Ensheathing a Polyoxometalate: Convenient Systematic Introduction of Organoimido Ligands at Terminal Oxo Sites in $[Mo_6O_{19}]^{2-}$

Joseph B. Strong,[†] Robert Ostrander,[‡]
Arnold L. Rheingold,[‡] and Eric A. Maatta*[,†]

Departments of Chemistry
Kansas State University
Manhattan, Kansas 66506-3701
University of Delaware
Newark, Delaware 19716

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Polyoxometalates comprise species presenting a remarkable variety of unusual structural, electrochemical, magnetic, and catalytic properties.[1] The introduction of rational means for the direct modification of polyoxometalate systems will likely stimulate further development and utility of these species. We report a simple and general method for the direct functionalization of the hexamolybdate cluster, $[Mo_6O_{19}]^{2-}$, through which peripheral oxo ligands can be systematically replaced by a variety of organoimido groups.[2]

Reaction of $[n\text{-}Bu_4N]_2[Mo_6O_{19}]$ with various organic isocyanates in hot pyridine occurs as shown in eq 1. Each of the three

$$[Bu_4N]_2[Mo_6O_{19}] + RNCO \rightarrow [Bu_4N]_2[Mo_6O_{18}(NR)] + CO_2 \quad (1)$$

1-Bu (R = *n*-Bu)
1-Cy (R = cyclohexyl)
1-Ar (R = 2,6-(*i*-Pr)$_2$C$_6$H$_3$)

monosubstituted hexamolybdate derivatives depicted in eq 1 has been characterized by elemental analysis, ^1H NMR spectroscopy, cyclic voltammetry, and single-crystal X-ray diffraction studies.[3] In each of these species, the organoimido substituent adopts a terminal position on the hexamolybdate cage.

In the case of the 2,6-(diisopropylphenyl)imido ligand (hereafter referred to as NAr), we have discovered that multiple functionalization is also readily achieved, as shown in eq 2. Thus

$$[Bu_4N]_2[Mo_6O_{19}] + x\text{ArNCO} \rightarrow [Bu_4N]_2[Mo_6O_{(19-x)}(NAr)_x] + xCO_2 \quad (2)$$

2 ($x = 2$)
4 ($x = 4$)
5 ($x = 5$)

far, hexamolybdate derivatives incorporating two (**2**),[4] four (**4**),[5] and five (**5**)[6] (NAr) groups have been prepared in one-step reactions between the hexamolybdate and varying amounts of ArNCO. Workup of all of the above reactions consists simply of evaporating solvent, washing the residue with Et$_2$O, and crystallizing from CH$_3$CN/Et$_2$O. Yields of crystalline material are as follows: **2**, 67%; **4**, 35%; **5**, 86%.

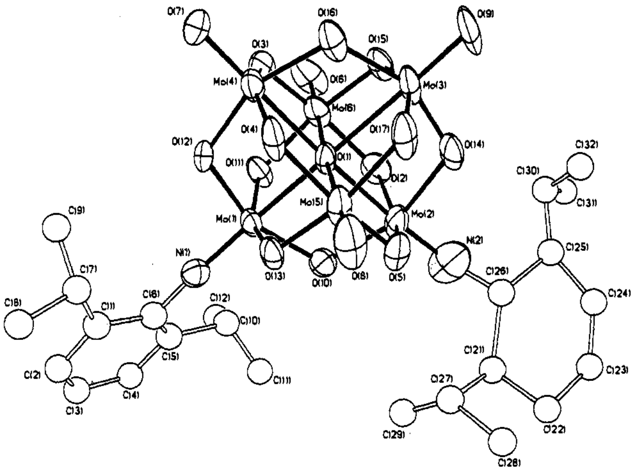

Figure 1. ORTEP representation of the structure of the $[Mo_6O_{17}(NAr)_2]^{2-}$ anion in **2** drawn with 35% probability ellipsoids.

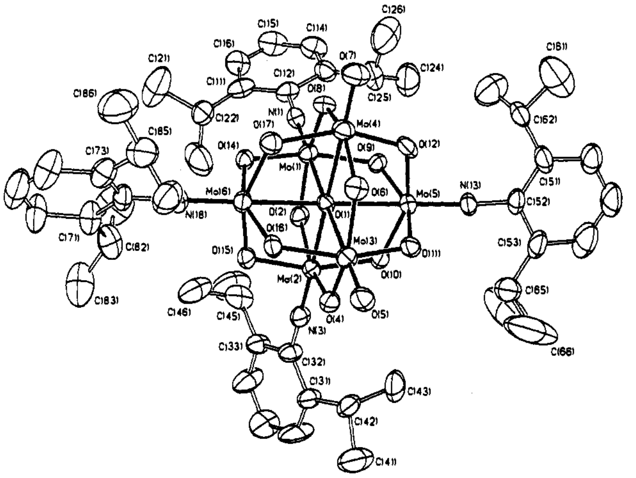

Figure 2. ORTEP representation of the structure of the $[Mo_6O_{15}(NAr)_4]^{2-}$ anion in **4**·2CH$_3$CN drawn with 35% probability ellipsoids. Selected bond lengths (Å) and angles (deg): Mo(1)–N(1), 1.760(10); Mo(2)–N(3), 1.710(10); Mo(5)–N(13), 1.731(11); Mo(6)–N(18), 1.742(11); Mo(3)–O(5), 1.704(8); Mo(4)–O(7), 1.686(9); Mo(1)–O(1), 2.267(7); Mo(2)–O(1), 2.243(7); Mo(3)–O(1), 2.388(7); Mo(4)–O(1), 2.406(7); Mo(5)–O(1), 2.292(8); Mo(6)–O(1), 2.282(8); Mo(1)–N(1)–C(12), 178.8(10); Mo(2)–N(3)–C(32), 177.8(9); Mo(5)–N(13)–C(52), 175.5(10); Mo(6)–N(18)–C(72), 178.5.

The molecular structures of $[Mo_6O_{17}(NAr)_2]^{2-}$ (**2**)[7] and $[Mo_6O_{15}(NAr)_4]^{2-}$ (**4**)[8] have been determined by single-crystal X-ray diffraction methods. In the case of the bis(imido) derivative **2** (Figure 1), the quality of the data set does not allow detailed structural analysis but the connectivity within the anion is clearly established. Contrary to expectations based on steric considerations, **2** adopts a *cis* structure with the imido groups occupying adjacent terminal positions on the hexamolybdate cage, suggesting that the presence of one imido substituent exerts an activating effect at proximal oxo sites. As shown in Figure 2, the tetrakis(NAr) derivative **4** similarly displays a structure in which the

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[†] Kansas State University.

[‡] University of Delaware.

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(2) The only previous examples of imido–polyoxometalates are $[Bu_4N]_2[Mo_6O_{18}(NR)]$ (R = *p*-tolyl and *t*-Bu): (a) Kang, H.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1988**, 1192. (b) Du, Y.; Rheingold, A. L.; Maatta, E. A. *J. Am. Chem. Soc.* **1992**, *114*, 345. (c) Clegg, W.; Errington, R. J.; Fraser, K. A.; Lax, C.; Richards, D. G. *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity*; Pope, M. T., Müller, A., Eds.; Kluwer Academic Publishers: Dordrecht, 1994; p 113.

(3) Complete details regarding these species will be published elsewhere.

(4) Anal. Calcd for $C_{56}H_{106}N_4O_{17}Mo_6$: C, 39.96; H, 6.35; N, 3.33. Found: C, 39.59; H, 6.49; N, 3.32. ^1H NMR (CD$_3$CN, 25 °C): δ 7.140 (d, C$_6$*H*$_3$(*m*), 4 H), 7.015 (m, C$_6$*H*$_3$(*p*), 2H), 3.908 (m, C*H*(CH$_3$)$_2$, 4 H), 3.110 (m, NC*H*$_2$, 16 H), 1.606 (m, C*H*$_2$, 16 H), 1.376 (m, C*H*$_2$, 16 H), 1.278 (m, CH(C*H*$_3$)$_2$, 24 H), 0.948 (t, C*H*$_3$, 24 H).

(5) Anal. Calcd for $C_{80}H_{140}N_6O_{15}Mo_6$: C, 48.00; H, 7.05; N, 4.20; O, 11.99. Found: C, 47.88; H, 7.02; N, 3.41; O, 11.61. ^1H NMR (CD$_3$CN, 25 °C): δ 7.102 (m, C$_6$*H*$_3$(*m*), 8 H), 6.951 (m, C$_6$*H*$_3$(*p*), 4 H), 3.985 (m, C*H*(CH$_3$)$_2$, 8 H), 3.077 (m, NC*H*$_2$, 16 H), 1.580 (m, C*H*$_2$, 16 H), 1.340 (m, C*H*$_2$, 16 H), 1.275 (m, CH(C*H*$_3$)$_2$, 48 H), 0.944 (t, C*H*$_3$, 24 H).

(6) Anal. Calcd for $C_{92}H_{157}N_7O_{14}Mo_6$: C, 51.14; H, 7.32; N, 4.54. Found: C, 51.16; H, 7.48; N, 4.61. ^1H NMR (CD$_3$CN, 25 °C): δ 7.060 (m, C$_6$*H*$_3$(*m*), 10 H), 6.900 (m, C$_6$*H*$_3$(*p*), 5 H), 4.033 (m, C*H*(CH$_3$)$_2$, 10 H), 3.064 (m, NC*H*$_2$, 16 H), 1.570 (m, C*H*$_2$, 16 H), 1.333 (m, C*H*$_2$, 16 H), 1.284 (m, CH(C*H*$_3$)$_2$, 60 H), 0.934 (t, C*H*$_3$, 24 H).

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two remaining terminal oxo sites are mutually *cis*, rather than the presumably less crowded alternative arrangement with four equatorially disposed NAr groups and *trans*-positioned oxo ligands.

Selected bond lengths and bond angles for **4** are collected in Figure 2; of note are the very long distances from Mo(3) and Mo(4) to O(1) of 2.388(7) and 2.406(7) Å, respectively. In the parent $[Mo_6O_{19}]^{2-}$ structure, analogous Mo–O bond lengths are 2.32 Å.[9]

The availability of these homologous oxo/(NAr) hexamolybdate derivatives provides an opportunity to examine how the electrochemical properties of the clusters respond to varying degrees of substitution. Cyclic voltammetry studies in acetonitrile were conducted on the hexamolybdate and its mono-, bis-, and tetrakis(NAr) derivatives. In Figure 3 are plotted the potentials of the first, reversible reductions observed for each of the four homologues (a second quasi-reversible process was also observed in each case). It is seen that each successive incorporation of an arylimido ligand renders the reduction potential less favorable by ca. 220 mV. For **5**, the onset of an irreversible process was noted at ca. −2000 mV. These data clearly indicate that the NAr ligand is a superior electron donor in comparison to an oxo ligand.[10]

Given the ready availability of various organic isocyanates, the present work suggests that it will be possible to logically design and rationally synthesize a broad range of hexamolybdate derivatives of potential utility. For example, it is now possible to conceive of incorporating hexamolybdate clusters into extended arrays, either by employing isocyanates bearing a reactive additional functionality or by using diisocyanate building blocks. An important question awaiting study is whether the enhanced electron donation provided by successive imido incorporation renders these hexamolybdate derivatives reactive toward various electrophiles.[11] We are exploring these and other ideas.

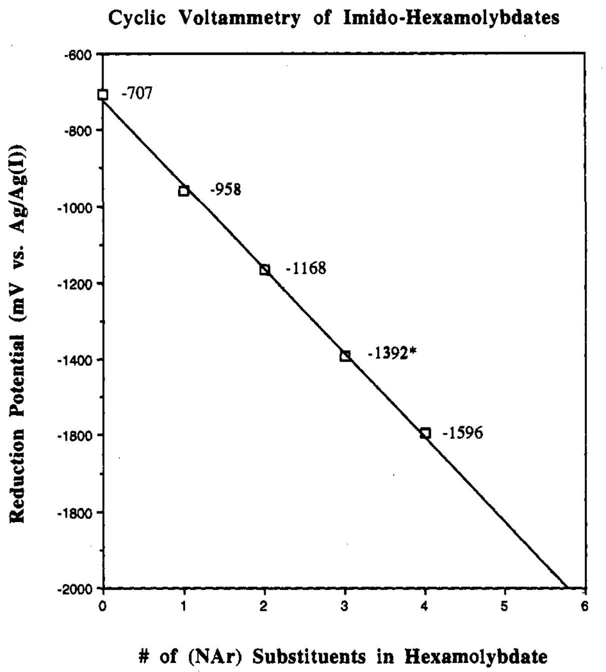

Figure 3. Reduction potentials of arylimido–hexamolybdate derivatives as determined by cyclic voltammetry. Conditions: MeCN solvent, 298 K, Pt working electrode, sweep rate 100 mV/s, $[Bu_4N]PF_6$ supporting electrolyte. The asterisk (*) indicates a minor wave observed in the CV of **4** and ascribed to $[Mo_6O_{16}(NAr)_3]^{2-}$.

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Supplementary Material Available: For **2** and **4**: tables of complete data collection information, atomic coordinates, bond distances, bond angles, anisotropic thermal parameters, and H-atom positional parameters (41 pages); structure factor tables (54 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(7) Crystal data for $C_{56}H_{106}N_4O_{17}Mo_6$ (**2**): orange-brown blocks, triclinic, $P\bar{1}$, a = 12.863(4) Å, b = 12.829(4) Å, c = 22.090(6) Å, α = 88.51(3)°, β = 86.21(3)°, γ = 78.19(3)°, V = 3560(2) Å^3, Z = 2; 11 207 independent reflections were collected (T = 238 K, $4° \leq 2\theta \leq 45°$), of which 5511 with $F_o > 4\sigma(F_o)$ were used in refinement. The centrosymmetric space group was chosen on the initial basis of E values and retained on the basis of the refinement statistics and molecular symmetry. A semiempirical absorption correction was applied (T_{max}/T_{min} = 1.19). All non-hydrogen atoms except carbon were refined anisotropically. H atoms were treated as idealized isotropic contributions. R = 9.42%, and R_w = 12.95%.

(8) Crystal data for $C_{84}H_{146}N_8O_{15}Mo_6$ ($4 \cdot 2CH_3CN$): orange crystals, monoclinic, $P2_1/n$, a = 16.227(9) Å, b = 22.868(7) Å, c = 26.766(13) Å, β = 93.30(4)°, V = 9916(8) Å^3, Z = 4; 13 279 independent reflections were collected (T = 233 K, $4° \leq 2\theta \leq 45°$), of which 7353 with $F_o > 4\sigma(F_o)$ were used in refinement. A semiempirical absorption correction was applied (T_{max}/T_{min} = 1.30). With the exception of the atoms in one disordered acetonitrile molecule, all non-hydrogen atoms were refined anisotropically. H atoms were treated as idealized isotropic contributions. R = 6.51%, and R_w = 8.45%.

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(11) See, for example, the following and references therein: (a) Knoth, W. H.; Harlow, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 4265. (b) Che, T. M.; Day, V. W.; Francesconi, L. C.; Fredrich, M. F.; Klemperer, W. G.; Shum, W. *Inorg. Chem.* **1985**, *24*, 4055. (c) Day, V. W.; Klemperer, W. G.; Schwartz, C. *J. Am. Chem. Soc.* **1987**, *109*, 6030.