Polyoxometalates

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Synthesis of Orthorhombic Mo-V-Sb Oxide Species by Assembly of Pentagonal Mo_6O_{21} Polyoxometalate Building Blocks**

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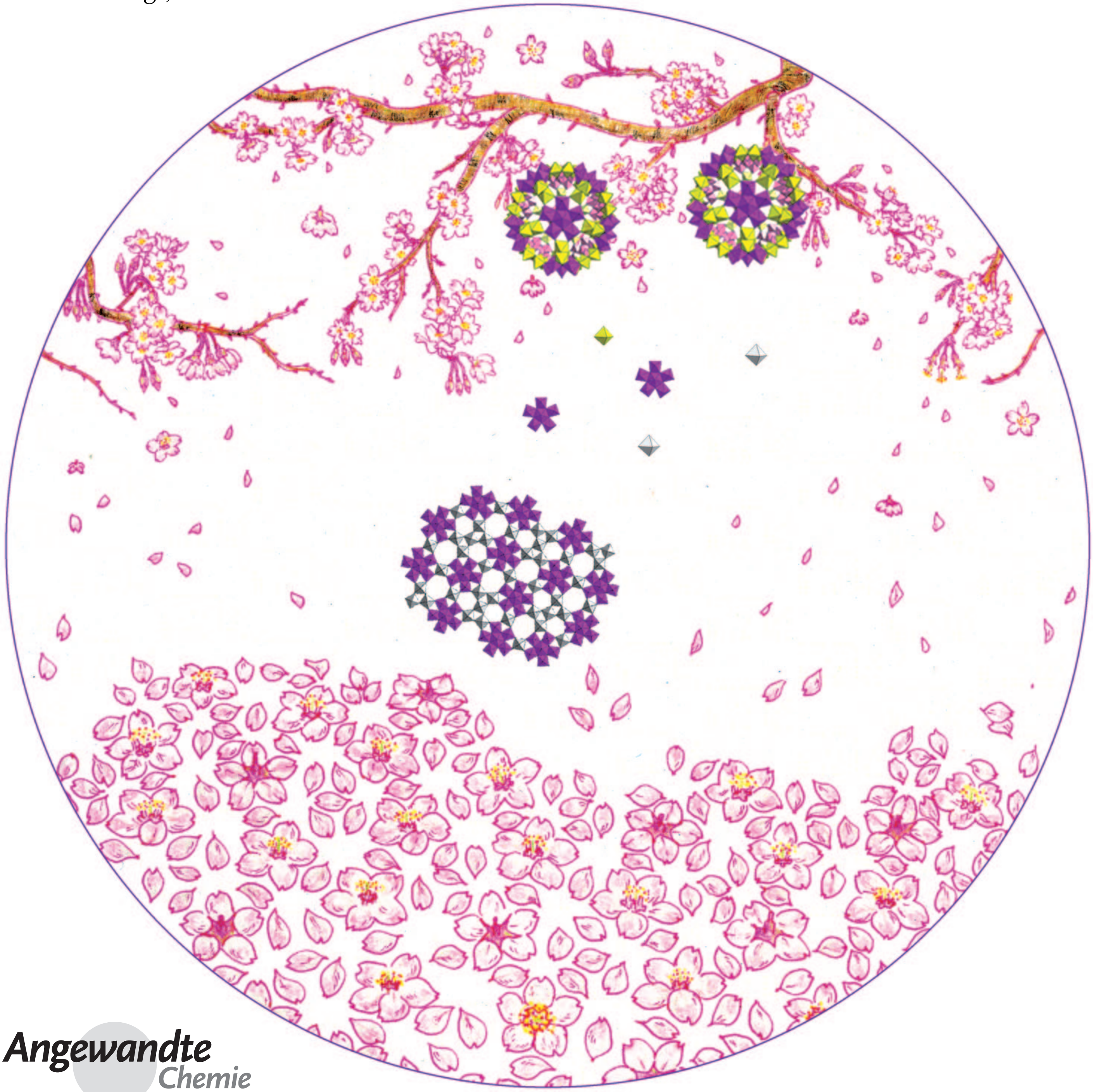

Construction of tailored crystalline solids assembled from molecular building blocks is a major topic in materials science.[1] Application of this approach, together with use of templating agents, has been particularly useful in the case of zeolites, owing to important applications in industry as catalysts and functional materials.[2]

Polyoxometalates (POMs) comprise a rich and diverse family of metal oxygen clusters made up of early transition metals (primarily tungsten and molybdenum) with unique redox, acidic, magnetic, and chemical properties. These compounds have promising applications in diverse disciplines, including catalysis, medicine, and materials science.[3] Furthermore, POM molecules have been attracting attention as building blocks for supramolecular inorganic materials.[4]

In polymolybdate chemistry, a new era of the pentagonal Mo building block $\{Mo_6O_{21}\}$ with a central pentagonal bipyramidal unit and five surrounding edge-sharing octahedra began with the discovery of the "big wheel" Mo_{154} anion by Müller and co-workers.[4b,5] They found several giant polyoxomolybdates with "hedgehog" (Mo_{368}), icosahedral (Mo_{132}), capped cyclic (Mo_{248}), and "basket" (Mo_{116}) architectures by exploiting a "virtual library" of pentagonal building blocks abundant in solution. The pentagonal $\{Mo_6O_{21}\}$ unit is well-known as a structural component in several molybdenum bronze frameworks.[6] However, rational construction of molybdenum-based oxides by assembly of pentagonal building blocks has not been achieved.

Herein, we describe the synthesis of a crystalline orthorhombic molybdenum–vanadium–antimony oxide (**1a**) by assembly of the pentagonal Mo building block with other Mo, V, and Sb moieties. Species **1a** is isostructural to orthorhombic Mo-V-Nb-Te oxide (**1b**) and Mo-V-Nb-Sb oxide (**1c**), which are the most promising oxidation catalysts for production of acrylonitrile and acrylic acid from propane; these oxides are known collectively as "M1 phases".[7] Orthorhombic Mo-V-based oxides (**1**) have a layered structure with a slab comprising six- and seven-membered rings of corner-sharing octahedra and pentagonal $\{M_6O_{21}\}$ units, in which Mo and V are the main elements (Figure 1, bottom). The Te or Sb atoms are thought to be located in both the six- and seven-membered rings, and the Nb atoms are thought to exist in the middle of the pentagonal units.[8]

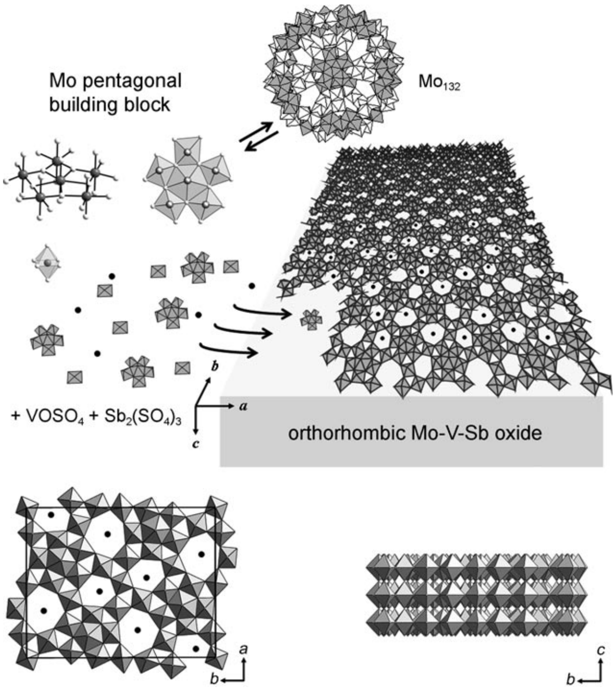

Figure 1. Plausible building-block reaction mechanism (top) and structure of orthorhombic Mo-V-Sb oxide (**1a**; bottom). Mo and V are in the center of polyhedra. Sb is represented by black circles, which occupy hexagonal and heptagonal channels in the oxide.

Recently, we used hydrothermal synthesis to prepare an orthorhombic Mo-V oxide (**1d**) that contains exclusively Mo and V as metal atoms.[9] We found that a ball-type polyoxomolybdate $Mo_{72}V_{30}$ ($[\{(Mo)Mo_5O_{21}(H_2O)_3(SO_4)\}_{12}(VO)_{30}(H_2O)_{20}]^{36-}$) complex formed in the reaction solution before the hydrothermal reaction.[10] The $Mo_{72}V_{30}$ complex contains

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12 pentagonal $[Mo_6O_{21}]^{6-}$ units connected by 30 vanadyl $[VO]^{2+}$ moieties,[11] and we proposed that this Mo pentagonal unit is probably a building block for the synthesis of **1d**. To determine the building-block mechanism, it is necessary to confirm that the pentagonal units in the metal oxide are composed of Mo. To date, crystals of **1d** have been too small (under 1 μm) to perform single-crystal structural analysis. Furthermore, successful Rietveld analysis of powder samples of **1d** has not yet been realized.[8a,b]

With the belief that the Mo pentagonal unit is a building block for orthorhombic Mo-V-based oxides (**1**; Figure 1), we have continued screening reaction conditions by using polyoxomolybdates containing the Mo pentagonal unit as a Mo source to obtain crystals large enough to conduct single-crystal analysis. Our choice of polyoxomolybdate was the Mo_{132} ($[\{(Mo)Mo_5O_{21}(H_2O)_6\}_{12}\{Mo_2O_4(CH_3CO_2)\}_{30}]^{42-}$) ion, in which 12 Mo pentagonal units were connected by 30 Mo_2 units to form ball-shaped molecules.[12] This choice was based on the following reason: kinetic stability of the Mo pentagonal unit was expected, because the Mo_2 connecting unit in the Mo_{132} molecule can be exchanged for other connecting units to form other ball-shaped polyoxomolybdates.[13]

Reaction of the Mo_{132} ion, $VOSO_4{\cdot}n\,H_2O$, and $Sb_2(SO_4)_3$ under hydrothermal conditions provides a well-crystallized orthorhombic Mo-V-Sb oxide (**1a**) with crystallite sizes up to 10 μm (Figure 2a and Supporting Information, Figure S1). Addition of the Sb cation was necessary to increase the crystal size. The presence of the pentagonal $[Mo_6O_{21}]^{6-}$ unit in reaction solution prior to the hydrothermal reaction was confirmed using Raman spectroscopy (Supporting Information, Figure S2, peak at ca. 880 cm^{-1}).[10]

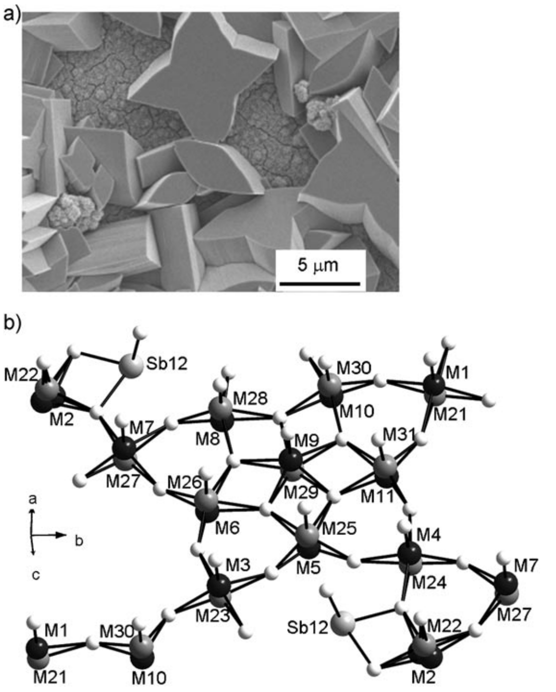

Figure 2. a) SEM image of orthorhombic Mo-V-Sb oxide (**1a**). b) Site map of an asymmetric unit in **1a** obtained from single-crystal structural analysis. Metals with high occupancy (black balls), low occupancy (gray balls), Sb (Sb12, large light-gray balls), and oxygen (small white balls).

X-ray single-crystal structure analysis of a crystal of **1a** was performed using synchrotron radiation, and this is the first successful single-crystal structural analysis of an orthorhombic Mo-V-based oxides (**1**). Metal coordinates, occupancies, and metal–oxygen bond lengths are summarized in Tables S1 and S2 in the Supporting Information. The pentagonal units are found to consist exclusively of Mo metal, and V is found predominantly in linking polyhedra connecting the pentagonal units. Both Mo and V metals occupy non-pentagonal-unit metal sites (M1–M4 and M7), with Mo occupancy ranging from 0.32 to 0.84. Mo and V in octahedral sites have out-of-center distortions with significant elongation of one apical M−O bond and corresponding shortening of the other apical M−O bond; these findings are similar to previous results obtained using a combined Rietveld analysis of synchrotron X-ray and neutron powder diffraction data of **1b**.[8d] The short apical distance ranged from 1.58 to 1.75 Å, the long distance ranged from 2.28 to 2.45 Å, and equatorial M−O bonds ranged from 1.77 to 2.09 Å; these distances are reasonable for molybdenum oxides containing pentagonal units.[6,8] Using single-crystal analysis, disordering of all metal sites along the z direction was detected (black and gray balls in Figure 2b), which is often observed in single-crystal structural analyses of polyoxomolybdates[5] and molybdenum oxides.[6] The occupancy ratios between the disordered metal sites in the pentagonal units (M5, M6, M8–M11 vs. M25, M26, M28–M31) are almost identical (0.75), while the ratio varies from 0.64 to 0.86 in other metal sites (M1–M4, M7 vs. M21–M24, 27). The direction of displacements of central metal atoms in the pentagonal columns are opposite to those in the five surrounding octahedra, because the metal–metal separations from the central atom (across the shared edges) are considerably shorter than those peripheral to the pentagonal rings. The Sb atom was found only in the hexagonal channel and was not detected in the heptagonal channel. This finding, based solely on the X-ray data, could indicate either absence or low occupancy such that Sb could not be distinguished from N and O atoms present as NH_4^+ and H_2O in the channels.

Contrast that may indicate the presence of Sb in heptagonal channels, in addition to the expected hexagonal occupancy, was detected using high-resolution (HR) TEM imaging along the [001] direction (Figure 3a and Supporting Information, Figure S3). Hexagonal and heptagonal channels without Sb spots were also observed, indicating that neither of the channels are fully occupied, although this result may be influenced by electron-beam-induced sublimation. More intense contrast was observed in the hexagonal channel (Sb1), and the contrast in heptagonal channels (Sb2) was weak and found in only a few heptagonal channels. This weak contrast (Sb2) could be simulated with approximately 30% occupancy for this heptagonal channel (Supporting Information, Figure S4). Furthermore, micropore volume of the Mo-V-Sb oxide was much smaller than that of orthorhombic Mo-V oxide (**1d**) in which the empty heptagonal channel is a micropore (Supporting Information, Figure S5).[9a] These results indicate that Sb may be present in the heptagonal channels at low occupancy.

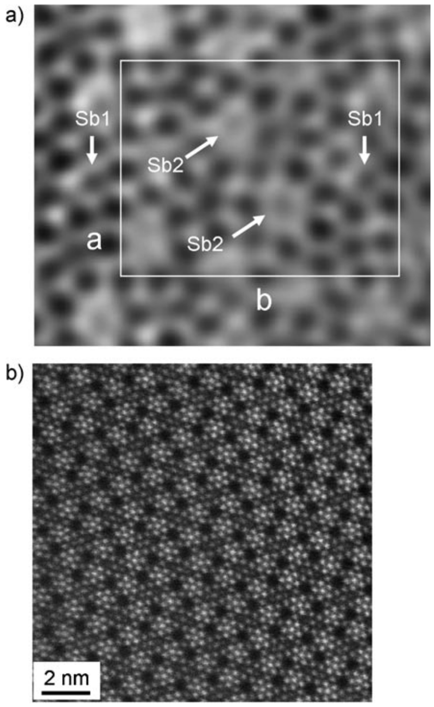

Figure 3. a) HR-TEM and b) HAADF-STEM images showing [001] projection of orthorhombic Mo-V-Sb oxide (**1a**). Sb1 and Sb2 in (a) indicate spots in hexagonal and heptagonal rings, respectively, and the unit cell is shown.

For high-resolution high-angle annular dark field (HAADF) STEM imaging, the contrast is roughly proportional to the square of the atomic number, providing enhanced Z contrast.[14] As clearly observed in Figure 3b and Supporting Information Figure S6, contrast from atomic columns in the pentagonal units is more pronounced than that from the other metal columns, indicating that occupancy of Mo as the higher Z species is dominant in the pentagonal units; this finding is consistent with the single-crystal structure analysis. The contrast from Sb is weak in the hexagonal channels owing to partial occupancy and is not clearly detected in the heptagonal channels.

We have presented, for the first time, results of a single-crystal structural analysis of the orthorhombic Mo-V-Sb oxide (**1a**), which is isostructural to the well-known orthorhombic Mo-V-Nb-Te oxide (**1b**, "M1 phase"). Although many structural analyses have been published to date, single-crystal structural analysis has not previously been successful.[8] This single-crystal analysis, together with HAADF-STEM imaging, revealed that the pentagonal unit metal centers were composed exclusively of Mo metal ions. Raman spectroscopy confirmed that the Mo pentagonal unit was supplied from the ball-type polyoxomolybdate Mo_{132} prior to the hydrothermal reaction (Supporting Information, Figure S2). This result provides new evidence that the pentagonal polyoxomolybdate ion $[Mo_6O_{21}]^{6-}$ is a building block for the synthesis of this orthorhombic Mo-V-Sb oxide, as the Mo pentagonal unit exists in both the dissolved precursor and the product (Figure 1). This is also the first example of a polyoxometalate being used as a building block for the synthesis of a metal oxide.

Orthorhombic Mo-V-based oxides (**1**) are promising oxidation catalysts[7] and are novel octahedral molecular sieves with micropores.[10] Elucidation of the formation mechanism together with structural information will lead to the development of strategies to design novel Mo-based catalysts and octahedral molecular sieves.

Experimental Section

Materials: All chemicals including distilled water were reagent-grade and used as supplied. The compound $(NH_4)_{42}[Mo_{132}(OAc)_{30}O_{372}(H_2O)_{72}]$ (Mo_{132}) was prepared according to the published procedure[12] and analyzed by IR and Raman spectroscopy.

Preparation of orthorhombic Mo-V-Sb oxide (**1a**): Mo_{132} (3.0 g, Mo: 13.8 mmol) was dissolved in water (40 mL) and heated at 353 K for 10 min before $VOSO_4 \cdot n H_2O$ (1.15 g, $n = 5.4$, 4.2 mmol) was added. After the solution was stirred at 353 K for 10 min, $Sb_2(SO_4)_3$ (0.71 g, Sb: 2.7 mmol) was added. The resulting slurry was stirred for 10 min at the same temperature and then transferred to a 50 mL teflon-lined stainless-steal autoclave with help of additional 10 mL water. Six teflon plates were inserted in the teflon liner, and the mixture was then heated at 448 K for 24 h. The gray solid (about 0.23 g) that formed on the teflon plates was collected, washed with water, and dried at 353 K overnight.

The presence of H_2O and NH_4^+, possibly in the porous channels and on the crystal surface, was confirmed by FT-IR spectroscopy (Figure S6 in the Supporting Information).

Formula from elemental analysis $Mo_{33.3}V_{6.7}Sb_{2.3}O_{114.3}(NH_4)_{3.2}(H_2O)_{0.5}$. Elemental analysis (%) calcd: Mo 55.9, V 6.0, Sb 4.9, O 32.2, N 0.78, H 0.22, S 0, total 99.8; found: Mo 56.3, V 6.4, Sb 4.5, O 31.7, N 0.49, H 0.32, S 0.

X-ray crystallography of **1a**: A single crystal was mounted on a carbon fiber using a micromanipulator under an optical microscope. Data were collected at 293 K under vacuum to measure reflection intensities accurately by reducing the air-scattered background. synchrotron radiation (12.0651 keV ($\lambda = 1.0276$ Å)) and a MAC Science low-temperature vacuum X-ray camera equipped with an imaging plate (IP) area detector in the BL02B1 beamline at Spring-8 were used. The frames were indexed and the reflections integrated with DENZO and subsequently scaled with SCALEPACK.[15a] An empirical correction for absorption anisotropy was applied to all intensity data by using PLATON-MULABS.[15b] The structure model was refined by full-matrix least-squares techniques on F^2 (SHELXL-97)[16a] using x, y, and z coordinates from orthorhombic Mo-V-Nb-Te oxide (**1b**) as starting parameters.[10d] All atoms were isotropically refined. All calculations were performed with the WinGX crystallographic software package.[16b] All metal atoms and oxygen atoms were refined isotropically, as their anisotropic refinements were unstable because of the small contribution of each atom to the total scattering intensity.

Crystal structure analysis for **1a** ($Mo_{32.34}V_{7.66}Sb_{2.10}O_{114.6}N_{3.20}H_{13.80}$): black plate, $0.007 \times 0.003 \times 0.001$ mm, orthorhombic, space group $Pba2$, $a = 21.166(1)$, $b = 26.620(1)$, $c = 4.009(1)$ Å, $V = 2258.8(6)$ Å^3, $Z = 1$, $\rho_{calcd} = 4.147$ Mg m^{-3}, $2\theta_{max} = 94.32°$, total measured reflections 17336, independent reflections 3211, $R_{int} = 0.0892$, empirical absorption correction based on measured intensities of equivalent reflections at different phi and omega values ($\mu = 15.956$ mm^{-1}, min./max. transmission 0.9286/0.9588), $R_1 = 0.0632$ for 2563 reflections with $I > 2\sigma(I)$ and $wR_2 = 0.2258$ for all reflections, 204 parameters, highest residual electron density 2.788 e Å^{-3}. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-420112.

Other characterization methods: Scanning electron microscopy (SEM) was performed on a JSM-7400F (JEOL) instrument. High-resolution transmission electron microscopy (HR-TEM) images were taken by an atomic-resolution high-voltage electron microscope at 800 kV (HITACHI, H-1500). Powder specimens were dispersed in CCl_4 and dropped onto a holey carbon-coated copper grid. Aberration-corrected HR-STEM at 200 kV was completed on a JEOL 2100F equipped with a CEOS Cs corrector on the illumination system. The geometrical aberrations were measured and controlled to provide less than a $\pi/4$ phase shift of the incoming electron waves over the probe-defining aperture of 14.5 mrad. HAADF-STEM images were acquired on a Fischione Model 3000 HAADF detector with a camera length such that the inner cut-off angle of the detector was 65.6 mrad. The scanning acquisition was synchronized to the 60 Hz AC electrical power to minimize 60 Hz noise in the images, and a pixel dwell time of 32 ms was chosen. Samples were prepared by grinding the as-prepared solid and dipping a holey-carbon coated Cu grid into the powder. Complete elemental analysis was carried out by Mikroanalytisches Labor Pascher (Remagen, Germany).

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