CO$_2$ Fixation

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Picking up 30 CO$_2$ Molecules by a Porous Metal Oxide Capsule Based on the Same Number of Receptors**

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Dedicated to Professor Michael T. Pope on the occasion of his 80th birthday

After the metal oxide clusters $\{Mo_{72}M_{30}\}$ ($M = V^{IV}$, Cr^{III}, Fe^{III}, Mo^{V}), $\{Mo_{132}\}$ (Keplerate-type), $\{Mo_{154}\}$, $\{Mo_{176}\}$, $\{Mo_{248}\}$ (wheel type), and also the $\{Mo_{368}\}$ (hedgehog type) and some tungsten analogues were discovered,[1] they were recognized as nanomaterials that allow a variety of research options in several disciplines. The corresponding results obtained from several groups refer to unusual chemical reactions (especially the work of Aida et al.[2]) as well as electronic and magnetic properties,[3] but also different aspects of materials science,[1g,4a,b] including catalysis.[4c–f] In particular, the spherical nanocapsules/Keplerates of the $(pentagon)_{12}(linker)_{30} \equiv \{(Mo)Mo_5\}_{12}\{Mo_2\}_{30} \equiv \{Mo_{132}\}$ type containing 20 well-defined pores have been extensively investigated because of their unique structures and the related properties. This refers in particular to the option of tuning the internal capsule functionalities (including important hydrophobic types), which reveals several interesting features especially regarding interactions of the capsules with the environment. If the capsules are transferred, for example, to solutions containing different constituents at their disposition, they exchange their interior correspondingly. One example is the extremely fast exchange of 30 lower-charged acetate ligands coordinated to the 30 $\{Mo^{V}_2O_4\}^{2+}$ linkers of the capsule $[\{(Mo^{VI})Mo^{VI}_5O_{21}(H_2O)_6\}_{12}\{Mo^{V}_2O_4(CH_3COO)\}_{30}]^{42-}$ **1a**[5] by the corresponding number of more highly charged sulfate ions present in the new environment.[6]

Herein we refer to a scenario based on the aqueous solution of **1a** into which CO$_2$ is bubbled, leading to the fast exchange of acetate by carbonate ligands inside the capsule while CO$_2$ can also react directly with the H$_2$O ligands of the $\{Mo^{V}_2O_4(H_2O)_2\}^{2+}$ linkers. Acidification of solutions of the carbonate-containing capsules leads easily to CO$_2$ release while CO$_2$ is also completely removed from the related solid upon standing and especially upon mild heating. The three different types of CO$_2$ integration into MOFs as promising materials[7a–c] have been recently shortly summarized:[7d] One refers to binding CO$_2$ to vacant coordination sites on metal atoms, another to physisorption of CO$_2$ by means of dipole interactions, while the authors themselves[7d] in their work refer to covalent bonding. In this context, the present results should be of interest.

The problem that had to be solved was to find the optimal, that is, limited pH range for the CO$_2$ uptake reaction because the (necessary) formation of the intermediate product HCO_3^- as well as the stability of **1a** in solution, like of each polyoxometalate, are strongly pH-dependent.[8] But after CO$_2$ was bubbled through an aqueous solution containing **1a** with a pH value of about 7, the capsule **2a** is quickly formed as the CO_3^{2-} ligands have a much higher affinity to the $\{Mo^{V}_2O_4\}^{2+}$ linkers than the less negatively charged acetate ligands. The resulting compound **2** could be isolated in crystalline form and was characterized spectroscopically by IR (based on the ^{13}C–^{12}C isotope shifts) and Raman spectra[9] and also by X-ray crystallography.[10a] The corresponding compound **3** was prepared using isotopically pure $^{13}CO_2$ and characterized by IR and ^{13}C NMR spectra (see below), while compound **4** was obtained in the same way as **2**, but in absence of formamidinium cations in the reaction mixture to investigate the pore-closing influence of the organic cations on the stability. Compound **4** was characterized by elemental analysis, spectroscopically, and the measurement of the unit-cell dimensions which are as expected practically identical to those of **2**, as the pore closing does not change the size of the spherical capsules.[10b]

$$(NH_4)_{52}\{HC(NH_2)_2\}_{20}[\{(Mo^{VI})Mo^{VI}_5O_{21}(H_2O)_6\}_{12}\{Mo^{V}_2O_4(CO_3)\}_{30}] \cdot L \equiv (NH_4)_{52}\{HC(NH_2)_2\}_{20} \cdot \mathbf{2a} \cdot L \quad (\mathbf{2})$$

L = lattice components (ca. 250 H$_2$O + 2 MoO$_3$ · H$_2$O) that are disordered because of the large voids between the giant capsules.

Compound **3** corresponds to **2** but contains $^{13}CO_3^{2-}$ ligands.

$$(NH_4)_{72}[\{(Mo^{VI})Mo^{VI}_5O_{21}(H_2O)_6\}_{12}\{Mo^{V}_2O_4(CO_3)\}_{30}] \cdot \text{ca. } 260\,H_2O \equiv (NH_4)_{72} \cdot \mathbf{4a} \cdot \text{ca. } 260\,H_2O \quad (\mathbf{4})$$

As the Raman spectrum of the aqueous solution containing **2** (Figure 1) shows, owing to the almost high icosahedral symmetry of its metal oxide skeleton, only very few characteristic lines this can be considered as an easy proof for the identification.[9] The IR spectra of **2** and **3** confirm the

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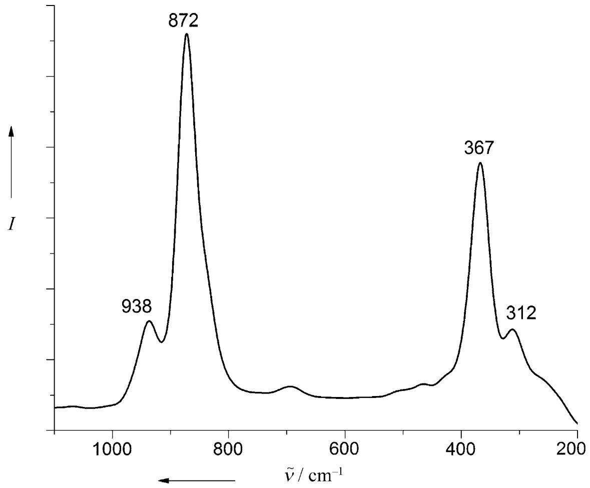

Figure 1. The extremely simple characteristic Raman spectrum (see text) of an aqueous solution of **2** ($\lambda_{ex} = 785$ nm) does not change over several hours. For the spectra of a solution of **4** and their time dependence, see the Supporting Information, Figure S2.

presence of CO_3^{2-} ions coordinated as bridging ligands to the $\{Mo^V{}_2O_4\}^{2+}$ linkers as they show the expected ^{12}C–^{13}C isotope shifts of about 30 cm^{-1} of the $\nu_{as}(CO)$ stretching vibrations (but not of the symmetric one) (Supporting Information, Figure S1); the isotope shifts are comparable to that of the $\nu_{as}(CO)$ stretching mode of $^{12}CO_2$ and $^{13}CO_2$.[11] The single-crystal X-ray structure analysis of **2**,[10a] which crystallizes in the cubic space group $Fm\bar{3}$, confirms the presence of 30 CO_3^{2-} anions coordinated as bridging ligands to the 30 linkers (Figure 2a), while the carbon atoms form the unique icosidodecahedron with all edges equal (Figure 2b). In the solid compound **2** the 20 pores are closed by 20 formamidinium cations, which interact with the $\{Mo_9O_9\}$ pores by hydrogen bonds (Figure 2c; for a corresponding example, see Ref. [12a]).

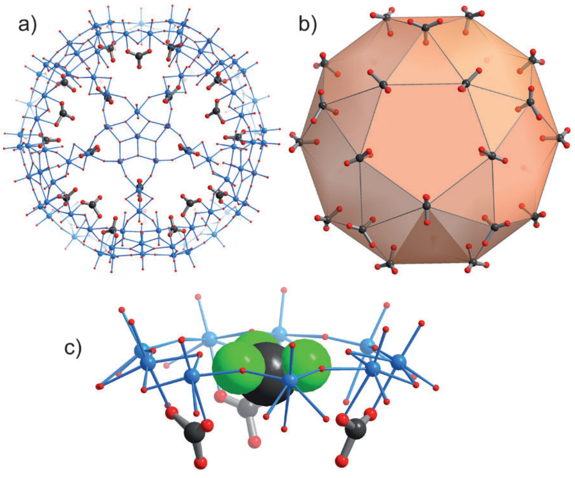

Figure 2. a) The structure of **2a** mostly in ball-and-stick representation, b) the icosidodecahedron spanned by the 30 carbonate C atoms, and c) one integrated (disordered) formamidinium cation as guest in a pore (O red, Mo blue, C black, N green).

The important results with respect to the chemical pathway and the stability of the new compound type in context with the release of CO_2 are as follows:

1) The fixation of CO_2 can occur either by fast exchange of the acetate ligands of **1a** by the more highy charged CO_3^{2-} ligands (primarily HCO_3^- is formed at pH 7) or by direct reaction of CO_2 with the H_2O ligands of the $\{Mo^V{}_2O_4(H_2O)_4\}^{2+}$ linkers. The latter argument is due to the fact that there is a pH dependent equilibrium between acetate and H_2O ligands in the capsule interior of **1a**.[4f,12b,13]
2) Aqueous solutions of **2a** are remarkably stable for several hours at pH 7, as confirmed by the characteristic Raman spectrum (as proof for the intact capsule skeleton; see Figure 1; regarding the comparatively less-stable **4a**, see the Supporting Information Figure S2) and ^{13}C NMR spectra (as confirmation of the presence of integrated CO_3^{2-} ligands; see below). The 30 CO_3^{2-} ions can, by formation of CO_2, be easily removed from the capsule upon addition of different acids/ligands to the solution. This allows compounds to be easily prepared with the related anions as ligands coordinated to the 30 linkers/receptors of the capsule. For the present relevant example, upon addition of acetic acid to the solution containing **4a**, the easily prepared compound **1**,[5] which is often used in materials science[1g] and the synthesis is reported even in a student textbook,[5c] is formed (for details, see the Supporting Information, Section S1). Of special interest in the context are the encapsulations of very weakly coordinating ligands, such as F^-, Cl^-, and BF_4^- ions but also H_2O.[4f] Generally speaking the capsule **2a** with the CO_3^{2-} ligands is highly reactive with respect to the exchange of the interior.
3) Solid **2** is stable at about 0 °C for a couple of days and at about −10 °C for at least two weeks; it releases CO_2 slowly but completely at room temperature (Supporting Information, Table 1). The capsules decompose because no ligands are present for the stabilization of the $\{Mo^V{}_2O_4\}^{2+}$ linkers after the carbonate decomposition, as in case of aqueous solution. Compound **4** decomposes more easily than **2** owing to the missing stabilization effect by pore closing (Supporting Information, Figure S2 and Table S1).

The ^{13}C NMR spectrum of a solution of **3** in water shows the expected signals in the relevant region[14] (Figure 3); that

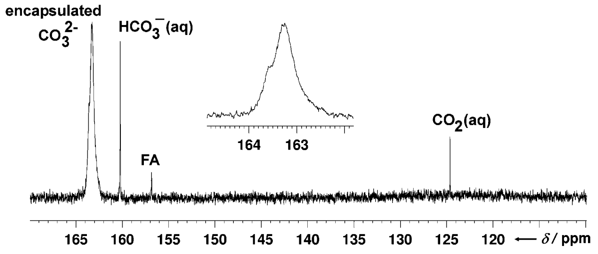

Figure 3. ^{13}C NMR spectrum of an aqueous solution of **3** (FA: formamidinium cation). The characteristic broad signal (for an explanation, see the Supporting Information, Figure S3) is also observed after bubbling CO_2 for only a short time into the solution (pH ca. 7) containing **1a**.

is, for HCO_3^-(aq), CO_2(aq), the formamidinium cation, and for the coordinated carbonate ligands as a broad signal. The latter signal is shifted compared to that of HCO_3^- to higher frequencies, comparable to scenarios with other anions coordinated to the positively charged linkers (see the Supporting Information, Figures S3 and S4 for further details, especially regarding the characteristic broad peak for integrated ligands). The latter peak (overall linewidth ca. 80 Hz) has a very weak shoulder that can be assigned to a small number of protonated carbonate ligands weakly interacting with the capsule by hydrogen bonds. The stability of the compound in water at a well-defined pH value of about 7 is remarkable: after several hours, even days, the decrease of the signal intensity of the carbonate ligands is practically not visible, while the intensity of the HCO_3^-(aq) signal is nearly constant and that of the CO_2(aq) increases very slowly, which is obviously accompanied by a small change in the pH that results in a very small low-frequency shift of the signal for the coordinated carbonate ligands. Importantly, the formation of **2a** is very fast, as the signal of the coordinated CO_3^{2-} ligands is observed after bubbling CO_2 for minutes through the aqueous solution (pH $\approx$ 7) containing **1a**.

A long-term ^{13}C EXSY spectrum does not show cross-peaks, which leads to the conclusion that there are practically no carbonate-based exchange equilibria between the capsule interior and the outside. The more highly charged CO_3^{2-} ions are more strongly attracted by the positively charged linkers than, for example, the less-charged acetate ligands for which correspondingly exchange is observed (for the related EXSY spectra, see Ref. [13]). Further evidence for the existence of **3a** in solution is given by the ^{13}C DOSY NMR spectrum (Figure 4; for related spectra of macroions with comparable sizes, see Ref. [15]).

In summary, apart from the option of picking up 30 CO_2 molecules in only one capsule, it is also noteworthy that the related cluster **2a** is comparably rather stable in solution over a well-defined pH range, while **2a**, because of the easy decomposition of the CO_3^{2-} ligands upon lowering the pH value of the corresponding solution, is a powerful highly reactive and unique starting material for the syntheses of capsules exhibiting other interiors, and especially those with weakly coordinating ligands, such as Cl^- or H_2O.[17]

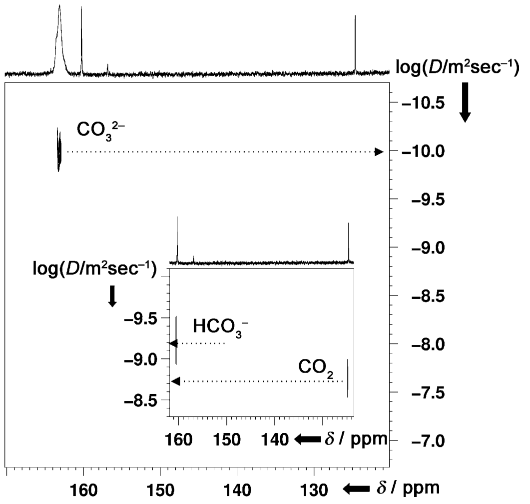

Figure 4. ^{13}C DOSY NMR spectrum of a solution of **3** in D_2O with the characteristic peak of the CO_3^{2-} ions integrated in the capsule. Inset: Spectrum with lower intensity levels to show the less intense signals of the smaller components; the signal of the formamidinium cation (^{13}C only in natural abundance) is not detected owing to the lack of sensitivity.

Experimental Section

All chemicals were of reagent grade and used as supplied. $^{13}CO_2$ (99 atom % ^{13}C) was supplied by Campro Scientific GmbH. Compound **1** was prepared according to a well-known preparation method[5] and characterized by IR and Raman spectroscopy.

2: CO_2 gas was bubbled rapidly (at least 3–4 bubbles per second) into a solution of **1** (2 g, 0.068 mmol) in water (100 mL) in a two-necked round-bottom flask for 10 min. After an ammonia solution (ca. 2.5 mL, 12.5 % in water) was added dropwise over a period of 1 h (while maintaining a continuous flow of CO_2) to keep the pH value constant at 7.0 for 1 h, formamidinium chloride (0.3 g, 3.72 mmol) was added and the solution was stirred, keeping the CO_2 bubbling constant for a further 10–15 min. The solution was then kept tightly closed by a rubber stopper (and parafilm to keep the rubber stopper fixed against the pressure generated from the dissolved CO_2). After 5–7 days, the (distorted) octahedrally shaped brown crystals that had precipitated were filtered through a glass frit and then washed with a small amount of ethanol and diethyl ether. The compound was dried for 2 min under suction and then quickly stored at −10 °C. Yield: 0.5 g (25 % based on Mo). Anal calcd (%) for $Mo_{134}O_{740}N_{92}C_{50}H_{852}$: C 2.19, H 3.13, N 4.70, Mo^V 20.98; found: C 2.5, H 3.6, N 5.0, Mo^V 21.6 (cerimetric titration). The smaller number of H_2O crystal water molecules found here (namely 200) corresponds to the weathering process, while the formula for **2** corresponds to the results of the X-ray crystallographic study as for example also described in Ref. [13]; for the stability, see the text; for the IR spectrum, see the Supporting Information, Figure S1. Using more formamidinium chloride (0.5 g) increases the yield (1.2 g/60 % based on Mo) but because of faster crystallization only gives a microcrystalline solid with the same spectroscopic data.

3: The compound was obtained in the same manner as **2**, but on a reduced scale, starting from a solution of **1** (0.2 g, 0.0068 mmol) in water (15 mL), using isotopically pure $^{13}CO_2$ and comparatively more formamidinium chloride (0.1 g, 1.25 mmol). The (distorted) octahedrally shaped deep-brown crystals separated after 3–5 days. The compound was dried for 2 min under suction and then quickly stored at −10 °C. Yield: 0.1 g (50 % based on Mo); for the IR spectrum, see the Supporting Information, Figure S1.

4: The compound was obtained in the same manner as **2**, but by adding NH_4Cl (0.25 g, 4.7 mmol) instead of formamidinium chloride. Elongated deep-brown octahedrally shaped crystals separated after 2–3 days. The compound was dried for 1 min under suction and then quickly stored at −10 °C. Yield: 0.5 g (25 % based on Mo). Anal calcd (%) for $Mo_{132}O_{734}N_{72}C_{30}H_{832}$: C 1.36, H 3.15, N 3.78, Mo^V 21.63; found: C 1.6, H 3.5, N 3.6, Mo^V 22.0; for the IR spectrum, see the Supporting Information, Figure S1.

The ^{13}C NMR spectra in D_2O were measured at 100 MHz on a BRUKER AVANCE spectrometer using standard parameters. For a possible degradation study, the experiment time for each spectrum was four hours. The ^{13}C DOSY NMR spectrum was recorded using a standard BRUKER pulse sequence (stebpgp1s) with a relaxation time of 10 s, a gradient pulse of 6 ms, and a diffusion delay of 150 ms. 32 experiments were measured with a linear gradient ramp from 2 to 95 % and 640 scans each; total experiment time ca. 60 h.

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[1] a) A. Müller, S. Roy in *The Chemistry of Nanomaterials: Synthesis Properties and Applications* (Eds.: C. N. R. Rao, A. Müller, A. K. Cheetham), Wiley-VCH, Weinheim, **2004**, pp. 452 – 475; b) D.-L. Long, E. Burkholder, L. Cronin, *Chem. Soc. Rev.* **2007**, *36*, 105 – 121; c) D.-L. Long, L. Cronin, *Chem. Eur. J.* **2006**, *12*, 3698 – 3706; d) L. Cronin in *Comprehensive Coordination Chemistry II: From Biology to Nanotechnology*, *Vol. 7* (Eds.: J. A. McCleverty, T. J. Meyer), Elsevier, Amsterdam, **2004**, pp. 1 – 56; e) D.-L. Long, R. Tsunashima, L. Cronin, *Angew. Chem.* **2010**, *122*, 1780 – 1803; *Angew. Chem. Int. Ed.* **2010**, *49*, 1736 – 1758; f) M. T. Pope in *Comprehensive Coordination Chemistry* II: *From Biology To Nanotechnology*, *Vol. 4* (Eds.: J. A. McCleverty, T. J. Meyer), Elsevier, Amsterdam, **2004**, pp. 635 – 678; g) A. Proust, R. Thouvenot, P. Gouzerh, *Chem. Commun.* **2008**, 1837 – 1852 (the last section refers to the properties and applications of the giant polyoxometalates); h) N. Hall, *Chem. Commun.* **2003**, 803 – 806; i) C. Schäffer, A. Merca, H. Bögge, A. M. Todea, M. L. Kistler, T. Liu, R. Thouvenot, P. Gouzerh, A. Müller, *Angew. Chem.* **2009**, *121*, 155 – 159; *Angew. Chem. Int. Ed.* **2009**, *48*, 149 – 153; j) A. M. Todea, A. Merca, H. Bögge, T. Glaser, L. Engelhardt, R. Prozorov, M. Luban, A. Müller, *Chem. Commun.* **2009**, 3351 – 3353 (the last two refer to the tungstates).

[2] a) M. A. Alam, Y.-S. Kim, S. Ogawa, A. Tsuda, N. Ishii, T. Aida, *Angew. Chem.* **2008**, *120*, 2100 – 2103; *Angew. Chem. Int. Ed.* **2008**, *47*, 2070 – 2073; b) A. Tsuda, E. Hirahara, Y.-S. Kim, H. Tanaka, T. Kawai, T. Aida, *Angew. Chem.* **2004**, *116*, 6487 – 6491; *Angew. Chem. Int. Ed.* **2004**, *43*, 6327 – 6331.

[3] a) D. Zhong, F. L. Sousa, A. Müller, L. Chi, H. Fuchs, *Angew. Chem.* **2011**, *123*, 7156 – 7159; *Angew. Chem. Int. Ed.* **2011**, *50*, 7018 – 7021; b) D. Gatteschi, R. Sessoli, J. Villain, *Molecular Nanomagnets*, Oxford University Press, Oxford, **2006**, pp. 299 – 301.

[4] a) A. Müller, S. Roy, *J. Mater. Chem.* **2005**, *15*, 4673 – 4677 (in the meantime, there are ca. 50 publications regarding materials science aspects); see also b) D. Fan, J. Hao in *Self-Assembled Structures: Properties and Applications in Solution and on Surfaces* (Ed.: J. Hao), CRC, Boca Raton, **2011**, pp. 141 – 173; c) M. Sadakane, K. Yamagata, K. Kodato, K. Endo, K. Toriumi, Y. Ozawa, T. Ozeki, T. Nagai, Y. Matsui, N. Sakaguchi, W. D. Pyrz, D. J. Buttrey, D. A. Blom, T. Vogt, W. Ueda, *Angew. Chem.* **2009**, *121*, 3840 – 3844; *Angew. Chem. Int. Ed.* **2009**, *48*, 3782 – 3786, and d) S.-i. Noro, R. Tsunashima, Y. Kamiya, K. Uemura, H. Kita, L. Cronin, T. Akutagawa, T. Nakamura, *Angew. Chem.* **2009**, *121*, 8859 – 8862; *Angew. Chem. Int. Ed.* **2009**, *48*, 8703 – 8706; e) N. V. Izarova, O. A. Kholdeeva, M. N. Sokolov, V. P. Fedin, *Russ. Chem. Bull. Int. Ed.* **2009**, *58*, 134 – 137; f) S. Kopilevich, A. Gil, M. Garcia-Ratés, J. B. Avalos, C. Bo, A. Müller, I. A. Weinstock, *J. Am. Chem. Soc.* **2012**, *134*, 13082 – 13088.

[5] a) A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtmann, F. Peters, *Angew. Chem.* **1998**, *110*, 3567 – 3571; *Angew. Chem. Int. Ed.* **1998**, *37*, 3359 – 3363; b) A. Müller, S. K. Das, E. Krickemeyer, C. Kuhlmann, *Inorg. Synth.* **2004**, *34*, 191 – 200; c) L. Cronin, E. Diemann, A. Müller in *Inorganic Experiments* (Ed.: J. D. Woollins), 2nd ed., Wiley-VCH, Weinheim, **2003**, pp. 340 – 346.

[6] A. Müller, Y. Zhou, H. Bögge, M. Schmidtmann, T. Mitra, E. T. K. Haupt, A. Berkle, *Angew. Chem.* **2006**, *118*, 474 – 479; *Angew. Chem. Int. Ed.* **2006**, *45*, 460 – 465.

[7] a) D. M. D'Alessandro, B. Smit, J. R. Long, *Angew. Chem.* **2010**, *122*, 6194 – 6219; *Angew. Chem. Int. Ed.* **2010**, *49*, 6058 – 6082; b) K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae, J. R. Long, *Chem. Rev.* **2012**, *112*, 724 – 781; c) J. Liu, P. K. Thallapally, B. P. McGrail, D. R. Brown, J. Liu, *Chem. Soc. Rev.* **2012**, *41*, 2308 – 2322; d) J. J. Gassensmith, H. Furukawa, R. A. Smaldone, R. S. Forgan, Y. Y. Botros, O. M. Yaghi, J. F. Stoddart, *J. Am. Chem. Soc.* **2011**, *133*, 15312 – 15315; see also e) S. Henke, R. A. Fischer, *J. Am. Chem. Soc.* **2011**, *133*, 2064 – 2067.

[8] a) F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, Wiley, New York, 6th ed., **1999**; b) M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer, Berlin, **1983**.

[9] For a corresponding example, see C. Schäffer, A. M. Todea, P. Gouzerh, A. Müller, *Chem. Commun.* **2012**, *48*, 350 – 352.

[10] a) Crystal data for **2**: $M = 28381.03\ \text{g mol}^{-1}$, $Mo_{134}C_{50}H_{956}N_{92}O_{792}$, cubic, space group $Fm\bar{3}$, $a = 45.1722(5)$, $V = 92175(2)\ \text{Å}^3$, $Z = 4$, $\rho = 2.045\ \text{g cm}^{-3}$, $\mu = 15.441\ \text{mm}^{-1}$, $F(000) = 55456$, crystal size $= 0.12 \times 0.09 \times 0.07\ \text{mm}^3$. A total of 86634 reflections ($1.69 < \Theta < 66.60°$) were collected, of which 7072 reflections were unique ($R(\text{int}) = 0.0329$). An empirical absorption correction using equivalent reflections was performed with the program SADABS 2008/1.[16] The structure was solved with the program SHELXS-97 and refined using SHELXL-97 to $R = 0.0840$ for 5276 reflections with $I > 2\sigma(I)$, $R = 0.1130$ for all reflections; max/min residual electron density 2.779 and $-0.848\ \text{e Å}^{-3}$. Crystals of **2** were removed from the mother liquor and immediately cooled to 100(2) K on a Bruker-AXS X8-Prospector diffractometer (three-circle diffractometer, Cu-Kα radiation, microfocus source, multilayer optics; ω and ϕ scans). (Structure graphics with DIAMOND 2.1 from K. Brandenburg, Crystal Impact GbR, **2001**.) It is possible to refine the structure also in space group $Fm\bar{3}m$. However, in that case the disordered atom sets A and B are related by symmetry (m), which makes it extremely difficult to get a clearly resolved picture of the anion framework. As the coordinates from the $Fm\bar{3}m$ refinement do not significantly differ from the $Fm\bar{3}$ set, the lower symmetric description of the crystal structure was chosen. CCDC 890756 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif; b) Crystal data for **4**: Cubic, $a = 45.071(6)$ Å, $V = 91560(16)\ \text{Å}^3$.

[11] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part A: Theory and Applications in Inorganic Chemistry*, Wiley, New York, 5th ed., **1997**; K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B: Applications in Coordination, Organometallic, and Bioinorganic Chemistry*, Wiley, New York, 5th ed., **1997**.

[12] a) T. Mitra, P. Miró, A.-R. Tomsa, A. Merca, H. Bögge, J. B. Ávalos, J. M. Poblet, C. Bo, A. Müller, *Chem. Eur. J.* **2009**, *15*, 1844 – 1852; b) A. Ziv, A. Grego, S. Kopilevich, L. Zeiri, P. Miro, C. Bo, A. Müller, I. A. Weinstock, *J. Am. Chem. Soc.* **2009**, *131*, 6380 – 6382.

[13] O. Petina, D. Rehder, E. T. K. Haupt, A. Grego, I. A. Weinstock, A. Merca, H. Bögge, J. Szakács, A. Müller, *Angew. Chem.* **2011**, *123*, 430 – 434; *Angew. Chem. Int. Ed.* **2011**, *50*, 410 – 414.

[14] a) M. J. Manos, A. D. Keramidas, J. D. Woollins, A. M. Z. Slawin, T. A. Kabanos, *J. Chem. Soc. Dalton Trans.* **2001**, 3419 – 3420; b) S. Garai, E. T. K. Haupt, A. Müller, unpublished results.

[15] S. Floquet, S. Brun, J.-F. Lemonnier, M. Henry, M.-A. Delsuc, Y. Prigent, E. Cadot, F. Taulelle, *J. Am. Chem. Soc.* **2009**, *131*, 17254 – 17259.

[16] G. M. Sheldrick, SADABS 2008/1 University of Göttingen, Göttingen, Germany, **2008**.

[17] Publications demonstrating vapor/gas sorptions of polyoxometalates but not directly related to the present discovery, mainly by Mizuno et al., should also be mentioned; see the Supporting Information, References S3–S10.