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Polyoxometalate Necklace

A Nanosized Molybdenum Oxide Wheel with a Unique Electronic-Necklace Structure: STM Study with Submolecular Resolution**

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The discovery of nanoscale molybdenum oxide based clusters with spherical as well as wheel and hedgehog-type shapes containing between 102 and 368 atoms[1–3]—belonging to the family of polyoxometalates[4]—was considered as a step forward in inorganic chemistry because it led to new length scales and to the study of new phenomena and this in particular for confinement scenarios.[1–3] Members of this family are the (considered herein) mixed-valence wheel-shaped diamagnetic clusters of the $\{Mo_{11}\}_n$ type ($n = 14, 16$)[3b] with multifunctional properties; they react specifically with the environment[5,6] and with themselves forming unique vesicles.[7,8] All the above mentioned clusters are of the Molybdenum Blue type.[2a] The wheel-shaped clusters are also of interest for materials science,[9–12]for example, for the generation of films (with surfactants),[10c–e] liquid crystals,[10a] as well as of molecular[11] and solid-state magnetic materials exhibiting conductivity properties[12a] and they are also of interest for catalysis.[12b] Furthermore, materials exhibiting internal nanospaces—such as the wheel-shaped species—allow phenomena/processes to be studied under confined conditions.[13] It is interesting when the electronic structure of a material can be directly correlated with its properties as in the two wheel-shaped mixed-valence molybdenum oxide based clusters of the type Mo_{154} (studied herein) and Mo_{176}. These contain 28 or 32 (partly delocalized) electrons, respectively, causing the blue color[2a,14a] and the related Vis absorption band with extremely large extinction coefficients, to which each Mo^{V} center contributes with the high value of $5\times10^3\,L\,mol^{-1}\,cm^{-1}$.[14a] (The larger Mo_{176}[14b] cluster is only considered herein for the comparison of the analogous electronic properties.[14a]) Though the color was known to scientists from Carl Wilhelm Scheele's early work in the 1770s,[2a,14a] its origin, discussed in numerous cases, was only recently disclosed.[14a] As the clusters played not only a role in different areas of materials science but also show a unique chemistry[15–18] it was our aim to learn more about the basic electronic structure (which is analogous for both the wheel-type clusters) especially of the Mo_{154} cluster by scanning tunneling microscopy (STM)/spectroscopy (STS), allowing us to obtain high spatial resolution down to the atomic regime.[19] The highest occupied molecular orbitals (HOMOs) of the tetradecameric Mo_{154} (formula in the legend of Figure 1) have mainly Mo-4d character, are occupied by 28 electrons (32 in case of the hexadecameric Mo_{176})[14a] and are confined to 14 $\{Mo^{V/VI}{}_5O_6\}$-type compartments—identical subunits of the necklace like structure—the focus of the present studies.

Mo_{154} clusters (for the preparation see Experimental Section[20,21]) deposited on single-crystalline gold (111) surfaces were measured by using STM at 78 K under ultrahigh vacuum (UHV) conditions. Figure 2 shows the STM topography with the clusters mostly adsorbed having their equatorial plane parallel to the substrate surface and clearly displaying ring-like features. Only few of the clusters are tilted or stand up with their equatorial plane perpendicular to the substrate surface giving an apparent height greater than the flat lying clusters (Figure S1, Supporting Information). No long-range ordering and no real close packing is obtained; the average nearest-neighbor distance is approximately 4 nm. The diameter of the wheels as obtained from STM (opposite maxima of the ring across the center hole) is in good agreement with the crystallographic data giving inner and outer diameters of 2.0 and 3.4 nm respectively.[20] In some cases also smaller particles (ca. 1 nm in size) were found on the substrate coexisting with the ring-like clusters (Figure S1 and S2, Supporting Information). They may originate from the decomposition of the complete clusters because of their sensitivity to O_2 especially in solution (but to a less extent), the preparation procedure on the Au substrate (i.e. by removing most of the water shell in the UHV), and the interactions with the metal surface. Remarkably, a movement of the small particles (induced by the STM tip) into the

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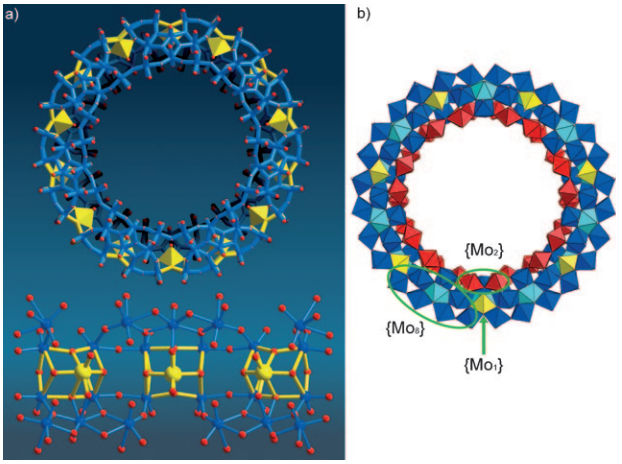

Figure 1. Structure of the nanosized Mo_{154}-type wheel (general formula $[\{Mo_2\}_{14-x}\{Mo_8\}_{14}\{Mo_1\}_{14}]^{(14+2x)-} \equiv [\{Mo^{VI}{}_2O_5(H_2O)_2\}^{2+}{}_{14-x}\{Mo^{VI/V}{}_8O_{26}(\mu_3\text{-}O)_2H(H_2O)_3Mo^{VI/V}\}^{3-}{}_{14}]^{(14+2x)-}$; x = number of missing $\{Mo_2\}$ groups). The studied compound contains 50% of the wheels with $x=1$ (see Refs. [14a, 20, 21] as well as Experimental Section). a) Ball and stick representation of the wheel and side-views of three of the 14 $\{Mo^{V/VI}{}_5O_6\}$ double cubane-type compartments (yellow) in which, according to bond valence sum calculations, practically all of the 4d electron density occurs[14a, 20] ($\{Mo^{V/VI}{}_1\}$ units of the wheel as well as the corresponding Mo atoms (enlarged) in the compartments in yellow; O red; other Mo blue). b) Polyhedral representation of the wheel based on 140 MoO_6 octahedra and 14 MoO_7 pentagonal bipyramids (cyan) forming the three types of basic building blocks ($\{Mo_8\}$: blue and cyan, $\{Mo_2\}$: red, and $\{Mo_1\}$: yellow; together these blocks form the $\{Mo_{11}\}$ unit[3b]).

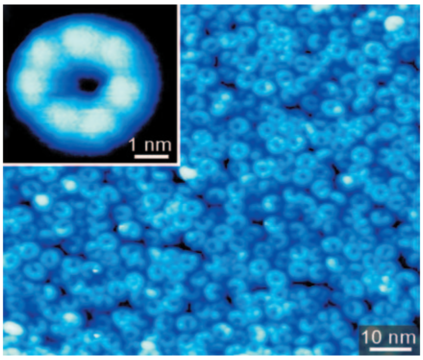

Figure 2. Constant current STM image of wheel shaped Mo_{154} clusters deposited on Au(111) ($V_{sample} = 3$ V, $I = 5$ pA). Inset: high-resolution STM image of the Mo_{154} cluster exhibiting sevenfold rotational symmetry with seven bright protrusions on the ring ($V_{sample} = 3$ V, $I = 2$ pA).

central cavity of the wheel is possible (Supporting Information Figure S3).

The sevenfold rotational symmetry of the Mo_{154} clusters is clearly visualized in our experiments, as shown in the inset of Figure 2. Most of the clusters show seven bright and rather broad protrusions, corresponding to seven repeat units with the central $\{Mo_5O_6\}$ compartments containing partially reduced $Mo^{V/VI}$ centers.

Figure 3a and b show STM images of the Mo_{154} clusters obtained with positive and negative bias voltage, displaying the distribution of unoccupied and occupied states, respectively. Applying a negative sample voltage, scanning of the STM tip may result eventually in the destruction of the clusters in the scanned region (Supporting Information, Figure S3). While both images exhibit sevenfold symmetry, the negative-bias image shows also fine structure subunits. To assign the observed features qualitatively we have performed simple molecular orbital (MO) calculations on the basis of the extended-Hückel method yielding three occupied energy bands which may be assigned (with increasing energy) to MoO σ-, MoO π-bonding levels, and those with mainly Mo-d character, which form the highest occupied molecular orbitals (HOMOs) containing the 28 4d electrons (see also legend of Figure 1).

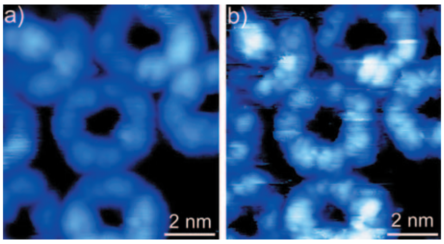

Figure 3. Bias dependent STM images of Mo_{154} clusters deposited on Au(111). a) Positive sample voltage ($V_{sample} = 3$ V, $I = 5$ pA) showing the spatial distribution of the unoccupied states. b) Negative sample voltage ($V_{sample} = -2$ V, $I = 5$ pA) showing the spatial distribution of the occupied states.

The spatial distributions for some of the MOs of the above mentioned type of bands/levels are shown in Figure S4 of the Supporting Information. Each single level shows a dominant electronic density on a part of the ring only, accompanied by a second region located diagonally opposite according to the approximate D_{7d} symmetry, like for the first LUMOs which have mainly Mo-4d character (example in Supporting Information, Figure S4a). A summation of the density distribution of all levels accounts well for the observed sevenfold diffuse electron delocalization-based compartmental regions, that is, a necklace type structure as observed in Figure 3. Interestingly, the localization of each of the higher energy MoO π-bonding levels is almost completely confined to only one of the fourteen compartments (Supporting Information, Figure S4c). Important, the finer features of the observed protrusions as seen in Figure 3b, can be assigned to the metal centers of the $\{Mo^{V/VI}{}_5O_6\}$ compartments containing the Mo-4d electrons (two delocalized in each; see also Figure S4a).

The local features of the molecular orbitals have been experimentally confirmed by scanning tunneling spectroscopy (STS), giving information about the distribution of the electronic density of states (DOS) inside a cluster. STS has been performed at different positions on the surface of the wheel-like clusters (Figure 4). The bright protrusions are caused by the units exhibiting $Mo^{V/VI}$ centers and the nodes in between by the Mo atoms with almost no 4d electron density. Whereas the steep increase of DOS at higher positive voltages results in all cases from the unoccupied states mainly π*-MoO in character, the weak features (shoulders) at lower positive

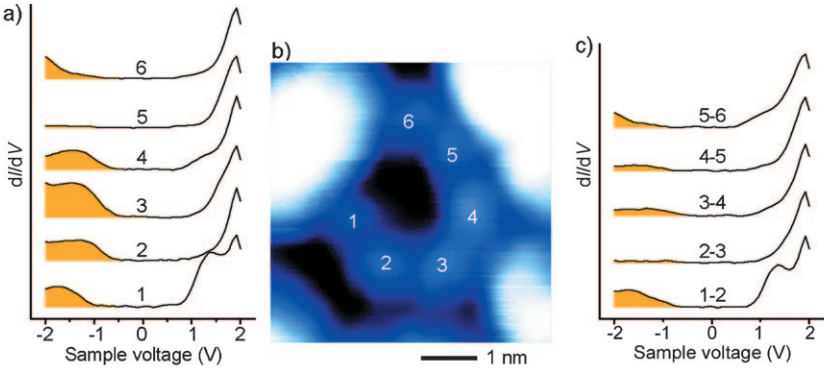

Figure 4. Differential conductivity (d*I*/d*V*) of the Mo_{154} cluster. a) d*I*/d*V* curves at the subunits 1–6 indicated in (b), c) d*I*/d*V* curves at the connections between the subunits. The colored areas show the occupied DOS (for further details see text). b) STM image of the measured cluster (3 V, 5 pA).

voltages can be assigned to the LUMOs originating from the unoccupied Mo-4d levels. The most obvious differences between the subunits and the connections appear at negative sample bias, which correspond to the occupied states, easily recognizable by comparing Figure 4a and Figure 4c. Moreover, the STS results indicate an energy gap (with very low or no DOS) slightly above 1 eV corresponding to the observed optical transition energies at about 1100 nm and 750 nm[14a] The latter corresponds to the long-known blue color of the Mo_{154} clusters in solution.[14a] Both bands may be assigned to HOMO→LUMO excitations, that is, $Mo^{V}\rightarrow Mo^{VI}$ intervalence charge transfer (IVCT) transitions. This agrees with the spectrum of the Mo_{176} cluster[14a] showing only higher extinction coefficients due to the presence of four more Mo^{V} centers.

Our STM/STS experiments unveil a necklace- or corrugated circular tube-like distribution of the 4d electrons in the Mo_{154} cluster. According to several experimental results, there are 28 spin-coupled Mo-4d electrons in total, leading to a $S=0$ spin ground state mostly located in the 14 linked $\{Mo^{V/VI}_{5}O_{6}\}$ compartments (having an average Mo bond valence sum of 5.6 which is the same as that of the related 16 compartments of the Mo_{176} cluster containing 32 4d electrons[14a]). The compartments—formed from four $Mo^{V/VI}$ atoms of the $\{Mo_8\}$ (according to the bond valence sums) and $\{Mo_1\}$ units—are linked by Mo-O-Mo bridges forming the necklace structure (see Figure 1). Importantly, resonance Raman spectroscopy[14a] also shows nicely that the 4d electrons are almost only delocalized in Mo-O-Mo-type bridges (the constituents of the 14 compartments) as the spectrum practically does not contain a band with high intensity due to the symmetrical $\nu(Mo{=}O_{terminal})$-type vibrations. The $\{Mo^{VI}_{2}\}$ units and four Mo atoms of the $\{Mo_8\}$ units not belonging to the $\{Mo^{V/VI}_{5}O_{6}\}$ units—for which darker features appear in STM images—do not contribute to the occupied Mo-4d frontier states. These Mo atoms have Mo bond valence sums of approximately 6.[14a,20]

To conclude, the nanosized Mo_{154} cluster with its unique electronic structure, is an intriguing nanoelectronic system in view of the localization of states within the 14 cluster compartments and the correlation of these states with optical properties of the cluster. These states, as investigated by STM/STS, originate from (bound) chemical states within the subunits and thus make the system different from conventional quantum dots carrying free electrons or excitonic states. It will be of interest to further study the possibility to stimulate these complex metal oxide nanoparticles by light (note the strong light absorption[14a]) and magnetic fields (especially with additionally incorporated paramagnetic centers)[11,12] as well as by electric fields (in the context of conductivity), but also to investigate how they act with respect to different types of catalytic processes.[12b] Activation of molecules can result if they are placed near areas containing the "flexible" Mo-4d electrons; in this context also the absorption of gases[12b] and the type of interaction with water[22] is of interest and that cations, such as Cu^{2+}, can be placed near to the $\{Mo^{V/VI}_{5}O_{6}\}$ compartments.[11,23] It would be interesting to extend the STM study to wheel derivatives, like those with different defects,[17b] different ring sizes/shapes,[24] and to those in which the wheels are linked.[25]

Experimental Section

Crystalline $Na_{15}[Mo^{VI}_{126}Mo^{V}_{28}O_{462}H_{14}(H_2O)_{70}]_{0.5}[Mo^{VI}_{124}Mo^{V}_{28}O_{457}H_{14}(H_2O)_{68}]_{0.5}\cdot$ca.400 H_2O (in the second constituent one $\{Mo_2\}$ group is missing) was prepared as described in Refs. [20,21]. Complete Mo_{154} cluster anions and defective ones with one $\{Mo_2\}$ unit missing at a ratio of 1:1 coexist in these crystals. They were dissolved in H_2O or CH_3OH at concentrations of 10–20 μM. The solution was then dropped onto an Au(111) single crystalline surface, which was cleaned by cycles of Ar^{+} sputtering and annealing in ultrahigh vacuum (UHV). The drop of solution was held on the substrate for around 10–20 seconds and the excess solvent was removed by a pipette. The substrate was then introduced into the UHV chamber (ca. 10^{-10} mbar) again and cooled to 78 K for STM measurements. An electrochemically etched tungsten tip was used. Mo_{154} clusters deposited on the Au(111) surface are sensitive to the scanning of the STM tip. Only at low tunneling currents (typically 2–10 pA), and relatively high positive sample bias (2–4.5 V) the clusters are stable during scanning. Movement and even decomposition of the POM clusters at the surface may be induced by tip scanning under lower bias and larger current conditions. For STS, the tip was located at a specific position upon the cluster and the differential conductance (d*I*/d*V*) as a function of bias voltage was measured by using a lock-in amplifier with a modulation frequency of 946.5 Hz and an amplitude of 50 mV, added to the dc-bias during STS measurement. In all cases the presence of O_2 was excluded.

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[1] a) D.-L. Long, R. Tsunashima, L. Cronin, *Angew. Chem.* **2010**, *122*, 1780–1803; *Angew. Chem. Int. Ed.* **2010**, *49*, 1736–1758;

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.

[2] a) P. Gouzerh, M. Che, *Actual. Chim.* **2006**, *298*, 9–22; b) J. W. Steed, D. R. Turner, K. J. Wallace, *Core Concepts in Supramolecular Chemistry and Nanochemistry*, Wiley, Chichester, **2007**, p. 289; c) J. R. Gispert, *Coordination Chemistry*, Wiley-VCH, Weinheim, **2008**, pp. 141–143; d) N. Hall, *Chem. Commun.* **2003**, 803–806 (Focus article); e) A. F. Holleman, N. Wiberg, *Lehrbuch der Anorganischen Chemie*, 102. Aufl., de Gruyter, Berlin, **2007**.

[3] 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) A. Müller, P. Kögerler, H. Bögge, *Struct. Bonding (Berlin)* **2000**, *96*, 203–236; there it is shown that the formula of the spherical $\{Mo_{132}\}$ capsule can be written as $\{Mo_{11}\}_{12}$—with high C_5 symmetry of the formal $\{Mo_{11}\}$ units—and of the wheels as $\{Mo_{11}\}_n$ ($n = 14, 16$) with lower symmetry of the units in which one $\{MoO_6\}$ octahedron is displaced; c) A. Müller, P. Kögerler, C. Kuhlmann, *Chem. Commun.* **1999**, 1347–1358.

[4] a) M. T. Pope, A. Müller, *Angew. Chem.* **1991**, *103*, 56–70; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 34–48; b) M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer, Berlin, **1983**.

[5] This can lead, for example, to coordination ligands like cystine with several functional groups to the internal cavity surface generating an interesting internal surface: A. Müller, S. K. Das, C. Kuhlmann, H. Bögge, M. Schmidtmann, E. Diemann, E. Krickemeyer, J. Hormes, H. Modrow, M. Schindler, *Chem. Commun.* **2001**, 655–656.

[6] A. Proust, R. Thouvenot, P. Gouzerh, *Chem. Commun.* **2008**, 1837–1852 (see last related section of the Review).

[7] See for example, a) T. Liu, E. Diemann, H. Li, A. W. M. Dress, A. Müller, *Nature* **2003**, *426*, 59–62; b) A. Müller, E. Diemann, C. Kuhlmann, W. Eimer, C. Serain, T. Tak, A. Knöchel, P. K. Pranzas, *Chem. Commun.* **2001**, 1928–1929.

[8] a) T. Liu, *Langmuir* **2010**, *26*, 9202–9213; b) T. Liu, E. Diemann, A. Müller, *J. Chem. Educ.* **2007**, *84*, 526–532.

[9] A. Müller, S. Roy, *J. Mater. Chem.* **2005**, *15*, 4673–4677.

[10] a) S. Polarz, B. Smarsly, M. Antonietti, *ChemPhysChem* **2001**, *2*, 457–461; see also: b) S. Polarz, B. Smarsly, C. Göltner, M. Antonietti, *Adv. Mater.* **2000**, *12*, 1503–1507; c) T. Akutagawa, R. Jin, R. Tunashima, S.-I. Noro, L. Cronin, T. Nakamura, *Langmuir* **2008**, *24*, 231–238; d) M. Clemente-León, T. Igo, H. Yashiro, T. Yamase, E. Coronado, *Langmuir* **2007**, *23*, 4042–4047; e) see also 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.

[11] A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtmann, P. Kögerler, C. Rosu, E. Beckmann, *Angew. Chem.* **2001**, *113*, 4158–4161; *Angew. Chem. Int. Ed.* **2001**, *40*, 4034–4037.

[12] a) H. Imai, T. Akutagawa, F. Kudo, M. Ito, K. Toyoda, S.-I. Noro, L. Cronin, T. Nakamura, *J. Am. Chem. Soc.* **2009**, *131*, 13578–13579; b) 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.

[13] A. Müller, S. Q. N. Shah, H. Bögge, M. Schmidtmann, *Nature* **1999**, *397*, 48–50 (nucleation/self-assembly processes within the wheels can lead to the formation of two new types of molybdenum oxide clusters thereby closing the cavity).

[14] a) A. Müller, C. Serain, *Acc. Chem. Res.* **2000**, *33*, 2–10; b) In the first published papers the number of protonations and correspondingly of the charges especially in the larger wheel species (for detailed reasons see Ref. [14a]) caused problems, as expected. These could later be solved for both, that is, the tetra- and hexadecameric species $[(MoO_3)_{154}(H_2O)_{70}H_{14}]^{14-}$ and $[(MoO_3)_{176}(H_2O)_{80}H_{16}]^{16-}$[3b] (see Refs [2a, 3a, 3c, 6, 9, 14a]; an interesting aspect: we can refer in both cases to reduced protonated molybdenum trioxide). The correct charge of the large ring with 16 Na^+ and 16 H^+ was given for example, in c) A. Müller, M. Koop, H. Bögge, M. Schmidtmann, C. Beugholt, *Chem. Commun.* **1998**, 1501–1502 (see also Ref. [16] where the compound was used for some unusual reactions). In this context, note that the clusters are rather strong acids in aqueous solution.

[15] Md. 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.

[16] 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.

[17] a) T. Yamase, S, Kumagai, P. V. Prokop, E. Ishikawa, A.-R. Tomsa, *Inorg. Chem.* **2010**, *49*, 9426–9437; b) S. Shishido, T. Ozeki, *J. Am. Chem. Soc.* **2008**, *130*, 10588–10595. In this paper a large number of new interesting structures is reported especially those with defects; see in particular Refs. [24–33] cited therein.

[18] a) H. N. Miras, G. J. T. Cooper, D.-L. Long, H. Bögge, A. Müller, C. Streb, L. Cronin, *Science* **2010**, *327*, 72–74; b) A. Müller, L. Toma, H. Bögge, M. Schmidtmann, P. Kögerler, *Chem. Commun.* **2003**, 2000–2001) (referring to the unprecedented integration of a 64-membered $\{KSO_4\}_{16}$ ring into the larger wheel).

[19] G. Binnig, H. Rohrer, C. Gerber, E. Weibel, *Phys. Rev. Lett.* **1983**, *50*, 120–123.

[20] A. Müller, S. K. Das, V. P. Fedin, E. Krickemeyer, C. Beugholt, H. Bögge, M. Schmidtmann, B. Hauptfleisch, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1187–1192.

[21] A. Müller, S. K. Das, E. Krickemeyer, C. Kuhlmann in *Inorganic Syntheses*, *Vol. 34* (Ed.: J. R. Shapley) Wiley, New York, **2004**, pp. 191–200.

[22] A. Oleinikova, H. Weingärtner, M. Chaplin, E. Diemann, H. Bögge, A. Müller, *ChemPhysChem* **2007**, *8*, 646–649.

[23] Correspondingly also the protons can be "positioned" there.[20]

[24] a) A. Müller, C. Beugholt, H. Bögge, M. Schmidtmann, *Inorg. Chem.* **2000**, *39*, 3112–3113; b) L. Cronin, C. Beugholt, E. Krickemeyer, M. Schmidtmann, H. Bögge, P. Kögerler, T. Kim, K. Luong, A. Müller, *Angew. Chem.* **2002**, *114*, 2929–2932; *Angew. Chem. Int. Ed.* **2002**, *41*, 2805–2808.

[25] A. Müller, S. Roy, *Eur. J. Inorg. Chem.* **2005**, 3561–3570.