Functionalisation of $[Mo_6O_{19}]^{2-}$ with Aromatic Amines: Synthesis and Structure of a Hexamolybdate Building Block with Linear Difunctionality

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In reactions between the hexamolybdate $[Mo_6O_{19}]^{2-}$ and 1,4-diaminobenzene, terminal oxides are replaced by 4-aminophenylimido ligands and the first structurally characterised polyoxometallate to contain functionalised organoimido ligands, $(Bu^n{}_4N)_2[Mo_6O_{17}(NC_6H_4NH_2)_2]$ **5**, is also the first example of a *trans*-bis(imido) derivative; further condensation also occurs to yield species in which hexamolybdate units are linked by 1,4-phenylenediimido bridges.

We are developing rational strategies for the surface modification of polyoxometallate structures whereby oxide ligands are replaced by organoimido groups. Maatta and coworkers have used phosphinimines to prepare arylimido hexamolybdates [eqn. (1)] and have reported the structure of $[Mo_6O_{18}(NC_6H_4Me\text{-}4)]^{2-}$.[1] This route is less useful for alkylimido analogues, but we have shown that reactions with isocyanates [eqn. (2)] afford aryl *and* alkyl derivatives and have structurally characterised the first alkylimido-substituted polyoxometalate, $[Mo_6O_{18}(NBu^t)]^{2-}$.[2] We have now found that aromatic amines will also react with $[Mo_6O_{19}]^{2-}$ in the presence of triethylamine [eqn. (3)], broadening the range of accessible organoimido-substituted molybdates. Using this route we have prepared and structurally characterised the tetrabutylammonium salts of $[Mo_6O_{18}(NC_6H_4Bu^t\text{-}4)]^{2-}$ and $[Mo_6O_{18}(NC_6H_3Pr^i{}_2\text{-}2,6)]^{2-}$, full details of these reactions will be published elsewhere.

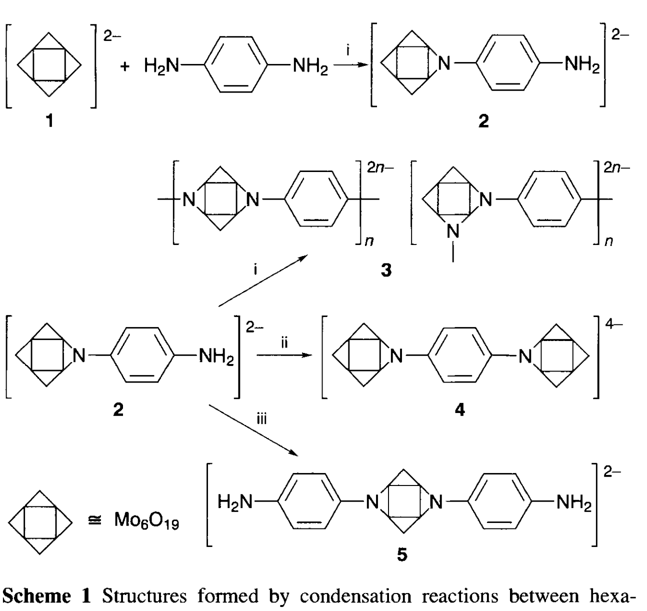
$$[Mo_6O_{19}]^{2-} + Ph_3P{=}NAr \rightarrow [Mo_6O_{18}(NAr)]^{2-} + Ph_3P{=}O \quad (1)$$

$$[Mo_6O_{19}]^{2-} + RNCO \rightarrow [Mo_6O_{18}(NR)]^{2-} + CO_2 \quad (2)$$

$$[Mo_6O_{19}]^{2-} + ArNH_2 \rightarrow [Mo_6O_{18}(NAr)]^{2-} + H_2O \quad (3)$$

Phenylenediimido ligands are attracting attention as a means of bridging higher oxidation-state transition metals with a non-labile, delocalised π system.[3] Following our determination of the first crystal structure of such a complex,[3e] we were keen to extend this strategy to polyoxometallates in view of the established redox properties of these molecular metal oxide structures. However, our attempts to react $(Bu^n{}_4N)_2[Mo_6O_{19}]$ **1** with 1,4-diisocyanatobenzene using similar conditions to those we had previously used in reactions with RNCO (*i.e.* MeCN or PhCN solvent, elevated temperatures) led to intractable products. [Maatta and coworkers have subsequently developed this approach successfully using dry pyridine as the solvent.[4]] Our efforts involving diamines have been more successful and we report here our preliminary studies of reactions between **1** and 1,4-diaminobenzene from which, by varying the stoichiometry, we have isolated phenylenediimido-bridged hexamolybdate compounds and the new *trans*-difunctionalised hexamolybdate $(Bu^n{}_4N)_2[Mo_6O_{17}(NC_6H_4NH_2)_2]$ **5**.

^1H NMR studies of the products from reactions between **1** and 1,4-diaminobenzene in benzonitrile at *ca.* 150 °C in the presence of triethylamine are indicative of the condensation processes shown in Scheme 1. The aromatic and amine resonances of the product from the reaction between **1** and 0.5 equiv. of diamine (after an initial recrystallisation from hot MeCN to remove unreacted starting material) are shown in Fig. 1(*a*). All chemical shifts are higher than those in the free diamine [δ 6.47 (C_6H_4), 3.60 (NH_2)]. The AB type pattern of an unsymmetrically substituted phenylene ring is probably due to the expected initial product of substitution **2**. This assignment is consistent with cyclic voltammetry results (see below) and microanalytical data for a purified sample. The singlets must be due to symmetrically substituted phenylene groups in either polymeric or oligomeric **3**, formed by further condensation at the free amino group in **2** (note that *cis*-disubstitution at each Mo_6 unit could feasibly give a cyclic tetramer), or to the bridged species **4**. After recrystallisation, the singlet at δ 7.21 and a much less intense singlet at δ 7.18 were the only peaks in the aromatic region. The singlet at δ 7.18 is due to the tetraanion **4** formed by condensation between **2** and hexamolybdate **1** which has also been synthesised by Maatta from **1** and 0.5 equiv. of 1,4-diisocyanatobenzene.[4] A sample of this mixture was further purified for microanalysis and the results are consistent with an oligomeric structure **3**.



Scheme 1 Structures formed by condensation reactions between hexametallate **1** and 1,4-diaminobenzene. *Reagents*: i, Et_3N (cat.); ii, $[Mo_6O_{19}]^{2-}$, Et_3N (cat.); iii, $H_2NC_6H_4NH_2$, Et_3N (cat.).

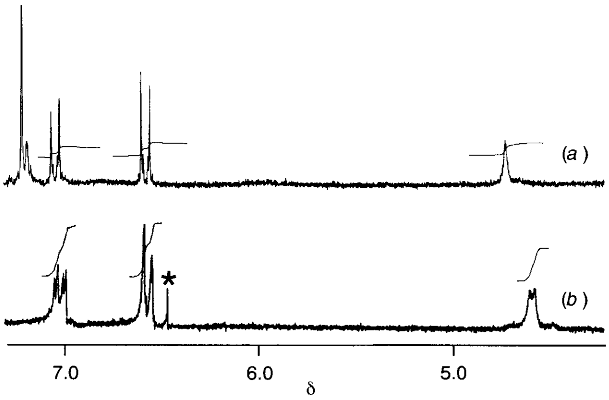


Fig. 1 Aromatic and amino resonances in the ^1H NMR spectra of the products from reactions between **1** and (*a*) 0.5 equiv. and (*b*) 2.0 equiv. of 1,4-diaminobenzene. The peak marked with an asterisk is due to $C_6H_4(NH_2)_2$-1,4.

In the reaction between **1** and 2.0 equiv. of 1,4-phenylenediamine, two (possibly isomeric) products having unsymmetric phenylene groups and different NH_2 chemical shifts from that in Fig. 1(*a*) are observed [Fig. 1(*b*)]. Recrystallisation afforded predominantly the component with the higher chemical shifts and a cation : ligand ratio of *ca.* 1 : 1, *i.e.* $(Bu^n_4N)_2[Mo_6O_{17}(NC_6H_4NH_2)_2]$ **5**, although microanalysis indicated some contamination by residual **1**. A crystal structure determination revealed a linear, centrosymmetric anion with terminal amine groups (Fig. 2).† This is the first *trans*-bis(imido)-hexamolybdate, the only other structurally characterised disubstituted imido derivatives[5] being *cis*-$[Mo_6O_{17}(NC_6Pr^i_2\text{-}1,6)_2]^{2-}$ and *cis*-$[Mo_6O_{17}(NPh)_2]^{2-}$, suggesting that the other signals in the ^1H NMR spectrum shown in Fig. 1(*b*) are due to the *cis* isomer of **5**. The Mo–N bond lengths and Mo–N–C angles are as expected for a multiply-bonded four electron donor organoimido ligand. As in other imido functionalised hexamolybdate structures,[1,2,5] the Mo–O bonds *trans* to the imido groups (2.24 Å) are substantially shorter than the other bonds to the central oxygen (2.35 Å). Also significant is the short–long bond alternation in the bridging bonds of the central Mo_4O_4 belt perpendicular to the long axis of the molecule. This cyclic pattern, as discussed by Day and Klemperer,[6] is disrupted in the other two Mo_4O_4 rings by the incorporation of Mo≡NAr groups, resulting in a decrease in the average bridging bond length to each Mo≡O group. The resulting charge distribution could explain the different bond lengths to the central oxygen.

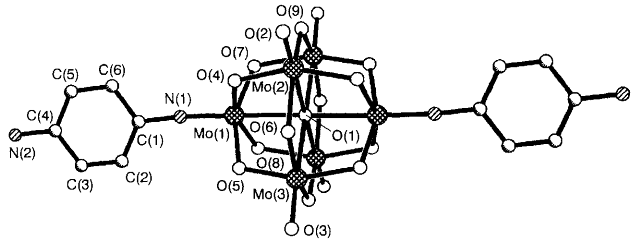


Fig. 2 Structure of the anion of **5**, without hydrogen atoms. Principal distances (Å) and angles (°): Mo(1)–O(1) 2.2402(7), Mo(2)–O(1) 2.3522(11), Mo(3)–O(1) 2.3526(10), Mo(1)–N(1) 1.743(4), Mo(2)–O(2) 1.696(4), Mo(3)–O(3) 1.688(3), Mo(1)–O(4) 1.927(3), Mo(1)–O(5) 1.960(3), Mo(1)–O(7) 1.927(3), Mo(1)–O(8) 1.958(3), Mo(2)–O(4) 1.917(3), Mo(2)–O(6) 2.006(3), Mo(2)–O(8′) 1.894(3), Mo(2)–O(9) 1.890(3), Mo(3)–O(5) 1.890(3), Mo(3)–O(6) 1.890(4), Mo(3)–O(7′) 1.916(3), Mo(3)–O(9′) 2.009(4), N(1)–C(1) 1.366(6), Mo(1)–N(1)–C(1) 175.2(4). The prime denotes an atom related by the inversion centre on O(1).

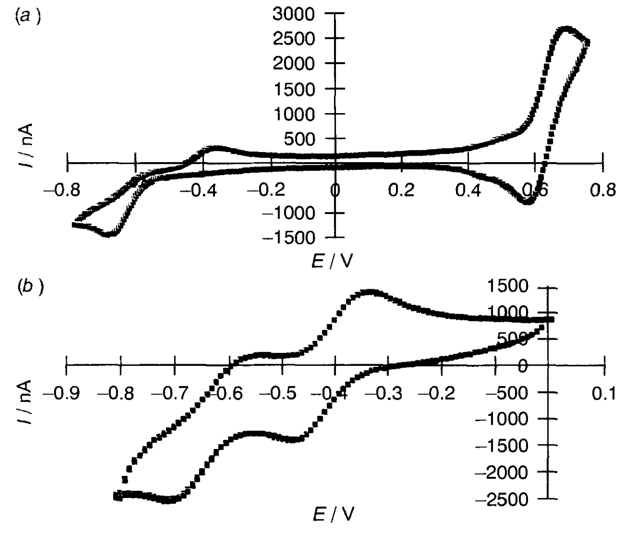


Fig. 3 Cyclic voltammograms of **5**: (*a*) single scan in the presence of $(\eta^5\text{-}C_5H_5)_2Fe$, 50 mV s^{-1}; (*b*) multiple scan, 529 m Vs^{-1}. *Conditions*: MeCN solvent, $(Bu^n_4N)BF_4$ supporting electrolyte, 1 mm diameter Pt disc working electrode, AgQRE, 298 K.

Fig. 3 shows the electrochemical behaviour of **5**. The single scan at 50 mV s^{-1} (*a*) contains no oxidation peak for the species formed by reduction at −1.24 V [*vs.* Fc/Fc$^+$ (Fc = ferrocene)], a chemical process generates a new species that is then oxidised at −1.02 V. The multiple scan plot (*b*) shows that this new species undergoes reversible reduction similar to that of **2**. This behaviour can be compared with the *reversible* one-electron reduction of **1** at −0.79 V (*vs.* Fc/Fc$^+$) and of $[Mo_6O_{17}(NC_6H_3Pr^i_2\text{-}1,6)_2]^{2-}$ at −1.25 V (*vs.* Fc/Fc$^+$).[5] This difference in reduction potentials between monosubstituted (**2** and **4**) and disubstituted (**3** and **5**) imidomolybdates has enabled us to distinguish between the products with AB type aromatic ^1H NMR resonances (**2** or **5**) and between those giving singlets (**3** or **4**).

The availability of polyoxometalates such as **2** and **5** bearing organic functional groups and the ability to link molecular oxides directly as in **3** and **4** are keys steps in the advancement of molecular architecture involving polyoxometallates. We now have the means to incorporate the redox properties of oxide fragments into large assemblies either by polymerisation or by incorporation of self-organising organic groups through further derivatisation.

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Footnote

† *Crystal data* for **5**·6MeCN: $C_{56}H_{102}Mo_6N_{12}O_{17}$, M_r = 1791.1, monoclinic, $P2_1/c$, a = 13.895(5), b = 16.343(6), c = 16.992(6) Å, β = 100.18(5)°, V = 3798(2) Å^3, Z = 2, ρ_{calc} = 1.566 g cm^{-3}, $F(000)$ = 1820, Mo-Kα radiation, λ = 0.71073 Å, μ = 1.027 mm^{-1}. The structure was determined by heavy atom methods and refined on F^2 for all 6704 independent reflections measured at 160 K with a Stoe-Siemens diffractometer ($2\theta_{max}$ = 50°), with anisotropic displacement parameters and with isotropic hydrogen atoms except for NH_2 and acetonitrile: $R' = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2} = 0.1146$ for all data, conventional R [on F values for 4768 reflections with $F_o^2 > 2\sigma(F_o)^2$] = 0.0377, goodness of fit = 1.045 on F^2 for all parameters. Programs: SHELXTL/PC and SHELX-93, G. M. Sheldrick, University of Göttingen. 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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