A superoctahedral complex derived from a polyoxometalate: the hexakis(arylimido)hexamolybdate anion $[Mo_6(NAr)_6O_{13}H]^{②}$

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Reaction of $[Mo_6O_{19}]^{2②}$ with an excess of 2,6-diisopropylphenyl isocyanate (ArNCO) affords the title anion in which the hexamolybdate framework serves as an octahedral nexus for six terminal arylimido ligands.

The rich diversity of structure and function afforded by various polyoxometalate clusters[1] is evidenced by their relevance in areas ranging from catalysis to chemotherapy to molecular magnetism.[2] In many instances, the global symmetry of a polyoxometalate ion conforms to that present within its core: for example, the idealized T_d symmetry of the Keggin phosphomolybdate $[Mo_{12}O_{40}P]^{3②}$ mirrors that of its encapsulated tetrahedral $[PO_4]^{3②}$ unit, while the idealized O_h symmetry of the Lindquist hexamolybdate $[Mo_6O_{19}]^{2②}$ reflects the octahedral environment surrounding its central $[O]^{2②}$ core. We were intrigued by the prospect of exploiting the radiating O_h symmetry of the hexamolybdate by using this anion as a nexus for the construction of a superoctahedral derivative. Although multiple functionalization of polyoxometalates has been achieved in the preparations of various organoimido derivatives of $[Mo_6O_{19}]^{2②}$,[3] and in the highly functionalized *p*-tolylimido complex $[Mo_{10}(NC_6H_4Me\text{-}p)_{12}O_{18}(py)_2]$,[4] a complete derivatization which maintained the global symmetry of the polyoxometalate parent had not been realized. Here we establish that the hexamolybdate ion can serve as an octahedrally directing template for the incorporation of six terminal arylimido ligands along the Cartesian axes of its framework.

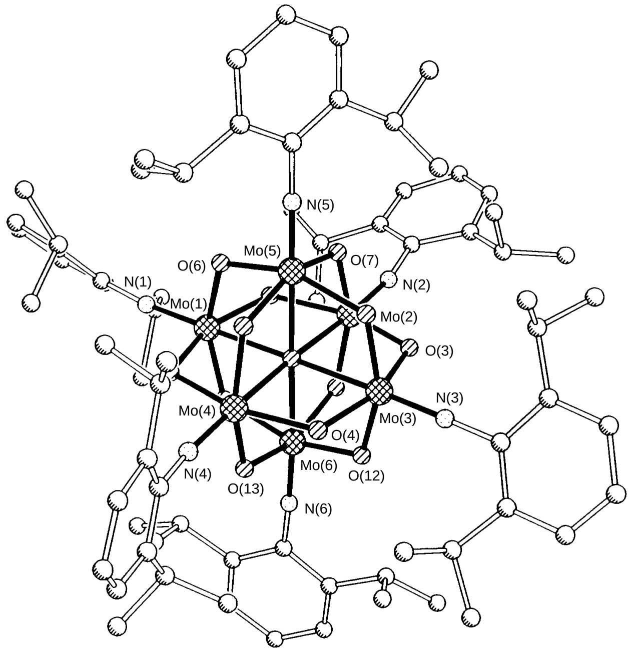

Fig. 1 Structure of the $[Mo_6(NAr)_6O_{13}H]^{②}$ anion of **1**. Selected bond lengths (Å) and angles (°): Mo(1)–N(1) 1.725(10), Mo(2)–N(2) 1.737(14), Mo(3)–N(3) 1.742(11), Mo(4)–N(4) 1.727(14), Mo(5)–N(5) 1.755(10), Mo(6)–N(6) 1.734(10), Mo(1)–N(1)–C(6) 172.7(9), Mo(2)–N(2)–C(18) 170.5(9), Mo(3)–N(3)–C(30) 176.6(10), Mo(4)–N(4)–C(42) 171.0(10), Mo(5)–N(5)–C(54) 175.0(12), Mo(6)–N(6)–C(66) 176.4(12).

Reaction of $[NBu_4]_2[Mo_6O_{19}]$ with a twenty-fold molar excess of 2,6-diisopropylphenyl isocyanate (ArNCO) in refluxing pyridine for three weeks occurs with the evolution of CO_2 and the development of a dark orange–red solution. After removal of volatiles under vacuum and washing the residue with ether (in which some of the product dissolves), a red solid was obtained. Fractional crystallization (CH_2Cl_2–Et_2O) led to the initial separation of crystalline $[NBu_4]_2[Mo_6O_{14}(NAr)_5]$;[3a] the remaining mother-liquor was concentrated and additional ether vapour was admitted causing the growth of dark red crystals of $[NBu_4][Mo_6(NAr)_6O_{13}H]$ **1**, as the monoetherate in *ca.* 20% yield.† At room temperature, a single arylimido environment is seen in the ^1H NMR spectrum of the complex. The incorporation of a proton into the hexamolybdate framework of **1** is without precedent among complexes derived from the $[Mo_6O_{19}]^{2②}$ system and testifies to the greatly enhanced electron donation provided by the arylimido ligand set. Although no ^1H NMR resonance for the bound proton was observed in either CD_3CN or $CDCl_3$ solution, a band at 3550 $cm^{②1}$ in the IR spectrum of **1** corroborates its presence; the most likely source of the proton is through reaction with adventitious water. The IR spectrum is devoid of bands assignable as ν(Mo≡O) in the 900–1000 $cm^{②1}$ region, containing only a single medium intensity absorption at 995 $cm^{②1}$, which may be associated with the Mo≡NAr units.

The molecular structure of the $[Mo_6(NAr)_6O_{13}H]^{②}$ anion as determined by single-crystal X-ray diffraction is shown in Fig. 1.‡ Six terminal arylimido ligands radiate from the octahedral Mo_6 core; the distance between opposed *para*-aryl carbon atoms averages 1.634 nm. The six Mo–N bond lengths span the range 1.725(10)–1.755(10) Å, and the associated Mo–N–C angles are all essentially linear [170.5(9)–176.6(10)°]. Comparison of the metrical data for the $\{Mo_6O_{13}\}$ core within **1** to that within the $[Mo_6O_{19}]^{2②}$ parent reveals little perturbation as a result of the introduction of the six arylimido ligands: in **1**, the distances from the central O(1) atom to the surrounding set of six Mo atoms average 2.313(9) Å, while in the hexamolybdate the corresponding average is 2.319(4) Å.[5] Similarly, the Mo–O distances involving the μ-O atoms of **1** span the range 1.903(7)–2.019(8) Å, while in $[Mo_6O_{19}]^{2②}$ analogous bond lengths range from 1.855(4) to 2.005(4) Å. Scrutiny of the metrical parameters of **1** reveals no evidence for the localization of the proton; most likely, it is disordered over the twelve μ-O atoms in the solid state.

We propose that in solution the proton undergoes rapid exchange throughout the set of μ-O atoms, thus accounting for both its non-observance and the equivalence of the six arylimido ligand environments in the ^1H NMR spectrum of **1**. A possible low-energy pathway for such a proton exchange can be visualized in the alternate view of the anion structure provided in Fig. 2, in which the isopropyl methyl groups have been omitted for clarity. Each particular μ-O atom can be seen to be have four nearest-neighbour oxygen atoms which, in combination, define two trigonal faces of the superoctahedron. These $O_b\cdots O_b$ separations within the anion average 2.70 Å, a value

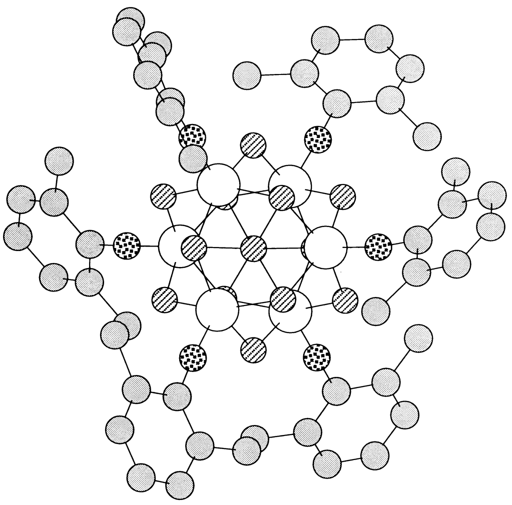

Fig. 2 Alternate view of the $[Mo_6(NAr)_6O_{13}H]^-$ anion emphasizing the $\{Mo_6O_{13}\}$ core

which is reminiscent of the corresponding 2.76 Å separation within ice[6] and which can enable facile proton migration *via* O–H···O interchanges.

If the superoctahedral derivatization of the hexamolybdate described herein can be replicated with organoimido ligands whose substituents bear appropriate remote functionality,[3c,7] then we can anticipate the designed construction of extended three-dimensional networks of tunable porosity; such systems are currently being explored.

We thank the Office of Basic Energy Sciences, Department of Energy (USA) for support of this work.

Footnotes

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† *Selected data* for **1**·Et_2O: $C_{92}H_{149}Mo_6N_7O_{14}$ requires (found) C, 51.33 (51.47); H, 6.98 (7.13); N, 4.55 (4.43%). ^1H NMR (400 MHz, CD_3CN, 298 K): δ 7.12 (d, 12 H, *m*-Ar), 6.99 (t, 6 H, *p*-Ar), 4.03 (spt, 12 H, CH), 3.21 (q, 4 H, OCH_2), 3.06 (m, 8 H, NCH_2), 1.58 (m, 8 H, CH_2), 1.30 (m, 8 H, CH_2), 1.29 (d, 72 H, $CHMe_2$), 1.14 (q, 6 H, ether CH_3), 0.96 (t, 12 H, CH_3). Selected IR bands (thin film/ KBr plate): 3550, 995, 765, 751, 722 cm^{-1}. UV–VIS (MeCN): λ_{max}(log ε/dm^3 mol^{-1} cm^{-1}) = 364(5.0), 271(5.1), 244(5.1), 208(5.2).

‡ *Crystal data* for **1**·Et_2O: Siemens R3m/V diffractometer, Mo-Kα radiation, 249 K; dark red plate, monoclinic, space group $P2_1/c$, a = 27.196(8), b = 14.874(2), c = 27.431(8) Å, β = 116.45(2)°, U = 9935(4) Å^3, Z = 4, M = 2152.9, μ = 0.795 mm^{-1}; 14087 independent reflections collected ($2\theta_{max}$ = 48°), 8291 observed [$F_o > 4\sigma(F_o)$] extinction correction, structure solved by direct methods and refined by full-matrix least squares (972 parameters), riding model (fixed isotropic U) for hydrogen atoms, $R(F)$ = 0.0684, $R(wF)$ = 0.0907. One of the butyl groups in the counter ion is severely disordered; the γ-carbon atom is disordered over two positions and the δ-carbon atom could not be located. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/458.

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Received in Bloomington, IN, USA, 13th March 1997; Com. 7/01782K