DCC-Assisted Esterification of a Polyoxometalate-Functionalized Phenol with Carboxylic Acids (DCC: Dicyclohexylcarbodiimide)

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In recent years the efforts to construct organic–inorganic hybrid functional materials based on covalently linked poly-oxometalates (POMs) have increased,[1] owing to the nano-sized geometry, molecular, and electronic structural diversity of the incorporated POM clusters and their significance in catalysis, medicine, and materials science.[2,3] One of the most important strategies for fabricating such hybrid materials is based on the functionalization of POM precursors with suitable organic ligands and the subsequent or concomitant coupling of the organically derived POMs through common organic synthetic techniques under controllable conditions.[1c,d] So far, a few hybrid materials with covalently anchored POMs have been successfully obtained, for instances, nanoscale molecular dumbbells of Lindquist type POMs,[4] catalytic POM terminated dendrimers,[5] and polymers with covalently bound POMs.[1d,6]

Amongst the organically derived POMs,[7] organoimido derivatives have gained increasing interest[1d,4,8,9] after the pioneering work of Maatta, Errington, and Proust,[10–12] as the organic π electrons in arylimido derivatives of POMs may extend their conjugation to the inorganic framework, which could give birth not only to "value-adding properties", but also to possible synergistic effects in resulting hybrid materials. Although the reaction chemistry of other types of organic derivatives of POMs has made considerable progress,[13] the side-chain reactivity of organoimido substituted POMs is relatively under developed,[1d] an area which is crucial for the development of POM-based hybrids. Herein, we report, for the first time, the synthesis and esterification reaction of a phenolic hydroxyl functionalized organoimido substituted hexamolybdate, $[(n\text{Bu}_4\text{N})_2]$-$[\text{Mo}_6\text{O}_{18}(\text{NAr})]$ (Ar = p-hydroxyl-o-toyl), $[(\text{Bu}_4\text{N})_2]$-**1**, with carboxylic acids in the presence of 1,3-dicyclohexylcarbodiimide (DCC) as a dehydrating agent.[14] This reaction opens a novel pathway to make hybrid materials, which contain covalently bonded POM clusters and organic conjugated segments, in more controllable and rational manner.

Compound $[(\text{Bu}_4\text{N})_2]$-**1** was synthesized according to previously reported procedures with some modification.[8] Scheme 1 shows the synthesis of the hybrid POMs $[(\text{Bu}_4\text{N})_2]$-**2a–e**, their yields are collected in Table 1.

First attempts to prepare the hybrid compounds $[(\text{Bu}_4\text{N})_2]$-**2a–e** by the reactions of $[(\text{Bu}_4\text{N})_2]$-**1** and acid chlorides failed since the derivatives decomposed into hexamolybdate by HCl, a strong acid, formed during the reactions. Although $[(\text{Bu}_4\text{N})_2]$-**2a** can be formed using acetic anhydride as the acylation agent, we observed that, in the presence of DCC, $[(\text{Bu}_4\text{N})_2]$-**2a–e** were both easily synthesized directly using carboxylic acids as acylation agents.[14] For example, when a mixture of $[(\text{Bu}_4\text{N})_2]$-**1**, one equivalent carboxylic acid such as acetic acid, p-methylbenzoic acid, p-chlorobenzoic acid, propanoic acid or acrylic acid, and one equivalent DCC was refluxed for 10 h in anhydrous acetonitrile, the esterification reaction proceeded smoothly, and $[(\text{Bu}_4\text{N})_2]$-**2a–e** were formed in good to excellent yields. Here, common to classic organic chemistry, DCC served as a dehydration agent and promoted the esterification and $[(\text{Bu}_4\text{N})_2]$-**1** behaved as a functionalized phenol during the reactions. Without DCC, however, the esterification of **1** is hard to take place even after refluxing for a prolonged time, which is totally different from common phenols.[14] Instead, the decomposition of **1** is observed, presumably owing to

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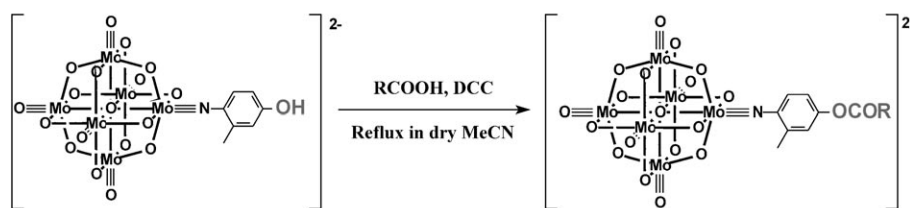
Scheme 1. Esterification of [(Bu$_4$N)$_2$]-**1** with carboxylic acids.

Table 1. The esterification of [(Bu$_4$N)$_2$]-**1** with selected carboxylic acids.[a]

Entry	R	t [h]	Products[b]	Yield[c] [%]
1	CH$_3$	10	[(Bu$_4$N)$_2$]-**2a**	82
2	p-C$_6$H$_4$CH$_3$	10	[(Bu$_4$N)$_2$]-**2b**	75
3	p-C$_6$H$_4$Cl	10	[(Bu$_4$N)$_2$]-**2c**	80
4	C$_2$H$_5$	10	[(Bu$_4$N)$_2$]-**2d**	77
5	C$_2$H$_3$	10	[(Bu$_4$N)$_2$]-**2e**	75

[a] Reaction conditions: [(Bu$_4$N)$_2$]-**1** (1.0 mmol), carboxylic acid (1.5 mmol), DCC (2.0 mmol), acetonitrile (20 mL), refluxing at 85 °C. [b] All products were characterized by ^{1}H NMR, UV/Vis and IR spectroscopy. [c] Isolated yield.

the limited stability under the reaction conditions and other characteristic in composition and electronic structure of the POM group vastly different from common functional groups, i.e., nitro or sulphonic groups, in organic chemistry.

The ^{1}HNMR spectra of these hybrids show clearly resolved signals, all of which can be unambiguously assigned. In [(Bu$_4$N)$_2$]-**1**, the signals for the aromatic protons appear as one singlet and two doublets at $\delta = 6.62$, 6.59, and 7.05 ppm, respectively. The methyl and hydroxyl protons attached to the benzene ring appear as singlets at $\delta = 2.56$ and 10.04 ppm, respectively. Compared to [(Bu$_4$N)$_2$]-**1**, although there is no obvious change of the methyl protons attached to the benzene ring, the hydroxyl signal was not observed for [(Bu$_4$N)$_2$]-**2a–e**, and there are the significant downfield shifts of the three aromatic protons, owing to the replacement of H atom by the electron-withdrawing acyl groups. Furthermore, there are several additional signals for [(Bu$_4$N)$_2$]-**2a–e**, which originate from the acyl groups of corresponding carboxylic acids. These facts imply that the hybrid [(Bu$_4$N)$_2$]-**1** has realized esterification reactions with carboxylic acids and the targeted hybrids have indeed formed.

The IR spectra of [(Bu$_4$N)$_2$]-**1**, [(Bu$_4$N)$_2$]-**2a–e** in the low wavenumber region ($\tilde{\nu} < 1000$ cm^{-1}) are similar to each other, owing to the same POM framework. However, they show obvious discrepancies in the high wavenumber region as a result of the incorporation of different organoimido ligands. In [(Bu$_4$N)$_2$]-**1**, there is a medium and wide band at $\tilde{\nu} = 3420$ cm^{-1} observed for the vibration of ν(O−H). As expected, this band is not observed for [(Bu$_4$N)$_2$]-**2a–e**, in accordance with the formation of esters, as a result of the acylation. Instead, there are the characteristic stretching vibrations of the C=O group observed as medium peaks at 1756,

1735, 1737, 1760, and 1740 cm^{-1}, in [(Bu$_4$N)$_2$]-**2a–e**, respectively, which definitely implies the formation of esters.

The electronic properties of these functionalized hexamolybdates were studied by UV/Vis absorption. The ligand to metal charge-transfer (LMCT) band for [Mo$_6$O$_{19}$]$^{2-}$ anion is at $\lambda = 325$ nm.[10a,11a] After functionalization, the lowest energy electronic transition is bathochromically shifted from the parent hexamolybdate anion to [(Bu$_4$N)$_2$]-**1** (365 nm) owing to strong electron-donating nature of the hydroxyl functionalized organoimido ligand, indicating that the Mo−N π bond is formed and delocalized with the organic conjugated π electrons.[15] On the contrary, after acylation of hybrid [(Bu$_4$N)$_2$]-**1**, this lowest energy electronic absorption is continuously hypochromatically shifted significantly from [(Bu$_4$N)$_2$]-**1** to hybrid [(Bu$_4$N)$_2$]-**2a** (354 nm), [(Bu$_4$N)$_2$]-**2d** (353 nm), [(Bu$_4$N)$_2$]-**2e** (352 nm), [(Bu$_4$N)$_2$]-**2b** (350 nm) and [(Bu$_4$N)$_2$]-**2c** (348 nm) because of the enhanced electron-withdrawing ability of the corresponding acyl groups. It also indicates that the -COO-bond is formed in hybrid [(Bu$_4$N)$_2$]-**2a–e** and that there are electronic interactions to some extent between the metal–oxygen cluster and the organic-conjugated ligands in all these hybrid compounds.

The crystal structures of [(Bu$_4$N)$_2$]-**1**, [(Bu$_4$N)$_2$]-**2a**, -**2c**, and -**2e** have been determined by single-crystal X-ray diffraction studies, which substantially confirm the targeted molecular structures. Figure 1 depicts the ORTEP diagrams of the molecular structures of the corresponding anions **1**, **2a**, **2c**, and **2e**, respectively. As can be seen, **2a**, **2c**, and **2e** are indeed assembled from **1** with the hydrogen atom of its hydroxyl group replaced by acetyl, p-chlorobenzoyl and acryloyl groups, respectively. The acetyl, p-chlorobenzoyl and acryloyl groups are linked to the organoimido substituted hexamolybdate with the C8-O19 bond lengths of 1.274(4), 1.360(12), 1.350(9) Å in **2a**, **2c**, and **2e**, respectively. Compared to their hexamolybdate cages in **1**, **2a**, **2c**, and **2e**, they all show some typical features of the reported organoimido derivatives in the literatures:[4,8,10–12] For example, their Mo−N bonds have substantial triple bond character, as evidenced by the short bond lengths (1.724(3), 1.721(2), 1.734(7), 1.701(8) Å in **1**, **2a**, **2c**, and **2e**, respectively) and nearly liner Mo−N−C bond angles (173.1(3)°, 173.2(2)°, 176.9(7)°, 174.8(9)° in **1**, **2a**, **2c**, and **2e**, respectively). After esterification, there are no obvious changes in the C−C bond distances of the corresponding aryl groups in **2a**, **2c**, and **2e** in comparison with **1**. However, there are considerably enlargements of the C4−O19 bond distances (1.353(5), 1.454(4), 1.414(11), 1.403(17) Å in **1**, **2a**, **2c**, and **2e**, respectively) related to the hydroxyl group of **1**, as a result of the acylation. In [(Bu$_4$N)$_2$]-**1**, there is an interesting supramolecular assembly originating from the hydrogen bonding interactions of the OH groups of cluster anions. A pair of O−

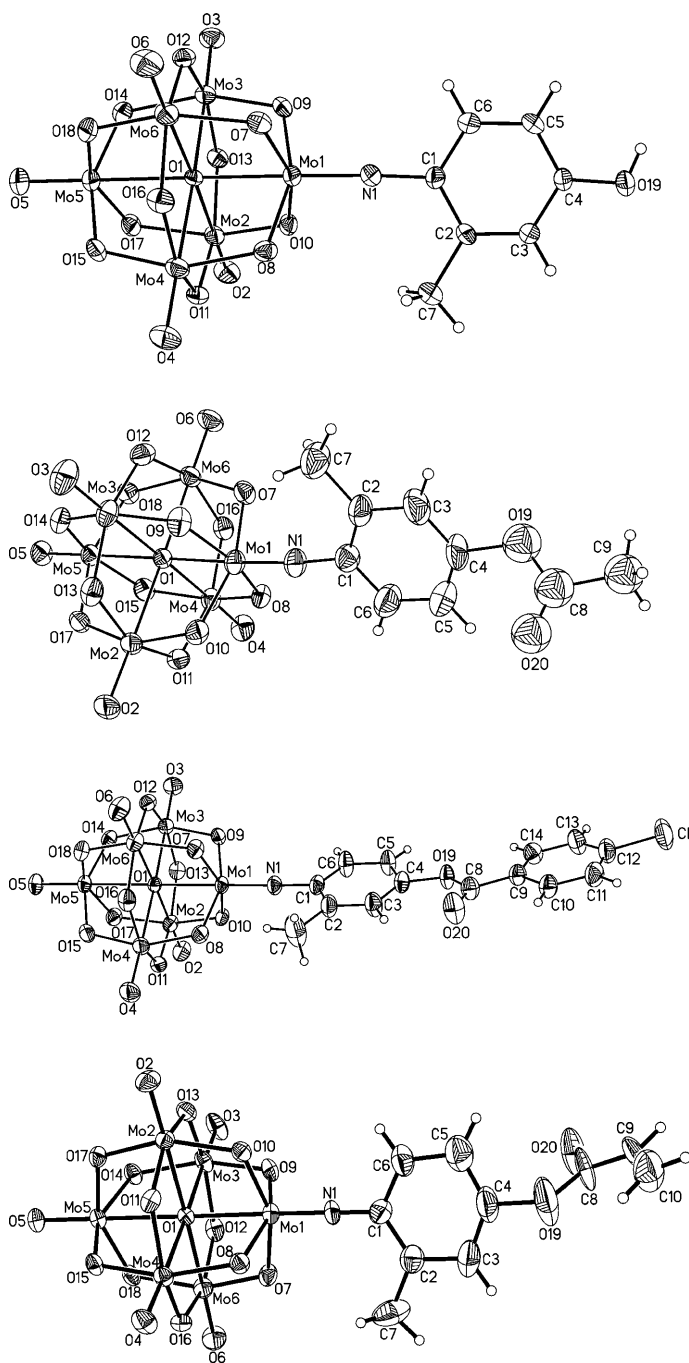Figure 2. 1D hydrogen bonding chain through O−H···O hydrogen bonds in the crystals of [(Bu₄N)₂]-**1**.

Figure 1. The ORTEP diagrams showing of molecular structures of the cluster anions **1**, **2a**, **2c**, and **2e** (from top to bottom) with atomic labeling schemes.

H···O hydrogen bonds (O19−H19···O7#1, 2.776(4) Å, 168.6°, symmetry code #1: $-x+1/2$, $y+1/2$, $-z+1/2$) between a cluster anion and its two neighbors arrange the cluster anions of **1** into 1D zigzag chain (Figure 2) parallel to the crystallographic *a* axis, in which the organoimido ligands are sandwiched by two rows of hexamolybdate clusters related by a 2_1 screw axis.

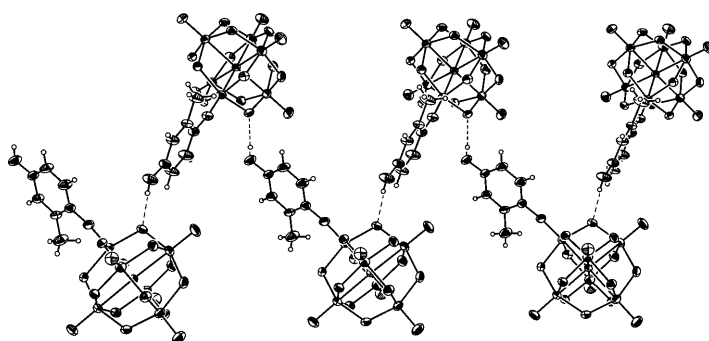In conclusion, we have successfully synthesized a novel organoimido derivative of hexamolybdate with a remote phe-

nolic-hydroxyl group, in which there is an interesting hydrogen-bonding supramolecular assembly in the solid state, and established that it can undergo an esterification reaction easily with various carboxylic acids. This study opens a way to prepare a new class of organic derivatives of POMs and corresponding hybrid materials. Extension of this esterification to other functionalized carboxylic acids, including cinnamic acids and bibasic acids, which are considered for making novel POM-based polymer hybrids and supramolecular building blocks, is also under study in our laboratory and will be published in subsequent papers.

Experimental Section

Synthesis of [(Bu₄N)₂]-1: A mixture of [Bu₄N]₄[α-Mo₈O₂₆] (1.0 mmol), DCC (2.5 mmol), the hydrochloride salt of 4-amino-*m*-cresol (1.34 mmol) was refluxed under nitrogen in anhydrous acetonitrile (10 mL) for about 12 h. During the course of the reaction the color of the solution changed into black-brown and some white precipitates (1, 3-dicyclohexylurea) were formed. The resulting brown-black solution was cooled down to room temperature and the brown precipitates were removed by filtration. Most of the acetonitrile was evaporated slowly in the open air. The black precipitate was collected by filtration, and recrystallized twice from the mixture of acetone and ethanol (1:1). The product was deposited as black-brown X-ray quality crystals in a yield of ≈70%. [(Bu₄N)₂]-**1**: ¹H NMR (300MHZ, [D₆]DMSO): $\delta = 0.98$ (t, 24H; CH₃, [Bu₄N]⁺), 1.60 (m, 16H; CH₂), 1.34 (m, 16H; CH₂, [Bu₄N]⁺), 2.56 (s, 3H; CH₃, CH₃Ar), 3.40 (t, 16H; NCH₂, [Bu₄N]⁺), 6.59 (d, 1H; ArH), 6.62 (s, 1H; ArH), 7.05 (d, 1H; AH), 10.04 ppm (s, Ar-OH); IR (KBr): $\tilde{\nu} = 975$ (m), 953 (s) [ν(Mo≡N, Mo=O)], 795 (s) [ν(MoOMo)], 3420 cm⁻¹ (m, w) [ν(OH)]; UV/Vis (MeCN): $\lambda_{max} = 226$, 252, 365 nm; elemental analysis (%) calcd for C₃₉H₇₉Mo₆N₃O₁₉ (1469.69): C 31.87, H 5.42, N 2.86; found: C 31.91, H 5.38, N 2.90.

Synthesis of [(Bu₄N)₂]-2: A mixture containing [(Bu₄N)₂]-**1** (1.0 mmol), a carboxylic acid (1.5 mmol) in anhydrous acetonitrile (15 mL) was heated ahead for 15 min, then was added DCC (2.0 mmol in 5 mL anhydrous acetonitrile). The reaction mixture was refluxed at a temperature of 85 °C for 10 h. After being cooled to room temperature, the resulting red-brown solution was filtered to remove some yellow-green precipitates. The red-brown filtrate was poured into 40 mL ice-water mixture with stirring continuously. Then the resulting brown solid product was collected by filtration. After being dried, the crude product was dissolved in 15 mL acetonitrile for recrystallization, and the product was obtained on evaporation as red-brown block crystals within 3 days (yield 75 to 82%). X-ray quality single crystals were grown in a test tube by slow dif-

fusion of the layered on Et_2O into an acetonitrile solution of the crude product.

Synthesis of [(Bu₄N)₂]-2 a: A mixture containing ([(Bu₄N)₂]-**1**) (1.0 mmol), acetic anhydride (1.0 mmol), and $NaHCO_3$ (1.0 mmol) was refluxed in anhydrous acetonitrile (20 mL) for about 10 H; then the resulting red-brown solution was filtered to remove some yellow-brown precipitates. The red-brown filtrate was poured into 40 mL ice-water mixture under continuous stirring, and the resulting red-brown solid product was collected by filtration. After being dried, the crude product was redissolved in 15 mL acetonitrile. The pure [(Bu₄N)₂]-**2 a** was deposited on evaporation as red-brown block crystals in ≈85 % yield within 3 days. X-ray quality single crystals were grown in a test tube by slow diffusion of the layered on Et_2O into an acetonitrile solution of the crude product.

Data for [(Bu₄N)₂]-2 a: ¹H NMR (300 MHz, [D₆]DMSO): $\delta = 0.96$ (t, 24 H; CH₃), 1.32 (sextet, 16 H; CH₂), 1.56 (m, 16 H; CH₃), 2.26 (s, 3 H; ArO-CO-CH₃), 2.55 (s, 3 H; CH₃-Ar), 3.16 (t, 16 H; NCH₂), 7.06 (d, 1 H; ArH), 7.08 (s, 1 H; ArH), 7.22 ppm (d, 1 H; ArH); IR (KBr): $\tilde{\nu} = 976$ (m), 952 (s) [ν(Mo=N, Mo=O)], 795 (s) [ν(MoOMo)], 1756 (m) [ν(C=O)], 1197 cm⁻¹ (m) [ν(C-O-C)]; UV/Vis (MeCN): $\lambda_{max} = 243$, 251, 354 nm; elemental analysis (%) calcd for C₄₁H₈₁Mo₆N₃O₂₀ (1511.73): C 32.58, H 5.40, N 2.78; found: C 32.45, H 5.32, N 2.70.

Data for [(Bu₄N)₂]-2 b: ¹H NMR(300 MHz, [D₆]DMSO): $\delta = 0.96$ (t, 24 H; CH₃), 1.32 (sextet, 16 H; CH₂) ,1.59 (m, 16 H; CH₃), 2.32 (s, 3 H; CH₃-Ar), 2.55 (s, 3 H; CH₃-Ar), 3.14 (t, 16 H; NCH₂), 7.06 (d, 1 H; ArH), 7.20 (s, 1 H; ArH), 7.22 (d, 1 H; ArH), 7.42 (d, 2 H; ArH), 7.88 ppm (d, 2 H; ArH); IR (KBr): $\tilde{\nu} = 973$ (m), 964 (s) [ν(Mo=N, Mo=O)], 797 (s) [ν(MoOMo)], 1735 (m) [ν(C=O)], 1210 cm⁻¹ (m) [ν(C-O-C)]; UV/Vis (MeCN): $\lambda_{max} = 245$, 253, 350 nm; elemental analysis (%) calcd for C₄₇H₈₅Mo₆N₃O₂₀ (1587.82): C 35.55, H 5.40, N 2.65; found: C 35.48, H 5.42, N 2.58.

Data for [(Bu₄N)₂]-2 c: ¹H NMR (300 MHz, [D₆]DMSO, 300k): $\delta = 0.96$ (t, 24 H; CH₃), 1.32 (sextet, 16 H; CH₂), 1.59(m, 16 H; CH₃), 2.59 (s, 3 H; CH₃-Ar), 3.14 (t, 16 H; NCH₂), 7.06 (d, 1 H; ArH), 7.26 (s, 1 H; ArH), 7.28 (d, 1 H; ArH), 7.58 (d, 2 H; ArH), 7.95 ppm (d, 2 H; ArH). IR (KBr): $\tilde{\nu} = 973$ (m), 952 (s) [ν(Mo=N, Mo=O)], 794 (s) [ν(MoOMo)], 1737 (m) [ν(C=O)], 1216 cm⁻¹ (m) [ν(C-O-C)]; UV/Vis (MeCN): $\lambda_{max} = 244$, 251, 348 nm; elemental analysis (%) calcd for C₄₆H₈₂ClMo₆N₃O₂₀ (1608.24): C 34.35, H 5.14, N 2.61; found: C 34.42, H 5.08, N 2.69. (1608.24):

Data for [(Bu₄N)₂]-2 d: ¹H NMR (300 MHz, [D₆]DMSO): $\delta = 0.94$ (t, 24 H; CH₃), 1.06 (t, 3 H; CH₃), 1.31 (sextet, 16 H; CH₂), 1.57 (m, 16 H; CH₃), 2.28 (q, 2 H; ArO-CO-CH₂), 2.55 (s, 3 H; CH₃-Ar), 3.16 (t, 16 H; NCH₂), 7.07 (d, 1 H; ArH), 7.14 (s, 1 H; ArH), 7.24 ppm (d, 1 H; ArH); IR (KBr): $\tilde{\nu} = 976$ (m), 952 (s) [ν(Mo=N, Mo=O)], 794 (s) [ν(MoOMo)], 1760 (m) [ν(C=O)], 1221 cm⁻¹ (m) [ν(C-O-C)]; UV/Vis (MeCN): $\lambda_{max} = 242$, 250, 353 nm; elemental analysis (%) calcd for C₄₂H₈₃Mo₆N₃O₂₀ (1525.75): C 33.06, H 5.48, N 2.75; found: C 33.19, H 5.40, N 2.71.

Data for [(Bu₄N)₂]-2 e: H NMR (300 MHz, [D₆]DMSO): $\delta = 0.94$ (t, 24 H; CH₃), 1.31 (sextet, 16 H; CH₂), 1.57 (m, 16 H; CH₃), 2.55 (s, 3 H; CH₃-Ar), 3.16 (t, 16 H; NCH₂), 6.16 (d, 1 H; =CH₂), 6.32 (d, 1 H; OOCCH=), 6.46 (d, 1 H; =CH₂), 7.06 (d, 1 H; ArH), 7.15 (s, 1 H; ArH), 7.23 ppm (d, 1 H; ArH); IR (KBr): $\tilde{\nu} = 976$ (m), 951 (s) [ν(Mo=N, Mo=O)], 792 (s) [ν(MoOMo)], 1740 (m) [ν(C=O)], 1213 cm⁻¹ (m) [ν(C-O-C)]; UV/Vis (MeCN): $\lambda_{max} = 228$, 250, 352 nm; elemental analysis (%) calcd for C₄₂H₈₁Mo₆N₃O₂₀ (1523.74): C 33.11, H 5.36, N 2.76; found: C 33.32, H 5.30, N 2.80.

Suitable crystals of [(Bu₄N)₂]-**1**, [(Bu₄N)₂]-**2 a**, **2 c**, and **2 e** were covered with mineral oil, mounted onto glass fibers, and transferred directly to a Bruker APEX CCD area-detector diffractometer at room temperature. Structures were solved by direct methods by using SHELXS-97 and refined against F^2 by full matrix least squares by using SHELXL-97. All non-hydrogen atoms were refined anisotropically, with the exception of some disordered atoms on the tetrabutylammonium cations, which were fixed after several cycles of refinement. Hydrogen atoms were located at their ideal calculated positions with riding model during the structure refinements. The largest peaks in the final difference Fourier map were of no chemical significance.

X-ray data for [(Bu₄N)₂]-1: C₃₉H₇₉Mo₆N₃O₁₉, $M_r = 14669.69$, monoclinic, space group $C2/c$, $a = 42.716(2)$ Å, $b = 12.7263(6)$ Å, $c = 23.8487(15)$ Å, $\beta = 120.165(2)°$, $V = 11208.9(10)$ Å³, $Z = 8$, $\rho_{calcd} = 1.742$ g cm⁻³, $T = 292(2)$ K, $F(000) = 5888$, $\mu(Mo_{K\alpha}) = 1.368$ mm⁻¹, block crystal with size = $0.30 \times 0.20 \times 0.10$ mm³, 43101 reflections measured, 11019 unique ($R_{int} = 0.0839$), 632 parameters, $R1 = 0.0408$ [$I > 2\sigma(I)$], $wR2 = 0.0763$ [$I > 2\sigma(I)$], GOF = 0.899.

X-ray data for [(Bu₄N)₂]-2 a: C₄₁H₈₁Mo₆N₃O₂₀, $M_r = 1511.73$, triclinic, space group $P\bar{1}$, $a = 12.6830(4)$ Å, $b = 12.8276(4)$ Å, $c = 19.4757(6)$ Å, $\alpha = 74.5620(10)°$, $\beta = 72.162(2)°$, $\gamma = 77.5080(10)°$, $V = 2875.87(16)$ Å³, $Z = 2$, $\rho_{calcd} = 1.746$ g cm⁻³, $T = 293(2)$ K, $F(000) = 1520$, $\mu(Mo_{K\alpha}) = 1.337$ mm⁻¹, block crystal size = $0.51 \times 0.13 \times 0.04$ mm³, 16913 reflections measured, 10094 unique ($R_{int} = 0.0490$), 604 parameters, $R1 = 0.0247$ [$I > 2\sigma(I)$], $wR2 = 0.0706$ [$I > 2\sigma(I)$], GOF = 1.082.

X-ray data for [(Bu₄N)₂]-2 c: C₄₆H₈₂ClMo₆N₃O₂₀, $M_r = 1608.24$, triclinic, space group $P\bar{1}$, $a = 12.3593(6)$ Å, $b = 12.9224(6)$ Å, $c = 20.4793(11)$ Å $\alpha = 78.010(3)°$, $\beta = 76.326(3)°$, $\gamma = 78.683(3)°$, $V = 3071.3(3)$ Å³, $Z = 2$, $\rho_{calcd} = 1.739$ g cm⁻³, $T = 293(2$ K, $F(000) = 1616$, $\mu(Mo_{K\alpha}) = 1.300$ mm⁻¹, block crystal with size = $0.52 \times 0.43 \times 0.21$ mm³, 20907 reflections measured, 10349 unique ($R_{int} = 0.0257$), 686 parameters, $R1 = 0.0406$ [$I > 2\sigma(I)$], $wR2 = 0.0892$ [$I > 2\sigma(I)$], GOF = 0.994.

X-ray data for [(Bu₄N)₂]-2 e: C₄₂H₈₁Mo₆N₃O₂₀, $M_r = 1523.74$, triclinic, space group $P\bar{1}$, $a = 12.7096(14)$ Å, $b = 12.9021(13)$ Å, $c = 19.504(2)$ Å, $\alpha = 73.892(4)°$, $\beta = 72.916(4)°$. $\gamma = 79.245(4)°$, $V = 2917.9(5)$ Å³, $Z = 2$, $\rho_{calcd} = 1.734$ g cm⁻³, $T = 293(2$ K, $F(000) = 1532$, $\mu(Mo_{K\alpha}) = 1.319$ mm⁻¹, plate crystal with size = $0.40 \times 0.21 \times 0.11$ mm³, 17634 reflections measured, 9743 unique ($R_{int} = 0.0364$), 598 parameters, $R1 = 0.0586$ [$I > 2\sigma(I)$], $wR2 = 0.1147$ [$I > 2\sigma(I)$], GOF = 1.018.

CCDC 691254 ([(Bu₄N)₂]-**1**), 691255 ([(Bu₄N)₂]-**2 a**), 691256 ([(Bu₄N)₂]-**2 c**), and 691257 ([(Bu₄N)₂]-**2 e**) contains the supplementary crystallographic 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

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