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# Syntheses, structures and characterizations of two organoimido derivatives of POMs containing sulfide groups



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# ABSTRACT

Two remote methylthio group functionalized organoimido derivatives of hexamolybdate,  $(Bu_4N)_2[Mo_6O_{18}(NC_6H_4-SCH_3-p)](1)$  and  $(Bu_4N)_2[Mo_6O_{18}(NC_6H_4-SCH_3-m)](2)$ , were synthesized through the refluxing reaction of octamolybdates, the hydrochloride salts of corresponding organic amines in anhydrous acetonitrile with dicyclohexylcarbodiimide (DCC) as dehydration agent. They are characterized by single crystal X-ray diffraction, FT-IR spectra, UV–Vis spectra, elemental analysis, <sup>1</sup>H NMR and cyclic voltammetry. X-ray structural study reveals that anion clusters of both compounds possess some typical structural features of mono-substituted hexamolybdate, and their anion clusters are connected into two dimensional network *via* intermolecular multiple C–H···O hydrogen bonds.

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# 1. Introduction

Polyoxometalates (POMs) are a class of discrete anion clusters which are made up of early transition metal ions (i.e. Mo, W, V, Nb and Ta) and oxo ligands [1,2]. They have drawn increasing attention on account of their diverse structures and potential applications in diverse fields including electrochemistry, catalysis, magnetism, medicine, photochemistry and semiconductor materials [3-5]. One notable virtue of POMs is that the structures and properties of POMs can be tuned via the surface modification of POMs, for example, terminal oxo atoms or bridged oxo atoms of POMs can be replaced by organic ligands [6,7]. Typical example of the hybrid compounds, the arylimido derivatives of POMs containing Mo-N multiple bond have drawn particular research interests owing to the so-called "synergistic interaction", which is resulted from the  $d-\pi$  conjugated interaction between the inorganic POM cluster and organic ligand [8,9]. Additionally, the attachment of organoimido ligands on POMs allows the introduction of different functional groups into POMs.

Up to now, many functional groups, e.g. hydroxyl [10], amido [11], halogen atom [12,13], alkyl [14], vinyl [15], acetenyl [12], ferrocene [16], carboxyl [17] and terpyridyl [18], have been introduced into the arylimido derivatives of hexamolybdates, which afford them the ability for further coordination or post-modification. However, the organoimido derivatives of hexamolyb-dates containing soft base (i.e. S or P) are still not reported.

Organosulfur compounds are widely distributed within the natural world and play an important role in the life process. They have important potentials and applications in the fields of materials, medicine, catalysts and organic transformations [19]. For example, *m*-methylthiobenzylamine is one kind of important intermediates to prepare thioridazine and mesoridazine, it can be used in the synthesis of organic compounds with antivirus activity [20], antitumoral activity [21], and anti-inflammatory activity [22]. Additionally, sulfur atom in thioether is a typical soft base with the affinity to soft acid (such as Ag(I), Cu(I)), therefore, thioether can be used to construct coordination compounds or polymers [23].

To explore the organoimido derivatives of POMs containing sulfide groups, 4-(methylthio)aniline and 3-(methylthio)aniline are chosen as sulfide ligands and successfully attached to hexamolybdates *via* Mo–N triple bond. We herein report the syntheses, characterizations, structures and electrochemical studies of  $(Bu_4N)_2[Mo_6O_{18}(NC_6H_4SCH_3-p)]$  (**1**) and  $(Bu_4N)_2[Mo_6O_{18}(NC_6H_4SCH_3-p)]$  (**1**)



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#### 2. Experimental details

#### 2.1. Materials and physical measurements

 $[Bu_4N]_4[\alpha-Mo_8O_{26}]$  was synthesized according to literature procedure [24] and confirmed by IR. The hydrochloride salts of corresponding amines were prepared by adding concentrated HCl into an ethanol solution of corresponding amines. Lots of colorless crystals were obtained after evaporation of solvent under vacuum pressure. Anhydrous acetonitrile was refluxed in the presence of CaH<sub>2</sub> and distilled prior to use. All other chemical reagents were of analytical grade and used as received without further purification. Elemental analyses were performed on Vario EL (Elementar An alysensysteme GmbH). FT-IR spectra were measured using KBr pellets and recorded on FT-IR spectrometer (PERKINELMER) spectrophotometer. UV-Vis spectra were measured in acetonitrile solution with UV-2700 spectrophotometer (Shimadzu). <sup>1</sup>H NMR spectra for both compounds were taken on a JEOL JNM-ECA300 NMR spectrometer at 300 K using DMSO-d<sub>6</sub> as solvent. Cyclic voltammetry were performed in DMF solutions at 25 °C in a high pure N<sub>2</sub> filled electrolytic cell using CHI750 electrochemical workstation. A Pt electrode was employing as the working electrode, double salt bridged saturated calomel electrode (SCE) as the reference electrode, and a Pt platelet electrode as the counter electrode. [Bu<sub>4</sub>N]PF<sub>6</sub> was used as the supporting electrolyte with a scan rate of 50 mV s<sup>-1</sup>.  $E_{pa}$  values were measured versus SCE, and [Bu<sub>4</sub>N]<sub>2</sub>[Mo<sub>6</sub>O<sub>19</sub>] was employed as the internal standard

#### 2.2. Synthesis of $(Bu_4N)_2[Mo_6O_{18}(NC_6H_4SCH_3-p)]$ (1)

A mixture of 2.15 g  $(Bu_4N)_4[\alpha-Mo_8O_{26}]$ , 0.23 g hydrochloride salt of 4-(methylthio)aniline and 0.43 g N,N'-dicyclohexylcarbodiimide (DCC) were refluxed at 100–110 °C in 20 mL dry acetonitrile. After 12 h, the resulting black-red solution was cooled to room temperature, and filtrated to remove the resulting white precipitates. The brown-red filtrate was left to evaporate the solvent without disturbance. Crude products were obtained after the volatilization of solvent. Lots of red block crystals were obtained in a yield of 70-80% through twice recrystallization from the mixed solvent of acetone/ethanol (1:1). <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>): 7.29(d, J = 8.6 Hz, 2H, ArH), 7.15(d, J = 8.6 Hz, 2H, ArH), 3.17(t, J = 8.4 Hz 16H, NCH<sub>2</sub>-,  $[Bu_4N]^+$ ), 2.37(s, 3H, -SCH<sub>3</sub>), 1.57(m, J = 7.8 Hz, 16H,  $-CH_2-$ ), 1.32(m, J = 7.2 Hz, 16H,  $-CH_2-$ ), 0.94, (t,  $I = 7.3 \text{ Hz} 24\text{H}, \text{ CH}_{3-}, [Bu_4\text{N}]^+)$ . IR(KBr pellet, cm<sup>-1</sup>): 3146(broad, m), 2961(m), 2933(w), 2873(m), 1627(w), 1573(w), 1479(m), 1400(m), 1380(w), 1093(m), 975(m, shoulder), 955(vs), 793(vs), 592(m). UV–Vis (MeCN):  $\lambda_{max}$  = 377 nm. Elemental Anal. Calc. for C<sub>39</sub>H<sub>79</sub>Mo<sub>6</sub>N<sub>3</sub>O<sub>19</sub>: C, 31.87; N, 2.86; H, 5.42. Found: C, 31.91; N, 2.90; H, 5.38%. E<sub>1/2</sub> (DCE): -0.390 V.

#### 2.3. Synthesis of $(Bu_4N)_2[Mo_6O_{18}(NC_6H_4SCH_3-m)]$ (2)

A mixture of 2.15 g (Bu<sub>4</sub>N)<sub>4</sub>[ $\alpha$ -Mo<sub>8</sub>O<sub>26</sub>], 0.23 g hydrochloride salt of 3-(methylthio)aniline and 0.43 g N,N'-dicyclohexylcarbodiimide (DCC) was refluxed at 100–110 °C in 20 mL of anhydrous acetonitrile. After 12 h, the resulting red solution was cooled to room temperature and filtrated to remove resulting white precipitates. The red filtrate was left alone without disturbance. Lots of red block crystals were obtained in a yield of 50–60% through twice recrystallization from the mixed solvent of acetone/ EtOH(1:1). <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 7.37(d, *J* = 8.1 Hz, 1H, ArH), 7.09(d, *J* = 6.9 Hz, 1H, ArH), 6.98(d, *J* = 6.9 Hz, 2H, ArH), 3.17(t, *J* = 8.1 Hz, 16H, NCH<sub>2</sub>–, [Bu<sub>4</sub>N]<sup>+</sup>), 2.50(s, 3H, –SCH<sub>3</sub>), 1.55(m, *J* = 7.7 Hz, 16H, –CH<sub>2</sub>–), 1.32(m, *J* = 7.7 Hz, 16H, –CH<sub>2</sub>–), 0.94, (t, *J* = 7.2 Hz, 24H, CH<sub>3</sub>–, [Bu<sub>4</sub>N]<sup>+</sup>). IR (KBr pellet, cm<sup>-1</sup>): 3460(m, br), 2960(m), 2933(shoulder), 2873(m), 1564(s), 1479(s), 1379(m), 1325(m), 1151(w), 1098(w), 1025(w), 975(m, shoulder), 955(vs), 784(vs), 595(w). UV–Vis(MeCN):  $\lambda_{max} = 228.5$ , 256, 336.5 nm. Elemental *Anal.* Calc. for C<sub>46</sub>H<sub>88</sub>Mo<sub>6</sub>N<sub>4</sub>O<sub>20</sub>: C, 34.69; H, 5.57; N, 3.52. Found: C, 35.26; H, 5.80; N, 3.50%. *E*<sub>1/2</sub> (DCE): -0.386 V.

### 2.4. X-ray crystallography

Suitable crystals were mounted on glass fibers and rapidly transferred onto the diffractometer. X-ray diffraction data of compounds 1 and 2 were collected on a Rigaku RAXIS-SPIDER IP diffractometer using graphite-monochromatized Mo K $\alpha$  radiation  $(\lambda = 0.71073 \text{ Å})$  at room temperature (293 ± 2 K). Data collection, data reduction, cell refinement and experiential absorption correction for compounds 1 and 2 were performed with the software package of Rigaku RAPID AUTO (Rigaku, 1998, Ver2.30). Structures of all compounds were solved by direct methods and refined against  $F^2$  by full matrix least squares. All non-hydrogen atoms, except disordered atoms, were refined anisotropically. Hydrogen atoms of ligands were generated geometrically. All calculations were performed using the program package of SHELXS-97 and SHELXL-97 [25,26]. A summary of X-ray crystal data of compounds 1-2 is presented in Table 1. ORTEP diagrams of anionic clusters of both compounds are shown in Fig. 1. The selected bond lengths and angles are listed in Table 2, the hydrogen bond data of compounds 1-2 are summarized in Table 3.

#### 3. Results and discussion

#### 3.1. Synthesis

In the last three decades, phosphinimines, isocyanates, and aromatic amines had been used to make organoimido derivatives of POMs. Especially, DCC-assisted dehydration protocol developed by Peng and Wei is a facile and high-yield method to make monosubstituted and bifunctionalized organoimido derivatives of POMs [27]. 4-(Methylthio)aniline and 3-(methylthio)aniline are chosen as imido-releasing reagents because they are of easy access. Title compounds are prepared *via* a one-pot reaction of octamolybdate, hydrochloride salts of corresponding organic amines and DCC with molecular ratio of 3:4:6 in dry acetonitrile.

#### 3.2. Crystal structure

Single crystal X-ray diffraction structural research reveals that compound **1** crystallizes in monoclinic system, P2(1)/c space group, and there is one crystallographically independent anion of  $[Mo_6O_{18}(NC_6H_4SCH_3-p)]^{2-}$  and two cations of  $(Bu_4N)^+$  in the asymmetric unit. As shown in Fig. 1, the six molybdenum atoms in the anion cluster of  $[Mo_6O_{18}(NC_6H_4SCH_3-p)]^{2-}$  are connected to one central oxygen atom O(1) to form a distorted octahedron with the Mo...Mo separation ranging from 3.231(1) to 3.295(1) Å. Mo(1) is six-coordinated with one nitrogen atom (Nt) from 4methylthio-aniline, four bridged oxygen atoms (Ob) and one centered  $\mu_6$ -O(1) (O<sub>c</sub>) to form a distorted octahedron. The other molybdenum atoms are six-coordinated with one terminal oxygen atom  $(O_t)$ , four bridged oxygen atoms  $(O_b)$  and one centered  $\mu_6$ -O(1) (O<sub>c</sub>) to form a distorted octahedron. The Mo-N bond in compound 1 demonstrates substantial triple bond character considering the short bond length (1.726(3)Å) and nearly liner Mo-N-C angle (173.13°). Thus, an organic-inorganic hybrid conjugated system is constructed between 4-methylthio-aniline and the hexamolybdates cluster through the Mo=N triple bond. The bond length of Mo(1) $\equiv$ N(1) (1.723(5)Å) is longer than that of Mo $\equiv$ O<sub>t</sub>

Table 1Crystallographic data of compounds 1–2.

Compound	1	2
Formula Formula weight	C <sub>39</sub> H <sub>79</sub> Mo <sub>6</sub> N <sub>3</sub> O <sub>18</sub> S 1485.75	C <sub>39</sub> H <sub>79</sub> Mo <sub>6</sub> N <sub>3</sub> O <sub>18</sub> S 1485.75
Crystal system	monoclinic	monoclinic
Space group	P2(1)/n	P2(1)/n
a (Å)	17.571(4)	18.164(4)
b (Å)	15.785(3)	15.485(3)
<i>c</i> (Å)	21.031(4)	20.980(4)
β (°)	104.61(3)	105.97(3)
$V(Å^3)$	5644(2)	5673(2)
Ζ	4	4
$D_{\text{calc.}}(g/\text{cm}^3)$	1.748	1.739
$\mu \text{ (mm}^{-1}\text{)}$	1.394	1.387
F(000)	2984	2984
$\theta$ for data collection	3.00-26.00	3.08-26.00
Reflections collection	37108	46031
Reflections unique	10 145	10979
R <sub>int</sub>	0.0368	0.0389
Independent reflections	10145	10972
GOF on F <sup>2</sup>	1.079	1.058
Final R	0.0529	0.0367
Final Rw	0.1661	0.1044

 $\begin{aligned} R &= \Sigma ||F_o| - |F_c||/\Sigma |F_o| \text{ and } Rw = [\Sigma [w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2} \text{ with } w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP], \text{ where } P &= (F_o^2 + 2F_c^2)/3. \text{ 1: } a = 0.0841, b = 5.7830; \text{ 2: } a = 0.0477, b = 4.6789. \end{aligned}$ 



Fig. 1.  $_{\mbox{\scriptsize ORTEP}}$  drawing of anion cluster of compounds 1 and 2 with 40% probability thermal ellipsoids.

 Table 2
 Selected bond lengths and angles of compounds 1–2.

1	2
1.429(9)	1.388(5)
1.723(5)	1.732(3)
1.667(4)-1.692(5)	1.676(3)-1.688(3)
1.861(5)-1.987(5)	1.871(3)-1.976(3)
2.227(4)-2.359(4)	2.218(2)-2.360(2)
160.2(6)	169.5(3)
	<b>1</b> 1.429(9) 1.723(5) 1.667(4)-1.692(5) 1.861(5)-1.987(5) 2.227(4)-2.359(4) 160.2(6)

Table 3

Summary of hydrogen bonds in compounds 1–2.
---------------------------------------------

D–H···A	$d(H{\cdots}A)$	$d(H{\cdot}{\cdot}{\cdot}A)$	$d(D{\cdots}A)$	<(DHA)
Compound 1				
$C(7) - H(7A) - O(11)^{\#1}$	0.96	2.41	3.273(10)	149.8
$C(5)-H(5A)\cdots O(4)^{#2}$	0.93	2.77	3.402(10)	126.5
$C(6)-H(6A)\cdots O(4)^{#2}$	0.93	2.72	3.350(9)	125.8
Symmetry code: $^{#1} -x +$	1, $-y + 2$ , $-z$	+ 2; <sup>#2</sup> -x + 3/	2, $y + 1/2$ , $-z +$	3/2
Compound 2				
$C(5) - H(5A) - O(4)^{\#1}$	0.93	2.59	3.251(6)	128.6
$C(6)-H(6A)\cdots O(4)^{\#1}$	0.93	2.77	3.330(5)	119.9
$C(7)-H(7A)\cdots O(13)^{#2}$	0.96	2.58	3.320(6)	133.8
$C(7)-H(7A)\cdots O(10)^{#2}$	0.96	2.69	3.624(8)	165.6
Symmetry code: $^{\#1}$ –x +	3/2, y + 1/2, -	-z + 3/2; = -x	x + 1, -y + 1, -z	+ 2

(1.668(5)–1.692(5) Å), because the electronegativity of nitrogen atom is less than that of oxygen atom. The Mo–O<sub>b</sub> bond length of imido-bearing molybdenum atom (Mo(1)–O(1) (2.227(4) Å)) is obviously shorter than that of other Mo–Oc bonds (2.315(2)–2.364(2) Å) owing to the so-called "*trans influence*"; the average separation of Mo(1)···Mo (3.239 Å) is slightly shorter than that of other Mo···Mo (3.291 Å). The –SCH<sub>3</sub> group stands on the para position of hexamolybdates, the bond length of S(1)–C(4) and S(1)–C(4) are 1.758(7) and 1.775(10) Å, respectively, which are slightly shorter than that of the ligand of NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>SCH<sub>3</sub>-*p* (1.765 Å and 1.788 Å) [28].

Compound **2** crystallizes in monoclinic system, P2(1)/n space group. There are two cations of  $[Bu_4N]^+$  and one anion of  $[Mo_6O_{18}(NC_6H_4SCH_3-m)]^{2-}$  in the asymmetric unit. The anion cluster structure of compound **2** is close to that of compound **1** except that the  $-SCH_3$  group stands on the meta position of the bound hexamolybdates.

Weak interactions, such as hydrogen bonds,  $\pi \cdots \pi$  interactions, and anion  $\dots \pi$  interactions play a key role in supramolecular assembly [29]. The intermolecular hydrogen-bond interactions are found in compound 1. As seen in Fig. 2, two adjacent anion clusters form a dimer with graph set symbol [30] of R2 2(24) via two C-H···O hydrogen bonds  $(C(7)-H(7A) - O(11)^{\#2} 3.273(10) \text{ Å},$ symmetry code<sup>#2</sup>: -x + 1, -y + 1, -z + 2). Those dimers are further connected into a 2D network through C-H. O hydrogen bonds  $(C(5)-H(5A)\cdots O(4)^{\#1} 3.402(10) \text{ Å}, C(6)-H(6A)\cdots O(4)^{\#1} 3.350(9) \text{ Å},$ symmetry code<sup>#1</sup>: -x + 3/2, y - 1/2, -z + 3/2). One five-membered hydrogen-bond ring with graph set symbol of R1 2(5) is formed via  $C(5)-H(5A)\cdots O(4)^{\#1}$  and  $C(6)-H(6A)\cdots O(4)^{\#1}$ . In compound 2, adjacent anion clusters form a dimer containing a large hydrogenbond ring with graph set symbol of R2 2(20) via four C-H-O hydrogen bonds  $(C(7)-H(7A)\cdots O(13)^{\#2} 3.320(6) \text{ Å}, C(7)-H(7A)\cdots O(10)^{\#2} 3.624(8) \text{ Å}, symmetry code^{\#2}: <math>-x + 1, -y + 1, -z + 2$ , and those dimers are further connected into a 2D network via four C-H···O hydrogen bonds  $(C(5)-H(5A)···O(4)^{\#1} 3.251(6) Å$ ,  $C(6)-H(6A)\cdots O(4)^{\#1}$  3.330(5) Å, symmetry code<sup>#1</sup>: -x + 3/2, y + 1/22, -z + 3/2) (Fig. 3).

# 3.3. UV-Vis absorption spectra

UV–Vis absorption spectra of compounds **1**, **2** and hexamolybdates were studied in the solvent of CH<sub>3</sub>CN (Fig. 4). The lowest energy electronic transition for compound **1** and **2** are found at around 376 and 336 nm, respectively, while that of (TBA)<sub>2</sub>[Mo<sub>6</sub>O<sub>19</sub>] appear at about 325 nm. The large bathchromic shift (51 nm) of the lowest energy electronic transition between compound **1** and hexamolybdate indicates the presence of a strong  $d-\pi$  conjugation interaction in compound **1** [10]. That is because the methylthio group in compound **1** lies on the para position of  $-[N=(Mo_6O_{18})]^{2-}$ . There is an electron-denoting conjugated interaction (+C) besides the electron-drawing inductive effects of –SMe



Fig. 2. Ball-and-stick viewing of two dimensional hydrogen bond network of compound 1 (Symmetry code: #1 -x + 1, -y + 2, -z + 2, #2 -x + 3/2, y + 1/2, -z + 3/2).



Fig. 3. Ball-and-stick viewing of two dimensional hydrogen bond network of compound 2 (Symmetry code:  $\frac{x_1}{2} - x + 3/2$ ,  $\frac{y_2}{2} - x + 1$ , -y + 1, -z + 2).

(–I) in compound **1**, but the electron-denoting ability of –SMe is stronger than its electron-drawing ability. Therefore, the methylthio group in compound **1** acted as electron-denoting functional group and favor the formation of the D– $\pi$ –A system in the anion of [Mo<sub>6</sub>O<sub>18</sub>(NC<sub>6</sub>H<sub>4</sub>SCH<sub>3</sub>-p)]<sup>2–</sup>, which renders the lowest energy electronic transition of compound **1** to shift to 376 nm. As for compound **2**, there is a small bathchromic shift (11 nm) of the lowest energy electronic transition compared to that of hexamolybdates, this is due to the methylthio group sites on the meta position of –N=(Mo<sub>6</sub>O<sub>18</sub>)<sup>2–</sup>. Electron-drawing inductive interaction (–I) is the only electronic interaction of the methylthio

group, which went against the electron transfer from the aryl ring to the hexamolybdates and resulted in a small bathchromic shift. The big difference of bathchromic shift between compound **1** and **2** indicates that the position of substituents plays an important role in the electron interaction and electronic spectra of organic derivatized POMs.

#### 3.4. FT-IR spectra

FT-IR spectra of compounds **1** and **2** demonstrate some similar features of monofunctionalized organoimido derivatives of



Fig. 4. UV–Vis spectra of compound  $1\ (\text{red, dashed}),\ 2\ (\text{blue, dotted})$  and hexamolybdates (black, straight).

hexamolybdate. In the IR spectrum of hexamolybdate, two strong peaks of Mo–O<sub>t</sub> and Mo–O<sub>b</sub>–Mo are found to appear at 957 and 798 cm<sup>-1</sup>, respectively. In the IR spectra of compounds **1** and **2**, the peaks of Mo $\equiv$ O<sub>t</sub> are split into two peaks with approximate 20 cm<sup>-1</sup> intervals. The shoulder peak around 975 cm<sup>-1</sup> (975 cm<sup>-1</sup> for **1** and **2**) is tentatively ascribed as Mo $\equiv$ N stretching vibration, and the strong peak around 955 cm<sup>-1</sup> (955 cm<sup>-1</sup> for **1** and **2**) is attributed to Mo $\equiv$ O<sub>t</sub> stretching vibration [14]. The Mo–O<sub>b</sub>–Mo stretching vibration is found at 793 cm<sup>-1</sup> in **1**, 795 cm<sup>-1</sup> in **2**, respectively, demonstrating a slight red-shift compared to that in [Mo<sub>6</sub>O<sub>19</sub>] owing to the attachment of organoimido ligand.

#### 3.5. <sup>1</sup>H NMR spectra

<sup>1</sup>H NMR spectra of compounds **1** and **2** in d<sub>6</sub>-DMSO solution display clearly resolved signals, all of which can be unambiguously assigned. The integration matches well with their structures. <sup>1</sup>H NMR signals of aryl hydrogen atoms in compound **1** appear at 7.29 and 7.15 ppm, while that of aryl hydrogen atoms in corresponding free amines locate at 7.07 and 6.56 ppm. The downfield shift of aryl hydrogen in compound **1** indicates that they are influenced by deshielding effect, in other words, POMs are an electron-drawing functional group. <sup>1</sup>H NMR signals of aryl hydrogen atoms in corresponding free at 6.96, 6.47 and 6.36 ppm. There is an obvious downfield chemical shift of aryl hydrogen atoms between compound **2** and 3-(methylthio)aniline owing to the electron-drawing effect of attached POMs cluster.

#### 3.6. Cyclic voltammetry

Electrochemical data of compounds **1**, **2** and hexamolybdates were recorded in *ca*. 1 mmol/L DMF solutions with [n-Bu<sub>4</sub>N]PF<sub>6</sub> (0.1 mol/L) as the supporting electrolyte. In the range of -1.6 to +1.6 V (versus SCE), both compounds **1** and **2** show a reversible redox possess (Table 4), which is found at -0.390 V for **1**, and -0.386 V for **2**, respectively. Under the same conditions, the parent of [Bu<sub>4</sub>N]<sub>2</sub>[Mo<sub>6</sub>O<sub>19</sub>] shows one reversible redox possess at -0.216 V. The cathodic shift of  $E_{1/2}$  of compounds **1** and **2** in relative to hexamolybdate is 0.174 V for **1**, and 0.170 V for **2**, respectively. The large cathodic shift suggests that they are more difficult to be reduced than their parent of [Mo<sub>6</sub>O<sub>19</sub>]<sup>2-</sup>, which means that title compounds have higher electronic density than hexamolybdates. This is because the negativity of nitrogen atom Table 4

Cyclic voltammetry data of hexamolybdates and compounds 1-2.

Compound	$E_{\rm pc}\left(V\right)$	$E_{\rm pa}\left(V\right)$	$E_{\rm pa} - E_{\rm pc}  (V)$	$E_{1/2}(V)$	Cathodic shift (V)
[Mo <sub>6</sub> O <sub>19</sub> ] <sup>2-</sup>	-0.268	-0.163	0.105	-0.216	0
1	-0.435	-0.346	0.089	-0.390	0.174
2	-0.439	-0.334	0.105	-0.386	0.170

is less than oxygen atom and the nitrogen atom is conjugated with aryl ring in aryl imido derivatives, therefore the aryl imido ligands are superior electron-denoting ligands in relative to oxygen atoms [10,14], which render compound **1** and **2** to bear higher electronic density than hexamolybdates.

#### 4. Conclusion

In summary, two organoimido derivatives of hexamolybdates containing methylthio groups,  $(Bu_4N)_2[Mo_6O_{18}(NC_6H_4-SCH_3-p)]$ (1) and  $(Bu_4N)_2[Mo_6O_{18}(NC_6H_4-SCH_3-m)]$  (2), were successfully prepared using DCC assisting dehydration protocol. Single crystal X-ray diffraction structural study reveals that the anion clusters of both compounds demonstrate typical monosubstituted structural features of hexamolybdates with different substituted position of methylthio groups. The lowest energy electronic transition of compound 1 shows a large bathchromic shift owing to the formation of D- $\pi$ -A system, while that of compound 2 shows a slight bathchromic shift. <sup>1</sup>H NMR of aryl hydrogen atoms in compounds 1 and 2 show obvious downfield shifts compared to that of free amine owing to the electron-withdrawing effect of POMs. CV study indicates that both compounds are more difficult to be reduced than (TBA)<sub>2</sub>[Mo<sub>6</sub>O<sub>19</sub>].

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#### Appendix A. Supplementary data

CCDC 1031869 and 1031870 contains the supplementary crystallographic data for compounds **1** and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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