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Unprecedented Rearrangement of Molybdenum(VI) Oxide to (μ_2-Oxido)-bis[dioxidomolybdenum(VI)] Hexamolybdate

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$MoO_2(acac)_2$ reacts with water, amides, sulfoxides, and phosphane oxides in aqueous methanol, under mild conditions, to afford a new family of molybdates of composition $[Mo_2O_5L_6][Mo_6O_{19}]$ (L = H_2O, dimethylformamide, dimethylacetamide, dimethyl sulfoxide, dibutyl sulfoxide, tributylphosphane oxide, triphenylphosphane oxide, hexamethylphosphoramide). The crystal and molecular structures of the two first structurally characterized (μ_2-oxido)bis[dioxidomolybdenum(VI)] hexamolybdates were established by X-ray diffraction analysis.

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Polymolybdates have played a significant role in molybdenum chemistry for more than a century. The contemporary interest in these compounds arises from their compositional range and structural versatility, as well as important optical, magnetic, catalytic, and medicinal properties.[1] The formation of a particular polymolybdate depends on the nature of the cation and the reaction conditions.[2] Hexamolybdates, despite their low relevance in aqueous media, are an important class of polyoxometalates because of the high symmetry of the anion and their concomitant capability to form interesting derivatives.[3]

Here we report the easy formation of several (μ_2-oxido)bis[dioxidomolybdenum(VI)] hexamolybdates of composition $[Mo_2O_5L_6][Mo_6O_{19}]$ [L = H_2O (**1**), dimethylformamide (dmf) (**2**), dimethylacetamide (dma) (**3**), dimethyl sulfoxide (dmso) (**4**), dibutyl sulfoxide (dbso) (**5**), tributylphosphane oxide ($OPBu_3$) (**6**), triphenylphosphane oxide ($OPPh_3$) (**7**), hexamethylphosphoramide (hmpa) (**8**)], as well as the crystal and molecular structure of the dmso and $OPBu_3$ derivatives, **4** and **6**, respectively. To the best of our knowledge, these compounds are the first hexamolybdates with dioxidomolybdenum(VI) cations reported to date, and **6** is the first to crystallize in a noncentrosymmetric polar crystal class. These compounds are of high potential interest since: (1) the possibility of functionalization of both anion[4] and cation through substitution of the terminal oxido groups opens up the way to new materials with unexplored properties, (2) the expected different capability of anion and cation to work as oxido transfer catalysts may enable selective transformations, and (3) the ionic nature of the compounds and the tuning of the cation by coordinated ligands expand the options to work in a wide range of conditions.

As part of an ongoing study on the reactivity of $MoO_2(acac)_2$ (acac = acetylacetonate), it was soon evident that the diketonate hydrolyzes rapid and completely in aqueous methanol to yield a white solid for which molybdenum analysis and weight difference after heating were consistent with a composition very close to $MoO_3{\cdot}0.75H_2O$. We propose the formulation **1** for this compound because the IR spectrum showed the characteristic pattern of dioxidomolybdenum compounds, along with bands that strongly support the presence of the hexamolybdate anion,[5] and the ^1H NMR spectrum in $[D_4]$methanol only showed the presence of water.

To further elucidate the nature of this product we performed several reactions of $MoO_2(acac)_2$ in methanol in the presence of various O-donor ligands that are either able to stabilize oxidomolybdenum(VI) hydrates as previously reported[6] or to replace water from the coordination sphere of molybdenum.[7] In this manner we were able to isolate in high yield compounds **2**–**8**.

We also studied the reactivity of a suspension of freshly precipitated $MoO_3{\cdot}nH_2O$ in methanol with the same ligands. In all cases partial formation of the corresponding $[Mo_2O_5L_6][Mo_6O_{19}]$ compounds was observed; the best result was obtained with the most basic ligand, hmpa.

According to these observations, the hydrolysis of $MoO_2(acac)_2$ in aqueous methanol leads to a hydrated molybdenum(VI) oxide that rearranges to the metastable $[Mo_2O_5(H_2O)_6][Mo_6O_{19}]$, which in turn reacts with strong O-donor ligands, such as amides, sulfoxides, and phosphane oxides, through replacement of coordinated water while respecting the preformed $[Mo_2O_5]$ and $[Mo_6O_{19}]$ cores.

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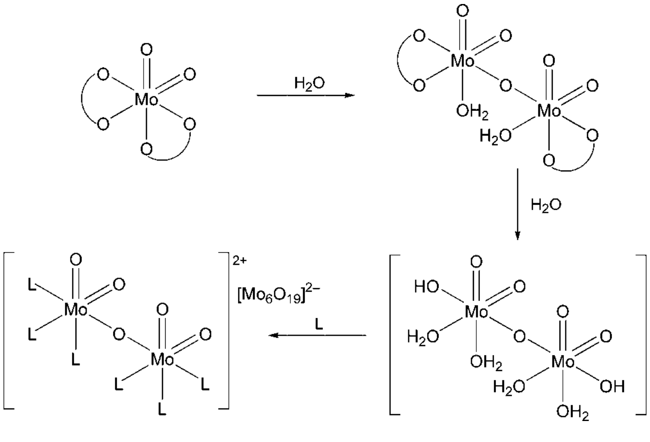
This process can be rationalized by assuming that the mentioned hydrolysis proceeds through a sequence of reactions as shown in Scheme 1, in which the formation of dinuclear species must play a relevant role, as evidenced by the easy formation of $Mo_2O_5(H_2O)_2(acac)_2$, which was recently characterized,[8] and the persistence of $[Mo_2O_5L_6]^{2+}$ cations in all compounds isolated.



Scheme 1. Suggested stepwise formation of $[Mo_2O_5L_6][Mo_6O_{19}]$.

Condensation and deprotonation of the dinuclear species $Mo_2O_5(H_2O)_4(OH)_2$ may lead to the formation of the $[Mo_6O_{19}]^{2-}$ anion, which could coexist for a while with the hydrated dinuclear cation $[Mo_2O_5(H_2O)_6]^{2+}$, which in turn is formed by protonation. According to this, when water is replaced by strong coordinating ligands $[Mo_2O_5L_6]$-$[Mo_6O_{19}]$ (**2**–**8**) were formed.

Compounds **1**–**8** were fully characterized by elemental analysis, and IR and ^1H NMR spectroscopy. The molecular structures of **4** and **6** were also confirmed by single-crystal X-ray diffraction,[9] and their dinuclear cations are shown in Figures 1 and 2, respectively.

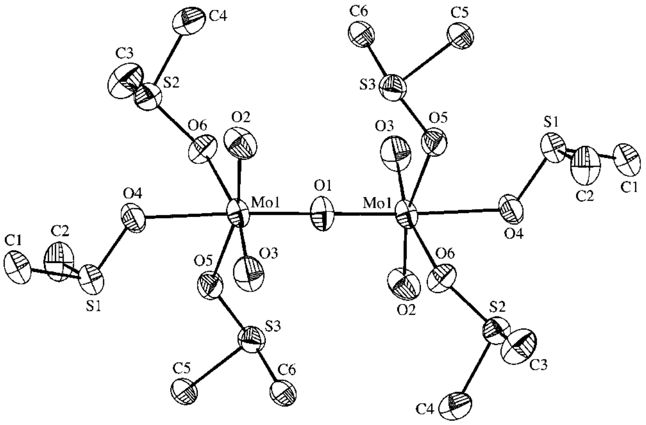


Figure 1. Crystal structure and atom-labeling scheme for $[Mo_2O_5(dmso)_6]^{2+}$ with thermal ellipsoids at the 50% probability level. The minor disorder component and hydrogen atoms are omitted for clarity.

Well-characterized compounds with the dication $[Mo_2O_5]^{2+}$ are rare, and to the best of our knowledge they are limited to $[Mo_2O_5L_2]^{2+}$ (L = *N*,*N*′,*N*′′-trimethyl-1,4,7-triazacyclononane, *N*,*N*′,*N*′′-tri-*tert*-butyl-1,4,7-triazacyclononane)[10–12] and $[Mo_2O_5L_6]^{2+}$ (L = $OPPh_3$).[13] For the cations from **4** and **6**, the Mo–O(t) and Mo–O(μ_2) bond lengths are similar to those reported for related cat-

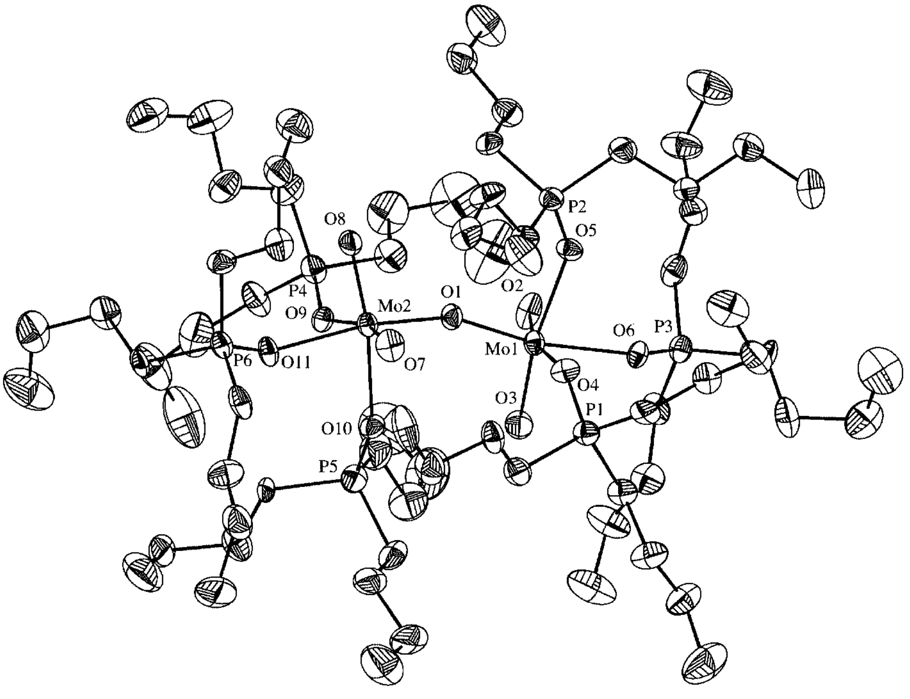


Figure 2. Crystal structure and atom-labeling scheme for $[Mo_2O_5(OPBu_3)_6]^{2+}$ with thermal ellipsoids at the 50% probability level. The minor disorder component and hydrogen atoms are omitted for clarity.

ions.[10–13] The cation from **4** has an inversion center at the oxygen bridge, which is analogous to cations reported in the literature; however, the angle Mo–O–Mo for the cation from **6** is 158.8(3)°, and this species is the first example of this type of cation that does not possess an inversion center.

The polyoxidoanion $[Mo_6O_{19}]^{2-}$ in **4** and **6** displays the well-known Lindqvist structure. The anion from **4** is highly symmetric, whereas that from **6** can be described as a distorted octahedron.

Whereas **4** crystallizes in the space group $P2_1/c$, quite common among the hexamolybdates previously reported, **6** crystallizes in the more interesting space group *P*2(1). To the best of our knowledge, this is the first hexamolybdate in an acentric space group that falls in a noncentrosymmetric polar crystal class.[14] This kind of material possesses all four of the noncentrosymmetric symmetry-dependent properties,[15] specifically enantiomorphism, optical activity, pyroelectricity, and piezoelectricity.

The catalytic activity of compounds **1**–**8** for oxido transfer processes from several oxygen sources to PPh_3 was been measured and compared with that of the prototypical $[Bu_4N]_2[Mo_6O_{19}]$. It is noteworthy that full oxidation of PPh_3 to $OPPh_3$ could be achieved under mild conditions with these compounds when oxygen was used as the oxidant, whereas $[Bu_4N]_2[Mo_6O_{19}]$ proved to be inactive in the same conditions.

In summary, we have developed a simple reaction route to prepare (μ_2-oxido)bis[dioxidomolybdenum(VI)] hexamolybdates from $MoO_2(acac)_2$. This easy procedure allows the reactions to be carried out in high yields under mild conditions. We have structurally characterized the two first members of this new family of hexamolybdates; one of them is the first hexamolybdate in a noncentrosymmetric polar crystal class. All these compounds show catalytic activity in oxidation processes with molecular oxygen as the oxidant. Further studies are currently being carried out in our laboratory.

Supporting Information (see footnote on the first page of this article): Full experimental details, structure refinement data and tables of bond lengths and bond angles for **4** and **6**.

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[9] CCDC-639298 (for **4**) and -639299 (for **6**) contain 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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