Synthesis and structural characterization of new inorganic–organic hybrid: arsenomolybdate compound with cytosinium cations

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Abstract. New organic–inorganic hybrid compound, with formula $(C_4H_6N_3O)_6[(HAsO_4)_2Mo_6O_{19}] \cdot 7H_2O$, was prepared and characterized by IR and UV–visible spectroscopies and X-ray diffraction techniques. Thermal analysis was performed to study their thermal stability. The crystal structure of the title compound (triclinic, space group $P - 1$, $Z = 2$) was determined by X-ray diffraction. The compound contains the polyanion $[(HAsO_4)_2Mo_6O_{19}]^{6-}$, which consists of the six molybdenum octahedral grouped into two parts consisting of four edge-sharing octahedral and two face-sharing octahedral, respectively, these two parts are connected by two corner-sharing O atoms to form a bent Mo_6 ring. The polyanion framework derives from the Strandberg type and it is a new isomer. The cytosinium cations (Cyt^+) are embedded in the channels and interact with the inorganic framework by way of $N-H \cdots O$ and $O-H \cdots O$ hydrogen bonds. Furthermore, the electrochemical property of this compound has been studied.

Keywords. Arsenomolybdate; crystal structure; thermal behaviour; infrared spectroscopy; cytosine.

1. Introduction

Polyoxometalates (POMs) have been a centre of research interest for a long time, as they exhibit a great variety of structures and rich diversity of remarkable properties.^{1–7} In the past decades, an important advance in polyoxometalate chemistry is the polyoxometalate-based organic–inorganic hybrid materials.^{8,9} Such materials not only demonstrate their fascinating structural diversities, but also provide new and exciting functional materials with interesting optical, electronic and magnetic or catalytic properties.^{10–12} In particular, polyoxomolybdates shows a great variety of structures and properties. A large number of compounds were synthesized and structurally characterized in the $A-Mo-P-O$ system, where A is an organic or inorganic cation.^{13–15} They exhibit varieties of novel frameworks. In contrast to the rich structural chemistry of molybdenum phosphates, the $Mo-As-O$ system remains relatively undeveloped. In recent years, chemists have obtained some compounds of $Mo-As-O$ system belonging to a new class of anion clusters distinctly different from Keggin ion $[AsMo_{12}O_{40}]^{3-}$ and Dawson polyanion $[As_2Mo_{18}O_{62}]^{6-}$, such as $[As_6Mo_4O_{22}H_2]^{4-}$,^{16,17} $[AsMo_8O_{30}]^{7-}$,¹⁸ $[(HAsO_4)_2(Mo_2O_5)]^{2-}$ ¹⁹ and $[As_3Mo_{12}O_{40}]^{5-}$.^{16,17} In order to obtain new materials with novel structures and interesting properties, we report here the synthesis and X-ray crystal structure of a novel inorganic–organic hybrid arsenomolybdate compound with cytosinium cations.

2. Experimental

2.1 Materials and measurements

All chemicals were purchased commercially and used without any further purification. Qualitative analysis by scanning electron microscopy (SEM) probe was performed using an apparatus of the type JOEL JSM-5400 (JOEL Ltd Tokyo, Japan). Infrared spectrum was recorded at room temperature on a Nicolet 470 FTIR spectrophotometer as KBr pellets in the $4000-400\text{ cm}^{-1}$ region. UV–vis spectrum was measured using a Perkin-Elmer Lambda 19 spectrophotometer in the $180-800\text{ nm}$ range. The TGA–DTA thermograms were obtained with 3.5 mg. Sample was placed in an open platinum crucible and heated, under air, from room temperature to 450°C with 5°C min^{-1} heating rate; an empty crucible was used as reference. A CHI 660 Electrochemical Workstation connected to a Digital-586 personal computer was used for control of the electrochemical measurements. A conventional three-electrode system was used. The working electrode was gold, platinum gauze was used as counter electrode and the saturated calomel electrode (SCE) was the reference electrode. The measurements were performed at room temperature.

2.2 Synthesis

A solution of cytosine base $C_4H_5N_3O$ (0.5 mmol) in 10 cm^3 of water was added, with vigorous stirring, to a mixture of $Na_2MoO_4 \cdot 2H_2O$ (1 mmol) and H_3AsO_4 (3 mmol) in 20 cm^3 of water, at room temperature with a starting pH 3 adjusted with glacial acetic acid. One week later, colourless

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Figure 1. SEM spectrum of $(\text{C}_4\text{H}_6\text{N}_3\text{O})_6[(\text{HAsO}_4)_2\text{Mo}_6\text{O}_{19}]\cdot 7\text{H}_2\text{O}$.

block crystals were grown by slow evaporation at room temperature. The qualitative analysis by SEM of one of the colourless stick-like crystals obtained revealed the presence of only Mo, As, C, N and O elements (figure 1). Elem. Anal. Found: Mo, 29.4; As, 7.65; C, 14.72; N, 12.87; O, 32.68 (%). Calcd: Mo, 29.7; As, 7.62; C, 14.58; N, 13.10; O, 32.68 (%).

3. Results and discussion

3.1 X-ray crystallographic study

Single crystal of the title compound with dimension $0.1 \times 0.2 \times 0.15 \text{ mm}^3$ was chosen for X-ray diffraction studies. Data were collected on an Enraf-Nonius CAD-4 diffractometer with $\text{MoK}\alpha$ monochromatic radiation ($\lambda = 0.71073 \text{ \AA}$)²⁰ at 293 K. Empirical absorption correction was applied using ψ -scan data.²¹ The structure was successfully developed in the non-centrosymmetric space group $P-1$, solved by the Patterson method using SHELXS-97^{22,23} and refined by the full-matrix least-squares method on F^2 using the SHELXL-97 crystallographic software package.^{22,23}

A total of 12460 reflections ($2.088^\circ < \theta < 26.978^\circ$) was collected, of which 12460 unique reflections [$R(\text{int}) = 0.0282$] were used. The structure was solved using SHELXS-97 and refined using SHELXL-97 to $R_1 = 0.060$, $wR_2 = 0.141$, for 9627 reflections with $I > 2\sigma(I)$. All non-hydrogen atoms were refined anisotropically. Attempt to locate the positions of some hydrogen atoms from different Fourier maps was given up. Further details of the X-ray structural analysis are given in table 1. The final atomic coordinates and equivalent temperature factors are presented in table 2. Selected bond lengths of 1 are listed in table 3. Structure graphics are drawn with DIAMOND 2.1.³⁶

Table 1. Crystal data and structure refinement for $(\text{C}_4\text{H}_6\text{N}_3\text{O})_6[(\text{HAsO}_4)_2\text{Mo}_6\text{O}_{19}]\cdot 7\text{H}_2\text{O}$.

Chemical formula	$(\text{C}_4\text{H}_6\text{N}_3\text{O})_6[(\text{HAsO}_4)_2\text{Mo}_6\text{O}_{19}]\cdot 7\text{H}_2\text{O}$
Formula weight	1956.14 g mol^{-1}
Crystal system	Triclinic
Space group	$P-1$
a ($\text{\AA}$)	11.0334(1)
b ($\text{\AA}$)	15.3654(1)
c ($\text{\AA}$)	18.3757(1)
α ($^\circ$)	101.710(1)
β ($^\circ$)	106.889(1)
γ ($^\circ$)	92.986(1)
V ($\text{\AA}^3$)	2898.30(4)
Z	2
T (K)	293(2)
$\mu_{\text{Mo(K}\alpha)}$ (mm^{-1})	2.445
R_1 [$I > 2\sigma(I)$]	0.033
wR_2	0.087

3.2 Structure description

Single-crystal X-ray structural analysis shows that the structure of $(\text{C}_4\text{H}_6\text{N}_3\text{O})_6[(\text{HAsO}_4)_2\text{Mo}_6\text{O}_{19}]\cdot 7\text{H}_2\text{O}$ consists of isolated $[(\text{HAsO}_4)_2\text{Mo}_6\text{O}_{19}]^{6-}$ cluster anions, protonated cytosine $(\text{C}_4\text{H}_6\text{N}_3\text{O})^+$ and water molecules. A projection of the structure, showing the displacement ellipsoids, is presented in figure 2. The $\{\text{As}_2\text{Mo}_6\}$ anion is formed by close packing of oxygen atoms with As and Mo atoms in the distorted tetrahedral and octahedral voids, respectively. A perspective view of the $[(\text{HAsO}_4)_2\text{Mo}_6\text{O}_{19}]^{6-}$ anion with its numbering scheme is shown in figure 3. The polyoxomolybdate cluster $[(\text{HAsO}_4)_2\text{Mo}_6\text{O}_{19}]^{6-}$ can be described as a ring of six distorted edge-, face- and corner-sharing MoO_6 octahedra with two HAsO_4 tetrahedra capped on each side. The arsenic As_2 subunit shares three oxo-groups

Table 2. The final atomic coordinates, fractional occupancies and equivalent temperature factors.

Atoms	<i>x</i>	<i>y</i>	<i>z</i>	Occupation	<i>U</i> _{eq}
As1	0.89840(4)	0.37987(3)	0.13234(2)	1	0.01417(9)
As2	0.78464(4)	0.35147(3)	0.30854(3)	1	0.01844(10)
Mo1	1.09704(4)	0.31269(2)	0.31203(2)	1	0.02039(9)
Mo2	0.71558(3)	0.16253(2)	0.02990(2)	1	0.01820(9)
Mo3	1.01929(4)	0.52302(2)	0.31915(2)	1	0.01973(9)
Mo4	1.00448(4)	0.15343(2)	0.11900(2)	1	0.02223(9)
Mo5	0.72134(4)	0.53518(2)	0.20821(2)	1	0.02023(9)
Mo6	0.55701(3)	0.33460(2)	0.12441(2)	1	0.01908(9)
O1	0.3206(6)	0.7690(5)	0.1488(6)	1	0.0277(14)
O2	0.2995(7)	0.3333(5)	0.3595(6)	1	0.0338(15)
O3	0.3837(8)	0.4967(8)	0.3816(8)	1	0.021(2)
O4	0.4855(11)	0.6391(8)	0.3018(10)	1	0.025(2)
O5	0.4080(8)	0.4723(7)	0.1603(8)	1	0.016(2)
O6	0.6442(8)	0.5120(9)	0.4841(7)	1	0.020(2)
O7	0.6614(7)	0.4993(7)	0.2814(7)	1	0.0159(18)
O8	0.5184(10)	0.3498(8)	0.3570(9)	1	0.021(2)
O9	0.8525(10)	0.6076(8)	0.4851(10)	1	0.026(2)
O10	0.8859(9)	0.4468(10)	0.6196(9)	1	0.029(3)
O11	0.9030(8)	0.4366(8)	0.3952(7)	1	0.019(2)
O12	0.7289(9)	0.3276(8)	0.4385(9)	1	0.019(2)
O13	0.1983(9)	0.4965(9)	−0.0648(8)	1	0.029(2)
O14	0.3579(9)	0.6411(7)	0.0257(9)	1	0.017(2)
O15	0.3653(8)	0.5281(8)	−0.1668(8)	1	0.020(2)
O16	0.5531(8)	0.5057(8)	0.0339(7)	1	0.019(2)
O17	0.3681(9)	0.3582(7)	−0.0433(10)	1	0.019(2)
O18	−0.1507(10)	0.6112(8)	−0.0222(10)	1	0.022(2)
O20	−0.0714(9)	0.4579(8)	−0.1056(9)	1	0.024(2)
O19	−0.3062(8)	0.4538(8)	−0.0954(8)	1	0.017(2)
O21	0.0176(8)	0.4864(9)	0.1510(7)	1	0.019(2)
O22	0.8050(8)	0.4919(8)	0.1544(7)	1	0.0147(17)
O23	−0.1323(9)	0.3279(8)	0.0399(9)	1	0.020(2)
O24	1.1431(10)	0.4419(10)	0.3995(9)	1	0.032(3)
O25	1.0019(11)	0.6020(9)	0.3365(10)	1	0.028(3)
O26	0.9672(10)	0.3151(8)	0.2474(9)	1	0.023(2)
O27	0.5779(11)	0.6308(8)	−0.1493(9)	1	0.024(2)
C1	0.4831(10)	0.4880(9)	−0.3193(8)	1	0.026(2)
C2	0.4856(10)	0.3513(8)	−0.1529(10)	1	0.023(2)
C3	0.3206(12)	0.8446(10)	0.3249(11)	1	0.033(3)
C4	0.1646(13)	0.6721(11)	0.1956(13)	1	0.045(4)
N1	0.3664(17)	0.3008(11)	0.5647(13)	1	0.057(4)
N2	0.1964(11)	0.3487(10)	0.1401(12)	1	0.036(3)
N3	0.2771(11)	0.1606(10)	0.3192(12)	1	0.033(3)
OB1	0.1950(18)	0.6527(19)	−0.3271(17)	1	0.098(11)
C5	0.019(2)	0.2745(16)	0.5357(19)	1	0.090(7)
C6	0.1775(19)	0.4146(17)	−0.3431(19)	1	0.097(8)
C7	0.0472(15)	0.3021(15)	−0.153(2)	1	0.086(7)
C8	0.6186(12)	0.2999(10)	0.4139(11)	1	0.013(2)
N4	0.5945(15)	0.2001(11)	0.4473(14)	1	0.023(3)
N5	0.4088(14)	0.3170(10)	−0.1140(13)	1	0.020(3)
N6	0.3559(16)	0.2210(10)	−0.1635(14)	1	0.021(3)
OB2	−0.0733(12)	0.2826(10)	0.1364(13)	1	0.016(3)
C9	−0.0497(15)	0.1790(11)	0.1189(12)	1	0.021(3)
C10	0.7112(13)	0.1491(12)	0.5247(13)	1	0.032(3)
C11	0.2678(12)	0.1889(10)	−0.1105(12)	1	0.023(3)
C12	0.0049(12)	0.1229(10)	0.2371(11)	1	0.026(3)
N7	1.1388(4)	0.2607(2)	0.3876(2)	1	0.0374(8)
N8	1.2418(3)	0.3516(2)	0.3046(2)	1	0.0324(8)
N9	1.0559(3)	0.2138(2)	0.22544(19)	1	0.0267(7)
OB3	1.0700(3)	0.4291(2)	0.37050(17)	1	0.0249(7)
C13	0.8926(3)	0.2830(2)	0.2951(2)	1	0.0293(7)

Table 2. (continued)

Atoms	<i>x</i>	<i>y</i>	<i>z</i>	Occupation	<i>U</i> _{eq}
C14	1.0084(3)	0.39953(18)	0.22311(17)	1	0.0191(6)
C15	0.6742(3)	0.2106(2)	−0.0488(2)	1	0.0318(8)
C16	0.6148(3)	0.0641(2)	−0.0005(2)	1	0.0282(7)
N10	0.6321(3)	0.22837(19)	0.09622(19)	1	0.0227(6)
N11	0.8690(3)	0.11165(19)	0.01905(19)	1	0.0231(7)
N12	0.8830(3)	0.26868(18)	0.09379(18)	1	0.0194(6)
OB4	0.8215(3)	0.13008(19)	0.14410(18)	1	0.0218(6)
C17	1.0048(4)	0.6015(2)	0.3963(2)	1	0.0334(8)
C18	1.1599(3)	0.5630(2)	0.3066(2)	1	0.0291(7)
C19	0.9046(3)	0.55980(19)	0.23112(17)	1	0.0197(6)
C20	0.8216(3)	0.45809(19)	0.30340(17)	1	0.0209(6)
N13	1.0531(4)	0.0517(2)	0.1276(3)	1	0.0421(10)
N14	1.1178(3)	0.2044(2)	0.0885(2)	1	0.0341(8)
N15	0.6985(4)	0.6144(2)	0.2837(2)	1	0.0339(8)
OB5	0.6798(4)	0.5809(2)	0.1290(2)	1	0.0347(8)
C21	0.5735(3)	0.4532(2)	0.19150(19)	1	0.0238(7)
C22	0.7542(3)	0.40430(19)	0.14382(18)	1	0.0197(6)
N16	0.4175(3)	0.2881(2)	0.1314(2)	1	0.0288(7)
N17	0.5100(3)	0.3611(2)	0.0356(2)	1	0.0302(7)
N18	0.6423(3)	0.3062(2)	0.24609(18)	1	0.0244(7)
C23	0.9406(3)	0.4371(2)	0.07517(18)	1	0.0241(7)
C24	0.7780(4)	0.3593(3)	0.4019(2)	1	0.0398(9)
OB6	1.2867(5)	0.6372(3)	0.1724(3)	1	0.0324(11)
OW1	1.2973(5)	0.4774(4)	0.0692(3)	1	0.0324(11)
OW2	1.2590(4)	0.4744(3)	0.1361(3)	1	0.0278(10)
OW3	1.3283(5)	0.5586(4)	0.0573(3)	1	0.0377(12)
OW4	1.3233(5)	0.6361(3)	0.1070(3)	0.59	0.0381(10)
OW5	1.2565(4)	0.5542(3)	0.1845(2)	0.41	0.0299(9)
OW6	1.2264(4)	0.4006(3)	0.1541(3)	0.42	0.0342(10)
OW7	1.2771(4)	0.7060(3)	0.2166(2)	0.58	0.0468(10)
OW8	0.7018(5)	−0.0659(3)	0.1858(3)	0.62	0.0352(12)
OW9	0.7521(4)	−0.1023(3)	0.0646(3)	0.38	0.0255(9)
OW10	0.7076(5)	−0.1936(3)	0.0542(3)	1	0.0322(11)

with the molybdate ring. In turn, two of these oxo-groups adopt the μ_2 -bridging mode, linking one molybdenum site and the arsenic, and the other one adopts the μ_3 -bridging mode, linking two molybdenum sites and the arsenic, while the As1 subunit shares three oxo-groups of six octahedral MoO_6 .

In these anions there are three categories of Mo–O bonds. Thus, the Mo is bonded to two terminal oxygen atoms with Mo–O distances in the 1.698(3)–1.736(3) Å range. The Mo–O bonds ranging from 1.891(3) to 2.256(3) Å are found with oxygen atoms bonded to two molybdenum atoms. The longest Mo–O distances, 2.198(3)–2.349(3) Å, appear with oxygen atoms coordinated to arsenic and molybdenum. The six-member ring is nearly planar with a mean deviation of 0.1775 Å, and the interatomic distance between As1 and As2 is 3.89(1) Å with the orientation of the As1–As2 vector to the ring being 57.9°. As atoms are surrounded by four oxygen atoms and exhibit distorted geometry, with As–O bond ranging from 1.646(3) to 1.715(3) Å and from 1.668(3) to

1.719(3) Å for As1 and As2, respectively. The O–As–O bond angles between 105.16(3)° and 114.53(3)°.

The title polyanion differs from a well-known Lindqvist type of structure $[\text{Mo}_6\text{O}_{19}]^{2-}$,²⁴ in which each Mo atom of the polyanion is coordinated by six O atoms (one terminal O_t , one central O_c and four bridging O_b) in a distorted octahedral arrangement, due to the displacement of Mo atoms towards the terminal O_t atoms. The six MoO_6 octahedra share a common vertex at the central O_c , and also each octahedron shares four edges with adjacent octahedral²⁵ and thus exhibits an approximate O_h symmetry, whereas the $[(\text{HAsO}_4)_2\text{Mo}_6\text{O}_{19}]^{6-}$ cluster has approximate C_1 symmetry.

BVS calculations²⁶ (<http://kristall.uni.mki.gwdg.de/softbv>) revealed that all the molybdenum atoms have valence sums ranging from 5.942 to 6.055, with an average value of 6.001, close to the ideal value of 6 for Mo^{VI} . The calculated average value of arsenic (V), oxygen (−II) atoms are 4.940 and 1.973, respectively. Moreover, these calculations indicated that the bridging oxygen atoms, O26 and O27, are protonated.

Table 3. Selected bond lengths (Å).

Bond lengths	
Mo1–O1	1.701(3)
Mo1–O2	1.729(3)
Mo1–O3	1.890(3)
Mo1–O4	1.976(3)
Mo1–O5	2.195(3)
Mo1–O6	2.345(3)
Mo2–O7	1.712(3)
Mo2–O8	1.720(3)
Mo2–O9	1.899(3)
Mo2–O10	1.946(3)
Mo2–O11	2.259(3)
Mo2–O12	2.254(3)
Mo3–O13	1.716(3)
Mo3–O14	1.734(3)
Mo3–O4	1.902(3)
Mo3–O15	1.947(3)
Mo3–O16	2.264(3)
Mo3–O6	2.285(3)
Mo4–O17	1.701(3)
Mo4–O18	1.725(3)
Mo4–O3	1.890(3)
Mo4–O10	1.961(3)
Mo4–O12	2.225(3)
Mo4–O11	2.316(3)
Mo5–O19	1.698(3)
Mo5–O20	1.738(3)
Mo5–O21	1.918(3)
Mo5–O15	1.942(3)
Mo5–O22	2.222(3)
Mo5–O16	2.354(3)
Mo6–O24	1.702(3)
Mo6–O23	1.713(3)
Mo6–O9	1.915(3)
Mo6–O21	1.949(3)
Mo6–O22	2.271(3)
Mo6–O25	2.300(3)
As1–O26	1.646(3)
As1–O11	1.691(3)
As1–O6	1.711(3)
As1–O22	1.715(3)
As2–O5	1.668(3)
As2–O25	1.668(3)
As2–O16	1.696(3)
As2–O27	1.719(3)
C1–OB1	1.226(6)
C1–N1	1.372(7)
C1–N2	1.378(6)
C2–C4	1.353(7)
C2–C3	1.419(7)
C3–N3	1.306(6)
C3–N2	1.368(6)
C4–N1	1.360(7)
C5–OB2	1.218(7)
C5–N5	1.368(6)
C5–N4	1.378(6)
C6–N6	1.322(6)
C6–N6	1.353(6)
C6–C7	1.418(6)

Table 3. (continued)

Bond lengths	
C7–C8	1.352(8)
C8–N5	1.357(7)
C9–OB3	1.223(6)
C9–N7	1.367(7)
C9–N8	1.384(7)
C10–N9	1.309(6)
C10–N8	1.357(6)
C10–C11	1.438(7)
C11–C12	1.328(8)
C12–N7	1.360(7)
C13–OB4	1.213(7)
C13–N10	1.372(6)
C13–N11	1.376(7)
C14–N12	1.307(6)
C14–N10	1.367(6)
C14–C15	1.430(7)
C15–C16	1.352(8)
C16–N11	1.351(8)
C17–OB5	1.246(8)
C17–N13	1.348(8)
C17–N14	1.365(8)
C18–N15	1.321(8)
C18–N13	1.356(8)
C18–C19	1.432(8)
C19–C20	1.325(10)
C20–N14	1.364(9)
C21–N17	1.317(6)
C21–N16	1.366(6)
C21–C23	1.424(6)
C22–OB6	1.215(6)
C22–N18	1.366(6)
C22–N16	1.382(6)
N18–C24	1.378(7)
C23–C24	1.337(7)

In the structure the Cyt⁺ ions, acting as charge-compensating cations and space-filling structural subunits, are connected to the three-dimensional (3D) supramolecular by N–H···O and O–H···N hydrogen bonds and aromatic π – π stacking interactions.

The arrangement of the [(HAsO₄)₂Mo₆O₁₉]^{6–} clusters and the cytosinium cations along the *b* axis is demonstrated in figure 4. As listed in table 4, OW–H···O, OW–H···OW and OW–H···N hydrogen bonds between the solvent water molecules, Cyt⁺ cations and the clusters have interatomic O···O and N···O distances ranging, respectively, from 2.648 to 3.405 Å and from 2.672 to 3.283 Å and the hydrogen-bond angles from 110.37° to 179.45°. It is noticeable that there also exist the N–H···N hydrogen bonds between two organic amines with interatomic distances between 2.672 and 3.283 Å and the close contact distance between some adjacent aromatic rings of Cyt⁺ contributes to the formation of the extensive π – π interactions (figure 5). These hydrogen bonds hold the components together into a 3D network and make the crystal structure of the compound more stable.

Figure 2. An ORTEP drawing of the asymmetric unit.

Figure 3. A polyhedral representation of the $[(\text{HAsO}_4)_2\text{Mo}_6\text{O}_{19}]^{6-}$ anion.

3.3 IR absorption spectrometry

Vibrational spectrum exhibits the characteristic bands associated with the building constituents from which the title material was synthesized: the polyoxoanion $[(\text{HAsO}_4)_2\text{Mo}_6\text{O}_{19}]^{6-}$, organic groups and water molecules. The IR spectrum of the title compound (figure 6) has some characteristic bands for the cytosine moiety.²⁷ The broad absorption observed in the region between 3200 and 2800 cm^{-1} can be assigned to the O–H, N–H and C–H stretching modes. Absorptions in 1620–1674 cm^{-1} are attributed to the stretching vibration of C=O and bending vibration of

the OH group of the water molecules. On the other hand, the title compound exhibits bands in the 1532–1100 cm^{-1} region, corresponding to the stretching vibrations C–C and C–N and bending vibration C–C–H. The low-wavenumber characteristic peaks at 923, 876, 828, 781, 668, 621, 574, 515 and 480 cm^{-1} are attributed to the $[(\text{HAsO}_4)_2\text{Mo}_6\text{O}_{19}]^{6-}$ polyoxoanions.²⁸

3.4 UV–visible spectra

The UV–visible absorption behaviour of the title compound was analysed in the 190–800 nm range using an aqueous

Figure 4. A packing view of compound along the [010] direction, showing the arrangement of the $[(\text{HASO}_4)\text{Mo}_6\text{O}_{19}]^{6-}$ clusters, cytosinium cations and the lattice water molecules in the crystal structure.

Table 4. Hydrogen-bonding geometry ($\text{\AA}$, $^\circ$).

D–H...A	D–H ($\text{\AA}$)	H...A ($\text{\AA}$)	D...A ($\text{\AA}$)	D–H...A ($^\circ$)
O26–HAS1...N17 ⁱ	0.821	2.171	2.846	139.52
O27–HAS2...OW1 ⁱⁱ	0.959	1.830	2.648	141.46
N3–H1...O23 ⁱⁱⁱ	0.756	2.377	2.864	123.37
N3–H1...O18	0.756	2.494	3.048	131.42
N3–H4...O6	0.914	2.355	3.029	130.49
N5–H11...OW2 ^{iv}	1.014	1.933	2.681	128.24
N6–H12...O17	1.146	2.575	3.240	115.57
N8–H14...O20	0.943	1.803	2.745	177.63
N7–H15...OB4 ^v	0.956	1.783	2.672	153.40
N11–H21...OW6 ^{vii}	0.932	2.452	3.000	117.62
N12–H23...O9 ^{ix}	0.740	2.152	2.814	149.35
N12–H23...O23 ^{ix}	0.740	2.646	3.224	136.75
N13–H26...N13 ^v	0.862	2.257	2.889	130.14
N13–H26...OW4 ^v	0.862	2.594	3.273	136.43
N15–H28...OW3 ⁱⁱⁱ	1.025	2.056	3.022	156.19
N15–H28...OB2 ⁱⁱ	1.025	2.577	3.283	125.70
N17–H35...O26	1.132	1.741	2.699	138.90
OW3–H1W3...O5	0.868	2.486	2.905	110.37
OW4–H1W4...N11 ^v	0.798	2.192	2.844	139.07
OW5–H1W5...O1 ^x	1.074	2.244	2.996	125.37
OW5–H2W5...OW8	0.855	2.109	2.693	125.07
OW7–H1W7...O17 ^{vi}	0.994	2.319	3.061	130.66
OW9–H1W9...OW7 ^{ix}	0.855	2.119	2.849	142.96
OW9–H2W9...OW4 ^v	0.990	2.263	3.069	137.81

ⁱ $-x+2, y+1, -z$; ⁱⁱ $-x+1, y+1, -z+1$; ⁱⁱⁱ $x+1, y, z$; ^{iv} $x, y-1, z$; ^v $-x+1, -y+2, -z+1$; ^{vi} $x-1, y, z$; ^{vii} $x, y+1, z$; ^{ix} $x, y+1, z$; ^x $-x+2, -y+1, -z+1$.

Figure 5. The π - π interactions in the compound.

Figure 6. FT-IR spectrum of $(\text{C}_4\text{H}_6\text{N}_3\text{O})_6[(\text{HAsO}_4)_2\text{Mo}_6\text{O}_{19}] \cdot 7\text{H}_2\text{O}$ between 4000 and 400 cm^{-1} .

Figure 7. UV-visible absorption spectrum of $(\text{C}_4\text{H}_6\text{N}_3\text{O})_6[(\text{HAsO}_4)_2\text{Mo}_6\text{O}_{19}] \cdot 7\text{H}_2\text{O}$.

Figure 8. The two curves corresponding to the DTA and TGA analysis of $(\text{C}_4\text{H}_6\text{N}_3\text{O})_6[(\text{HAsO}_4)_2\text{Mo}_6\text{O}_{19}] \cdot 7\text{H}_2\text{O}$.

Figure 9. Cyclic voltammogram of compound in 1 mol l^{-1} H_2SO_4 solution at a scan rate of 100 mV s^{-1} .

solution. The electronic spectrum of compound is shown in figure 7, giving two evident bands at 200 and 270 nm. They are attributed to the ligand-to-metal charge transfers of Ot-Mo and μ -O-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.²⁹⁻³¹

3.5 Thermal analysis

The two curves corresponding to the DTA and TGA analysis of $(\text{C}_4\text{H}_6\text{N}_3\text{O})_6[(\text{HAsO}_4)_2\text{Mo}_6\text{O}_{19}] \cdot 7\text{H}_2\text{O}$ are given in figure 8. The DTA curve shows that this compound undertakes a series of endothermic and exothermic peaks in a wide temperature range (100–420°C). The DTA curve shows three endothermic peaks characterized by a weight loss of 8.5% observed on the TGA curve in the range 100–200°C. This thermal phenomenon corresponds to the loss of seven water

molecules. The DTA curve exhibits also several endothermic peaks between 300 and 400°C, which can be attributed to the degradation of the organic moiety.

3.6 Electrochemical property

The redox behaviour of the title compound was investigated by cyclic voltammogram in the 1 M H₂SO₄ aqueous solution, shown in figure 9. It can be seen that in the potential range from –600 to 1100 mV, three quasi-reversible redox peaks appear and the mean peak potentials $E_{1/2} = (E_{pa} + E_{pc})/2$ are 0.741(I), 0.570(II) and 0.086(III) mV. The I–I', II–II' and III–III' should be ascribed to three consecutive two-electron processes of molybdenum.^{32,33}

4. Conclusion

It is important to remark that polyanions consisting of a ring of six polyhedral MoO_x ($x = 5, 6$) capped above and below by arsenate groups are limited to the three isomers of [H_xAs₂Mo₆O₂₆]^{(6–x)–}, [As^V₂Mo₆O₂₆]^{6–}, [As^V₂Mo₆O₂₆ (H₂O)]^{6–34} and [(RAs)₂Mo₆O₂₄]^{4–} ($R = \text{CH}_3, \text{C}_6\text{H}_5, \text{p-C}_6\text{H}_4\text{NH}_2$).³⁵ In summary new compounds, including [(HAsO₄)₂Mo₆O₁₉]^{6–} type anion polyoxomolybdate, have been isolated under the conventional solution method. The crystal structure of the title compound has been elucidated by X-ray crystallography and confirmed by EDS, IR, UV and TG–DTA. There are extensive hydrogen-bonding interactions between the cluster, the cytosinium counter-ions and the water molecules, generating a 3D supramolecular network.

Supplementary material

CCDC 903129 contains the supplementary crystallographic data for this paper. 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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