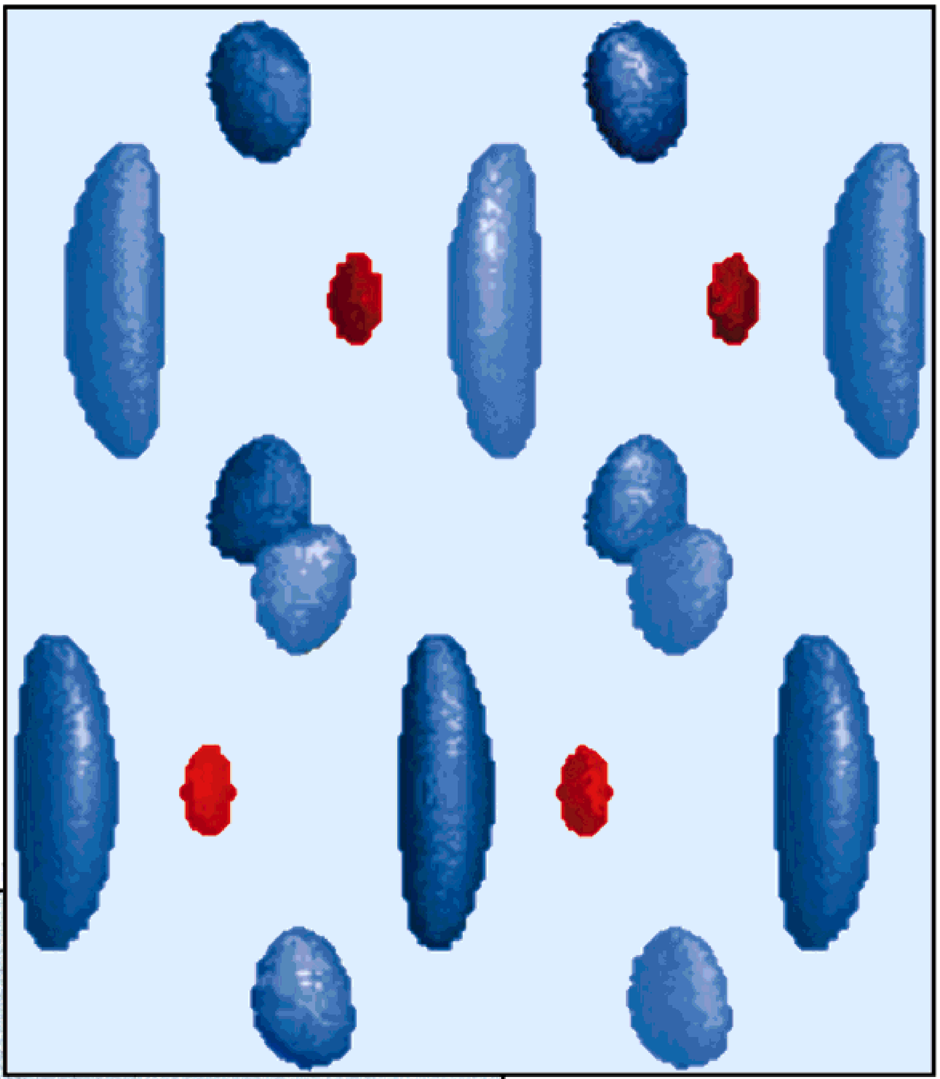
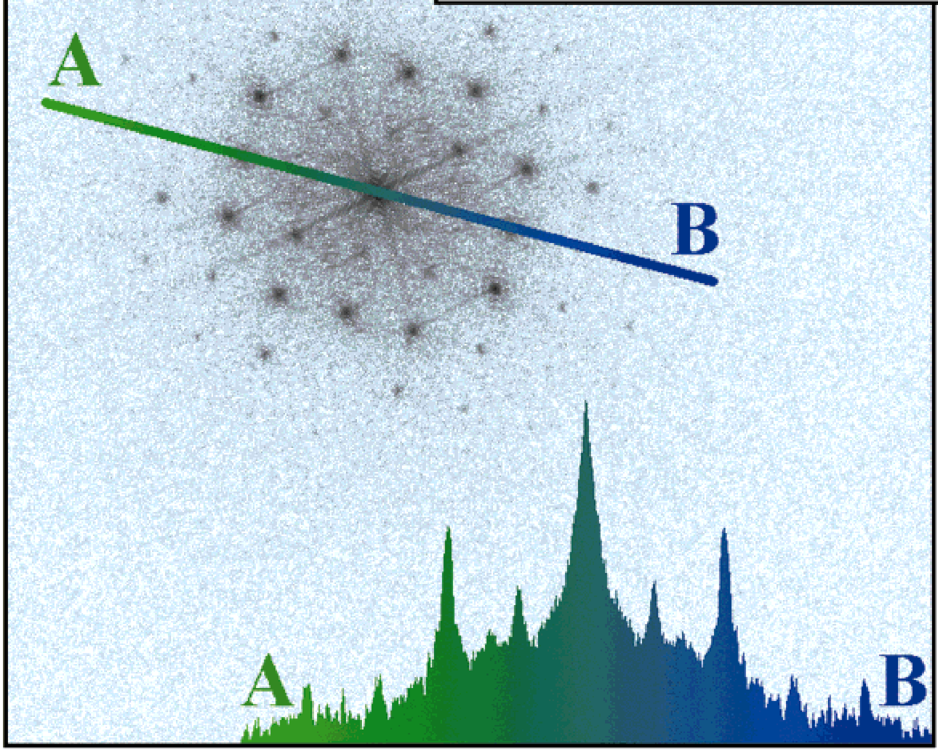
The crystal structure of colloidal Pd_3P was determined from high-resolution transmission electron microscopy images. A three-dimensional image of the structure (picture top right, viewed along [001]) was calculated by combining data from the Fourier transforms of the images (bottom left).





The positions of both the palladium (blue) and the phosphorus atoms (red) could be determined. More information about this new possibility in structure elucidation is provided by Bovin et al. on the following pages.

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The First Structure Determination of Nanosized Colloidal Particles of Pd_3P by High-Resolution Electron Microscopy[**]

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Reine Wallenberg, Jan-Olle Malm, Günter Schmid, and
Thomas Kubicki

The determination of the crystal structures of materials whose particle size is intermediate between those of clusters and colloidal particles is important, since their chemical and physical properties are structure-dependent. Nanosized crystalline particles are used in many important areas, such as catalysis, vapor deposition of metals, photoelectronics, solar cells, and powder metallurgy. Future developments in the fields of lasers, magnetic disks, photocells, and quantum devices will exploit the quantized electron energy levels of clusters. Single crystal X-ray diffraction, which is the most common technique for structure determination, is of very limited applicability for collecting data from nanosized crystalline particles. A combination of high-resolution transmission electron microscopy (HRTEM) images, recorded with the electron beam along different crystallographic directions, and selected-area electron diffraction (SAED) data is more useful for structure determination of very small crystals. Recent developments in recording images with a linear gray scale, by using slow-scan CCD cameras (CCD = charge-coupled device), allow quantitative evaluation of micrographs. Many previous structure determinations from HRTEM images used data that contained information on two dimensions and were recorded along one short axis of the unit cell.[1, 2] The atomic positions along the short axis were deduced from geometrical and chemical considerations. A full three-dimensional reconstruction that combines HRTEM images from several crystallographic directions is preferable.[3] Here we show how HRTEM images were used for the first time to determine the positions of the palladium and phosphorus atoms in the crystal structure of colloidal Pd_3P particles with a size range of 15–20 nm.

The solid-state structure of Pd_3P has been determined by X-ray diffraction.[5] The compound crystallizes in the space group *Pnma* ($a = 0.5980$, $b = 0.7440$, $c = 0.5164$ nm) and has the same structural type as cementite Fe_3C[6] and Pd_3B.[7] From hundreds of HRTEM images, 23 that were recorded parallel to crystallographic directions with low indices and exhibited high resolution were selected and subjected to image processing. Image simulations showed that multiple diffraction in these palladium-containing particles starts to affect the relative amplitudes of the reflections at a crystal thickness exceeding 5–7 nm.[8] In our case we assumed that the particles were approximately spherical and that only close to the edge of the crystal would the crystal thickness lie below this range. Therefore, the particle core was excluded from the image-processing procedure by masking. The resulting images resemble the perspective view of a pitted olive; two examples are shown in Figure 1. For image processing, 23 images from 17 particles, which were recorded with the electron beam parallel to the directions [100], [010], [110], [011], and [113], were selected. Image processing was performed with the Semper software of the company Synoptics. Each image was Fourier transformed (see Figure 2) and corrected for the effect of the contrast transfer function (CTF) of the objective lens. The focus of the microscope was estimated from the Fourier transform of amorphous material present on the surface of the particles. A full correction was performed with a Wiener filter.[9] Images of several particles and images recorded at different foci showed identical measured phases after focus correction (0 or π, since the structure is centrosymmetric). Amplitudes and phases with a signal-to-noise ratio greater than or equal to 3 were extracted from the focus-corrected Fourier transforms. The variation in amplitudes between different images of the same direction was typically around 30%. The origin was shifted to the correct phase origin of the projection, and the symmetry of the projection was imposed on the amplitudes and phases. The symmetry was chosen in accordance with the space group *Pnma* of the

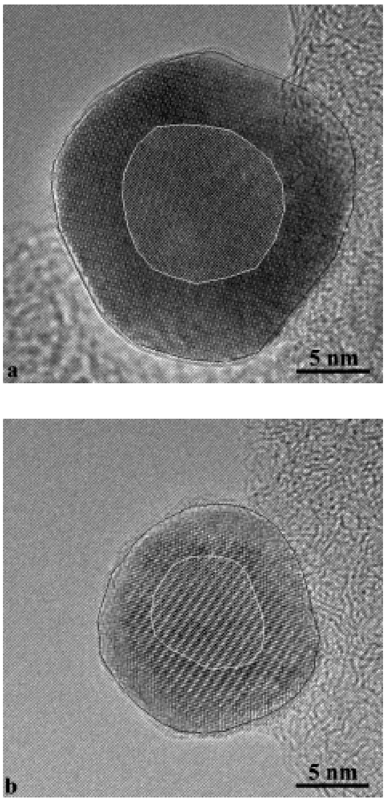

Figure 1. HRTEM images of two colloidal particles, recorded with the electron beam parallel to [010] (a) and [011] (b). The central part of the particles is masked out to avoid multiple-scattering effects in image processing.

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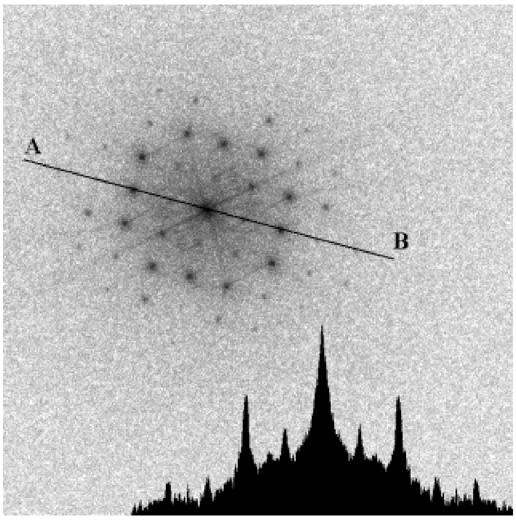

Figure 2. Fourier transform of the HRTEM image of a particle recorded along [010]. A line scan (along A – B)is shown bottom right.

bulk phase of Pd_3P, which also agreed with the lattice parameters and symmetry of the images, as determined by measuring the phase differences after imposition of the symmetry. The amplitudes and phases obtained from several images and directions were scaled together and combined. Thus from 26 unique reflections, 17 with a resolution of 0.17 nm were obtained (Table 1). The three-dimensional crystal potential (structure) was finally calculated by an inverse Fourier transform. The positions of the palladium and phosphorus atoms were directly determined from the positions of the peaks in the three-dimensional image (Figure 3).

Table 1. Structure factors used in the inverse Fourier transform.

h	k	l	$F/10^5$
0	0	2	2.49
0	1	1	– 0.221
0	2	2	1.57
1	0	1	0.450
1	0	2	– 3.69
1	1	1	0.160
1	1	2	– 1.65
1	2	1	– 0.136
1	2	2	– 1.87
2	0	0	– 1.14
2	0	1	– 3.02
2	0	2	– 1.36
2	1	1	– 3.00
2	2	0	0.959
2	2	1	0.777
3	0	1	– 3.90
3	1	1	0.750

The palladium atoms are located in the positions ($x = 0.04$, $y = 0.25$, $z = 0.88$) and ($x = 0.21$, $y = 0.04$, $z = 0.35$) and are comparable to the palladium atom positions in the X-ray structure ($x = 0.03$, $y = 0.25$, $z = 0.87$) and ($x = 0.18$, $y = 0.06$, $z = 0.34$).[5] Note, however, that the atomic positions in a small particle are not necessarily the same as in the bulk structure. The deviations between the positions determined by X-ray diffraction and those obtained by electron miscroscopy are 0.017 nm and 0.027 nm. The P atom is located in center of the triply capped trigonal prism of Pd atoms and has the coordinates $x = 0.84$, $y = 0.25$, $z = 0.35$. In the X-ray crystal structure, the P atom occupies the position $x = 0.88$, $y = 0.25$, $z = 0.46$. The P centers cannot be as precisely localized as the Pd centers, because of the relatively low electron-scattering power of phosphorus. The difference in the P positions of the two structures is 0.060 nm. The Pd – P distances in the triply capped trigonal prism lie between 0.203 and 0.299 nm (0.231 – 0.314 nm in the structure determined by X-ray diffraction). The Pd – Pd distances within the trigonal prism lie in the range 0.306 – 0.331 nm; hence, the trigonal prism in the colloidal particles is more regular than that in the crystals (Pd – Pd 0.278 – 0.322 nm). The regular polyhedron and the chemically reasonable bond lengths further support this structure determination. Attempts were made to repeat the determination without masking out the core of the particles, but due to severe multiple scattering, no clear peaks were found in the inverse Fourier transform.

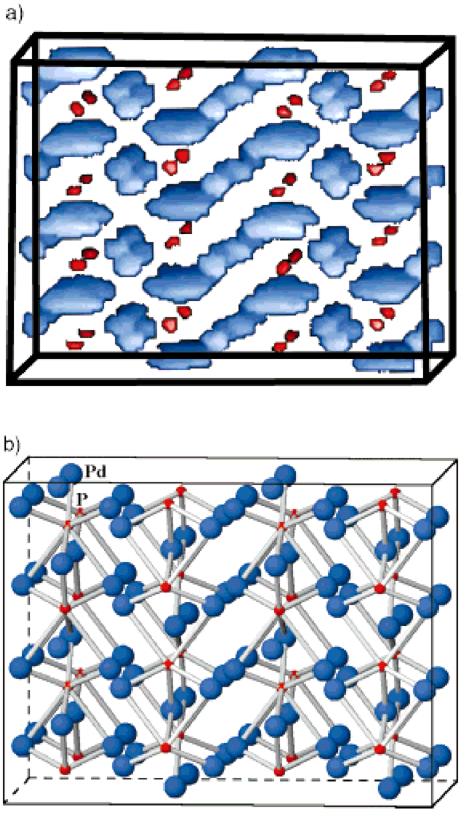

Figure 3. Three-dimensional depictions of the structure of Pd_3P. a) Calculated by inverse Fourier transform. b) Structural model calculated from Figure 3a.

Experimental Section

The compound $Pd_4B_6Cl(PBu_3)$[4] was used as the precursor for the colloidal particles and was heated under vacuum on an activated-carbon support (ca. 2 wt % Pd) to temperatures between 350 and 950°C. The palladium clusters, which had an initial size of 2 nm, coalesced and reacted when the temperature was increased. At 850 °C formation of carbon nanocapsules was observed. The size distribution of the particles subjected to higher temperatures was broad, but the majority of the particles were in the size range of 10–30 nm. Nanoprobe EDXS and EELS analysis revealed a composition of Pd_3P for most of the particles. Above 500°C the initial 2 nm clusters reacted only with the phosphorus atoms of the ligand shell, since neither boron nor carbon could be detected in the larger particles. The samples containing the palladium phosphide colloids were supported on lacy carbon film on a copper grid and investigated in a JEM-4000EX electron microscope, which was operated at 400 kV and a structural resolution of about 0.16 nm ($C_s = 1.0$, $C_c = 2.5$ mm, spread of focus about 60 Å, and semiconvergence angle 0.50 mrad). The crystal structure images were recorded at magnification of about 300000 × (3.4 pixels per 1.7 Å) with a slow-scan CCD camera (Gatan 694). Two particles imaged along different directions are shown in Figure 1. All images were recorded in the linear range of the CCD camera (0–12000 gray levels). The particles are too small to be oriented by stage tilting when the microscope is in diffraction mode, so correctly aligned particles must be sought among randomly oriented particles.

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[1] S. Hovmöller, A. Sjögren, G. Farrants, M. Sundberg, B.-O. Marinder, *Nature* **1994**, 311, 238.
[2] T. E. Weirich, R. Ramlau, A. Simon, S. Hovmöller, X. Zou, *Nature* **1996**, 382, 144.
[3] K. H. Downing, H. Meisheng, H.-H. Wenk, M. A. O'Keefe, *Nature* **1990**, 348, 525.
[4] G. Schmid, E. Schöps, J.-O. Malm, J.-O. Bovin, *Z. Anorg. Allg. Chem.* **1994**, 620, 1170.
[5] S. Rundqvist, L.-O. Gullman, *Acta Chem. Scand.* **1960**, 14, 2246.
[6] B. Aronsson, S. Rundqvist, *Acta. Crystallogr.* **1962**, 15, 878.
[7] E. Stenberg, *Acta. Chem. Scand.* **1961**, 15, 861.
[8] MacTempas v.1.6.7, Total Resolution, CA, USA.
[9] W. O. Saxton, *Scanning Microsc. Suppl.* **1988**, *2*, 213.

Formation of a Ring-Shaped Reduced "Metal Oxide" with the Simple Composition $[(MoO_3)_{176}(H_2O)_{80}H_{32}]$**

Achim Müller,* Erich Krickemeyer, Hartmut Bögge, Marc Schmidtmann, Christian Beugholt, Paul Kögerler, and Canzhong Lu

Dedicated to Professor Heribert Offermanns on the occasion of his 60th birthday

Two years ago, we reported on the ring-shaped polyoxometalate ion **1**.[1a–c] We have now succeeded in obtaining crystals which contain an even larger ring-shaped cluster formed by a conservative self-organization process. Remarkably, it represents a simple reduced, protonated, and hydrated molecular metal oxide, built up from 176 molybdenum and 608 oxygen atoms.[2] Based upon the number of metal atoms, it seems to be the largest discrete inorganic species characterized by single-crystal X-ray structure analysis.[3] Its large cavity (diameter 2.3 nm) opens new perspectives for host–guest and supramolecular chemistry.

$[Mo_{154}(NO)_{14}O_{448}(H_2O)_{70}H_{28}]^{14-}$ **1**

$[(MoO_3)_{176}(H_2O)_{80}H_{32}]$ **2**

After acidifying an aqueous solution of lithium molybdate (about 1M) followed by reduction with tin(II) chloride at room temperature, dark blue rhombic-bipyramidal crystals (crystal class *mmm*) of a compound containing cluster **2** precipitate together with chemically identical amorphous material from the dark blue reaction mixture. The blue compound contains cluster **2** together with additional, partly disordered lattice components (crystal water as well as small amounts of Li^+ and Cl^- ions; see Experimental Section). The compound was characterized by elemental analyses, cerimetric titration of the formal number of Mo^V centers, thermogravimetric analysis (to determine the crystal water content), bond valence sum calculations (to determine the number and position of protonated oxygen atoms as well as the formal number of Mo^V centers[4]), spectroscopic methods (IR, Raman, UV/Vis and NIR spectroscopy), EHMO calculations, and single-crystal X-ray structure analysis.[5]

Remarkably, **2** shows the stoichiometry of a protonated reduced molecular molybdenum trioxide with coordinated H_2O ligands. Despite the significantly different properties of **1** and **2**, a structural comparison shows striking similarities. According to a related building-block scheme for the cluster types $[\{Mo_2\}\{Mo_8\}\{Mo_1\}]_{\underline{n}} \equiv [\{Mo_2^{VI}O_5(H_2O)_2\}\{Mo_8^{VI/V}XO_{25}(OH)_2(H_2O)_3Mo^{VI/V}\}]_n$, **1** can be formulated as a tetradecamer (with $n = 14$ and X = NO) and **2** as a hexadecamer (with $n = 16$ and X = O; Figure 1).[1b, 6–8] This confirms that the $\{Mo_8\}$ units, connected by building units of the type $\{Mo_1\}$ and $\{Mo_2\}$ in **1** and **2**, represent a special type of building block that occurs in several polyoxometalate structures.[1a,b, 6–8] A more detailed structural comparison of both systems shows that the inner regions of the rings, which are mainly built up by $\{Mo_2\}$ units, are less tightly bound in **1**. This causes the rings to be slightly domed in the corresponding regions and can—upon decreasing the negative charge of the ring—easily lead to a release of $\{Mo_2\}^{2+}$ groups with further consequences for the reactivity in the case of **1**.[7, 8] Further unusual condensation reactions in the case of **2** can occur at the relatively tightly bound $\{Mo_2\}$ groups result in the formation of polyoxometalate fragments in the inner regions of the rings. These condensations lead to the formation of structures with a kind of "hubcap" caused by a novel type of molecular growth. In general however, the growth of polyoxometalates by condensation is only observed if the overall ion charge increases with a concomitant, approximately constant charge per molybdenum center. This ensures the solubility of the clusters and prevents not only the molecular units from forming the oxidic solid (showing translational

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