

# Synthesis, spectroscopic studies and crystal structure of a polyoxoanion cluster incorporating *para*-bromophenylimido ligand, $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{18}(\text{NC}_6\text{H}_4\text{Br-}p)]$

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## Abstract

An organic–inorganic hybrid compound,  $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{18}(\text{NAr})]$  ( $\text{Ar} = p\text{-BrC}_6\text{H}_4$ ) has been synthesized via the DCC dehydrating protocol of the reaction of  $[\alpha\text{-Mo}_8\text{O}_{26}]^{4-}$  with 4-bromoaniline hydrochloride in anhydrous acetonitrile, which has been characterized by UV–Vis spectra, <sup>1</sup>H NMR and single crystal X-ray diffraction study. By comparing the UV–Vis spectra, which were used to monitor the reaction, the optimum preparative condition for this compound was also determined. This compound crystallizes in the monoclinic space group  $P2_1/n$ , which is featured in a terminal *para*-bromophenylimido group linked to an Mo atom of a hexamolybdate cluster by a Mo–N triply bond. In addition, there are  $\pi$ – $\pi$  dimerization of the neighboring cluster anions through the parallel aromatic rings in their crystals.

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**Keywords:** Organoimido derivatives; Polyoxometalates; DCC; Aromatic amine halides; Organic/inorganic hybrids; Crystal structure

## 1. Introduction

The organoimido derivatives of polyoxometalates have gained tremendous interest in the last decade owing to their unusual structure, electrochemical, magnetic, catalytic, anti-microbial and anti-tumor properties [1–4]. Up to date, a number of organoimido derivatives of Lindqvist type polyoxometalates [4] such as the hexamolybdate ion,  $[\text{Mo}_6\text{O}_{19}]^{2-}$  and hexatungstate ion,  $[\text{W}_6\text{O}_{19}]^{2-}$ , have been directly or indirectly synthesized via three types of reactions, which include reactions with phosphinimines [5], isocyanates [6] and aromatic amines [7] or aromatic amines plus *N,N'*-dicyclohexylcarbodiimide [8]. However, such

donor–acceptor systems usually require that their ligands must be charge donors. So, those ligands covalently linked polyoxometalates are donor groups in such hybrid materials previously reported in the literatures [5–8]. Attempts to explore those POMs incorporating an aromatic amine ligand with an electron-withdrawing group have not been successful because such organic conjugated molecules and the POMs are both charge acceptors, which makes difficulty for covalently linking them each other. Very recently, based on the DCC dehydrating protocol, we have developed a new approach to synthesize such hybrid materials by using  $\alpha$ -octamolybdate ( $[\alpha\text{-Mo}_8\text{O}_{26}]^{4-}$ ) as the starting cluster [9]. The reaction of  $[\alpha\text{-Mo}_8\text{O}_{26}]^{4-}$  with aromatic amines and their hydrochlorides can easily take place under much more milder conditions and in the meanwhile monofunctionalized organoimido derivatives of  $[\text{Mo}_6\text{O}_{19}]^{2-}$  even bearing an electron-withdrawing group were selectively synthesized

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in high purity and moderate yield. In this paper, we hope to report the synthesis and structural characterization of the arylimido derivative,  $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{18}(\equiv\text{NAR})]$ , AR = *p*-BrC<sub>6</sub>H<sub>4</sub> (**1**). To the best of our knowledge, the hybrid compound **1** represents the first structurally characterized example of an organoimido derivative of hexamolybdate incorporating a phenylimido ligand with a bromo group [9], which is also an important building block for constructing novel organic/inorganic hybrids based on polyoxometalates with controllable organic synthesis technology such as the Pd-mediated carbon–carbon coupling reactions [10].

## 2. Experimental

### 2.1. Synthesis of **1**

Scheme 1 shows the synthesis of the hybrid material **1**: a mixture of  $(\text{Bu}_4\text{N})_4[\alpha\text{-Mo}_8\text{O}_{26}]$  (1.0 mmol), 4-bromoaniline hydrochloride (2.0 mmol) and *N,N'*-dicyclohexylcarbodiimide (DCC) (3.4 mmol) was refluxed in anhydrous acetonitrile (10 mL) for about 6 h, a large amount of white precipitates formed, which was confirmed to be dicyclohexylurea, and a dark-red solution was obtained. After cooling the suspension to room temperature, the white precipitates were removed away by filtration. And then while most of acetonitrile was allowed to slowly evaporate out, the product deposited from the filtrate as red colloid-like solid. The product was collected by filtration, washed successively with ethanol (EtOH) and ethyl ether (Et<sub>2</sub>O) several times, and then recrystallized twice from a mixed solution of acetone and ethyl alcohol (1:1), **1** is obtained in the moderate yield of ca. 50–60%, based on  $(\text{Bu}_4\text{N})_4[\alpha\text{-Mo}_8\text{O}_{26}]$ . Compound **1** is well soluble in most of common organic solvents such as acetone, acetonitrile and *N,N*-dimethylformamide.

### 2.2. General characterization

The elemental analysis was performed on a Vario EL analyses system. <sup>1</sup>H NMR and UV–Vis spectra were carried out on a Bruker AV-600 nuclear magnetic resonance spectrometer and a TU-1221 UV–Vis spectrophotometer, respectively.

Elemental analysis (%) calcd. for Compound **1** C<sub>38</sub>H<sub>76</sub>N<sub>3</sub>O<sub>18</sub>BrMo<sub>6</sub>: C, 30.06; H, 5.04; N, 2.77. Found: C, 30.22; H, 5.00; N, 2.72%. <sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>CN, 300 K, ppm): δ = 0.99 (t, 24 H, CH<sub>3</sub>–, [Bu<sub>4</sub>N]<sup>+</sup>), 1.39 (m, 16H, –CH<sub>2</sub>–, [Bu<sub>4</sub>N]<sup>+</sup>), 1.63 (m, 16H, –CH<sub>2</sub>–, [Bu<sub>4</sub>N]<sup>+</sup>), 3.12 (t, 16H, NCH<sub>2</sub>–, [Bu<sub>4</sub>N]<sup>+</sup>), 7.57, 7.56 (d, 2H, *o*-ArH), 7.15, 7.14 (d, 2H, *m*-ArH). UV/Vis (MeCN):

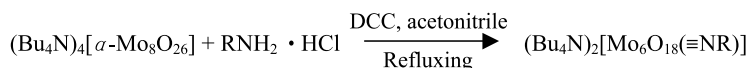
$\lambda_{\text{max}}/\text{nm}$  ( $\epsilon/\text{M}^{-1}\text{cm}^{-1}$ ) = 223 ( $3.2 \times 10^4$ ), 258 ( $3.3 \times 10^4$ ), 341 ( $2.0 \times 10^4$ ). Crystals suitable for single crystal X-ray diffraction were grown from a mixed solution of acetone and ethanol (1:1).

### 2.3. Structure determination

A suitable single crystal having approximate dimensions  $0.4 \times 0.3 \times 0.2\text{ mm}^3$  was mounted on a glass fiber. The measurement was made on a Bruker Smart Apex CCD diffractometer. Data collection was performed at 293 K by using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ). The raw frame data was processed using SAINT [11] and SADABS [12] to yield the reflection data. Subsequent calculations were carried out using SHELXTL program [13]. The structure was solved by direct methods and refinement was performed by full-matrix least-squares analysis. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at their ideal positions. Data collection and structure determination result for Compound **1** is summarized in Table 1. Table 2 contains atomic positions and equivalent temperature factors for non-H

Table 1  
Crystal data and structure refinement parameters for **1**

Empirical formula	C <sub>38</sub> H <sub>76</sub> N <sub>3</sub> O <sub>18</sub> BrMo <sub>6</sub>
Formula weight	1518.57
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> (Å)	17.627(4)
<i>b</i> (Å)	17.735(4)
<i>c</i> (Å)	19.340(4)
$\beta$ (°)	114.43(3)
Volume (Å <sup>3</sup> )	5504.5(19)
<i>Z</i>	4
Density (calculated) (Mg/m <sup>3</sup> )	1.832
Absorption coefficient (mm <sup>−1</sup> )	2.117
<i>F</i> (000)	3024
Crystal size (mm <sup>3</sup> )	0.4 × 0.3 × 0.2
$\theta$ Range for data collection (°)	2.30–22.50
Index ranges	−13 ≤ <i>h</i> ≤ 18, −19 ≤ <i>k</i> ≤ 18, −20 ≤ <i>l</i> ≤ 20
Reflections collected	24016
Independent reflections [ <i>R</i> <sub>int</sub> ]	7181 [0.0959]
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	7181/0/595
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.089
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0767, <i>wR</i> <sub>2</sub> = 0.1559
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.1194, <i>wR</i> <sub>2</sub> = 0.1720
Largest difference in peak and hole (e Å <sup>−3</sup> )	0.670 and −1.431



Scheme 1. Synthesis of  $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{18}(\equiv\text{NR})]$  with R = *p*-BrC<sub>6</sub>H<sub>4</sub>.

Table 2  
Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **1**

Atom	x	y	Z	$U_{\text{eq}}$
Mo(1)	−585(1)	2859(1)	2156(1)	68(1)
Mo(2)	−1081(1)	1530(1)	3057(1)	49(1)
Mo(3)	−1272(1)	1266(1)	1303(1)	57(1)
Mo(4)	691(1)	1746(1)	1808(1)	51(1)
Mo(5)	876(1)	2023(1)	3561(1)	56(1)
Mo(6)	209(1)	395(1)	2726(1)	50(1)
O(1)	−194(5)	1659(4)	2437(4)	37(2)
O(2)	−1694(6)	1453(6)	3513(6)	75(3)
O(3)	−2030(6)	961(8)	503(6)	94(4)
O(4)	1322(6)	1803(6)	1360(6)	73(3)
O(5)	1670(6)	2289(7)	4374(5)	86(4)
O(6)	480(7)	−502(6)	2927(6)	82(3)
O(7)	−577(5)	552(5)	3179(5)	48(2)
O(8)	−17(5)	1857(5)	3850(5)	54(2)
O(9)	1000(5)	941(5)	3563(5)	57(3)
O(10)	−374(6)	1400(5)	1011(5)	61(3)
O(11)	−1779(5)	1259(5)	2043(5)	57(3)
O(12)	−1404(6)	2352(6)	1293(6)	72(3)
O(13)	−758(6)	343(5)	1783(5)	57(3)
O(14)	197(6)	2716(5)	1685(5)	65(3)
O(15)	818(5)	706(5)	2157(5)	57(3)
O(16)	1386(5)	2016(5)	2824(5)	56(3)
O(17)	392(6)	2945(5)	3113(5)	64(3)
O(18)	−1209(6)	2560(5)	2719(6)	62(3)
N(1)	−826(10)	3786(7)	1976(10)	100(5)
C(1)	−777(11)	4570(11)	1915(10)	82(5)
C(2)	−240(13)	4946(15)	1625(13)	121(8)
C(3)	−218(17)	5688(13)	1501(11)	121(8)
C(4)	−753(13)	6129(11)	1702(11)	84(6)
C(5)	−1255(13)	5826(12)	2037(11)	100(7)
C(6)	−1268(13)	5071(14)	2149(11)	108(7)
Br	−788(2)	7159(1)	1525(2)	177(2)

$U_{\text{eq}}$  is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

atoms. Selected bond lengths and angles are presented in Table 3.

### 3. Results and discussion

#### 3.1. Synthesis

As shown in Scheme 1, when *para*-bromoaniline hydrochloride salts reacts with  $[\alpha\text{-Mo}_8\text{O}_{26}]^{4-}$ , the product is the monofunctionalized organoimido derivatives of hexamolybdate, and with increasing the amount of the hydrochloride salt, the amount of product will also increase. Apparently, the hydrochloride salt is, in fact, a proton carrier to introduce the proton into the reaction mixture. While more work needs to be done to shed light on the detailed reaction mechanism, the likely role of the proton is to complex with DCC and hence to increase the electrophilic ability of DCC to oxo group of the Mo–O bond. Additionally, it also promotes the conversion of an octamolybdate to the hexamolybdate though a degradation and re-assembly process since in an acidic organic solvent, a hexamolybdate and its derivatives are much more stable than an octamolybdate [10c]. On the other hand, according

Table 3  
Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for **1**

Mo(1)–N(1)	1.698(13)	Mo(2)–O(2)	1.660(9)
Mo(1)–O(18)	1.915(9)	Mo(2)–O(11)	1.896(9)
Mo(1)–O(12)	1.919(11)	Mo(2)–O(7)	1.918(8)
Mo(1)–O(17)	1.944(10)	Mo(2)–O(18)	1.922(9)
Mo(1)–O(14)	1.958(10)	Mo(2)–O(8)	1.956(9)
Mo(1)–O(1)	2.234(8)	Mo(2)–O(1)	2.341(8)
Mo(3)–O(3)	1.662(9)	Mo(4)–O(4)	1.671(9)
Mo(3)–O(10)	1.904(10)	Mo(4)–O(14)	1.897(9)
Mo(3)–O(13)	1.916(10)	Mo(4)–O(16)	1.898(9)
Mo(3)–O(12)	1.938(10)	Mo(4)–O(15)	1.945(9)
Mo(3)–O(11)	1.977(9)	Mo(4)–O(10)	1.970(9)
Mo(3)–O(1)	2.337(8)	Mo(4)–O(1)	2.347(8)
Mo(5)–O(5)	1.684(9)	Mo(6)–O(6)	1.659(10)
Mo(5)–O(17)	1.882(10)	Mo(6)–O(9)	1.907(9)
Mo(5)–O(8)	1.899(9)	Mo(6)–O(15)	1.908(9)
Mo(5)–O(9)	1.931(9)	Mo(6)–O(13)	1.916(9)
Mo(5)–O(16)	1.974(9)	Mo(6)–O(7)	1.942(9)
Mo(5)–O(1)	2.304(8)	Mo(6)–O(1)	2.349(8)
N(1)–C(1)	1.40(2)	C(1)–C(6)	1.44(2)
C(1)–C(2)	1.45(3)	C(4)–C(5)	1.40(3)
C(2)–C(3)	1.34(3)	C(4)–Br	1.854(19)
C(3)–C(4)	1.40(3)	C(5)–C(6)	1.36(3)
N(1)–Mo(1)–O(18)	103.3(5)	N(1)–Mo(1)–O(1)	176.7(6)
N(1)–Mo(1)–O(12)	104.0(7)	O(18)–Mo(1)–O(1)	77.9(3)
O(18)–Mo(1)–O(12)	87.9(4)	O(12)–Mo(1)–O(1)	79.1(3)
N(1)–Mo(1)–O(17)	99.6(7)	O(17)–Mo(1)–O(1)	77.3(3)
O(18)–Mo(1)–O(17)	88.3(4)	O(14)–Mo(1)–O(1)	77.5(3)
O(12)–Mo(1)–O(17)	156.4(4)	C(1)–N(1)–Mo(1)	163.6(14)
N(1)–Mo(1)–O(14)	101.2(5)	N(1)–C(1)–C(6)	121.3(19)
O(18)–Mo(1)–O(14)	155.4(4)	N(1)–C(1)–C(2)	124.3(19)
O(12)–Mo(1)–O(14)	87.5(4)		
O(17)–Mo(1)–O(14)	86.3(4)		

to our investigation, under the same conditions, there is no metathesis reaction occurred between  $[\alpha\text{-Mo}_8\text{O}_{26}]^{4-}$  and *para*-bromoaniline, except for the oxidation of the amine. The optimum reaction conditions such as the amount of each raw material and the reaction time can be obtained by monitoring the reaction system with TLC, UV–Vis or  $^1\text{H}$  NMR technology. In this work, by comparing UV–Vis spectroscopy of the product from different conditions (see Fig. 1), a favorable routine was obtained and is given in Section 2.

Compound **1** is well soluble in most of common organic solvents such as acetone, acetonitrile and *N,N*-dimethylformamide. Its composition and structure was firstly obtained from elemental analysis,  $^1\text{H}$  NMR and UV/Vis spectroscopic studies. It was confirmed finally by X-ray single crystal diffraction analysis.

#### 3.2. NMR spectroscopy

The  $^1\text{H}$  NMR spectrum (in  $\text{CD}_3\text{CN}$ ) of compound **1** shows clearly resolved signals, all of which can be unambiguously assigned (see Fig. 2). The integration matches well with the assumed structure (see Fig. 4). Compared to the  $^1\text{H}$  NMR spectrum of the corresponding free amine, the protons of **1**, except for those in the tetrabutylammonium cation, all exhibit significantly downfield chemical

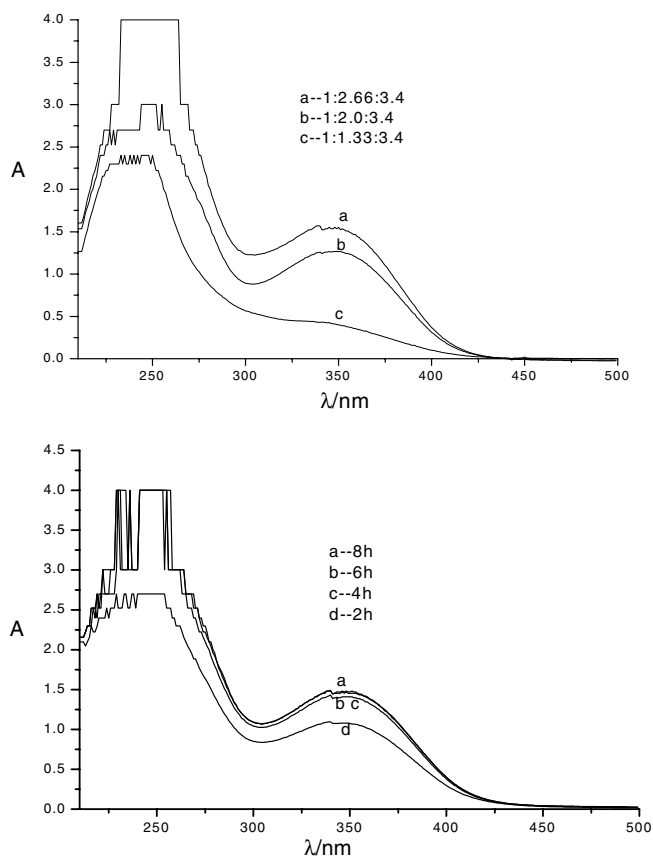


Fig. 1. Effects of the amount of raw materials and the reaction time on the product.

shifts, indicating the much weaker shielding nature of the  $[\text{Mo}_5\text{O}_{18}(\text{Mo}\equiv\text{N})]^{2-}$  than the amino group  $\text{NH}_2^-$ .

### 3.3. UV-Vis spectroscopy

Fig. 3 shows the UV/Vis absorption spectra of the tetrabutylammonium salts of  $[\alpha\text{-Mo}_8\text{O}_{26}]^{4-}$ ,  $[\text{Mo}_6\text{O}_{19}]^{2-}$ , and **1**. The lowest energy electronic transition at 325 nm in  $[\text{Mo}_6\text{O}_{19}]^{2-}$  was assigned to a L → M charge-transfer transition from the oxygen  $\pi$ -type HOMO to the molybdenum

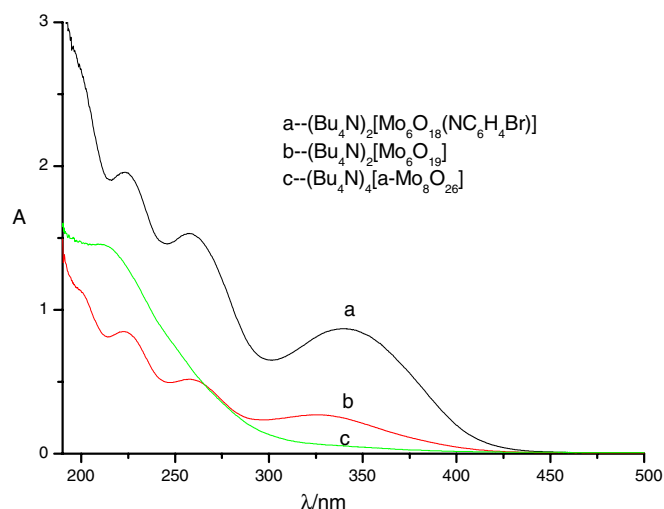


Fig. 3. UV/Vis absorption spectra of  $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{19}]$ ,  $(\text{Bu}_4\text{N})_4[\alpha\text{-Mo}_8\text{O}_{26}]$  and **1**.

$\pi$ -type LUMO, which is bathochromically shifted by more than 16 nm and becomes considerably more intense in **1** (341 nm), indicating that the Mo–N  $\pi$ -bond is formed in this organoimido derivative. In other words, there is a strong electronic interaction between the metal oxygen cluster and the organic conjugated ligand.

### 3.4. Crystal structure

The molecular structure of **1** has been determined by X-ray single-crystal diffraction. Compound **1** crystallizes in the monoclinic space group  $P2_1/n$ , which is *iso*-structural with previously reported a *para*-chlorophenylimido hexamolybdate [9]. For the sake of simplicity, only the structure of the cluster anion of **1** in an asymmetric unit is shown in Fig. 4. In the cluster anion of **1**, the arylimido ligand is bound to a terminal position at the hexamolybdate in a monodentate fashion. The Mo–N bond distance of 1.698(13) Å and the C–N–Mo bond angle of 163.6(14)° are typical of organoimido groups bonded at an octahedral  $d^0$  metal center and are consistent with a substantial degree

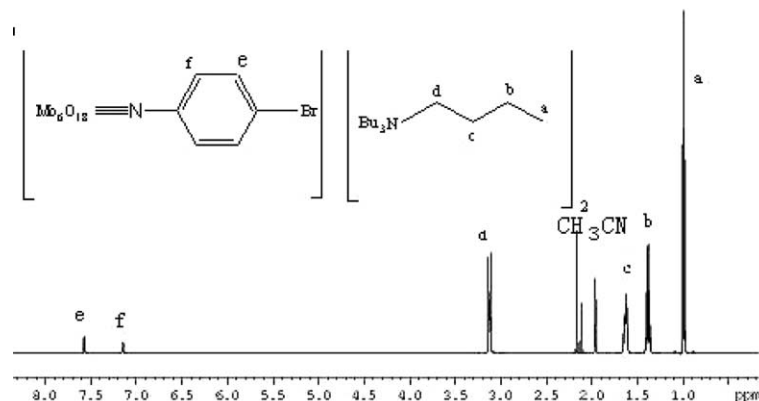


Fig. 2.  $^1\text{H}$  NMR spectrum of compound **1**.

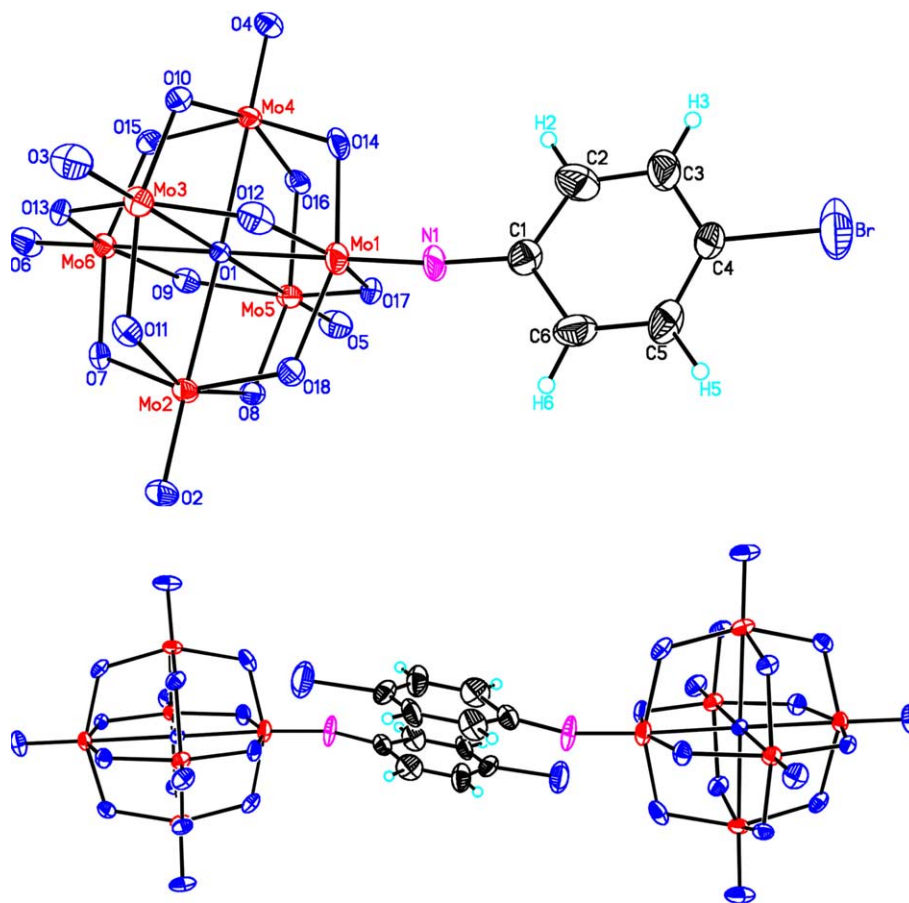


Fig. 4. ORTEP drawings of the cluster anion and its dimer of **1**.

of Mo≡N triple bond character [14]. Compared to the parent hexamolybdate and other derivatives, the bond lengths of the five remaining terminal oxo ligands of **1** do not vary significantly. The Mo(1)–O(1) distance between the Mo atom with imido group and the central oxygen atom within the cluster anion cage is remarkably shorter than the other Mo–O(1) distances, and such an analogous contraction has also been observed in the other imido derivatives of Lindqvist hexametalates [5–10]. Considerable variations are seen in the bond lengths involving the doubly bridging oxygen atoms coordinated to the Mo atom with imido group, which is again consistent with the other imido derivatives of Lindqvist hexametalates reported so far [5–10].

An interesting structure feature that should be mentioned here is the dimerization of the cluster anions of **1** in the crystals through  $\pi$ – $\pi$  stacking interaction between the parallel phenyl rings attached to Mo(1) atoms of two neighboring cluster anions. The existence of such a supramolecular  $\pi$ – $\pi$  interaction between the pairs of cluster anions is clearly indicated by the short vertical phenyl ring separation of 3.888 Å.

#### 4. Conclusion

In summary, an arylimido derivative of the hexamolybdate bearing a remote bromo group has been successfully

synthesized in reasonably yield and structurally characterized. With aromatic amine bromides widely accessible and much cheaper than the corresponding iodides, this study maybe opens an alternative way to efficiently construct novel hybrid molecular materials containing covalently bonded metal–oxygen clusters and organic conjugated segments. In addition, the phenomenon of supramolecular dimerization of cluster anions will be helpful for their future application in polyoxometalate-based organic–inorganic hybrid molecular materials.

#### 5. Supplementary materials

CCDC No. 249899 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB 21EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk).

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