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Crystal Structure Analysis of $[(\mathrm{IMo_7O_{26}})_2]^{6-}$ — A Missing Link between Molecular and Solid Oxides

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Introduction

Most metal elements and many non-metal elements hydrolyze to form oligonuclear cations or anions such as $[\mathrm{Al_{13}O_4(OH)_{24}(OH_2)_{12}}]^{7+}$ and $[\mathrm{Mo_7O_{24}}]^{6-}$ [1]. When looking at the structures of these polications 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. Oxygen atoms accommodate non-oxygen atoms in their interstices in either group of compound. The track of direct relevance, however, seems to end here. One stumbles when he/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. A link between molecular oxides and solid oxides has been missing. Very recently, we have found this missing link and have analyzed its crystal structure.

Results

Reaction of $\mathrm{MoO_4^{2-}}$ and $\mathrm{HIO_4}$ lead to the formation of a new molecular oxide $[(\mathrm{IMo_7O_{26}})_2]^{6-}$ as a crystalline $[(n\text{-}\mathrm{C_4H_9})_4\mathrm{N}]^+$ salt. Crystals suitable for x-ray structural analysis, a double salt $[(\mathrm{C_6H_5})_4\mathrm{P}]_4[(n\text{-}\mathrm{C_4H_9})_4\mathrm{N}]_2[(\mathrm{IMo_7O_{26}})_2]\cdot 3\mathrm{CH_3CN}$, could be obtained by the reaction of $[(n\text{-}\mathrm{C_4H_9})_4\mathrm{N}]_6[(\mathrm{IMo_7O_{26}})_2]$ with $[(\mathrm{C_6H_5})_4\mathrm{P}]\mathrm{Br}$ in acetonitrile. It is, at 115(2) K, monoclinic, space group $P2_1/c$, with a = 18.9475(1) Å, b = 27.4414(1) Å, c = 17.4546(1), β = 116.3999(3)°, V = 8128.99(7) Å^3, and Z = 4. A colorless crystal of dimensions $0.32 \times 0.10 \times 0.05$ mm^3 was used for data collection. Diffraction data were collected on a Rigaku MERCURY CCD system at the NW2 beamline of PF-AR, using 18.00 keV (λ = 0.6890 Å) monochromatized X-ray beam. The final agreement factors were R = 0.0228 for 21005 reflections with $F^2 > 2\sigma(F^2)$ and $wR(F^2)$ = 0.0814 for 24189 unique reflections.

Discussion

The single-crystal x-ray diffraction study of the double salt revealed that the anionic molecular oxide has a novel type of structure shown in Figure 1. 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 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 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 a compactness of being fully close-packed, and 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. Given the prevalence of Keggin-type species and their derivatives, it is possible that $[(\mathrm{IMo_7O_{26}})_2]^{6-}$ is a representative of a large group of molecular oxides of similar structures.

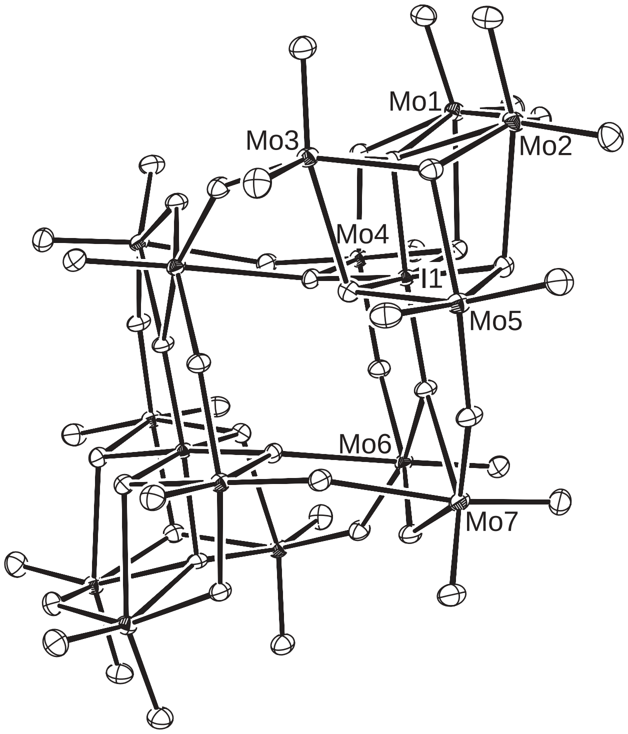

Figure 1. Structure of $[(\mathrm{IMo_7O_{26}})_2]^{6-}$. Displacement ellipsoids are drawn to encompass 50 % probability levels. Only heavy atoms are labeled for clarity.

References

[1] C. F. Baes, Jr. and R. E. Mesmer, “The Hydrolysis of Cations” (Wiley, New York, 1976).

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