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Methoxide of an Anderson-Type Polyoxometalate and Its Conversion to a New Type of Species, $[\mathrm{IMo_9O_{32}(OH)(OH_2)_3}]^{4-}$[†]

Daisuke Honda,[‡] Tomoji Ozeki,[*,§] and Atsushi Yagasaki[*,‡]

Department of Chemistry, Kwansei Gakuin University, Sanda 669-1337, Japan, and Department of Chemistry and Materials Science, Tokyo Institute of Technology, Tokyo 152-8551, Japan

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A totally new type of polyoxometalate, $[\mathrm{IMo_9O_{32}(OH)(OH_2)_3}]^{4-}$, has been synthesized by reacting $[\mathrm{IMo_6O_{22}(OMe)_2}]^{3-}$ with water. The $[\mathrm{IMo_9O_{32}(OH)(OH_2)_3}]^{4-}$ anion further transforms into $[(\mathrm{IMo_7O_{26}})_2]^{6-}$, a molecular oxide that has a rutile core, in dry acetonitrile, while it stays intact for several hours in wet acetonitrile.

Polyoxometalate chemistry has made a giant leap during the last score of years.[1] However, its development has largely depended on the progress made for the Keggin and related species that have tetrahedral heteroatoms. Many different species that contain tetrahedral heteroatoms have been reported since a milestone review was published in 1983.[2] The progress for the species of octahedral heteroatoms, on the other hand, has been far slower. The situation for this class of polyoxometalates has not changed much since 1983, and even experts of the field can name only a handful of newer structures.[3−13] Reaction chemistry of the species of octahedral heteroatoms has largely been left unexplored.

Recently we discovered a novel type of polymolybdate that has a rutile structure core, $[(\mathrm{IMo_7O_{26}})_2]^{6-}$.[13] The isolation of this compound was a little tricky. The tetrabutylammonium (TBA) salt of $[(\mathrm{IMo_7O_{26}})_2]^{6-}$ was obtained by crystallizing a compound prepared by adding TBABr to an acidic solution of $[\mathrm{IMo_6O_{24}}]^{5-}$.[14,15] However, the IR spectra of the initial material thus prepared (**1**; Figure S1 in the Supporting Information) and the final crystals obtained were totally different. This indicates that some structural reorganization takes place during crystallization. During an effort to fully characterize this initial material, we have isolated a novel type of polymolybdate as well as a methoxide of $[\mathrm{IMo_6O_{24}}]^{5-}$.

A dimethoxide of $[\mathrm{IMo_6O_{24}}]^{5-}$ was obtained by reacting **1** with methanol as a TBA salt.[16] X-ray crystal structure analysis revealed that the dimethoxide anion, $[\mathrm{IMo_6O_{22}(OMe)_2}]^{3-}$, has the structure shown in Figure 1 (see also the figure given in the graphical table of contents).[17] It has the same basic

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[*] To whom correspondence should be addressed. E-mail: tozeki@cms.titech.ac.jp (T.O.), yagasaki@kwansei.ac.jp (A.Y.).

[†] Dedicated to Professor Yukiyoshi Sasaki on the occasion of his 77th anniversary.

[‡] Kwansei Gakuin University.

[§] Tokyo Institute of Technology.

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(16) $\mathrm{Na_2MoO_4 \cdot 2H_2O}$ (3.20 g, 13.2 mmol) was dissolved in 17.7 mL of 1.05 M HCl (18.6 mmol). $\mathrm{HIO_4 \cdot 2H_2O}$ (0.500 g, 2.19 mmol) was added to this solution. The mixture was stirred for 5 min, during which time colorless precipitates formed. It was further stirred for 15 min at 70−75 °C to yield a clear solution. A solution of TBABr (2.83 g, 8.78 mmol, in 5 mL of water) was then added to the solution, and stirring was continued on the resulting slurry at 70 °C for 30 min. The mixture was filtered, and the pale yellow solids collected were dried in vacuo over $\mathrm{P_2O_5}$ for 12 h to yield 3.31 g of the intermediate product, **1**. A total of 0.43 g of **1** was dissolved in 15 mL of methanol, and the solution was filtered to remove a small amount of solids left undissolved. The crystals that appeared after allowing the filtrate to stand at ambient temperature for 24 h were collected by filtration and dried in vacuo over $\mathrm{P_2O_5}$ for 12 h to yield 0.15 g of $\mathrm{TBA_3[IMo_6O_{22}(OMe)_2]}$ (8.1×10^{-5} mol, 28% based on Mo). Anal. Calcd for $\mathrm{C_{50}H_{114}N_3IMo_6O_{24}}$: C, 32.56; H, 6.23; N, 2.28; I, 6.9; Mo, 31.2. Found: C, 32.10; H, 6.20; N, 2.03; I, 7.2; Mo, 30.9. IR (Nujol mull, 1050−400 cm^{-1}): 1013 (m), 943 (vs), 925 (vs), 907 (vs), 892 (m), 880 (w), 750 (s), 733 (s), 701 (vs), 666 (s), 641 (m), 624 (m), 556 (vs), 478 (m), 473 (m). ^{1}H NMR (CD$_3$CN): δ (ppm) 0.97 (t, C*H*$_3$CH$_2$CH$_2$CH$_2$N), 1.37 (m, CH$_3$C*H*$_2$CH$_2$CH$_2$N), 1.62 (m, CH$_3$CH$_2$C*H*$_2$CH$_2$N), 3.11 (m, CH$_3$CH$_2$CH$_2$C*H*$_2$N), 4.30 (s, C*H*$_3$O), 4.31 (s, C*H*$_3$O). The ^{1}H NMR of $\mathrm{TBA_3[IMo_6O_{22}(OMe)_2]}$ gives two peaks assignable to the methoxy groups in roughly a 2:1 ratio (see above), although the methoxy groups of the anion are equivalent in the solid state. Partial hydrolysis of the methoxy group is one possible explanation but has been excluded because the intensity ratio of these peaks does not change with the concentration of the compound or the amount of methanol in solution. We currently have no solid explanation for this observation.

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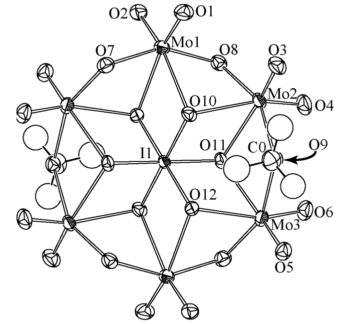

Figure 1. Structure of $[IMo_6O_{22}(OMe)_2]^{3-}$.

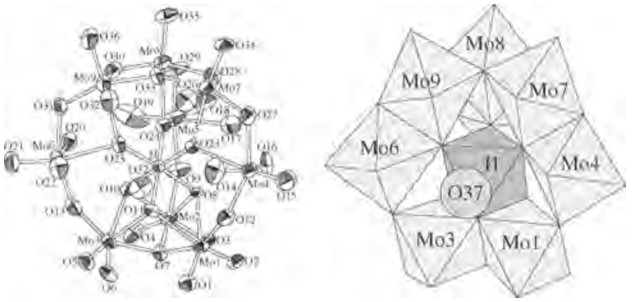

Figure 2. Structure of $[IMo_9O_{32}(OH)(OH_2)_3]^{4-}$ (left) and its polyhedral representaion (right).

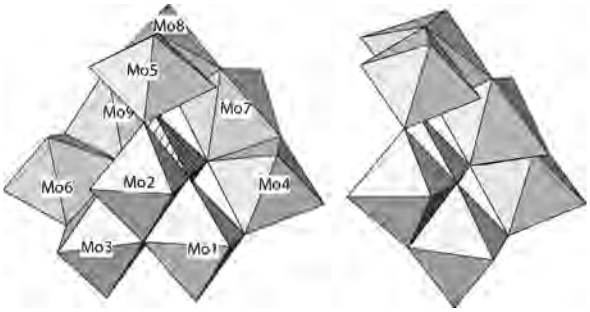

Figure 3. Polyhedral models of $[IMo_9O_{32}(OH)(OH_2)_3]^{4-}$ (left) and $[MeAsW_7O_{27}H]^{7-}$ (right). The MeAs group is omitted for clarity.

structure as the parent $[IMo_6O_{24}]^{5-}$ anion,[18] but two of the OMo_2 oxygens in the parent anion are replaced by methoxy groups in a centrosymmetric manner. The methyl groups stick out from the surface of the Anderson anion almost at right angles. It is interesting to note that there are no terminal methoxy groups in the structure, unlike in $[Mo_8O_{24}(OCH_3)_4]^{4-}$, where both terminal and bridging oxygens are replaced by methoxy groups.[19] They do not occupy the triply bridging sites either. Selective methylation of OMo_2 oxygen was also observed in the direct methylation of $[PMo_{12}O_{40}]^{3-}$ by trimethyloxonium.[20]

The dimethoxide anion seems to be stable in an acetonitrile solution. It gives basically identical IR spectra in the solid phase and in solution (Figure S2 in the Supporting Information). It does get hydrolyzed and releases methanol when H_2O is added to the solution. However, the IR spectra of the solution do not change significantly even after adding 120 equiv of H_2O and allowing the solution to stand for 24 h (Figure S3 in the Supporting Information), suggesting that the Anderson framework of the anion is maintained in solution under these conditions.

Despite the apparent stability of the Anderson framework in solution, a species of a totally different structure was obtained when ethyl acetate was added to a moist acetonitrile solution of $TBA_3[IMo_6O_{22}(OMe)_2]$.[21] Figure 2 shows the structure of this new molybdoperiodate anion, $[IMo_9O_{32}(OH)(OH_2)_3]^{4-}$.[22] The figure may be mistaken as that of a Keggin-related species at first sight. In fact, the ring made up from Mo1, Mo4, Mo7, Mo9, Mo6, Mo3, and the oxygens that bridge them is very similar to the Mo_6O_6 ring observed in the structure of the Keggin and related species.[23] However, the unit that sits inside the cage made up from the molybdenum and oxygen atoms for the current compound is an octahedral IO_6 unit, not a tetrahedral AO_4 unit.

The $[IMo_9O_{32}(OH)(OH_2)_3]^{4-}$ anion has a closer structural relevance to $[CH_3AsW_7O_{26}(OH)]^{7-}$ (Figure 3).[24] The former anion ideally has an *m* (C_s) symmetry, with the mirror plane going through I, Mo2, Mo5, and Mo8. The moiety made up from the octahedra that are centered by those atoms and the ones by Mo1, Mo4, and Mo7 (or, alternatively, Mo3, Mo6, and Mo9) has the same geometry as the W_7O_{27} framework of $[CH_3AsW_7O_{26}(OH)]^{7-}$. In other words, if we fuse two IMo_6O_{27} units of the W_7O_{27} structure in a manner that they share the I and three Mo atoms, we get the $[IMo_9O_{32}(OH)(OH_2)_3]^{4-}$ anion.

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(17) Single crystals of $TBA_3[IMo_6O_{22}(OMe)_2]$ at 85(2) K: monoclinic, space group $P2_1/n$, with $a = 10.4009(1)$ Å, $b = 14.6658(3)$ Å, $c = 23.5395(4)$ Å, $\beta = 100.324(1)°$, $V = 3532.5(1)$ Å^3, and $Z = 2$. A colorless crystal of dimensions $0.48 \times 0.30 \times 0.14$ mm^3 was used for data collection. Diffraction data were collected on a Bruker SMART CCD diffractometer using Mo Kα radiation. The final agreement factors were $R = 0.0343$ for 9714 reflections with $F^2 > 2\sigma(F^2)$ and $wR(F^2) = 0.0788$ for 10 755 unique reflections.

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(21) $TBA_3[IMo_6O_{22}(OMe)_2]$ (0.20 g, 0.11 mmol) was dissolved in 2.5 mL of acetonitrile. Water (0.23 mL, 13 mmol) was added to this solution, and the mixture was stirred for 7.5 h. A total of 8.8 mL of ethyl acetate was then added to the solution. The crystals that appeared after allowing the solution to stand for 16 h at ambient temperature were collected by filtration and dried in vacuo over P_2O_5 for 8 h to yield 64 mg of $TBA_4[IMo_9O_{32}(OH)(OH_2)_3]\cdot H_2O$ (0.025 mmol, 34% based on Mo). Anal. Calcd for $C_{64}H_{153}N_4IMo_9O_{37}$: C, 30.01; H, 6.02; N, 2.19; Mo, 33.7. Found: C, 30.29; H, 6.07; N, 2.07; Mo, 33.6. IR (Nujol mull, 1000−400 cm^{-1}): 944 (s), 924 (vs), 911 (vs), 890 (m), 850 (sh), 821 (vs), 809 (vs), 758 (s), 734 (sh), 723 (m), 696 (m), 667 (m), 648 (m), 627 (sh), 569 (w), 546 (w), 516 (w), 496 (w), 428 (w), 414 (w), 401 (w). The same compound can be obtained by using diethyl ether instead of ethyl acetate.

(22) Single crystals of $TBA_4[IMo_9O_{32}(OH)(OH_2)_3]\cdot H_2O$ at 123(2) K: orthorhombic, space group $Pna2_1$, with $a = 24.549(1)$ Å, $b = 17.979(1)$ Å, $c = 22.860(1)$ Å, $V = 10089.6(8)$ Å^3, and $Z = 4$. A colorless crystal of dimensions $0.44 \times 0.12 \times 0.12$ mm^3 was used for data collection. Diffraction data were collected on a MAC Science DIP LABO system installed on the BL04B2 bending magnet beamline of the SPring-8 syncrotron facility using a 37.78-keV ($\lambda = 0.3282$ Å) monochromatized X-ray beam. The final agreement factors were $R = 0.0641$ for 17 360 reflections with $F^2 > 2\sigma(F^2)$ and $wR(F^2) = 0.1763$ for 18 130 unique reflections. For details of the data collection system, see: Ozeki, T.; Kusaka, K.; Honma, N.; Nakamura, Y.; Nakamura, S.; Oike, S.; Yasuda, N.; Imura, H.; Uekusa, H.; Isshiki, M.; Katayama, C.; Ohashi, Y. *Chem. Lett.* **2001**, 804−805.

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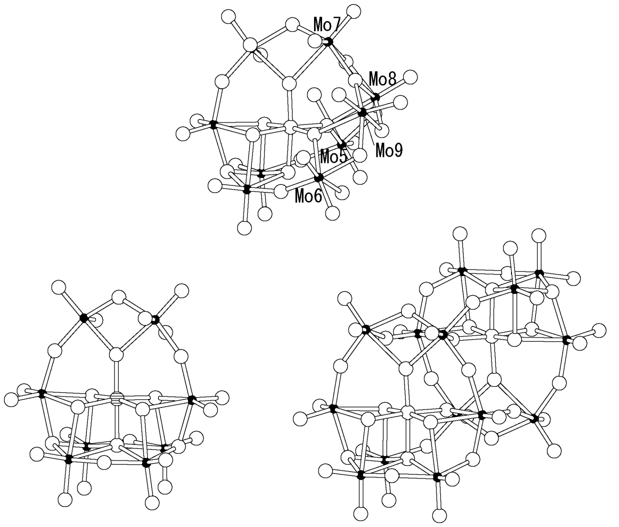

Figure 4. Structures of $[IMo_9O_{32}(OH)(OH_2)_3]^{4-}$ (top), $[TeMo_8O_{29}(OH_2)]^{4-}$ (bottom left), and $[(IMo_7O_{26})_2]^{6-}$ (bottom right).

The structure of $[IMo_9O_{32}(OH)(OH_2)_3]^{4-}$ also has a close relationship with those of $[TeMo_8O_{29}(OH_2)]^{4-}$ and $[(IMo_7O_{26})_2]^{6-}$ (Figure 4; see also the figure given in the graphical table of contents).[7,13] If we tear up the bottom part of $[TeMo_8O_{29}(OH_2)]^{4-}$ and insert a Mo unit, we get the structure of $[IMo_9O_{32}(OH)(OH_2)_3]^{4-}$. If we remove two MoO_6 octahedra from this teared up part (those centered by Mo_5 and Mo_8), we get the structure of the monomeric unit of $[(IMo_7O_{26})_2]^{6-}$.

Three of the Mo atoms in $[IMo_9O_{32}(OH)(OH_2)_3]^{4-}$ (Mo4, Mo5, and Mo6) have three nonbridging Mo−O bonds. This violation of Lipscomb's rule,[25,26] however, is of apparent nature. One of those three Mo−O bonds in each case is much longer than the other two (Mo4−O14 2.36 Å, Mo4−O15 1.68 Å, Mo4−O16 1.66 Å; Mo5−O17 2.39 Å, Mo5−O18 1.68 Å, Mo5−O19 1.68 Å; Mo6−O20 2.36 Å, Mo6−O21 1.70 Å, Mo6−O22 1.70 Å), suggesting that it is actually a $Mo-OH_2$ bond. Unlike the majority of the (apparent and strict) anti-Lipscomb polyoxometalates reported so far,[27−31] the terminal Mo−O bonds in the current compound are aligned in *mer* geometry, not in *fac*. The *mer* arrangement of two terminal Mo−O and one (terminal) $Mo-OH_2$ bonds has been observed in $[TeMo_8O_{29}(OH_2)]^{4-}$ and $[CH_3AsMo_6O_{21}(OH_2)_6]^{2-}$.[7,32] The charge neutrality of the crystal requires one more oxygen be protonated in the $[IMo_9O_{32}(OH)(OH_2)_3]^{4-}$ anion, just as the formula tells. Although the X-ray data were not very decisive on this matter, we tentatively propose that either O26 or O28 is protonated. The bond valence sums[33,34] for these oxygen atoms are 1.4 and significantly smaller than the values for the other oxygen atoms.

Another point that merits mention is the location of the noncoordinating water molecule (O37). It locates itself as if to fill the void of the layer that is made up from four terminal oxygen atoms: O14, O22, O26, and O32. It is close to O14 and O11 (O37···O14 2.75 Å, O37···O11 2.78 Å) and seems to be hydrogen-bonded to these two atoms.

In contrast to $[IMo_6O_{22}(OMe)_2]^{3-}$, the $[IMo_9O_{32}(OH)(OH_2)_3]^{4-}$ anion exhibits totally different behaviors in dry and moist acetonitrile. It undergoes spontaneous reorganization in dry acetonitrile and transforms into $[(IMo_7O_{26})_2]^{6-}$ (Figure S4 in the Supporting Information). In moist acetonitrile that contains 90 equiv of water, on the other hand, the framework of $[IMo_9O_{32}(OH)(OH_2)_3]^{4-}$ is maintained for more than several hours (Figure S5 in the Supporting Information). It does decompose after a longer period of time or if more water is added to the solution but never into $[(IMo_7O_{26})_2]^{6-}$ when the solution contains this much water. Because the IR spectra of $TBA_4[IMo_9O_{32}(OH)(OH_2)_3]$ are extremely similar to those of the mystery starting compound **1**, we now believe that **1** is actually $TBA_4[IMo_9O_{32}(OH)(OH_2)_3]$ in a less crystalline and somewhat lower purity form.

Here we have discovered an interesting series of reactions that accompanies structural change. Experiments to reveal further reaction chemistry of the molybdoperiodate system are underway.

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Supporting Information Available: Crystallographic data and solution and solid-state IR spectra for $TBA_3[IMo_6O_{22}(OMe)_2]$ and $TBA_4[IMo_9O_{32}(OH)(OH_2)_3]\cdot H_2O$, together with the IR spectra of **1** and $TBA_6[(IMo_7O_{26})_2]$. This material is available free of charge via the Internet at http://pubs.acs.org.

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