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A novel nanomolecular organic–inorganic hybrid compound: $Na_2[NH(CH_2CH_2OH)_3]_4\{Mo_{36}O_{112}(OH_2)_{14}[OHCH_2CH_2NH(CH_2CH_2OH)_2]_2\} \cdot nH_2O$ ($n \approx 72$) exhibiting a supramolecular one-dimensional chainlike structure

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Abstract

A novel nanomolecular organic–inorganic hybrid compound, $Na_2[NH(CH_2CH_2OH)_3]_4\{Mo_{36}O_{112}(OH_2)_{14}$ $[OHCH_2CH_2NH(CH_2CH_2OH)_2]_2\} \cdot nH_2O$ ($n \approx 72$) (**1**), was synthesized in aqueous acidic medium with a high yield (85%) and characterized by single crystal X-ray crystallography, IR spectroscopy, ^1H NMR, XRD and TG analysis. Compound **1** exhibits a supramolecular one-dimensional chainlike structure which consists of nanosized $\{[Mo_{36}O_{112}(H_2O)_{14}(HOC_2H_4)_2NHC_2H_4OH]_2\}^{6-}$ anions ($\{Mo_{36}(TEAH^+)_2\}$ for short) and cage-like dimers of $TEAH^+$ cations ($TEAH^+$ = protonated triethanolamine). In the $\{Mo_{36}(TEAH^+)_2\}$ anion, two $TEAH^+$ cations connect to one ring-like $\{[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$ ($\{Mo_{36}\}$ for short) anion by covalent bonds via replacing two water ligands by the alkoxy ligands. The $\{Mo_{36}(TEAH^+)_2\}$ unit could be considered as nanosized chelating ligand with [2N, 4O] donor sets. Crystal Data: triclinic, P-1, $a = 16.019(9)$ Å, $b = 17.372(4)$ Å, $c = 18.287(2)$ Å, $\alpha = 101.410(0)^\circ$, $\beta = 95.904(0)^\circ$, $\gamma = 116.332(0)^\circ$, $Z = 1$.

Keywords: Polyoxometalates; Organic–inorganic hybrid; $\{Mo_{36}\}$ cluster; Nanomolecular

1. Introduction

Polyoxoalkoxometalates, since the pioneering work in the early 1980s [1,2], have attracted continuous attention and now form the largest subclass of polyoxometalate derivatives [3–5]. A number of strategies have been developed to address the manipulation of the designs of novel compositions and architectures. Early work has been thoroughly reviewed by Pope [6,7], Zubieta [3,4,8], Gouzerh [5] and their co-workers. Though a lot of organic components have been employed to construct organic–inorganic hybrid polyoxometalates, the polyoxoalkoxometalates based on isopolymolybdates and branched ligands with [N, 3O] donor sets, which are of interest in this paper, are largely unexplored in a way.

As one of the macroisopolyanions, the ring-like centrosymmetric $[Mo_{36}O_{112}(OH_2)_{16}]^{8-}$ has been synthesized for a long time [9,10], and recently used as building block, with several structurally characterized examples now known, in the nanomolecular polymers of $\{(H_2O)MoO_{2.5}[Mo_{36}O_{108}(NO)_4(H_2O)_{16}]O_{2.5}Mo(H_2O)\}^{12-}\}_n$, in the mesoporous hydrogen-bonded organic–inorganic framework of $\{[Mo_{36}O_{112}(OH_2)_{16}](H_2bipy)_4\}28H_2O$, and in the one-, two-, and three-dimensional extended structures in which $\{Mo_{36}\}$ anionic units are linked by lanthanide cations [11–13].

Our attempt to link $\{Mo_{36}\}$ anionic units by comparatively less oxophilic transitional metals was inspired from the work of N.V. Izarova et al. which illustrated the synthesis of compounds containing $\{Mo_{36}\}$ building blocks linked by highly oxophilic lanthanide cations. However, the attempt failed, but the result enlightened us on paying our attention to the functionalization of $\{Mo_{36}\}$ anion through the replacement of oxo ligands by functional groups such as TEA.

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So far, to our knowledge, only a few examples based on isopolymolybdates and branched ligands with [N, 3O] donor sets have been reported. The $[Mo_2O_5(NTA)_2]^{2-}$ (NTA = nitrilotriacetate) anion contains an $O_2MoOMoO_2$ core with the core-bridging O atom lying on a crystallographic centre of symmetry, and the ligand is tridentate with coordination through one N atom and two carboxylate groups [14]. The Mo_2L_2 (L = (S,S,S)-triisopropanolaminate) shows a central Mo = Mo unit of distance 2.15(3) Å coordinated to two triolate ligands which each has two chelating arms and one that spans the Mo = Mo band [15].

In addition to dimolybdenum isopolyoxometalates, there are several simple molybdenum examples, such as $[MoO_2(TEA)]$, $\{MoO_3[OOCCH_2]_2N[CH_2COO]\}^{3-}$, $[MoO(O\text{-}O)(NTA)]^-$, $[Mo(V)(hidpa)_2]^-$ (hidpa = oxyimino dipropionate), $[MoO_2(HL)(MeOH)]$ (L = dianionic Schiff base), $[MoO_2L]$ (L = alkoxo-rich Schiff-bases) [16–21].

Herein, we report a novel organic-inorganic hybrid compound, $Na_2[NH(CH_2CH_2OH)_3]_4\{Mo_{36}O_{112}(OH_2)_{14}[OHCH_2CH_2NH(CH_2CH_2OH)_2]_2\}\cdot nH_2O$ ($n \approx 72$) (**1**), in which two $TEAH^+$ cations connect to one ring-like $\{[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$ ($\{Mo_{36}\}$ for short) anion cluster by covalent bonds via replacing two water ligands by the alkoxy ligands. Compound **1** is the second organic–inorganic hybird compound based on $\{Mo_{36}\}$ unit, however, it is the first time that organic component connect to $\{Mo_{36}\}$ unit via covalent band. In contrast with the compounds mentioned above, $\{Mo_{36}(TEAH^+)_2\}$ is active towards coordination, and could be considered as nanosized chelating ligand with [2N, 4O] donor sets. Thus, $\{Mo_{36}(TEAH^+)_2\}$ could be potentially used as building block to construct novel coordinated polymers including organometallic components.

2. Experimental details

2.1. General procedures

All chemicals were analytical reagents, commercially purchased, and used without further purification. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. Mo was determined by a PLASMA-SPEC(I) ICP atomic emission spectrometer. IR spectrum was recorded in the range 400–4000 cm^{-1} on an Alpha Centaurt FT/IR spectrophotometer using KBr pellets. TG analysis was performed on a Perkin-Elmer TGA7 instrument in N_2 atmosphere with a heating rate of 10 °C min^{-1} between 40 and 800 °C. ^1H NMR spectrum in D_2O solution was recorded on an INOVA 500NMR spectrometer, and XRD was recorded on a D/max IIIc diffractometer.

2.2. Synthesis of compound

Triethanolamine (1.5 g, 10.1 mmol) was dissolved in distilled water (50 mL), followed by the addition of $Na_2MoO_4\cdot 2H_2O$ (1.5 g, 6.2 mmol). Hydrochloric acid (37%) was added to adjust the pH value of the solution to about 2, and then L-ascorbic acid aqueous solution (0.6 mL, 0.5 mol/L) was added with vigorous stirring for about 1 h. Blue rhombic crystals with a yield of 87% (based upon Mo) were obtained after about 5 days. Anal. calcd. (%) for $H_{268}C_{36}N_6O_{216}Na_2Mo_{36}$: H, 3.48; C, 5.58; N, 1.08; Mo, 44.61. Found (%): H, 3.6; C, 5.5; N, 1.2; Mo, 43.5. IR (KBr, cm^{-1}) for 1: $\tilde{\nu} = 3600\text{–}3200$ ($N^+\text{–}H$), 1450–1400 ($R\text{–}CH_2\text{–}R$), 1092–1060 ($CH_2\text{–}OH$) and 959–876, 850 (Mo = O, Mo–O–Mo) (see Fig. 3).

2.3. X-ray crystallography

The X-ray powder diffraction revealed that product **1** was a pure-phase material. The pattern of the powder sample was consistent with simulated single-crystal pattern, which had relative higher intensity (Fig. S1).

Crystal suitable for single-crystal X-ray diffraction was glued to a thin glass fiber with epoxy resin and mounted to a Bruker Smart APEX II CCD diffractometer with graphite-monochromated Mo $K\alpha$ (0.71073 Å) radiation in the ψ-scanning mode at 293 K. The structure was solved by the direct method and refined by full-matrix least squares on F^2 using the SHELXTL-97 software [22]. All of the non-hydrogen atoms were refined anisotropically except some disordered $TEAH^+$ and solvent water moleculars. Restraint structural refinements were applied to the bond lengths of N–C, C–C and C–O. Partial hydrogen atoms on $TEAH^+$ were located from the Fourier difference map. Crystal parameters and details of the data collection and structure refinements were listed in Table 1. CCDC reference no. for **1**: 612348.

3. Results and discussion

While preparing compound **1**, the addition of L-ascorbic acid seems to be necessary. In the absence of L-ascorbic acid or decreasing the amount of it, crystals comprising $\{Mo_{36}\}$ and $TEAH^+$ were obtained, but in which $TEAH^+$ only played the role of counterions [23].

Compound **1** crystallizes as a triclinic system with half of the $\{Mo_{36}(TEAH^+)_2\}$ (i.e., $\{Mo_{18}TEAH^+\}$) anion cluster, one Na cation, and two partial disordered protonated TEA cations ($TEAH^+$) found in the asymmetric unit, plus some positions that are indentified as solvent water molecules. The other half of the $\{Mo_{36}(TEAH^+)_2\}$ is related by a center of symmetry. Each $\{Mo_{18}\}$ moiety of the $\{Mo_{36}\}$ cluster shares a protonated terminal O atom (see O8H) with one $TEAH^+$, and the position of the terminal O atom is occupied by a coordinated water molecule in the structure of previously reported $[Mo_{36}O_{112}(OH_2)_{16}]^{8-}$ anion cluster. Two centrosymmetric $\{Mo_{18}TEAH^+\}$ moieties are connected via sharing the edges (O35-O42 and $O35^i$-$O42^i$) of two MoO_6 octahedra (see Mo12 and $Mo12^i$) ($i = -x+1, -y+1, -z+2$).

Table 1
Crystal data and structure refinement for 1

Empirical formula	C36 H26 Mo36 N6 Na2 O163
$Fw(\mathrm{g\,mol^{-1}})$	6650.45
Temp (K)	293(2)
λ(Å)	0.71073
Crystal system	Triclinic
Space group	P-1
a (Å)	16.019(9)
b (Å)	17.372(4)
c (Å)	18.287(2)
α (deg)	101.410(0)
β (deg)	95.904(0)
γ (deg)	116.332(0)
V (Å^3)	4364.6(7)
Z	1
Dc (mg m^{-3})	2.536
Abs coeff. (mm^{-1})	2.618
$R_1[I>2\sigma(I)]^a$	0.0388
$wR_2[I>2\sigma(I)]^b$	0.1162
R_1(all data)^a	0.0437
R_{w2}(all data)^b	0.1191
Goofness-of-fit on F^2	1.067

[a] $R_1 = \Sigma\,||F_o| - |F_c||/\Sigma|F_o|$,
[b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table 2
BVS of Mo atoms in $\{Mo_{18}TEAH^+\}$ asymmetric unit

Atom no	Bond valence sum	% Deviation from assumed oxide state
Mo1	6.022	0
Mo2	6.043	1
Mo3	6.059	1
Mo4	6.074	1
Mo5	6.029	0
Mo6	6.180	3
Mo7	6.201	3
Mo8	5.929	1
Mo9	5.912	1
Mo10	5.982	0
Mo11	6.049	1
Mo12	6.046	1
Mo13	6.107	2
Mo14	6.054	1
Mo15	6.056	1
Mo16	6.121	2
Mo17	6.056	1
Mo18	6.010	0

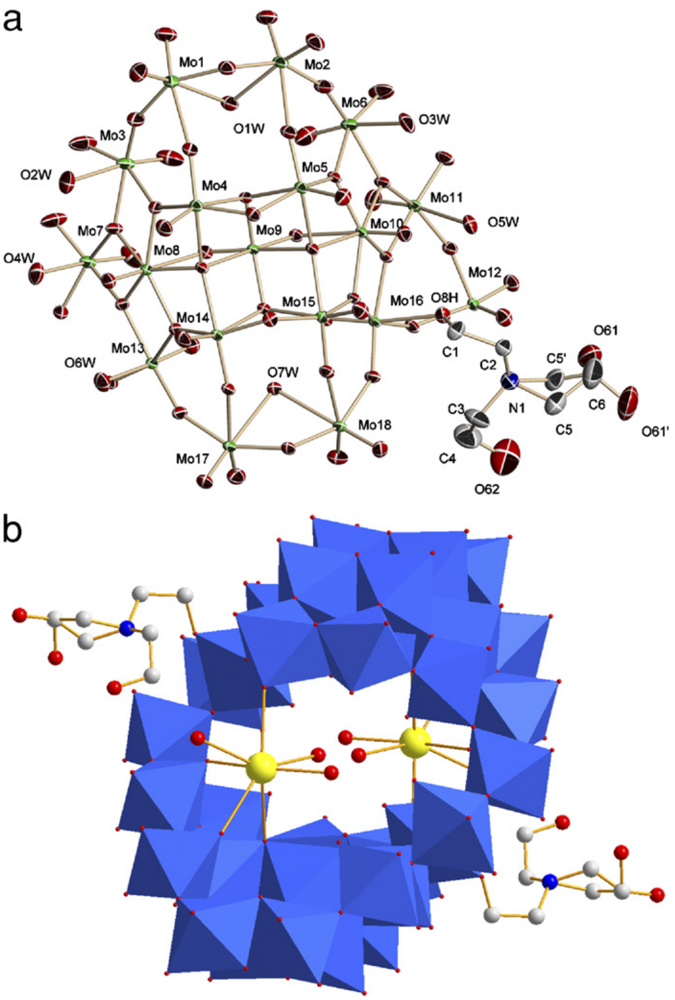

Fig. 1. Ellipsoid and polyhedral representations. (a) $\{Mo_{18}(TEAH^+)\}$ in the asymmetric unit consists of $\{Mo_{18}\}$ and $TEAH^+$ connected by sharing one O atom (O8H) which coordinates to Mo16. (b) $\{Mo_{36}(TEAH^+)_2\}$ unit with two seven-coordianted Na cations at the opening of the ringlike architecture. In (a) and (b), Mo—green; O—red; C—gray; N—blue; Na—yellow.

In order to identify the valences of Mo atoms in $\{Mo_{36}(TEAH^+)_2\}$, both theory calculations and experiments have been carried out. The bond valence sum (BVS) [24] values are in the range of 5.912–6.201 (see Table 2). There is no response in EPR spectrum and no characteristic absorption in electronic spectrum. In the ^{1}H NMR spectrum of **1** (see Fig. S2), only aliphatic protons ($-CH_2-$ in $TEAH^+$, $\delta = 3.896$ and 3.435 ppm) are resolved as the protons present in the clusters are not observed owing to rapid exchange with solvent. The well-defined resonance signals suggest that the ^{1}H NMR spectrum is not influenced by other paramagnetic material. All experimental results and theory calculations are in agreement with the absence of reduced Mo(V) atoms. The blue color of the crystals might be attributed to the partial charge transfer from $TEAH^+$ to $\{Mo_{36}\}$ inorganic fragment.

As shown in Fig. 1(a), the inorganic fragment of $\{Mo_{18}TEAH^+\}$ moiety is constructed from 16 $\{MoO_6\}$ pseudo-octahedra and two $\{MoO_7\}$ distorted pentagonal bipyramids. The coordination number of Mo(VI) is six or seven. Based on the coordinated oxygen atoms, the coordination environments around the Mo atoms can be classified into seven types of polyhedra: one $\{Mo(\mu\text{-}O_6)\}$ (see Mo9), one $\{(O=)Mo(\mu\text{-}O_4)(OH_2)\}$ (see Mo13), one $\{(O=)Mo(\mu\text{-}O_4)[OHCH_2CH_2N(CH_2CH_2OH)_2]\}$ (see Mo16), four $\{(O=)Mo(\mu\text{-}O_5)\}$ (see Mo4, Mo5, Mo14, and Mo15), eight $\{(O=)_2Mo(\mu\text{-}O_3)(OH_2)\}$ (see Mo1, Mo2, Mo3, Mo6, Mo7, Mo11, Mo17, and Mo18), one $\{(O=)_2Mo(\mu\text{-}O_4)\}$

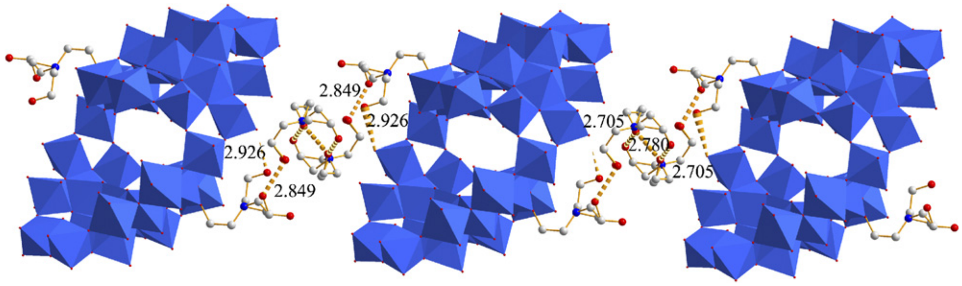

Fig. 2. Compound **1** exhibits a supramolecular one-dimensional chainlike structure consisting of {$Mo_{18}(TEAH^+)$} and dimers of $TEAH^+$. The lengths of hydrogen bonds between the {$Mo_{18}(TEAH^+)$} and dimers of $TEAH^+$ is 2.849 Å, and in the dimers are 2.705 and 2.780 Å.

(see Mo12) pseudo-octahedra and two {(O =)Mo(μ-O_6)} (see Mo8 and Mo10) distorted pentagonal bipyramids, which are connected by edge share and corner share.

In the structure of {$Mo_{36}O_{112}(H_2O)_{14}[(HOC_2H_4)_2NHC_2H_4OH]_2$}$^{6-}$, the 14 coordinated water molecules are well defined, and all the positional and thermal parameters of them are obtained with considerable precision. It is interesting to notice that the coordinated water molecules not only come from the terminal oxygen, but also come from the bridging oxygen of the anion cluster, and the absence of them would result in the partial collapse of the {$Mo_{36}(TEAH^+)_2$} skeleton.

Each Na cation is surrounded by seven O atoms including three terminal and one bridging oxygen atoms coming from {$Mo_{36}(TEAH^+)_2$} and three solvent water molecules, and the lengths of Na–O bonds are in the range of 2.465–3.013 Å. Considering the inorganic isopolyoxometlate segment of {$Mo_{36}(TEAH^+)_2$} has no difference with previously reported {$[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$ cluster in essence, the role of Na cations is only to compensate the negative charges of the cluster anion.

As shown in Fig. 1(b), the structure of {$Mo_{36}(TEAH^+)_2$} anion cluster looks like a ringlike architecture which shows a large internal cavity of approximately 0.7 × 0.5 nm, two seven-coordinated Na cations occupy the opening of the ring, and one alkoxy branch of $TEAH^+$ connect to inorganic {Mo_{36}} fragment and the other two alkoxy branches stretch outside.

Compound **1** shows a supramolecular one-dimension chainlike structure which is built by connecting {$Mo_{36}(TEAH^+)_2$} and the dimers of $TEAH^+$ with intermolecular hydrogen bonds (Fig. 2). The bonds connecting the synthons are a series of H-bonds, exhibiting a zigzag type line (range O···O = 2.7–2.9 Å). In {$Mo_{36}(TEAH^+)_2$}, the four alkoxies which are free of coordination play different roles in the packing of the synthons. Two hyoxyl oxygen atoms of $TEAH^+$ (see O62 and O62^i) interact with the terminal O atoms of {Mo_{36}} fragment (see O26 and O26^i) via intramolecular hydrogen bonds (O···O = 2.926 Å), in contrast, the other hyoxyl oxygen atoms (see O61 and O61^i) interact with the dimers of $TEAH^+$ via intermolecular hydrogen bonds (O···O = 2.849 Å). In addition, three relatively stronger hydrogen bonds are identified in the dimer of $TEAH^+$ (O···O = 2.705 and 2.078 Å). The supramolecular chainlike structure looks like a beautiful string of "pearls" in which the "pearls" are exactly the 36-molybdate clusters and the thread is the list of invisible H-bonds decorated by the dimers of $TEAH^+$.

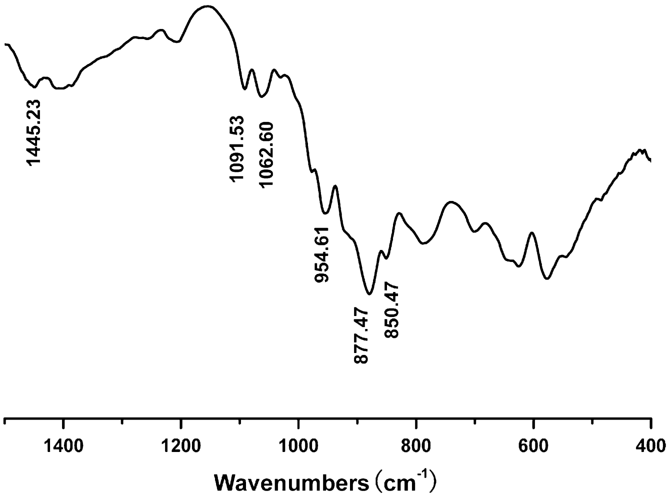

Fig. 3. Infrared spectrum of **1**.

The remarkable branched ligand with [N, 3O] doner sets, TEA, seized our attention because not only its excellent dissolubility but also its coordinate ability to various metals. TEA is an amino alcohol used in a large number of commercial applications, such as herbicides, surface-active agents, corrosion inhibitors and cement additives [25]. Because of its double actions as both a tertiary amine and a primary alcohol, TEA readily coordinates to metal ions to form complexes and also stabilizes the anions by hydrogen bonding. TEA widely coordinate with various metals from alkali metals to alkaline earth metals, transition metals, as well as rare earth metals, such as K, Ca, Ba, Y, Ti, V, Mo, Mn, Co, Ni, Cu, Zn, Al, Ge, Ln [14d,15].

The characteristic of compound **1** is the unique behavior of the connection of $TEAH^+$ and {Mo_{36}}. For each half of the {$Mo_{36}(TEAH^+)_2$}, i.e., {$Mo_{18}TEAH^+$}, perhaps by reason of steric hindrance, only one of the three hydroxyl O donors of one $TEAH^+$ coordinates with Mo (see O8H), and the residual two hydroxyl O atoms, could be considered as participants in hydrogen bonding interactions. Thus, the $\{Mo_{36}(TEAH^+)_2\}$ is active towards coordination because it could be considered as nanosized chelating ligand with [2N, 4O] donor sets. That is to say, $\{Mo_{36}(TEAH^+)_2\}$ could potentially coordinate with two metal atoms (range from alkali metals, alkaline earth metals, transition metals, to rare earth metals, or combination of them) via chelating effect in the opposite directions, which affords the chance of not only confirming discrete compounds but also constructing coordination polymers including organometallic components.

Reminiscent of R.W. Saalfrank's metal-centered, six-membered, metallic Wheels of $[M_6Cl_6(L)_6]$ ($M =$ Fe, In, Mn, Cu; $L = RN(C_2H_4O)_2$; $R =$ Me, benzyl, and even huger organic components) exploiting the behavior of coordination of $RN(C_2H_4O)_2$ ligands, $\{Mo_{36}(TEAH^+)_2\}$ maybe play the role of organic–inorganic hybrid analog taking the place of the organic component in such system [26].

It seems impossible to determine the precise water content of **1** only depending on single crystal X-ray crystallography, because not only most of the crystallization water molecules are badly disordered, but also they rapidly lose part of the hydrate water when the crystals are isolated from the solution [9]. There are some relatively big isolated residual peaks in the Fourier difference map of compound **1** which could not be identified for keeping the stability of structure refinements, which might result from the badly disorders of water molecules at several sets of positions.

The TGA study was carried out from 40 to 800 °C. The thermal behavior of compound **1** was similar to that of $\{[Mo_{36}O_{112}(OH_2)_{16}](H_2bipy)_4\}28H_2O$ [13] which was reported as the first organic–inorganic example based on $\{Mo_{36}\}$. As shown in Fig. S3, the curve shows a first step of weight loss (40–360 °C) which is attributed to the dehydration of the compound (crystallization and coordination water molecules) (found: 20.01%; calc.: 20.00%). A second weight loss (360–518 °C) is assigned to the decomposition of the organic components. Notice that one very complex process is observed, from 520 to 680 °C for compound **1**, which includes the weight loss and weight increase that might be due to the coagulation of MoO_3. With the temperature increasing, MoO_3 could be obtained in the course of the sequent loss of the coordination water and the organic components and then sublimate because of the exothermic reaction during the decomposition of the organic components. Accompanied with the gradual cease of the exothermic course, the coagulation of MoO_3 predominates and the slow weight increase appears. For temperature over 680 °C, the TG curve shows a sharp weight loss indicating the rapid sublimation of MoO_3.

4. Conclusion

In summary, we have synthesized a novel organic–inorganic hybrid compound **1**, which is the first compound comprising $\{Mo_{36}\}$ and $TEAH^+$ connected by covalent bonds. Compound **1** shows a supramolecular one-dimension chainlike structure. The $\{Mo_{36}(TEAH^+)_2\}$ is active towards coordination because it could be considered as nanosized chelating ligand with [2N, 4O] donor sets. Future work will aim to introduce various properties, for example magnetic property, into the $\{Mo_{36}\}$ system via connecting functionalized $\{Mo_{36}(TEAH^+)_2\}$ building blocks with various metals. The functionalizations of other polyoxometalates are also of interest for us.

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Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2006.10.041.

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