

## Polyoxometalate Clusters as Building Blocks: Preparation and Structure of Bis(hexamolybdate) Complexes Covalently Bridged by Organodiimido Ligands

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Covalently linked polyoxometalate clusters are produced in the reaction of organic diisocyanates with  $[\text{Bu}_4\text{N}]_2[\text{Mo}_6\text{O}_{19}]$ , suggesting the development of extended interconnected networks incorporating polyoxometalate ions.

Polyoxoanions of the early transition metals ('polyoxometalate clusters')<sup>1</sup> offer a fascinating diversity of structural, electrochemical, magnetic and catalytic properties. Typically, the structures of these polyoxoanions are built up from edge- and corner-shared octahedra and as such, are reminiscent of the close-packed structures of metal oxide lattices.<sup>2</sup> The structure<sup>3</sup> of the hexamolybdate cluster  $[\text{Mo}_6\text{O}_{19}]^{2-}$  features six terminal oxygen atoms aligned along the Cartesian axes. If the terminal oxygen atoms could be rendered as reactive sites, the hexamolybdate could serve as an octahedrally-directing template with which to build new types of interconnected extended polyoxometalate networks analogous to the beautiful and diverse examples of cascade molecules (arborols) which are now the focus of intense activity in the field of supramolecular chemistry.<sup>4</sup> Given recent demonstrations of direct<sup>5</sup> and multiple<sup>6</sup> functionalization of the terminal oxo sites in the hexamolybdate to afford the corresponding organoimido derivatives, we became interested in linking hexamolybdate cages using organodi-imido<sup>7-9</sup> bridging ligands. We now report our first successes in that endeavour through the syntheses and characterization of complexes of the form  $[\text{Bu}_4\text{N}]_4[(\text{Mo}_5\text{O}_{18})\text{Mo}\equiv\text{N}-\text{Z}-\text{N}\equiv\text{Mo}(\text{Mo}_5\text{O}_{18})]$ , **1**, ( $\text{Z} = p\text{-C}_6\text{H}_4$ , **1a**;  $\text{Z} = p\text{-(C}_6\text{H}_3\text{Me)}$ , **1b**;  $\text{Z} = 1,4\text{-cyclo-C}_6\text{H}_{10}$ , **1c**).

Reaction of  $[\text{Bu}_4\text{N}]_2[\text{Mo}_6\text{O}_{19}]$  with 0.5 equiv. of various diisocyanates in dry pyridine occurs with evolution of  $\text{CO}_2$  and formation of the corresponding organodi-imido bridged bis(hexamolybdate) derivatives (Scheme 1).<sup>†</sup> Complexes **1** are soluble in acetonitrile, pyridine and nitromethane, somewhat soluble in 1,2-dichloroethane, and insoluble in diethyl ether, benzene, and hexane. The <sup>1</sup>H NMR spectrum of the *p*-phenylenediimido system **1a** displays a characteristic singlet for the phenylene protons ( $\delta = 7.18$ ) indicative of a symmetric binding mode for the  $[\text{N}-\text{C}_6\text{H}_4-\text{N}]$  bridge. The protons attached to the  $\alpha$ -carbons of the cyclohexyl ring in **1c** are shifted significantly downfield ( $\delta = 4.74$ ), suggesting that they are rendered somewhat acidic upon incorporation into the diimido ligand framework.<sup>10</sup> The IR spectra of complexes **1** are very similar to that of  $[\text{Bu}_4\text{N}]_2[\text{Mo}_6\text{O}_{19}]$ , except for the presence of a medium-intensity shoulder absorption at  $970\text{ cm}^{-1}$ ; while this

feature may derive from a component associated with the  $[\text{Mo}\equiv\text{N}-\text{Z}-\text{N}\equiv\text{Mo}]$  unit, we note that similar bands have been reported in the spectra of, *e.g.*, the  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ti}(\text{M}_5\text{O}_{18})]^{3-}$  systems ( $\text{M} = \text{Mo}, \text{W}$ ) of Klemperer,<sup>11</sup> and thus this band may be associated with a stretching vibration of the unique *trans*- $\text{Mo}\equiv\text{O}$  unit of the substituted clusters.

The electronic spectrum of **1c** in acetonitrile contains bands at 240 ( $\epsilon = 3.117 \times 10^4$ ) and 322 nm ( $\epsilon = 1.45 \times 10^4$ ); in comparison, the spectrum of the cyclohexylimido monohexamolybdate system  $[\text{Mo}_6\text{O}_{18}(\text{NCy})]^{2-}$  displays bands at 211 nm ( $\epsilon = 3.48 \times 10^4$ ) and 325 nm ( $\epsilon = 7.00 \times 10^3$ ).<sup>6a</sup> The corresponding spectrum of **1a** displays bands at 257 ( $\epsilon = 4.44 \times 10^4$ ) and 424 nm ( $\epsilon = 4.65 \times 10^4$ ) while that of the 2,6-diisopropylphenylimido analogue  $[\text{Mo}_6\text{O}_{18}(\text{NAr})]^{2-}$  contains bands at 211 ( $\epsilon = 4.29 \times 10^4$ ) and 351 nm ( $\epsilon = 1.90 \times 10^4$ ).<sup>6a</sup>

The structure of the anion within **1c**† (Fig. 1) consists of two terminally substituted imido-hexamolybdate cages bridged by a *trans*-1,4-disubstituted cyclohexane ring. An inversion centre resides at the centroid of the cyclohexane unit. The imido-hexamolybdate substituents of the cyclohexane are poised in a diaxial arrangement. The short Mo–N bond length [1.685(19)

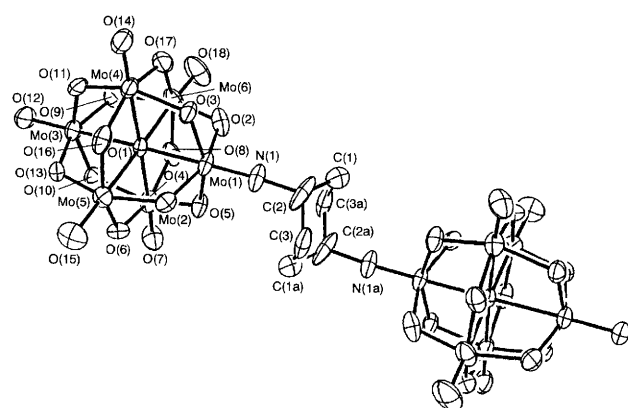
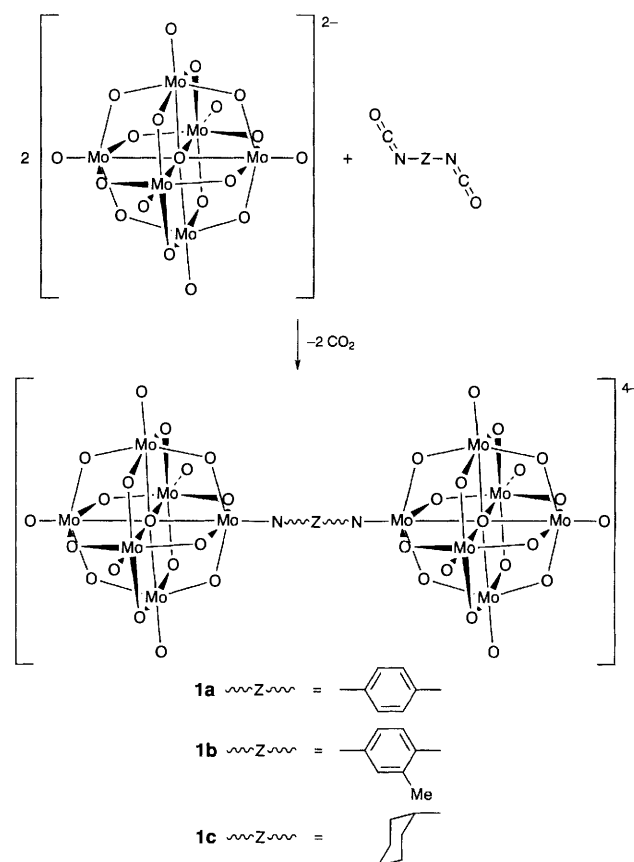


Fig. 1 ORTEP representation of the structure of the *trans*-1,4-cyclohexyldiimido bis(hexamolybdate) tetraanion within **1c**



Scheme 1 Synthesis of organodi-imido bridged bis(hexamolybdate) complexes **1**

Å] and nearly linear Mo–N–C angle [174.3(22)°] are typical of Mo≡NR interactions in Mo<sup>VI</sup> imido complexes. As has been observed previously,<sup>5,6</sup> the bond from the imido-bearing Mo(1) atom to the central O(1) atom is substantially shorter [2.211(12) Å] than the other Mo–O(1) interactions (2.34 Å avg.). There are no appreciable variations in the terminal Mo=O bond lengths, which span the narrow range from 1.679(16)–1.728(13) Å. Bond lengths involving the μ<sup>2</sup>-oxygen atoms show considerable variations, however, ranging from 1.873(18) to 1.974(13) Å.

Preliminary experiments reveal a rich electrochemistry for complexes **1**. Cyclic voltammetry studies in dimethylformamide (298 K; Pt working electrode; 200 mV<sup>-1</sup> s; [Bu<sub>4</sub>N]PF<sub>6</sub> supporting electrolyte) reveal two quasi-reversible reduction waves for **1c** with *E*<sub>1/2</sub> values of –1165 and –2008 mV (vs. Ag/Ag<sup>+</sup>). For **1a**, a quasi-reversible reduction centered at –980 mV is followed by a reversible reduction at –1524 mV; the onset of a third irreversible reduction can be seen at –2178 mV. These are one-electron processes, as demonstrated by comparisons of peak currents to those of known amounts of ferrocene (*E*<sub>1/2</sub> = +66 mV) added as an internal standard.

This study has demonstrated the construction of soluble redox-active systems incorporating hexamolybdate frameworks and, when coupled with our previous demonstration of multiple functionalization of [Mo<sub>6</sub>O<sub>19</sub>]<sup>2-</sup>, suggests that the synthesis of extended networks comprising covalently linked polyoxometalate systems is an achievable goal.

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## Footnotes

† *Preparation and Characterization*: [Bu<sub>4</sub>N]<sub>2</sub>[Mo<sub>6</sub>O<sub>19</sub>] (1.1 mmol) and the appropriate diisocyanate (0.56 mmol) were stirred in dry pyridine (60 cm<sup>3</sup>) under N<sub>2</sub> for 3 d (**1a** and **1b** at 95 °C; **1c** at 25 °C), whereupon volatiles were removed by vacuum. Thereafter, complexes **1a** and **1b** were washed with CH<sub>2</sub>Cl<sub>2</sub> (ca. 50 cm<sup>3</sup>). After vacuum drying, examination of the crude products by <sup>1</sup>H NMR spectroscopy revealed the following yields (based on relative integrations): **1a**, 60%; **1b**, 60%; **1c**, 80%. Red (**1a** and **1b**) or yellow–orange (**1c**) crystals of each complex were grown with difficulty by careful diffusion of Et<sub>2</sub>O vapour into MeNO<sub>2</sub> solutions at room temperature. For **1a** C<sub>70</sub>H<sub>148</sub>N<sub>6</sub>O<sub>36</sub>Mo<sub>12</sub>. δ<sub>H</sub> (CD<sub>3</sub>CN, 23 °C) 7.18 (s, 4 H, C<sub>6</sub>H<sub>4</sub>), 3.09 (m, 32 H, NCH<sub>2</sub>), 1.60 (m, 32 H, CH<sub>2</sub>), 1.35 (m, 32 H, CH<sub>2</sub>), 0.96 (48 H, t, <sup>2</sup>J = 7, CH<sub>3</sub>). For **1b**, C<sub>71</sub>H<sub>150</sub>N<sub>6</sub>O<sub>36</sub>Mo<sub>12</sub>. δ<sub>H</sub> 7.16–6.98 (3 H, m, C<sub>6</sub>H<sub>3</sub>), 3.09 (32 H, m, NCH<sub>2</sub>), 2.50 (3 H, s, ring CH<sub>3</sub>), 1.60 (32 H, m, CH<sub>2</sub>), 1.35 (32 H, m, CH<sub>2</sub>), 0.96 (48 H, t, <sup>2</sup>J = 7 CH<sub>3</sub>). For **1c**, C<sub>70</sub>H<sub>154</sub>N<sub>6</sub>O<sub>36</sub>Mo<sub>12</sub>. δ<sub>H</sub> 4.74 (2 H, s, CH), 3.11 (32 H, m, NCH<sub>2</sub>), 2.25 (4 H, d, <sup>2</sup>J = 10, ring CH<sub>2</sub>), 1.92 (4 H partially obscured d, <sup>2</sup>J = 10, ring CH<sub>2</sub>), 1.61 (32 H, m, CH<sub>2</sub>), 1.35 (32 H, m, CH<sub>2</sub>), and 0.97 (48 H, t, <sup>2</sup>J = 7, CH<sub>3</sub>).

‡ *Crystal data* for **1c** Orange block (0.22 × 0.26 × 0.34 mm), triclinic, *P* $\bar{1}$ , *a* = 12.066(4), *b* = 12.424(6), *c* = 19.463(9) Å, α = 107.38(2), β =

92.17(1), γ = 99.35(1)°, *V* = 2736(2) Å<sup>3</sup>, *Z* = 1, Mo–Kα (λ = 0.71073 Å), μ = 1.396 mm<sup>-1</sup>, *D*<sub>c</sub> = 1.704, *T* = 295 K. Using a Siemens R3m/V diffractometer, a total of 8876 reflections (8589 independent) were collected (4° ≤ 2θ ≤ 45°), of which 3933 with *F*<sub>o</sub> > 5σ*F*<sub>o</sub> were used in refinement. An empirical absorption correction was applied to the data. The structure was solved by direct methods and expanded by a succession of difference Fourier syntheses. While the anionic portion of the structure is fully ordered, the two tetrabutylammonium cations are highly disordered. The appearance of the disorder suggests that at least two N-atom sites exist within each cation. Occupations were assigned values of either 0.5 or 1.0 according to their thermal parameters and apparent alkyl-chain position, and the total was adjusted to the correct stoichiometry. All non-hydrogen atoms of the anions were refined with anisotropic thermal parameters and those of the cations were isotropically refined. No attempt was made to locate or assign hydrogen atoms. All calculations used the software contained in the SHELXTL(PC) software libraries (G. Sheldrick, Siemens XRD, Madison, WI). The quantity minimized in refinement was Σw(*F*<sub>o</sub> – *F*<sub>c</sub>)<sup>2</sup>, where w<sup>-1</sup> = σ<sup>2</sup>(*F*) + 0.0025*F*<sup>2</sup>. At convergence (417 parameters refined), *R* = 0.0736, w*R* = 0.1080, GOF = 1.67, largest difference peak = 1.20 eÅ<sup>-3</sup>, largest difference hole = –0.57 eÅ<sup>-3</sup>. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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