(\text{OH})_6) \cdot 18\text{H}_2\text{O}$, only three oxygen atoms: (O(13), O(18) and O(23)) of the anion are involved in the coordination of the six independent Li^+ ions (Fig. 3).

In the present structure, the telluric acid molecule is a nearly regular octahedron, with an average Te2-OH bond length of 1.921 (3) Å and an average O-Te2-O angles of 83.333 (1)°. These distances and angles are of the same magnitude in accordance with previous observations of $\text{Te}(\text{OH})_6$ involved in other molybdotellurates:

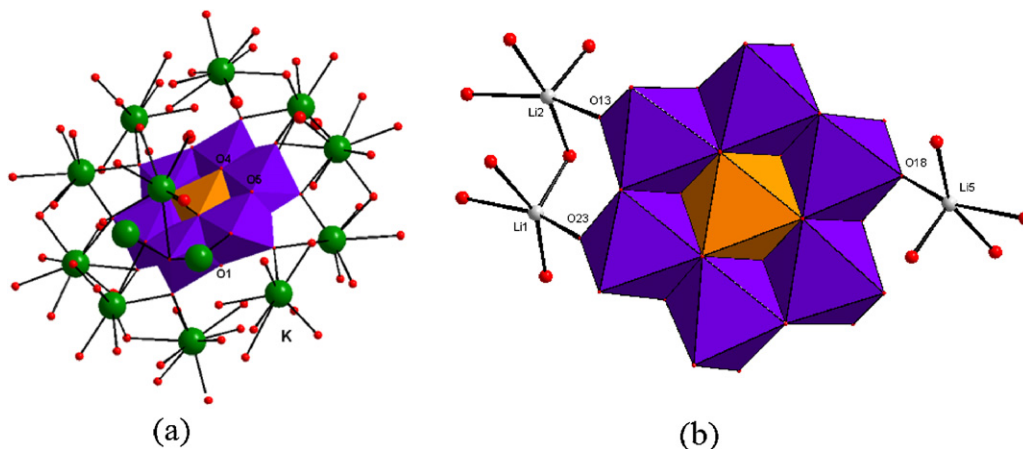


Fig. 3. The $(\text{TeMo}_6\text{O}_{24})^{6-}$ anion environment in **1**(a) and in $\text{Li}_6(\text{TeMo}_6\text{O}_{24})(\text{Te}(\text{OH})_6) \cdot 18\text{H}_2\text{O}$ (b).

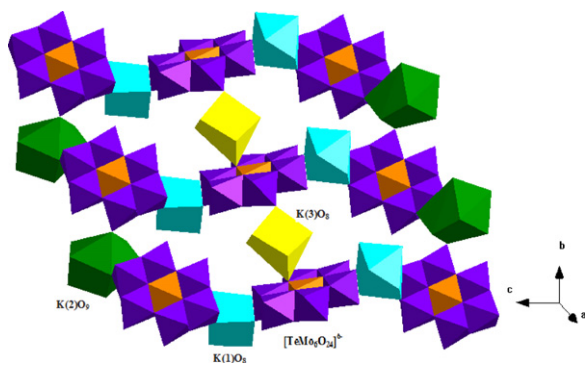


Fig. 4. A view showing the association between $[\text{TeMo}_6\text{O}_{24}]^{6-}$ and the polyhedral KO_n .

$\text{Rb}_6\text{TeMo}_6\text{O}_{24} \cdot \text{Te}(\text{OH})_6 \cdot 6\text{H}_2\text{O}$, $\text{Cs}_6\text{TeMo}_6\text{O}_{24} \cdot 2\text{Te}(\text{OH})_6 \cdot 4\text{H}_2\text{O}$, $(\text{NH}_4)_6\text{TeMo}_6\text{O}_{24} \cdot \text{Te}(\text{OH})_6 \cdot 7\text{H}_2\text{O}$, $\text{Li}_6(\text{TeMo}_6\text{O}_{24}) \cdot \text{Te}(\text{OH})_6 \cdot 18\text{H}_2\text{O}$.

The Anderson ($\text{TeMo}_6\text{O}_{24}$) $^{6-}$ polyanions are assembled in a 1-D chain through the coordination of the terminal oxygen atoms and the potassium K1 cations. Then, each chain is connected to two other parallel chains through $\text{K}(2)$ and $\text{K}(3)$ to yield a 2D layer (Fig. 4). The neighboring layers are further held together by extensive hydrogen-bonding and telluric acid molecule $\text{Te}(\text{OH})_6$ forming a 3D open framework structure (Figs. 5 and 6). The K^+ ions occupy three distinct sites. Its environment is consisted of eight O atoms for K1 , K3 and nine O atoms for K2 , with K-O distances ranging from 2.731 (5) to 3.403 (4) Å, 2.730 (4) to 3.191 (1) Å and 2.746 (1) to 3.363 (6) Å for K1 , K2 and K3 , respectively.

As listed in Table 4, $\text{OW-H} \dots \text{O}$, $\text{OW-H} \dots \text{OW}$ and $\text{OW-H} \dots \text{N}$ hydrogen bonds between the solvent water molecules, clusters and $\text{Te}(\text{OH})_6$ have interatomic $\text{OW} \dots \text{O}$ distances ranging from 0.914 Å to 1.119 Å and hydrogen-bond angles from 110.78° to 163.18° . These hydrogen bonds hold the components together into a three-dimensional network and make the crystal structure of the compound more stable.

3.3. IR absorption spectroscopy

For a MoO_6 vibration ion having O_h symmetry, there are six fundamental vibrations, symmetric stretching mode ν_1 ,

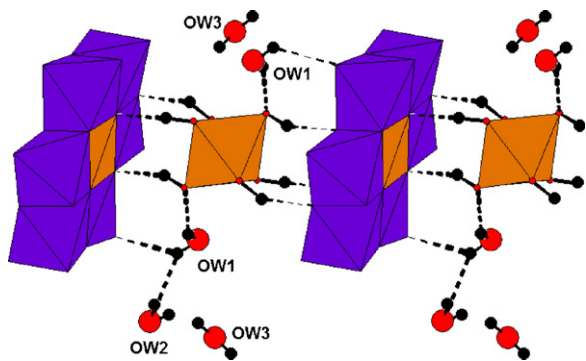


Fig. 5. A view showing the hydrogen-bonding interactions between water molecules, $\text{Te}(\text{OH})_6$ groups and terminal oxygen atoms of polyoxoanions.

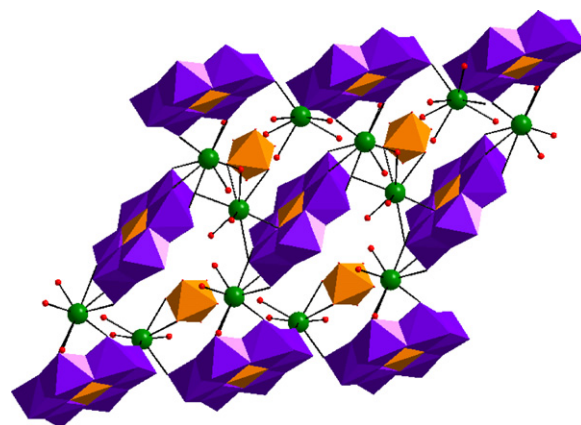


Fig. 6. The three-dimensional supramolecular framework of 1. Water molecules atoms are omitted for clarity.

asymmetric stretching modes ν_2 and ν_3 , asymmetric bending mode ν_4 , symmetric bending mode ν_5 , and inactive mode ν_6 .

In the crystal, the MoO_6 octahedral ions lose their O_h symmetry by the sharing oxygen atoms with TeO_6 group. Since there are three different Mo-O distances and different O-Mo-O angles in the crystal, the spectrum is expected to be very complex with separate frequencies for the individual Mo-O distances and O-Mo-O angles.

As shown in Fig. 7, the spectra can be divided into the following typical regions: 3600 and 2800 cm^{-1} (O-H and N-H stretchings), 1650 and 1400 cm^{-1} (O-H and N-H bendings). The low-wavenumber characteristic peaks are attributed to the Anderson anion $[\text{TeMo}_6\text{O}_{24}]^{6-}$ [20]: 1000 and 800 cm^{-1} (Mo-O_t vibrations), 750 and 550 cm^{-1} (fundamentally Mo-O_b modes) and below 450 cm^{-1} (Mo-O_c , and some other modes). Between 550 and 500 cm^{-1} , it is possible to observe some bands attributable to water liberations.

3.4. UV-visible spectra

When water was used as solvent, the UV spectrum of compound 1 (Fig. 8) exhibits two peaks at 202 and 244 nm

Table 4
Hydrogen-bonding geometry (Å, °).

D-H...A	D-H	H...A	D...A	D-H...A
O13-H1...O1 ^{xiii}	0.980	1.796	2.664	145.71
O14-H2...OW1 ^{xi}	1.119	2.612	3.186	110.78
O15-H3...O4 ^{xiv}	0.914	1.785	2.637	153.94
OW1-H11...O15 ^{xvi}	0.970	2.057	2.868	139.90
OW1-H12...O11 ^{ix}	0.970	2.227	2.925	127.98
OW1-H12...OW2 ⁱⁱⁱ	0.970	2.575	3.402	143.21
OW1-H12...O12 ⁱⁱⁱ	0.970	2.606	3.096	111.46
OW2-H21...N ⁱⁱⁱ	0.970	2.327	3.114	137.71
OW2-H22...O6	0.970	1.807	2.750	163.18
OW3-H31...N	0.970	2.052	2.858	139.18
OW3-H31...N ^{xv}	0.970	2.273	3.192	157.74
OW3-H31...OW3 ^{xv}	0.970	2.461	3.153	128.09
OW3-H32...O8 ⁱ	0.970	2.437	3.092	124.49

Symmetry codes: (i) $-x+1/2, -y+1/2, -z+1$; (iii) $-x+1, -y, -z+1$; (ix) $x-1/2, -y+1/2, z+1/2$; (xi) $x, -y, z-1/2$; (xiii) $x+1/2, y-1/2, z$; (xiv) $x+1/2, y+1/2, z$; (xv) $-x+1, y, -z+3/2$; (xvi) $x, -y, z+1/2$

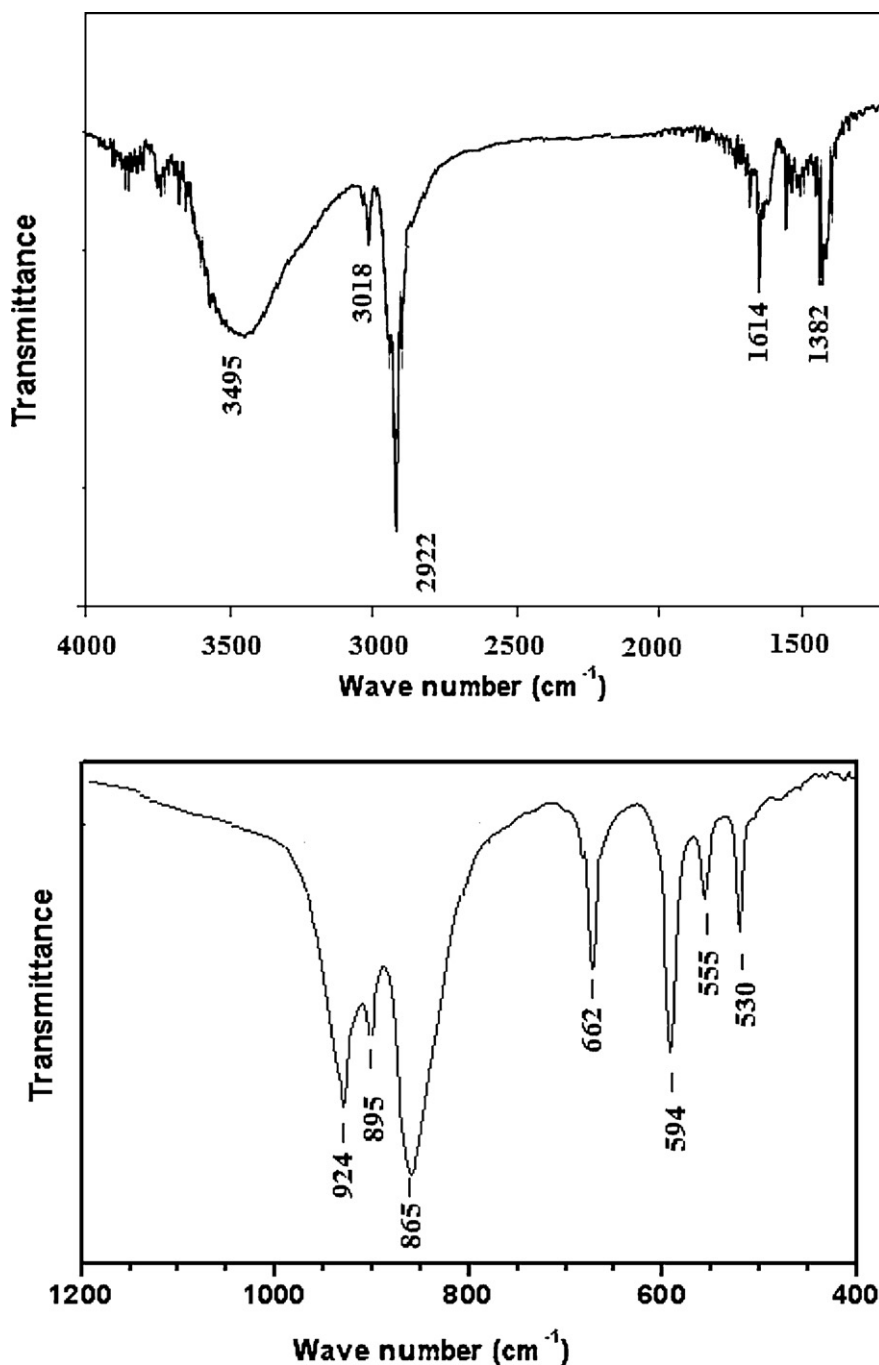


Fig. 7. IR spectrum of $K_5NH_4[ToMo_6O_{24}].Te(OH)_6.6H_2O$.

ascribed to the ligand-to-metal charge transfers (LMCT) of $O_t \rightarrow Mo$ and $O_b \rightarrow Mo$, respectively, where electrons are promoted from the low-energy electronic states, mainly comprised of oxygen 2p orbitals, to the high-energy states, which are mainly comprised of metal d orbitals [21–23].

3.5. Thermal analysis

Thermogravimetric and differential thermal analyses (TG–DTA) curves of the compound **1** are shown in Fig. 9.

The TGA curve of the structure shows four steps of decomposition. The first corresponds to the elimination of two water molecules per formula unit (weight loss observed 2.23%) in the temperature range 100–223 °C. This dehydration is related to the first endothermic peak on the DTA curve with a maximum elimination at 145 °C. The second process starts at 223 °C and is complete at 282 °C, which corresponds to the remaining four crystallization water molecules (weight loss observed 6.68%). The third and the fourth effect at 318 °C and 347 °C,

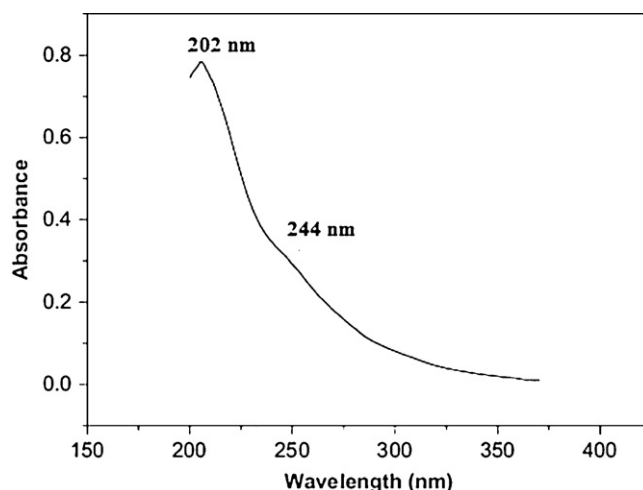


Fig. 8. UV-visible absorption spectrum of the compound $K_5(NH_4)(TeMo_6O_{24})(Te(OH)_6).6(H_2O)$.

respectively correspond probably to the removal of NH_4^+ cation and to the decomposition of the compound. Further heating shows no noticeable loss in between 400 °C and 700 °C.

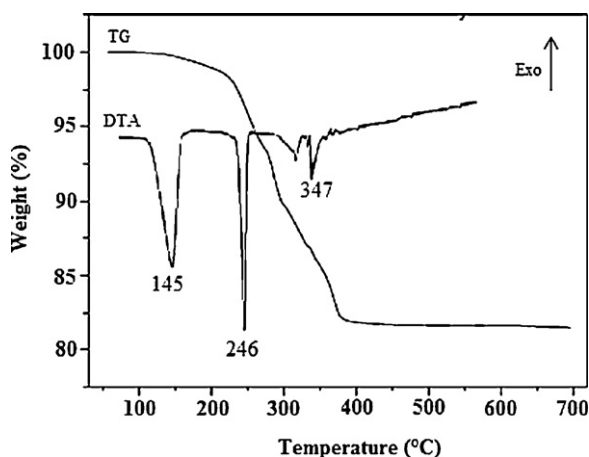


Fig. 9. TG-DTA thermograms of $K_5NH_4[TeMo_6O_{24}].Te(OH)_6.6H_2O$.

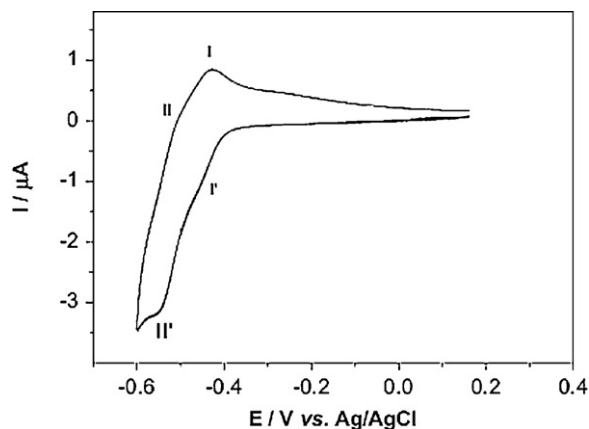


Fig. 10. CV of compound 1 in 1 mol L^{-1} H_2SO_4 solution at a scan rate of 100 $mV s^{-1}$.

3.6. Electrochemical behavior

The Anderson structure contains not only MoO_6 octahedra with single terminal oxygen but also octahedra containing cis terminal oxygen; so it is electrochemically active and can be reduced. Cyclic voltammetry on the compound 1 was carried out in 1 mol L^{-1} H_2SO_4 aqueous solution in the potential range from -600 to 400 mV. Fig. 10 shows the typical cyclic voltammetric behaviors of the compound at scan rate 10 $mV s^{-1}$. It can be seen that two redox peaks appear and the mean peak potential $E_{1/2} = (E_p + E_{pc})/2$ are -440 mV (I-I') and -533 mV (II-II') (vsAg/AgCl), respectively. The two peaks I-I' and II-II' may be attributed to the redox of the $Mo^{VI/V}$ in the polyanion framework.

4. Conclusion

In summary, new compounds have been isolated under conventional solution method by controlling the pH value of the reactive system. The crystal structure of the title compound has been elucidated by X-ray crystallography and confirmed by EDS, IR, UV and TG-DTA. The main geometrical feature of this structure is the existence of $(TeMo_6O_{24})^{6-}$ clusters. These clusters are connected to the $Te(OH)_6$ groups through hydrogen bonds and potassium ions to form three-dimensional framework.

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