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SYNTHESIS AND CHARACTERIZATION OF A PURE INORGANIC 3D NETWORK BASED ON THE $[Sr_2P_9HMo_{12}O_{71}]^{20-}$ CLUSTER AND STRONTIUM(II) LINKERS

M.M. Ftini

Laboratoire de matériaux et cristallochimie (LMC), Faculté des sciences Monastir, Tunisie
E-mail: mohamedmongi@yahoo.fr

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Novel supramolecular networks based on an anionic polymolybdophosphate cluster $Sr_{10}(H_2O)_{12}[Sr_2P_9HMo_{12}O_{71}]$ is hydrothermally synthesized and structurally characterized by single crystal X-ray diffraction, thermogravimetric analysis, infrared, ultraviolet spectroscopy, and cyclic voltammetry in an aqueous solution. It crystallizes in the orthorhombic space group *Pnmm* (No. 59) with $a = 12.699(1)$, $b = 14.914(1)$, $c = 23.851(2)$ Å and $Z = 2$. The compound is made up of unusual shaped-cage $[Sr_2P_9HMo_{12}O_{71}]^{20-}$. The strontium cations are divided in two kinds. The first occupy vacant sites in the $[P_9Mo_{12}O_{68}]^{n-}$ polyoxoanions unit and the second $[Sr(H_2O)_6]^{2+}$, $[Sr(H_2O)_4]^{2+}$, and $[Sr(H_2O)_2]^{2+}$ serve to bridge together the adjacent polymolybdophosphate clusters to yield unprecedented three-dimensional pure inorganic assemblies of the shaped-cage polymolybdophosphate clusters.

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INTRODUCTION

Polyoxometalate (POM)-based organic-inorganic hybrid compounds have attracted great interest in recent years because of their theoretical and practical applications in catalysis, molecular adsorption, medicine, electroconductivity, magnetism, and photochemistry [1—22]. As was indicated by Zubieta, polyoxomolybdate anions, which have oxygen-rich compositions can be used as building blocks to construct the structure of new materials having secondary transition metal complexes and/or organic ligands as linkers [23—26].

Great interest has been paid to assisting the self-assembly of molybdenum phosphate precursor subunits, the building blocks unit can be assembled *via* the 4*f* metal center, alkaline metal or transition metal cations yielding to sandwich-shaped molybdenum phosphate building blocks such as $(NH_4)_{11}[Ln(PMo_{11}O_{39})_2]\cdot 16H_2O$, (Ln = Ce, Sm, Dy …) [27]; $(Hen)_6[M_2(H_2O)Mo_{12}O_{24}(OH)_6(H_2PO_4)_3\cdot\cdot(HPO_4)_4(PO_4)]\cdot 4H_2O$ (M = Na, K) [28], $(H_2dien)_4[CaMo_{12}O_{24}(OH)_6(HPO_4)_8]\cdot 7.82H_2O$ [29]. $Na_{15}Mn_{10}[(Mo_2O_3)_3(HPO_4)(PO_4)_3(OH)_3]_4(PO_4)\cdot 48H_2O$, $Na_{12}Co_3[(PO_4)_4Mo_6O_{12}(OH)_3]_2\cdot 44H_2O$ [30], $Na_7Mn_4Fe_6[(Mo_2O_3)_3(HPO_4)_2(PO_4)_2(OH)_3]_4(PO_4)\cdot 50H_2O$ [31], $(4,4'\text{-}H_2bpy)[Ni(4,4'\text{-}bpy)(H_2O)_2Ni_{0.5}\cdot\cdot Mo_6(OH)_3O_{12}(HPO_4)_4]\cdot 2H_2O$ [32]. Recently, it is worth noting that most of these studies are based on non-classical heteropolyanions, thus, the hydrothermal technique has been extensively used and proved to be an efficient way to prepare some polymolybdophosphate clusters having a basket-shaped clusters based on the inorganic basket $[P_6Mo_{18}O_{73}]^{11-}$. The cluster can be divided into two fragments. The first is a tetra-vacant, lacunary derivative from the Wells—Dawson $[P_2Mo_{14}]$ heteropolymolyb-

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date fragment forming the basket body. The second fragment is the handle of the [P_4Mo_4O] basket. To the best of our knowledge few of supramolecular materials based on the basket-like $[P_6Mo_{18}O_{73}]^{11-}$ cage have been reported and refers to $[H_2dmpip]_5[KP_6Mo_{18}O_{73}]$ [33], $[Cu(phen)(H_2O)_3]\cdot[\{Cu(phen)(H_2O)_2\}\{Cu(phen)(H_2O)\}_3\{SrP_6Mo_{18}O_{73}\}]\cdot 3H_2O$ [34], $[Cu_4(bpy)_4(H_2O)_4KP_6Mo_{18}O_{71}\cdot(OH)_2]\cdot 7H_2O$ [35], $(H_2imi)_6(Himi)_4[\{Sr(H_2O)_4\}_2\{SrP_6Mo_{18}O_{73}\}_2]\cdot 17H_2O$ compounds [36]. Our aim was, firstly, to synthesize new supramolecular materials based on giant non-classical polymolybdophosphate clusters using simple molybdate as the starting materials and strontium cations as linkers under hydrothermal conditions and changing the pH value and, secondly, to participate in the expanding field of investigation. Herein, we report the hydrothermal synthesis and single X-ray diffraction of the supramolecular material based, to our knowledge, on the first example of the $[Sr_2HP_9Mo_{12}O_{71}]$ shaped-cage cluster. The infrared (IR), thermogravimetric analysis (TGA), UV visible and the electrochemical behavior of the title compound were also investigated.

EXPERIMENTAL

Hydrothermal synthesis. This product was hydrothermally synthesized under autogenous pressure in a 25 ml Teflon-lined reactor. A mixture of $(NH_4)_6Mo_7O_{24}\cdot 6H_2O$ (1.27 g, 1.00 mmol) and $SrCO_3$ (0.015 g, 0.1 mmol) was dissolved in 15 ml of distilled water. Then it was neutralized to pH = 3.1 with 3 ml of phosphoric acid (H_3PO_4) under continuous stirring for half an hour. The mixture was sealed in a 25 ml Teflon reactor and heated at 180 °C for 3 days. The autoclave was cooled at 5° per h to room temperature. The transparent block crystals were collected by filtration through a filter paper, washed with cold water, and dried under vacuum.

Single crystal X-ray diffraction. The data were collected on an Enraf-Nonius CAD4 diffractometer at 293 K using graphite monochromated MoK_α radiation (λ = 0.71073 Å). Empirical absorption corrections were applied. The structures were solved by direct methods using the SHELXS97 program [37] and refined by full-matrix least-squares methods based on F^2 using the SHELXL-97 program [38] included in the WINGX software package [39]. The crystal data and structure refinement are summarized in Table 1. The CCDC reference number 1043328 contains the supplementary crystallo-

Table 1

Crystal data and structure refinement for the $Sr_{10}(H_2O)_{12}[Sr_2P_9HMo_{12}O_{71}]$ *compound*

Empirical formula	$Sr_{10}(H_2O)_{12}[Sr_2P_9HMo_{12}O_{71}]$
Formula weight	3834.5
Crystal system	Orthorhombic
Space group	*Pnmm* (No. 59)
Cell parameters: *a*, *b*, *c*, Å	12.699(1), 14.914(1), 23.851(2)
V, Å^3; *Z*	4517.0(7); 2
D_{calc}, g/cm^3	2.187
Temperature, K	293(2)
Diffractometer	Enraf-Nonius CAD4
Monochromator	Graphite
Radiation	MoK_α (λ = 0.71073 Å)
hkl range	$-1 \le h \le 12$; $0 \le k \le 14$; $0 \le l \le 22$
θ range (deg.)	2.106—19.960
Reflections collected / observed	2243 / 1133
Number of parameters	295
Goodness-of-fit	1.009
R_1 / wR_2 (obs)	0.0485 / 0.1470
Weighting scheme	$w = 1/[\sigma^2\|F_0\|^2 + (0.1720P)^2 + 18.1685P]$, where $P = (\|F_0\|^2 + 2\|F_c\|^2)/3$

$R_1 = \sum(|F_0| - |F_c|) / \sum|F_0|$. $wR_2 = [\sum w(|F_0| - |F_c|)^2 / \sum w|F_0|^2]^{1/2}$.

graphic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

RESULTS AND DISCUSSION

Crystal structures. The single crystal X-ray diffraction analysis revealed that the title compound $Sr_{10}(H_2O)_{12}[Sr_2P_9HMo_{12}O_{71}]$ is constructed from anionic $[Sr_2P_9HMo_{12}O_{71}]^{20-}$ as the primary building block unit of the three-dimensional structure, twelve water molecules, and ten strontium(II) cations. The anionic unit is based on the shaped-cage $[Sr_2P_9HMo_{12}O_{71}]^{20-}$ clusters. The structure of $[Sr_2P_9HMo_{12}O_{71}]^{20-}$ polymolybdophophate clusters has been determined and can be separated into two $\{P_3Mo_6\}$ subunits. The $\{P_3Mo_6\}$ unit consists of six MoO_6 octahedra and three PO_4 tetrahedra. Three MoO_6 octahedra are linked together, sharing edges, to form a Mo_3O_{13} fragment. The other three PO_4 tetrahedra and three MoO_6 octahedra are alternatively linked to the inside of the Mo_3O_{13} fragment. The PO_4 tetrahedra share the double bonded oxygen atom of the Mo_3O_{13} subunit and two oxygen atoms with two different MoO_6 octahedra. Three MoO_6 octahedra share the terminal oxygen atom from the Mo_3O_{13} fragment and two oxygen atoms from two PO_4 tetrahedra. The connection mode resulting in a nest-shaped cluster, two nest-shaped clusters were joined to each other *via* three peripheral PO_4 tetrahedra by sharing terminal oxygen atoms resulting in a $[Sr_2P_9HMo_{12}O_{68}]^{20-}$ polymolybdophosphate cage-shaped cluster as shown in Fig. 1. All the molybdenum atoms in the cage-shaped cluster were part of distorted MoO_6 octahedra, the Mo—O bond lengths are in the range of 1.70(2)—2.27(2) Å, and the *cis*-O—Mo—O angles are in the range of 69.4(1)—103.6(1)°. The phosphorus atoms are tetrahedrally coordinated by oxygen atoms, and the P—O bond lengths are in the range of 1.41(7)—1.60(4) Å, the O—P—O angles are in the range of 104.8(2)—121(7)°. In the structure of the $[Sr_2P_9HMo_{12}O_{71}]^{20-}$ cluster, all nine phosphorous atoms are in the outside of the cluster and can be regarded as peripheral PO_4 tetrahedra. Whereas in other polymolybdophosphate, the shaped-basket $\{P_6Mo_{18}O_{73}\}$ anion was made up by two parts: the $\{P_4Mo_4\}$ handle consisting of four MoO_6 octahedra and four peripheral PO_4 tetrahedra and the basket body $\{P_2Mo_{14}\}$ unit, similar to the tetravacant Wells—Dawson structure type in which the PO_4 tetrahedra are inside the cluster and can be regarded as interstitial phosphorous atoms such as in $[H_2dmpip]_5[KP_6Mo_{18}O_{73}]$ [33], $[Cu(phen)(H_2O)_3]\cdot\cdot[\{Cu(phen)(H_2O)_2\}\{Cu(phen)(H_2O)\}_3\{SrP_6Mo_{18}O_{73}\}]\cdot 3H_2O$ [34], $[Cu_4(bpy)_4\cdot(H_2O)_4KP_6Mo_{18}O_{71}\cdot\cdot(OH)_2]\cdot 7H_2O$ [35], and $(H_2imi)_6(Himi)_4[\{Sr(H_2O)_4\}_2\{SrP_6Mo_{18}O_{73}\}_2]\cdot 17H_2O$ [36] compounds.

It is worth mentioning that the strontium(II) cation $Sr(1)^{2+}$ in the central cavity of the polymolybdophosphate cluster is encapsulated and having a seven-coordinated environment. The Sr(1)—O bond lengths range from 2.27(3) to 2.71(2) Å. During the self-assembly process the strontium cation stabilizes the whole polymolybdophosphate cluster yielding to the $[Sr_2P_9HMo_{12}O_{71}]^{20-}$ anions.

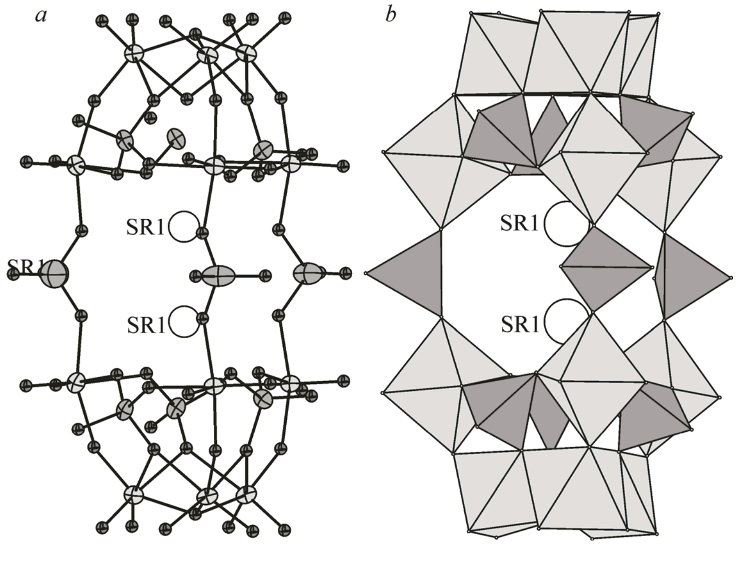

Fig. 1. Representation of the cage-shaped $[Sr_2P_9HMo_{12}O_{71}]^{20-}$ polymolybdophosphate cluster: ball and stick representation (*a*); polyhedral representation (*b*)

Table 2

Selected bond lengths (Å) *for the* $Sr_{10}(H_2O)_{12}[Sr_2P_9HMo_{12}O_{71}]$ *compound*

Bond	Distance	Bond	Distance	Bond	Distance	Bond	Distance
Mo1—O9	1.71(2)	Mo2—O19	1.71(2)	Mo3—O23	1.71(2)	P3—O1^{vi}	1.52(3)
Mo1—O9^{viii}	1.71(2)	Mo2—O19^{viii}	1.71(2)	Mo3—O20	1.73(2)	P3—O1	1.52(3)
Mo1—O4	1.85(3)	Mo2—O1	1.93(3)	Mo3—O17	1.97(2)	P3—O21	1.58(6)
Mo1—O6	2.03(3)	Mo2—O4	1.97(3)	Mo3—O22	1.99(3)	P3—O21^{iii}	1.58(6)
Mo1—O7	2.27(2)	Mo2—O10^{iv}	2.21(2)	Mo3—O3	2.15(2)		
Mo1—O7^{viii}	2.27(2)	Mo2—O10^{v}	2.21(2)	Mo3—O5	2.16(2)		
Mo4—O18^{iv}	1.71(2)	P1—O15	1.41(7)	P2—O8	1.54(4)	P4—O10	1.51(2)
Mo4—O13^{iv}	1.72(3)	P1—O26	1.50(7)	P2—O5^{viii}	1.55(2)	P4—O3	1.53(2)
Mo4—O17^{iv}	1.88(2)	P1—O22	1.56(3)	P2—O5	1.55(2)	P4—O11^{v}	1.57(3)
Mo4—O6	1.994(8)	P1—O22^{vi}	1.56(3)	P2—O2	1.60(4)	P4—O7^{v}	1.57(2)
Mo4—O7^{viii}	2.060(16)						
Mo4—O2	2.25(2)						

Symmetry codes: ^{i} $-x+2, -y+2, -z+1$; ^{ii} $-x+2, y+1/2, -z+1$; ^{iii} $x, -y+3/2, z$; ^{iv} $x, y, -z+1/2$; ^{v} $-x+3, -y+2, -z+1$; ^{vi} $x, -y+5/2, z$; ^{vii} $x, y, -z+3/2$; ^{viii} $-x+2, y-1/2, -z+1$; ^{ix} $-x+3, y-1/2, -z+1$; ^{x} $x, -y+3/2, -z+3/2$; ^{xi} $x, -y+5/2, -z+1/2$.

The Sr(3) and Sr(4) cations act as linkers between two cage-shaped polymolybdophosphate clusters, Firstly, the Sr(3) atom shares two terminal O(18) and O(9) oxygen atoms from the same cluster and share one terminal O(19) oxygen atom from MoO_6 octahedra and the O(11) oxygen atom from PO_4 tetrahedra deriving from the second cluster. A terminal Ow(2) water molecule completes the coordination sphere of Sr(3), The Sr(3)—O bond distances are in the range of 2.54(3)—2.94(3) Å. Secondly, the Sr(4) ions share four oxygen atoms with the first cluster, two terminal O(9) and O(19) oxygen atoms, one double bridged O(4) oxygen atom, and O(11)^{v} from the PO_4 tetrahedron. With the second cluster, Sr(4) ions are linked to two terminal O(18) oxygen atoms from MoO_6 octahedra and O(11) from the PO_4 tetrahedron. The Sr(4) cation has the eight-coordinated environment achieved by two coordinated Ow(3) and Ow(4) water molecules. The Sr(4)—O bond lengths are in the range of 2.71(4)—3.13(4) Å. The interlinked mode of the cage-shaped cluster *via* Sr(3) and Sr(4) ions, generating a two dimensional supramolecular layer, as shown in Fig. 2.

In the packing arrangement, the adjacent layers are linked together *via* Sr(2) strontium cations leading to the formation of a three-dimensional supramolecular network (Fig. 3). The Sr(2) center exhibits the eight-coordination geometry formed by four oxygen atoms (O(23), O(23)^{viii}, O(13)^{v}, O(13)^{iv}) and four coordinated water molecules (Ow(1), Ow(3), Ow(3)^{viii}, and Ow(4)). The Sr(2)—O bond

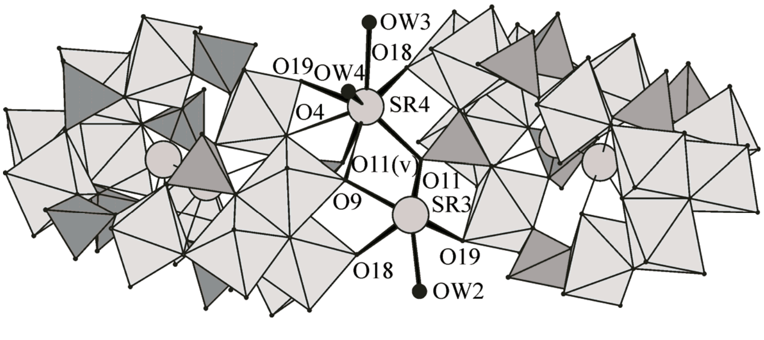

Fig. 2. Association mode between clusters *via* Sr(3) and Sr(4) in the 2D network

lengths are in the range of 2.45(4)—2.66(2) Å. In the three-dimensional network of the title compound there are four crystallographically independent strontium atoms (Sr(1), Sr(2), Sr(3), and Sr(4)) which exhibit various sorts of coordination geometries. Sr(1) ions are fully encapsulated in the central cavity of the cage-shaped clusters and serve to stabilize the whole polymolybdophosphate clusters, exhibiting a seven-coordinated mode. The Sr(3) and Sr(4) cations acting as linkers between the clusters yielding two-dimensional layers, where Sr(3) is five coordinated and four connected whereas Sr(4) is eight coordinated and six connected. The Sr(2) ions associate together two dimensional layers yielding a three dimensional building block. Sr(2) ions are eight coordinated and four connected.

IR and thermal analyses. IR spectra of the title compound were recorded in KBr pellets in the range 4000—400 cm^{-1} at room temperature. The peaks at 1076—1145 cm^{-1} are associated with ν(P—O) vibrations. The strong bonds at 878—950 cm^{-1} in the IR spectrum were assigned to the M—O terminal stretching vibrations; peaks at 739—844 cm^{-1} were assigned to ν(Mo—O—Mo) vibrations. The broad bands around 3215 cm^{-1} were ascribed to ν(O—H) of the water molecules.

To investigate the thermal stabilities of the title compound, the TG analyses were performed under the flowing dry N_2 atmosphere in the range 25—800 °C. The TG curve exhibits a two-step weight-loss process between 25 and 800 °C. The first weight loss of 5.7 % in the temperature range 260—345 °C is attributable to the removal of water molecules (calculated value 5.6 % for $10H_2O$). The second step of approximately 3.8 % occurs between 640 °C and 700 °C and is probably due to the evaporation of P_2O_5 (calculated value 3.7 %). All the observed weight losses from the TG curves are in accordance with the molecular formula of the title compound.

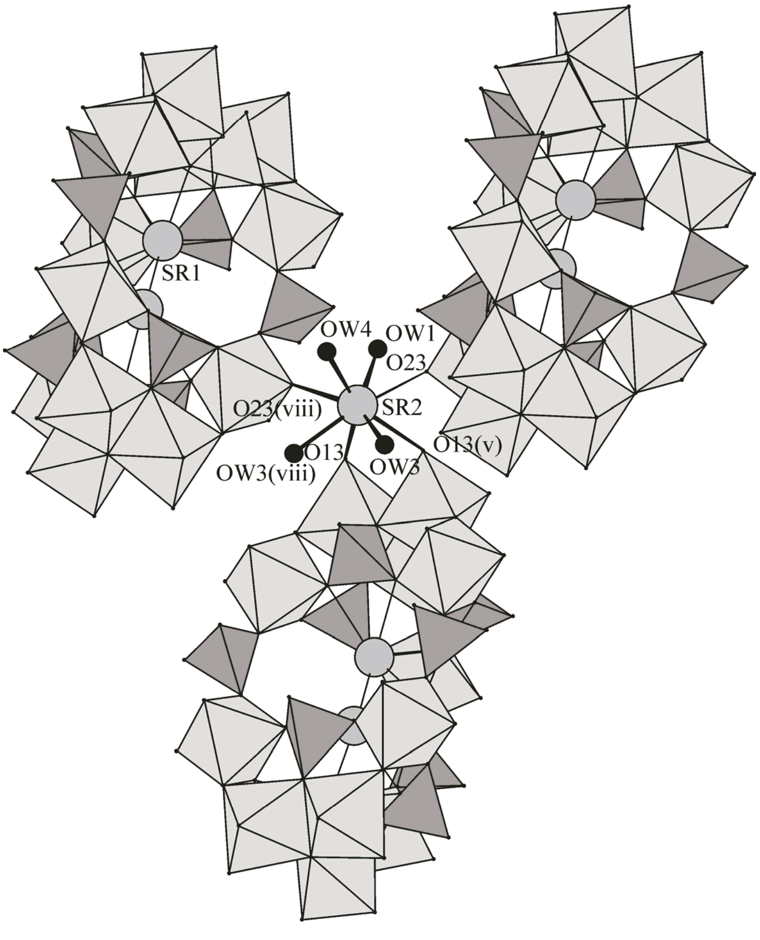

Fig. 3. Connection mode between 2D layers *via* Sr(2) ions in the 3D structure of the title compound

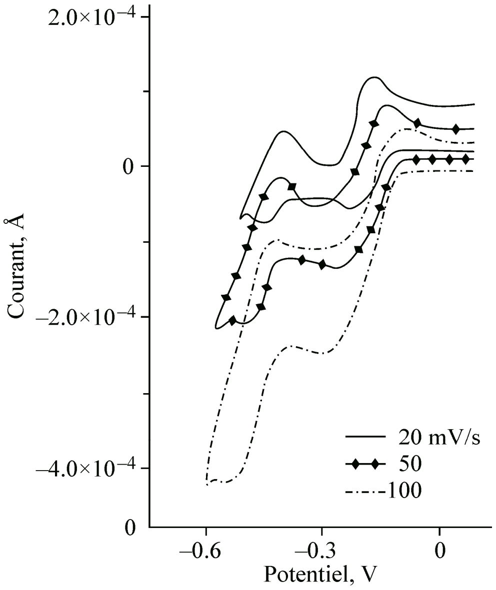

Fig. 4. Cyclic voltammograms of $Sr_{10}(H_2O)_{12}[Sr_2P_9HMo_{12}O_{71}]$ in H_2SO_4 at the Pt electrode at different scan rates: 20, 50, and 100 mV/s

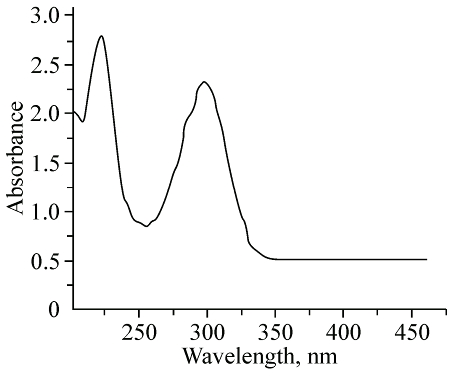

Fig. 5. UV-visible absorption spectrum of the $Sr_{10}(H_2O)_{12}[Sr_2P_9HMo_{12}O_{71}]$ compound

Electrochemical behavior. The electrochemical behavior of the title compound was studied by cyclic voltammetry in 1 M H_2SO_4 aqueous solutions at different scan rates. Platinum electrodes were used as the working electrode and the counter electrode, the reference electrode was an Ag/AgCl electrode. The cyclic voltammetric behaviors at different scan rates were recorded in a potential range from +100 to –600 mV (Fig. 4). Two reversible redox peaks with the half-wave potentials were estimated and reported as the average values of the anodic (E_{pa}) and cathodic (E_{pc}) peak potential $E_{1/2} = (E_{pa} + E_{pc})/2$ at –0.480 and –0.228 V, corresponding to two consecutive two-electron processes of $Mo^{VI/V}$ in the polymolybdophosphate framework. When the scan rates varied from 20 to 100 mV/s, the peak potentials changed gradually. The cathodic peak potentials shifted to the negative direction and the corresponding anodic peak potentials shifted to the positive direction. In addition, the peak-to-peak separation between the corresponding anodic and cathodic peaks increased, but the average peak potentials did not change on the whole. The peak currents were proportional to the scan rate, which indicates that the redox process is surface controlled.

UV-visible absorption spectrum. In order to study the solution optical property, the title compound was slightly dissolved in water. The UV-visible absorption behavior was analyzed in the range 200—500 nm. The obtained spectrum (Fig. 5) exhibits two strong absorptions bands centered at 225 and 300 nm. The strong higher energy band can be ascribed to the charge transfer transition from the terminal oxygen atoms to the molybdenum center ($O_t \rightarrow Mo$) in the Mo=O bonds, whereas the second lower energy band was attributed to the electronic transition between the bridged oxygen atoms and molybdenum atoms ($O_b \rightarrow Mo$) of the Mo—O—Mo bonds [40—42].

CONCLUSIONS

In this paper, we report the hydrothermal synthesis and crystal structure of a novel three-dimensional supramolecular material based on the cage-shaped polymolybdophosphate cluster and Sr^{2+} cations as linking elements. The electrochemical behavior has revealed that strontium molybdophosphate exhibits two successive reversible reductions in the negative potential range. The UV spectra of the title compound in the aqueous solution display two absorption peaks, appearing at 235 and 300 nm respectively. The higher spectral band can be attributed to the charge transfer $p\pi(O_t) \rightarrow d\pi^*(Mo)$, and the lower one was assigned to the $d\pi$—$p\pi$—$d\pi$ charge transfer of ($O_b \rightarrow Mo$) bonds. In the TG analysis the whole weight loss (9.5 %) is consistent with the calculated value (9.3 %). The ongoing other efforts were concentrated on the introduction of other alkali-earth metal ions into the molybdenum phosphate reactions to get new cage-shaped clusters as building blocks.

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