Inorganic Chemistry
· Communication

[(IMo$_7$O$_{26}$)$_2$]$^{6-}$: A Missing Link between Molecular and Solid Oxides

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

A new molecular oxide, [(IMo$_7$O$_{26}$)$_2$]$^{6-}$, that has a self-contained structure has been synthesized. Its structural relevance both to the rutile structure and several molecular oxides that had been classified as "strange ones with odd structures" has given some insights as to why those species assume such structures. The novel yet self-contained nature of the structure suggests the existence of a new class of molecular oxides of related structures.

Virtually all metal elements and many nonmetal elements hydrolyze to form oligomeric cations or anions such as [Al$_{13}$O$_4$(OH)$_{24}$(OH$_2$)$_{12}$]$^{7+}$ and [Mo$_7$O$_{24}$]$^{6-}$.[1] When looking at the molecular models of these polycations and polyanions, collectively referred to as molecular oxides, one cannot help comparing them to solid oxides. Both compounds consist of oxygen and one or more non-oxygen elements. Non-oxygen atoms occupy the interstices between oxygen atoms in either group of compound. The track of direct relevance, however, seems to end here. One stumbles when he or she tries to relate molecular oxides to solid oxides any further. One major problem here is the fact that very few molecular oxides have structures directly related to those of solid oxides. For instance, Keggin-type species and their derivatives form the largest group of molecular oxide that is very rich in variety.[2,3] Those are the species one encounters most frequently in the literature. However, no solid oxide has a structure that is built up from or can be directly compared to Keggin-type structures. Rutile and rutile-type structures are very common for solid oxides.[4] On the other hand, virtually no molecular oxide has been observed to assume such structure, the only exception being [Sb$_8$O$_{12}$(OH)$_{20}$]$^{4-}$.[5]

In short, a link between molecular oxides and solid oxides has been missing. Very recently, we have found this missing link.

A new molecular oxide, [(IMo$_7$O$_{26}$)$_2$]$^{6-}$, was synthesized by reacting MoO$_4$$^{2-}$ and HIO$_4$ as a crystalline [(*n*-C$_4$H$_9$)$_4$N]$^+$ salt.[6] Although crystals of this salt were unsuitable for X-ray structural analysis, suitable crystals of a double salt [(C$_6$H$_5$)$_4$P]$_4$-[(*n*-C$_4$H$_9$)$_4$N]$_2$[(IMo$_7$O$_{26}$)$_2$]·3CH$_3$CN could be obtained by reacting [(*n*-C$_4$H$_9$)$_4$N]$_6$[(IMo$_7$O$_{26}$)$_2$] with [(C$_6$H$_5$)$_4$P]Br in acetonitrile.[7] The single-crystal X-ray diffraction study of the double salt revealed that the anionic molecular oxide has a novel type of structure depicted in Figure 1.[8] The figure may easily be mistaken as that of a partial structure of some solid oxide, but that is not without reason. The anion contains rutile structure in its central part. This moiety of rutile structure is sandwiched between parts that assume rock salt

* To whom correspondence should be addressed. E-mail: yagasaki@kwansei.ac.jp.

† Kwansei Gakuin University.

‡ Tokyo Institute of Technology.

(1) Baes, C. F., Jr.; Mesmer, R. E. *The Hydrolysis of Cations*; Wiley: New York, 1976.
(2) Yagasaki, A. *Hyoumen* **1996**, *34*, 474−482.
(3) *Chem. Rev.* **1998**, *98*, 1.
(4) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Oxford University Press: Oxford, 1984; pp 247−252.
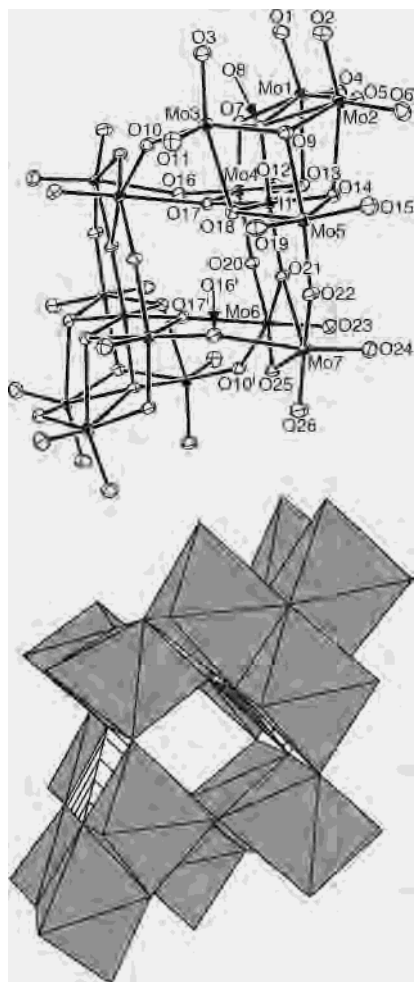(5) Nakano, H.; Ozawa, Y.; Yagasaki, A. *J. Am. Chem. Soc.* **1995**, *117*, 12007−12008.

(6) Na$_2$MoO$_4$·2H$_2$O (3.20 g, 13.2 mmol) was dissolved in 19.0 mL of 1.05 M HNO$_3$ (20.0 mmol). The solution was heated to 60 °C before HIO$_4$·2H$_2$O (0.500 g, 2.19 mmol) was added with stirring. To this hot solution was added a solution of [(*n*-C$_4$H$_9$)$_4$N]Br (2.10 g, 6.50 mmol, in 4 mL of H$_2$O) with vigorous stirring to form colorless precipitate. The mixture was left stirring for 30 min at 60 °C. The precipitate was then collected by filtration, washed with 30 mL of H$_2$O, and dried under vacuum to yield 2.47 g of pale yellow powder. Purification was accomplished by dissolving 1.00 g of this powder in 5 mL of CH$_3$CN, adding 10 mL of Et$_2$O with stirring, filtering off a small amount of microcrystals that formed, and adding 5 mL of Et$_2$O gently to the filtrate. Crystals of analytically pure [(*n*-C$_4$H$_9$)$_4$N]$_6$-[(IMo$_7$O$_{26}$)$_2$] were obtained by allowing the mixture to stand for 24 h (0.427 g, 0.110 mmol, 28.7% yield based on Mo). Anal. Calcd for C$_{96}$H$_{216}$N$_6$I$_2$Mo$_{14}$O$_{52}$: C, 29.69; H, 5.61; N, 2.16; I, 6.5; Mo, 34.6. Found: C, 29.73; H, 5.70; N, 2.19; I, 5.8; Mo, 34.1. Infrared (Nujol mull, 400−1000 cm^{-1}): 405(w), 418(w), 446(w), 476(w), 515(w), 536(m), 568(m), 614(s), 637(sh), 652(vs), 667(vs), 694(vs), 719(vs), 812(s), 864(s), 888(s), 911(s), 925(vs), 946(s), 960(sh).
(7) To a solution of [(*n*-C$_4$H$_9$)$_4$N]$_6$[(IMo$_7$O$_{26}$)$_2$] (0.050 g, 0.013 mmol, in 2.5 mL of acetonitrile) was added 1 mL of a solution of [(C$_6$H$_5$)$_4$P]Br (0.030 g, 0.072 mmol, in 2 mL of acetonitrile). Colorless plate-shaped crystals appeared in 24 h (0.021 g, 4.8 μmol, 37% yield based on Mo).
(8) Single crystals of [(C$_6$H$_5$)$_4$P]$_4$[(*n*-C$_4$H$_9$)$_4$N]$_2$[(IMo$_7$O$_{26}$)$_2$]·3CH$_3$CN are, at 115(2) K, monoclinic, space group *P*2$_1$/*c*, with *a* = 18.9475(1) Å, *b* = 27.4414(1) Å, *c* = 17.4546(1) Å, *β* = 116.3999(3)°, *V* = 8128.99-(7) Å^3, and *Z* = 4. A colorless crystal of dimensions 0.32 × 0.10 × 0.05 mm^3 was used for data collection. Diffraction data were collected on a Rigaku MERCURY CCD system installed on the NW2 beam line of the Advanced Ring (AR), the Photon Factory (PF) of the High Energy Accelerator Research Organization (KEK), using 18.00 keV (λ = 0.6890 Å) monochromatized X-ray beam. The final agreement factors were *R* = 0.0228 for 21005 reflections with *F*^{2} > 2σ(*F*^{2}) and *wR*(*F*^{2}) = 0.0814 for 24189 unique reflections.

Figure 1. Structure of $[(IMo_7O_{26})_2]^{6-}$ (top) and its polyhedral representation (bottom). Displacement ellipsoids are drawn to encompass 50% probability levels. Atoms labeled with a superscript i are related to those without a superscript by the crystallographic inversion center at (0, 0, 0). Selected distances (Å): I1−O17 1.8477(14), I1−O21 1.8692(14), I1−O13 1.8813(14), I1−O18 1.8850(14), I1−O14 1.8863(14), I1−O8 1.9497(13), Mo1−O4 1.7022(16), Mo1−O1 1.7041(15), Mo1−O7 1.9311(15), Mo1−O5 1.9551(15), Mo1−O13 2.3281(14), Mo1−O8 2.4217(14), Mo2−O6 1.6992(16), Mo2−O2 1.7059(15), Mo2−O5 1.8872(15), Mo2−O9 2.0582(15), Mo2−O8 2.3122(14), Mo2−O14 2.3258(14), Mo3−O11 1.6924(16), Mo3−O3 1.7051(15), Mo3−O10 1.9437(15), Mo3−O9 2.0271(15), Mo3−O18 2.2576(14), Mo3−O8 2.3184(14), Mo4−O12 1.7027(15), Mo4−O16 1.7290(15), Mo4−O7 1.8938(14), Mo4−O20 1.9658(14), Mo4−O13 2.2626(14), Mo4−O17 2.2997(14), Mo5−O15 1.6997(16), Mo5−O19 1.7109(16), Mo5−O22 1.8675(14), Mo5−O9 2.1144(14), Mo5−O18 2.2688(15), Mo5−O14 2.2979(14), Mo6−O23 1.6916(15), Mo6−O20 1.8317(14), Mo6−O10^i 1.8471(14), Mo6−O25 1.8896(15), Mo6−O21 2.1899(14), Mo6−O17^i 2.3662(14), Mo7−O26 1.7057(16), Mo7−O24 1.7081(16), Mo7−O22 1.9201(14), Mo7−O25 1.9367(15), Mo7−O16^i 2.2848(15), Mo7−O21 2.3395(14).

structure. The entire molecular anion is made up of arrays of close-packed oxygens and Mo and I atoms that occupy the octahedral interstices between oxygen layers. The Mo3 atom locates itself on a "turning point". It occupies the site which is vacant in the rutile structure, although five of the six oxygens around it belong to the central rutile core. The layers of close-packed oxygens are stacked in a sequence ABCBCA, resulting in a chhc packing. The mixing of cubic and hexagonal close-packing makes a fascinating, self-contained arrangement. It has the compactness of being fully

close-packed, yet lacks the ability to propagate indefinitely. It is interesting to note that the Keggin structure is also made up of a self-contained, hexagonal−cubic hybrid close-packed arrangement.[9] Given the prevalence of Keggin-type species and their derivatives, it is possible that $[(IMo_7O_{26})_2]^{6-}$ is a representative of a large group of molecular oxides of similar structures. The literature data suggests it actually is.

In Figure 2, the structure of $[(IMo_7O_{26})_2]^{6-}$ viewed from another direction is depicted together with those of some other species. Each of these species has largely been dismissed as a "strange compound with an odd structure" so far. They all contain Mo_6 rings. This is not at all rare. But their rings are all bent, unlike the Mo_6 rings in well-known Anderson species (e.g., $[IMo_6O_{24}]^{5-}$ and $[TeMo_6O_{24}]^{6-})$[10,11] and $[\alpha\text{-}Mo_8O_{26}]^{4-}$[12] which have planar Mo_6 rings. There has not been any explanation why the Mo_6 ring in these "odd" species undergo such deformation. However, their structural similarity to $[(IMo_7O_{26})_2]^{6-}$, and hence the relevance to rutile structure, is now strikingly clear. As can be noticed from its formula, $[(IMo_7O_{26})_2]^{6-}$ has a dimeric structure. The structure of its monomeric moiety, IMo_7O_{26}, is extremely similar to that of $[TeMo_8O_{29}(OH_2)]^{4-}$ (Figure 2b).[13] One of the Mo atoms in the latter is 5-coordinated and has a vacant coordination site (unshaded square pyramid in Figure 2b). Another Mo atom in this compound (one just behind the unshaded square pyramid) has virtual 5-coordination with a water molecule bound only loosely to its sixth coordination site. If we remove the water molecule and an MoO_3 unit from $[TeMo_8O_{29}(OH_2)]^{4-}$ and unite two of them through the coordinatively unsaturated 5-coordination sites, we obtain the structure of $[(IMo_7O_{26})_2]^{6-}$.

What is more interesting is the close relationship between $[(C_6H_5As)_2Mo_6O_{24}(OH_2)]^{4-}$ (Figure 2c)[14] and $[(IMo_7O_{26})_2]^{6-}$. The anion $[(C_6H_5As)_2Mo_6O_{24}(OH_2)]^{4-}$ contains a water molecule in its structure that makes its Mo_6 ring deformed and nonplanar. Why this anion encloses a water molecule to form such a distorted structure, which is known as Matsumoto structure, has not been understood at all and left as a total mystery. With the structure of $[(IMo_7O_{26})_2]^{6-}$ that contains a rutile-type core at hand, we can now at least speculate that $[(C_6H_5As)_2Mo_6O_{24}(OH_2)]^{4-}$ assumes such a "strange" structure because it can be more like a solid oxide this way. A molecular oxide of dimeric Matsumoto structure, $[\{(C_6H_5P)Mo_6O_{21}(OH_2)_3\}_2]^{4-}$, has also been isolated and structurally characterized (Figure 2d).[15] Here the structural relevance to $[(IMo_7O_{26})_2]^{6-}$ is even more apparent. The species shown in Figure 2b−d are not "odd ones". They are the ones that are closer to solid oxides.

The unique structural feature of $[(IMo_7O_{26})_2]^{6-}$ suggests that the current discovery is just a tip of an iceberg and this

(9) Linnett, J. W. *J. Chem. Soc.* **1961**, 3796−3803.
(10) Kondo, H.; Kobayashi, A.; Sasaki, Y. *Acta Crystallogr., Sect. B* **1980**, *B36*, 661−664.
(11) Evans, H. T., Jr. *Acta Crystallogr., Sect. B* **1974**, *B30*, 2095−2100.
(12) Fuchs, J.; Hartl, H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 375−376.
(13) Ichida, H.; Yagasaki, A. *J. Chem. Soc., Chem. Commun.* **1991**, 27−28.
(14) Matsumoto, K. Y. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 492−498.
(15) Lyxell, D.-G.; Boström, D.; Hashimoto, M.; Pettersson, L. *Acta Crystallogr., Sect. B* **1998**, *B54*, 424−430.
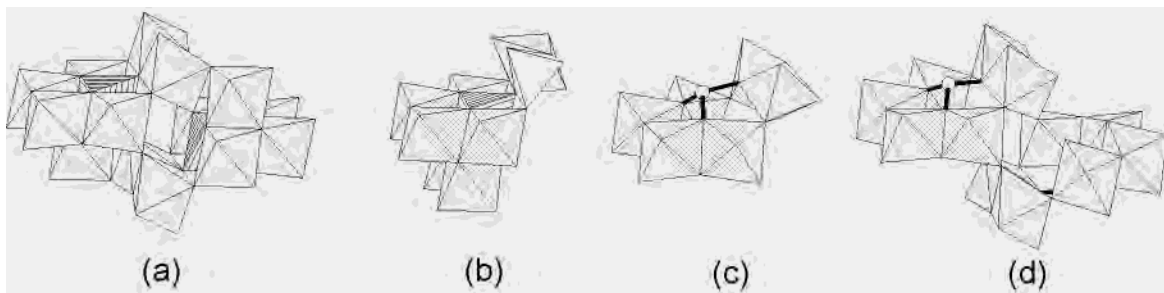
Figure 2. Structures of $[(IMo_7O_{26})_2]^{6-}$ (a), $[TeMo_8O_{29}(OH_2)]^{4-}$ (b), $[(C_6H_5As)_2Mo_6O_{24}(OH_2)]^{4-}$ (c), and $[\{(C_6H_5P)Mo_6O_{21}(OH_2)_3\}_2]^{4-}$ (d). The IO_6 and TeO_6 units are shaded by lines. The MoO_6 units are shaded by dots. The coordinatively unsaturated MoO_5 unit is represented by an unshaded square pyramid. As and P atoms are represented by small circles. Organic groups are omitted for clarity.

type of structure may actually be a prevalent one in the world of molecular oxides as mentioned above. Recent isolation of $[Mo_8O_{26}(OH)]^{5-}$,[16] which also has Matsumoto structure, supports this theory. The common feature of these and other species shown in Figure 2 is that they are synthesized using large organic cations. These nonclassical cations are poorer electron acceptors and much less hydrophilic than classical inorganic cations such as Na^+. These atoms would have smaller interactions with the surface oxygens of molecular oxides. This in turn would enhance the molecular nature of these species. A new field of rutile-type molecular oxide

would be opened up by further pursuing nonaqueous chemistry of molecular oxides.

Supporting Information Available: Crystallographic data for $[(C_6H_5)_4P]_4[(n\text{-}C_4H_9)_4N]_2[(IMo_7O_{26})_2]\cdot3CH_3CN$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0490425

(16) Fidalgo, E. G.; Neels, A.; Stoeckli-Evans, H.; Süss-Fink, G. *Polyhedron* **2002**, *21*, 1921−1928.