$3.27\,mm^{-1}$; $T = 98$ K, $2\theta_{max} = 54°$. Data were collected on a Mercury CCD area detector coupled with a Rigaku AFC-8S diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation (0.7107 Å) using CrystalClear (Rigaku Co.). Total reflections collected 30371. Data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied by using REQABA (min./max. transmission: 0.61/1.01). The structures were solved on a Silicon Graphics O2 computer system using teXsan, version 1.11 (Molecular Structure Co.). The initial position of rhenium atoms were determined by direct methods and other atoms were located using Fourier and difference Fourier techniques. Re, Sb, and Se atoms were refined anisotropically. Other non-hydrogen atoms were refined isotropically. With the exception of hydrogen atoms of crystal solvents, all hydrogen atoms were located at the calculated positions. One tolyl group was refined by using a rigid model. Full-matrix least-square refinement was employed against *F*. Final *R* and R_w values were 0.084 and 0.122 for 8842 observed reflections ($I > 3.5\sigma(I)$) and 735 variable parameters. Max./min. residual electron density were $2.87/-1.60\,e\,Å^{-3}$, both near Re atoms. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-170237. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[28] J. R. Long, A. S. Williamson, R. H. Holm, *Angew. Chem.* **1995**, *107*, 248–251; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 226–229.

[29] J. R. Long, L. S. McCarty, R. H. Holm, *J. Am. Chem. Soc.* **1996**, *118*, 4603–4616.

[30] Z. Zheng, R. H. Holm, *Inorg. Chem.* **1997**, *36*, 5173–5178.

[31] Z. Zheng, J. R. Long, R. H. Holm, *J. Am. Chem. Soc.* **1997**, *119*, 2163–2171.

[32] N. G. Naumov, A. V. Virovets, M. N. Sokolov, S. B. Artemkina, V. E. Fedorov, *Angew. Chem.* **1998**, *110*, 2043–2045; *Angew. Chem. Int. Ed.* **1998**, *37*, 1943–1945.

[33] M. W. Willer, J. R. Long, C. C. McLauchlan, R. H. Holm, *Inorg. Chem.* **1998**, *37*, 328–333.

[34] L. G. Beauvais, M. P. Shores, J. R. Long, *Chem. Mater.* **1998**, *10*, 3783–3786.

[35] A preliminary X-ray structural analysis of **5** revealed the suggested structure. (T. Yoshimura, unpublished result).

[36] R. Arratia-Perez, L. Hernandez-Acevedo, *J. Chem. Phys.* **1999**, *110*, 2529–2532.

[37] R. Arratia-Perez, L. Hernandez-Acevedo, *J. Chem. Phys.* **1999**, *111*, 168–172.

[38] C. Guilbaud, A. Deluzet, B. Domercq, P. Molinie, C. Coulon, K. Boubekeur, P. Batail, *Chem. Commun.* **1999**, 1867–1868.

[39] H. Honda, T. Noro, K. Tanaka, E. Miyoshi, *J. Chem. Phys.* **2001**, *114*, 10791–10797.

[40] L. Alvarez-Thon, L. Hermandez-Acevedo, R. Arratia-Perez, *J. Chem. Phys.* **2001**, *115*, 726–730.

[41] $[Re_6S_8(CH_3CN)_6](BF_4)_2$ was prepared from $(Bu_4N)_3[Re_6S_8I_6]$ in a manner similar to the μ_3-Se analogue.[31]

[42] $[Re_6S_8(CH_3CN)_6](SbF_6)_2$ was prepared by the method used to prepare $[Re_6Se_8(CH_3CN)_6](BF_4)_2$[31] but using $AgSbF_6$ in place of $AgBF_4$.

Photochemical Formation of Tire-Shaped Molybdenum Blues: Topology of a Defect Anion, $[Mo_{142}O_{432}H_{28}(H_2O)_{58}]^{12-}$**

Toshihiro Yamase* and Petra V. Prokop

UV irradiation (corresponding to the O → Mo ligand-to-metal charge-transfer photoexcitation) of isopolyoxomolybdates in aqueous solutions containing electron donors (such as alkylammonium cations, alcohols, and aliphatic carboxylates) results in formation of high-nuclearity mixed-valence species as a result of reduction self-assembly processes based on the dehydrative condensation at $[Mo^{V}O_5(OH)]$ sites produced photochemically in the polyoxomolybdate lattice:[1, 2] $[Mo_7O_{24}]^{6-}$ and β-$[Mo_8O_{26}]^{4-}$, which are dominant species at pH levels of 5.4 and 3.3 respectively, are converted into $[Mo_{14}O_{46}]^{10-}$ ($\{Mo_{14}\}$) $= [(Mo^{V}Mo^{VI}_{6}O_{23})_2]^{10-}$ and $[H_{14}Mo_{37}O_{112}]^{12-} = \{[H_{10}Mo^{V}_{12}O_{40}(Mo^{VI}O_2)_3][H_2Mo^{V}_{6}Mo^{VI}_{5}O_{33}]_2\}^{12-}$, respectively.

In our extension of the solution photolysis of isopolyoxomolybdates to $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$ ($\{Mo_{36}\}$), which is the dominant species at pH 1–2 and higher-Mo concentrations ($\geq 10^{-2}$ M), we found the photochemical formation of a variety of car-tire-shaped giant molybdenum blues. These were also formed by thermal reduction[3–8] of Na_2MoO_4 with reducing agents such as iron, ascorbic acid, $NH_2OH \cdot HCl$, $N_2H_4 \cdot H_2SO_4$, and $Na_2S_2O_4$ under strongly acidic conditions (pH ≈ 1). The structure of $\{Mo_{36}\}$ consists of a centrosymmetric arrangement of two $\{Mo_{18}\}$ subunits, each of which is viewed as a Mo_7O_{24} group encircled by edge- and corner-shared MoO_6 octahedra (Figure 1).[9] We describe here a diamagnetic blue 28-electron reduced species ($\{Mo_{142}\}$ **1a**) produced photochemically through the degradative self-assembly of $\{Mo_{36}\}$ and discuss size and shape for the ring clusters derived from $\{Mo_{36}\}$ on the basis of the successive two-electron reduction dehydrative–condensation processes similar to the reductive dimerization of $[Mo_7O_{24}]^{6-}$ to $\{Mo_{14}\}$.[1]

$[Mo^{V}_{28}Mo^{VI}_{114}O_{432}H_{28}(H_2O)_{58}]^{12-}$ **1a**

The title anion (Figure 2a) has been isolated as $[NH_3i Pr]^+$ salt **1**[10–12] the structure of which is quite similar to that reported for $Na_{26}[Mo^{V}_{28}Mo^{VI}_{114}O_{432}H_{14}(H_2O)_{58}] \cdot$ ca. $300\,H_2O$ thermally produced in the $Na_2MoO_4 \cdot 2\,H_2O/Na_2SO_4/N_2H_4 \cdot H_2SO_4/H_2SO_4$ system.[4]

$[NH_3i Pr]_{10}H_2[Mo^{V}_{28}Mo^{VI}_{114}O_{404}(OH)_{28}(H_2O)_{58}] \cdot 90\,H_2O$ **1**

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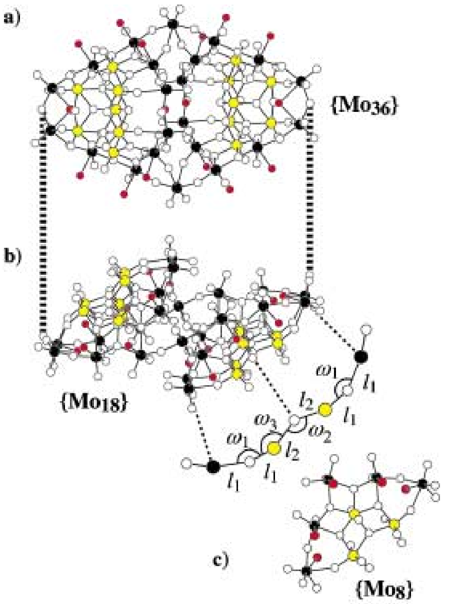

Figure 1. Structure of the $\{Mo_{36}\}$ unit (a), which is formed by connecting two $\{Mo_{18}\}$ units (b). Curvature of the Mo-O-Mo bond array (b) for the $\{Mo_8\}$ block (c) observed in the $\{Mo_{18}\}$ unit. For the Mo_7O_{24} moiety: Mo atoms: yellow; aqua-ligand oxygen atoms: red. The edge-shared Mo atoms are black.

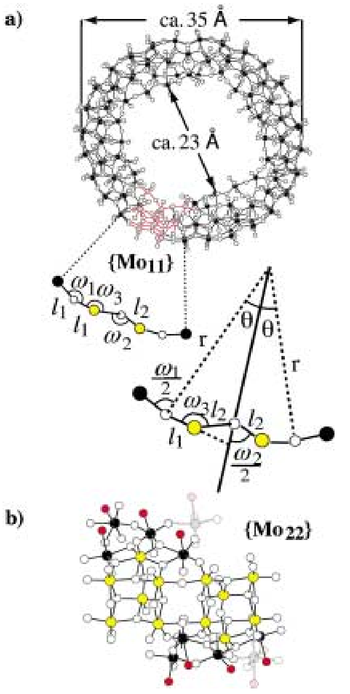

Figure 2. a) Structure of **1a** and curvature of the Mo-O-Mo bond array for the $\{Mo_{11}\}$ subunit (red bonds) for estimation of the ring radius. b) Structure of the $\{Mo_{22}\}$ unit, formed by connection of two $\{Mo_{11}\}$ subunits. For the mono-lacunary Mo_6O_{23} moiety: Mo atoms: yellow; aqua-ligand oxygen atoms: red. Two $\{Mo_1\}$ linkers are shown with dotted bonds.

The degree of protonation was estimated on the basis of the calculation of the bond valence sums (Σs),[13] although exact determination of the degree of protonation was a problem. The Σs calculation for **1a** indicates 28 singly and 58 doubly protonated oxygen atoms. Ten of the singly protonated oxygen atoms (for $0.7 \leq \Sigma s \leq 1.2$) are μ_3-O atoms situated in the equatorial plane and link two Mo atoms in incomplete double-cubane-type compartments of the mono-lacunary Mo_6O_{23} moieties as well as another Mo atom that also lies in this plane (Figure 2b). The remaining OH^- ligands are coordinated at terminal positions to other octahedral Mo sites. Of the doubly protonated O atoms (terminal aqua ligands), 42 aqua ligands are coordinated to the Mo atoms (one aqua ligand per Mo) for three edge-shared octahedra encircling the pentagonal-bipyramidal seven-coordinate Mo site at the each end of 14 mono-lacunary Mo_6O_{23} groups, which are arranged both above and below the ring plane. The remaining 16 aqua ligands are coordinated to 16 corner-shared octahedral Mo sites (one for each) as linkers (Figure 2b). The manganometric redox titration shows the presence of 27.5 Mo^V centers in **1**. Since 10 $[NH_3\textit{i}Pr]^+$ ions and 90 crystal water molecules in **1** are determined by X-ray crystallography and the overall number of Mo^V centers in **1a** is likely to be 28, the coordination of 28 OH^- ions and 58 aqua ligands in **1a** (as estimated by the Σs calculation) enables us to formulate **1** as given (with the additional two protons to balance the charge).

Compound **1a** as a discrete anion is a defect species derived formally by removing six sets of $[Mo(H_2O)O_2(\mu\text{-}O)Mo(H_2O)O_2]^{2+}$ units ($\{Mo_2\}$) for the construction of the inner rings from a hypothetical tire-shaped cluster **2**, which consists of 140 MoO_6 octahedra and 14 MoO_7 pentagonal bipyramids, with approximately D_{7d} symmetry. The half-deprotonated species $\{Mo_{154}\}$, **2a** has been thermally isolated in the $Na_2MoO_4 \cdot 2H_2O/Na_2S_2O_4/HCl$ system, and the structure of **2a** has been described as a tetradecamer (with approximate D_{7d} symmetry) of a conjugated group consisting of three different building blocks as $[\{Mo_8\}+\{Mo_2\}+\{Mo_1\}]$:[4, 5] the $\{Mo_8\}$ unit is observed in a quarter moiety of $\{Mo_{36}\}$ and neighboring $\{Mo_8\}$ units above and below the equator of the ring are linked by a $\{Mo_1\}$ unit that lies in the equator (Figure 1 and 2).

$[Mo^{V}_{28}Mo^{VI}_{126}O_{462}H_{28}(H_2O)_{70}]$ **2**

$[Mo^{V}_{28}Mo^{VI}_{126}O_{462}H_{14}(H_2O)_{70}]^{14-}$ **2a**

Since **2a** is built up by reductive degradation of $\{Mo_{36}\}$ to $\{Mo_8\}$, if $\{Mo_8\}$ is one of three building blocks, the coordination mode of the $\{Mo_8\}$ unit should be retained through the degradation of $\{Mo_{36}\}$ (Figure 1c). One can remark that two (as bridging ligands) of five aqua ligands in $\{Mo_8\}$ are replaced by μ_3-O atoms lying in the equator for both **1a** and **2a** (Figure 2b).[4, 5] In conjunction with that the coordination mode for other three aqua ligands in $\{Mo_8\}$ is retained in **1a** (although in some of the MoO_6 octahedra the terminal O and aqua ligands change their positions), such replacement implies that four MoO_6 octahedra incorporating the bridging aqua ligands in $\{Mo_{18}\}$ are degradatively liberated through the reductive self-assembly reaction of $\{Mo_{36}\}$. Thus, the structure of $\{Mo_{154}\}$ could be simply described as a tetradecamer of the $\{Mo_{11}\}$ subunits related by S_{14} symmetry, each of which is the mono-lacunary Mo_6O_{23} group containing a seven-coordinate Mo site at the end where an additional three edge-shared MoO_6 octahedra are attached and symmetrically linked by two corner-sharing MoO_6 octahedra as linkers (Figure 2). In the photochemical formation of $\{Mo_{14}\}$ (with the *cis*-configuration of Mo_7O_{23} moieties) as a result of the dimeric condensation of the one-electron reduced species of $[Mo_7O_{24}]^{6-}$ (incorporated in $\{Mo_{36}\}$), two electrons are delocalized over the central linear Mo–O–Mo linkages (with Mo-O-Mo bond angles (ω_1) of 174.4 and 175.0° and Mo–O bond lengths (l_1) of 1.87 – 1.89 Å) with approximately C_{2v} symmetry (Figure 3 a).[1] In **1a** or **2a**, the Mo–O–Mo bonds linking the neighboring mono-lacunary Mo_6O_{23} groups above and below the equator of the ring have large Mo-O-Mo bond angles ($\omega_1 = 156 - 160°$, average, 158°) and approximately symmetric Mo–O bonds ($l_1 = 1.80 - 1.95$ Å, average, 1.88 Å) (Figure 2 a). This let us conceive an idea that in the photochemical self-assembly of $\{Mo_{36}\}$ ($=2\{Mo_{18}\}$) to $\{Mo_{142}\}$ or $\{Mo_{154}\}$ the successive dehydrative condensation of two $\{Mo_{18}\}$ halves occurs in a mode similar to the photodimerization of $[Mo_7O_{24}]^{6-}$ to $\{Mo_{14}\}$ where the pentagonal-bipyramid-associated moiety is removed from an alternate half of $\{Mo_{18}\}$ because of steric hindrance between the bulky moieties, after the liberation of all the MoO_6 octahedra associated with the bridging aqua ligands (Figure 3 b). Then, the attachment of a corner-shared MoO_6 octahedron (as an additional linker) to each remaining half results in the formation of a $\{(Mo_{11})_2\} \equiv \{Mo_{22}\}$ unit (two-electron reduced species) which will enable photochemical two-electron reduction again (one-electron reduction for each $\{Mo_{11}\}$ subunit). Thus, the successive degradative – dehydration condensation on every two-electron photoreduction continues to build up a ring structure with *trans* orientation of the seven-coordinate Mo-site entities in neighboring $\{Mo_{11}\}$ subunits and with further attachment of the MoO_6 linker for the inner-ring formation. The partial lack of linkers leads to the formation of a tire-shaped defect structure.

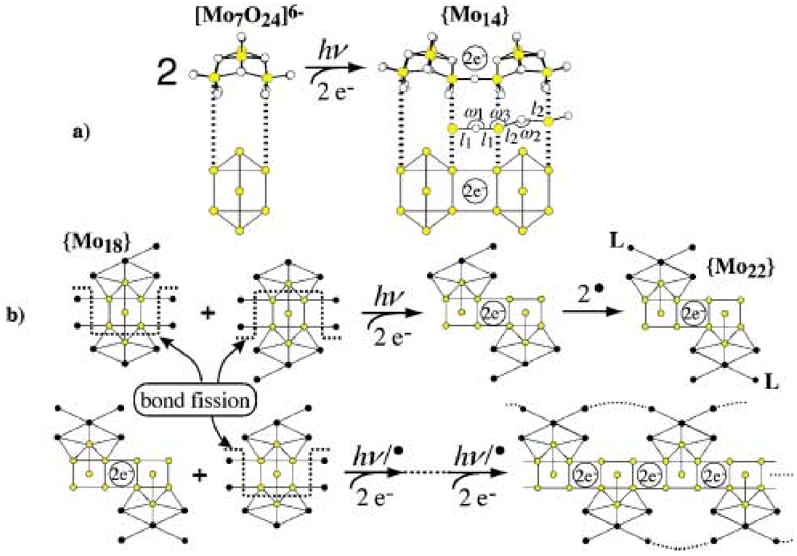

Figure 3. Schematic representations for the photodimerization of $[Mo_7O_{24}]^{6-}$ to $[(Mo^{V}Mo^{VI}_{6}O_{23})_2]^{10-}$ ($\{Mo_{14}\}$) (a) and for the photochemical formation of giant tire-shaped clusters from $\{Mo_{36}\}$ (2 $\{Mo_{18}\}$) and $\{Mo_{22}\}$ (b). Mo_7O_{24}-related moiety Mo atoms are yellow. All the O atoms are omitted for clarity in (b); L = linker.

A small curvature of the Mo-O-Mo bonds linking the mono-lacunary Mo_6O_{23} associated moieties for **1a** (Figure 2 b) let us estimate both size (the outer O ··· O diameter, $D = 2r$) and number (n) of $\{Mo_{22}\}$ building block (as formally four-electron reduced species) for a full-ring construction of $\{Mo_{154}\}$. By using Mo-O-Mo and O-Mo-O bond angles (ω_2 and ω_3, respectively) and Mo–O bond lengths (l_2) for the incomplete double-cubane-type compartments above and below the equator, we can estimate a full ring with $D \approx 34$ Å as a heptamer ($\{Mo_{154}\}$, 28-electron reduced species) of $\{Mo_{22}\}$, since the ring size estimated from ω_1 (156 – 160°, av 158°), ω_2 (137 – 145°, 140°), ω_3 (153 – 161°, 157°), l_1 (1.80 – 1.95 Å, 1.88 Å), and l_2 (1.95 – 2.13 Å, 2.04 Å) for **1a** give $n = 6.5$ and $D = 31$ Å. The estimated value is very close to $D \approx 35$ Å for **1a**. On the other hand, in the case where the $\{Mo_8\}$ unit (Figure 1 c) observed for a quarter moiety of $\{Mo_{36}\}$ is a building block for the ring formation, values of ω_1 (151.9 – 155.7°, av 154.3°), ω_2 (144.0 and 141.6°, 142.8°), ω_3 (155.0 – 157.6°, 155.9°), l_1 (1.71 – 1.75 Å, 1.73 Å), and l_2 (2.08 – 2.15 Å, 2.12 Å) for $\{Mo_{36}\}$[9] show a large displacement ($D \approx 24$ Å as a ring corresponding to a pentamer of $\{Mo_{22}\}$ unit) from the value for **1a** or **2a**. Furthermore, a curvature (with $\omega_1 = 174.7°$ (av), $\omega_2 = 152.6 - 154.3°$, 153.3°, $\omega_3 = 156.6 - 157.8°$, 157.3°, $l_1 = 1.88$ Å (av), and $l_2 = 2.13$ Å) of the central Mo-O-Mo bond array for the$\{Mo_{14}\}$ building unit (Figure 3 a)[1] let us estimate a ring of 7.5 units, indicates the plausible construction of either heptamer (with $D \approx 35$ Å) or octamer (with $D \approx 40$ Å) of the $\{Mo_{14}\}$ unit. The outer size for either full ring by $\{Mo_{14}\}$ is also close to that of $\{Mo_{154}\}$ or $\{Mo_{176}\}$ ($\equiv [Mo^{V}_{32}Mo^{VI}_{144}O_{528}H_{32}(H_2O)_{80}]$[7]). These results strongly suggest that **2a** is built up by the reductive propagation of seven $\{Mo_{22}\}$ (or fourteen $\{Mo_{11}\}$) units (associated with the $\{Mo_{14}\}$ formation) rather than by the self-assembly of the three different building blocks as $[\{Mo_8\} + \{Mo_2\} + \{Mo_1\}]$. The above mechanism proposed for the formation of tire-shaped molybdenum blues manifests that both $\{Mo_{154}\}$ as the heptamer of $\{Mo_{22}\}$ units (formally four-electron reduced species) and $\{Mo_{142}\}$ as its defect species lacking six pairs of the two $\{Mo_1\}$ linkers are 28-electron reduced species. These Mo 4d electrons are diamagnetically delocalized above and below the equator of the ring through Mo–O–Mo linkages (Mo-O-Mo bond angles of 125 – 163°) among corner-shared MoO_6 octahedra for **1a**.[14]

The choice of electron donor, duration of photolysis, and solution pH provide great flexibility with regard to structure within this class of compounds by allowing the tuning of the absence of linkers and the extent of protonation. Molybdenum blue photochemistry provides not only the opportunity to investigate the mechanism of degradation self-assembly processes but also a basis for the molecular design of nanosized ring clusters.

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[1] T. Yamase, *J. Chem. Soc. Dalton Trans.* **1991**, 3055.
[2] T. Yamase, E.Ishikawa, *Langmuir* **2000**, *16*, 9023.
[3] A. Müller, S. Q. N. Shah, H. Bögge, M. Schmidtmann, *Nature* **1999**, *397*, 48.
[4] A. Müller, C. Beugholt, M. Koop, S. K. Das, M. Schmidtmann, H. Bögge, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1960.
[5] A. Müller, S. K. Das, V. P. Fedin, E. Krickemeyer, C. Beugholt, H. Bögge, M. Schmidtmann, B. Hauptfleisch, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1187.
[6] C.-C. Jiang, Y.-G. Wei, Q. Liu, S.-W. Zhang, M.-C. Shao, Y.-Q. Tang, *Chem. Commun.* **1998**, 1937.
[7] A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtmann, C. Beugholt, P. Kögerler, C. Lu, *Angew. Chem.* **1998**, *110*, 1278; *Angew. Chem. Int. Ed.* **1998**, *37*, 1220.
[8] A. Müller, E. Krickemeyer, J. Meyer, H. Bögge, F. Peters, W. Plass, E. Diemann, S. Dillinger, F. Nonnenbruch, M. Randerath, C. Menke, *Angew. Chem.* **1995**, *107*, 2293; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2122.
[9] B. Krebs, S. Stiller, K. H. Tytko, J. Mehmke, *Eur. J. Solid State Inorg. Chem.* **1991**, *28*, 883.
[10] NH_2iPr (0.68 mL, 8.0 mmol) with $HClO_4$ acidification (pH 2.0) was added to a solution of $Na_8[Mo_{36}O_{112}(H_2O)_{16}]\cdot 58\,H_2O$, (0.4 g, 0.06 mmol) synthesized according to the method in reference [9], in H_2O (78 mL). Photolysis (two weeks; 500 W superhigh-pressure mercury lamp) of the resulting solution after degassing led to a deep blue solution. After cooling at 4 °C rhombohedral plate crystals of **1**, obtained as uniform crystalline material after 4 weeks, were collected by filtration and dried. Yield: 0.18 g (50 % based on Mo), elemental analysis calcd (%): N 0.59, C 1.51, H 1.80; found: N 0.99, C 2.22, H 1.98. The higher N, C, and H values than expected from the given formula are presumably attributed to the high adsorption (corresponding to about six molecules per **1**) of $[NH_3iPr]ClO_4$ on the highly water-soluble crystalline material of **1**, as suggested by the presence of Cl in the elemental analysis. IR (KBr pellet): $\tilde{\nu} = 1.618$ (m, $\delta(H_2O)$), 972(m), 908(w), 746(s), 631(s), 555(s) cm^{-1}; λ(nm) (ε_M) = 747 ($1.3 \times 10^5\,L\,mol^{-1}\,cm^{-1}$), 1076 ($1.0 \times 10^5\,L\,mol^{-1}\,cm^{-1}$).
[11] Space group $P2_1/n$, $a = 32.316(1)$, $b = 18.021(1)$, $c = 58.618(2)$ Å, $\beta = 98.388(2)^\circ$, $V = 33\,771(2)$ Å^3, $Z = 2$, $\rho = 2.34\,g\,cm^{-3}$, $\mu = 26.4\,cm^{-1}$, $F(000) = 22\,560$. Crystal dimensions $0.2 \times 0.1 \times 0.02$ mm. Crystal was coated with paraffin oil and mounted in a 20 micron nylon loop material. Intensity data were measured on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71071$ Å) at 103 K. Data collection using a ω scan at a scan width of 0.3° and $\chi = 45^\circ$ in five runs (with 600 frames for each) of $-75.0^\circ < \omega < 105^\circ$, $\phi = 0^\circ$; $-55.0^\circ < \omega < 125^\circ$, $\phi = 0^\circ$; $-55.0^\circ < \omega < 125^\circ$, $\phi = 90^\circ$; $-55.0^\circ < \omega < 125^\circ$, $\phi = 180^\circ$; $-55.0^\circ < \omega < 125^\circ$, $\phi = 270^\circ$. A crystal-to-detector distance was 95.35 mm. The detector swing angle for the first run was 15.5° and for other runs 35.5°. A total of 78 689 reflections was collected of which 325 154 unique reflections ($R_{int} = 0.098$) were used. Lorentz polarization factors were applied and an empirical absorption correction using equivalent reflections was performed with the program ABSCOR (T. Higashi, *Program for Absorption Correction*, Rigaku Corporation, Tokyo, **1995**). The structure was solved by direct methods and refined (1817 parameters) by using the TEXSAN software package (SHELXS 97) to $R = 0.094$ for a full-matrix least-squares refinement procedure (29 739 unique reflections with $I > 3\sigma(I)$). Further details on the crystal structure investigation 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-171234.
[12] The X-ray powder diffraction (XRD) pattern of **1** shows (002), (010), and (200) peaks at $d = 30$, 18, and 16 Å respectively, and an intensive angle peak at $d = 28$ Å. The latter peak corresponds to one of the diameter spacings (35 – 23 Å) for the car-tire-shaped ring and seems to be characteristic of the mesostructured nature, since $Na_8[Mo_{36}O_{112}(H_2O)_{16}]\cdot 58\,H_2O$ as a starting material gives no low-angle peak at $2\theta < 5^\circ$ ($Cu_{K\alpha} = 1.54056$ Å).
[13] I. D. Brown, K. K. Wu, *Acta Crystallogr. Sect. B* **1976**, *32*, 1952.
[14] T. Yamase, *Chem. Rev.* **1998**, *98*, 307.

Direct Evidence for the Nonrandom Nature of Al Substitution in Zeolite ZSM-5: An Investigation by ^{27}Al MAS and MQ MAS NMR**

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Many important properties of aluminosilicate zeolites, most notably their Brønsted acidity and hence catalytic performance, depend primarily on the framework Al content, that is, the extent of isomorphous substitution of Si by Al. However, even in materials with the same framework structure and composition, the location of catalytically active sites can differ according to the manner in which Al atoms are spatially distributed over the available tetrahedral sites (T-sites) in a given zeolite lattice. Therefore, detailed knowledge of the local ordering of Al atoms in these microporous materials is the starting point for systematically manipulating the distribution of acidic sites within the pore architecture.

Zeolite ZSM-5 (MFI topology) is one of the industrially most important zeolites. It typically crystallizes in the orthorhombic space group *Pnma*, and 12 crystallographically distinct T-sites with equal populations exist in the ZSM-5 framework.[1] A fundamental, recurring question regarding this type of zeolite structure is whether the acidic sites (that is, Al atoms on T sites) are spatially ordered. Recently, Olson et al.[2] carried out Rietveld refinement of synchrotron powder X-ray diffraction (XRD) data on a Cs-ZSM-5 zeolite with 5.8 Al atoms per unit cell (Si/Al = 15.6) and showed that Cs^+ ions are located in three different extraframework sites. They speculated that Al atoms may be unequally distributed over the 12 distinct T-sites of the ZSM-5 framework. However, because of the very similar scattering powers of Si and Al for X-rays and the difficulties in obtaining large single crystals, especially at high Al concentrations, it is very difficult, or even impossible, to directly locate Al atoms by conventional diffraction methods. Although many quantum chemical studies have also addressed this issue,[3] the nature of

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Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

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