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Transmission electron microscopic and small angle X-ray diffraction investigations of $Au_{55}(PPh_3)_{12}Cl_6$ microcrystals†

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Micrometer sized crystals of close packed $Au_{55}(PPh_3)_{12}Cl_6$ clusters are formed from dichloromethane solution and are investigated by transmission electron microscopy and small angle X-ray diffraction.

After a period of almost 20 years of investigation of the cluster compound $Au_{55}(PPh_3)_{12}Cl_6$ since its first synthesis we have now succeeded in making microcrystals in preparative amount. Transmission electron microscopic studies and small angle X-ray diffraction indicate a simple close packed arrangement of the spherical clusters correlating with an effective cluster distance of 2.3 nm in very good agreement with the actual cluster size of 2.1–2.2 nm.

The cluster compound $Au_{55}(PPh_3)_{12}Cl_6$ was first described in 1981.[1] In the meantime a large number of papers followed, describing its chemical and physical properties.[2–8] The compound became of extraordinary significance owing to its quantum size behavior. With respect to this property Au_{55} clusters are the most promising particles for applications in future nanoelectronics.[9]

The development of the physical and chemical characteristics of the easily available $Au_{55}(PPh_3)_{12}Cl_6$ cluster[10] was accompanied by the disadvantage of its non-crystalline nature. Thus, solid state investigations had to be performed with pellets or thin layers. Investigations of solutions suffered from their ready decomposition so that much effort has been required to reach our present knowledge of this cluster.

We have now succeeded in obtaining microcrystals of $Au_{55}(PPh_3)_{12}Cl_6$ in preparative quantities. The reason for having failed to obtain such crystalline particles previously is simply because they are too small to be distinguished directly and because long-standing electron microscopic investigations were exclusively focused on the imaging of single clusters from very dilute solutions. However, fast evaporation of the solvent from concentrated dichloromethane solutions of $Au_{55}(PPh_3)_{12}Cl_6$ results in the formation of well shaped crystals in the size range of hundreds of nanometers up to a few micrometers. Transmission electron microscopy (TEM) and small angle X-ray diffraction (SAXRD) of such microcrystals were used to establish their structure. Samples for the TEM investigations were simply prepared from a drop of a saturated solution of $Au_{55}(PPh_3)_{12}Cl_6$ in CH_2Cl_2 added onto the grid. After evaporation of the solvent the TEM images showed well shaped, mainly hexagonal, crystals (Fig. 1).

In contrast to the case of dilute solutions, only a few single clusters could be observed. Magnification of such crystals established their monocrystalline character. The high magnification of a crystal edge in Fig. 2, thin enough for TEM, allowed the determination of more structural details.

The distance between parallel columns is 2.0–2.1 nm. Supposing a fcc arrangement of the clusters, this distance corresponds to an effective cluster distance of 2.3–2.4 nm, in good agreement with the calculated cluster diameter if van der Waals distances between the PPh_3 ligands of neighboring clusters are considered. Cluster distances of 2.3 nm could also directly be determined from the TEM image in Fig. 2. Fig. 3

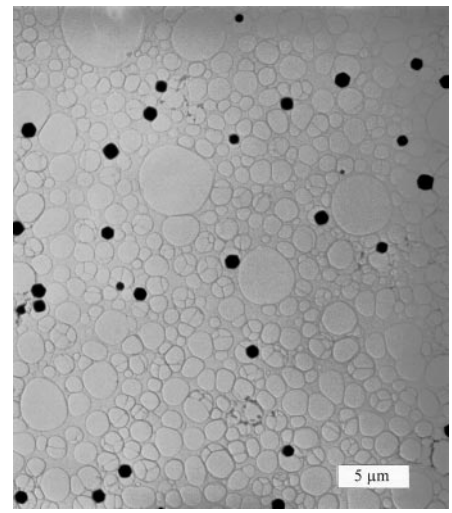

Fig. 1 Transmission electron microscopic (TEM) image of well shaped microcrystals of $Au_{55}(PPh_3)_{12}Cl_6$. Most of the crystals are *ca.* 1 μm in diameter.

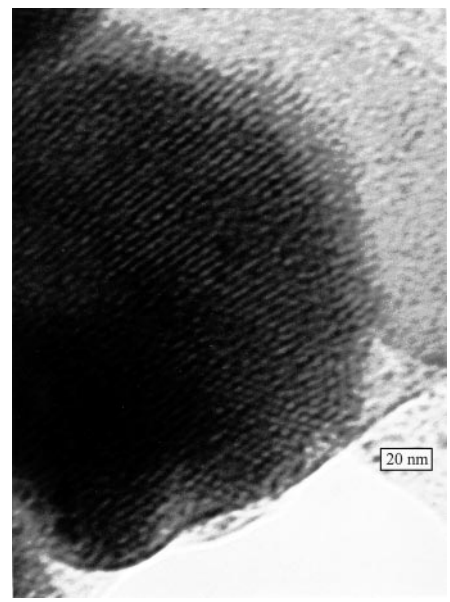

Fig. 2 High resolution TEM image of a $Au_{55}(PPh_3)_{12}Cl_6$ microcrystal. The monocrystalline particle shows cluster rows with a separation of 2.0–2.1 nm in accord with a hexagonal close-packed arrangement of the spherical clusters. The cluster distance can be determined as 2.3 nm.

† Dedicated to Professor Helmut Werner on the occasion of his 65th birthday.

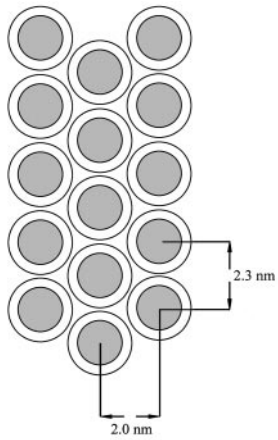

Fig. 3 Schematic view of the cluster arrangement in the microcrystals.

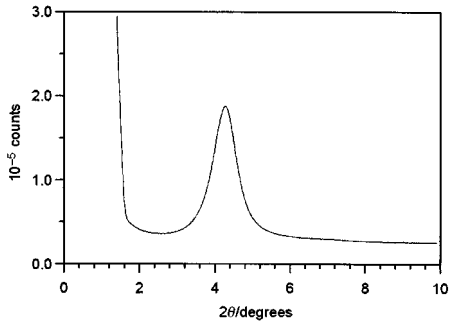

Fig. 4 Result of small angle X-ray diffraction (SAXRD) measurements on $Au_{55}(PPh_3)_{12}Cl_6$ microcrystals. The 2θ angle of 4.3° corresponds to a *d* value of 2.05 nm, in accord with the TEM results.

schematically represents the situation observed in the high resolution TEM images.

Samples for SAXRD experiments have also been prepared by fast evaporation of the solvent of concentrated dichloromethane solutions of $Au_{55}(PPh_3)_{12}Cl_6$. The black powder consisted almost exclusively of microcrystals as shown in Fig. 1. The result of the SAXRD experiments is shown in Fig. 4.

Only one strong reflection of 2θ = 4.3° is registered, corresponding to a *d*-value of 2.05 nm in accord with the average distance from TEM of 2.05 nm. This might correspond to a hexagonal close packing, if observed along the [111] direction.

Based on our knowledge of the quantum size behavior of individual clusters, the availability of nanocrystalline microcrystals now opens new routes for their use in three-dimensional single electron tunneling (SET) devices. A crystal of the size of $1 \times 1 \times 1$ μm contains *ca.* 10^8 clusters. The combination of such microcrystals by appropriate linkers is in principle possible and so could be a vehicle to a future nanotechnology.

Notes and references

‡ *Sample preparation*: the synthesis of $Au_{55}(PPh_3)_{12}Cl_6$ was carried out following ref. 10. For TEM investigations, a drop of a concentrated solution of $Au_{55}(PPh_3)_{12}Cl_6$ in dichloromethane, was added onto a carbon covered grid and dried. SAXRD measurements were performed with the powdery cluster material as synthesized.

TEM images were accomplished with a Philips FEG CM 200 microscope while for SAXRD measurements a Siemens D 5000 was used.

1 G. Schmid, R. Boese, R. Pfeil, F. Bandermann, S. Meyer, G. H. M. Calis and J. W. A. van der Velden, *Chem. Ber.*, 1981, **114**, 3634.
2 Summarizing the literature up to 1994; G. Schmid, in *Clusters and Colloids-From Theory to Applications*, ed. G. Schmid, VCH, Weinheim, 1994.
3 B. A. Smith, J. Z. Zhang, U. Giebel and G. Schmid, *Chem. Phys. Lett.*, 1997, **270**, 139.
4 Y. Volokitin, J. Sinzig, L. J. de Jongh, G. Schmid and I. I. Moiseev, *Nature*, 1996, **384**, 621.
5 L. F. Chi, M. Hartig, T. Drechsler, Th. Schwaak, C. Seidel, H. Fuchs and G. Schmid, *Appl. Phys. A*, 1998, **66**, 187.
6 L. F. Chi, S. Rakers, M. Hartig, H. Fuchs and G. Schmid, *Thin Solid Films*, 1998, **327**–**329**, 520.
7 G. Schmid and L. F. Chi, *Adv. Mater.*, 1998, **10**, 515.
8 G. Schmid, R. Pugin, J.-O. Malm and J.-O. Bovin, *Eur. J. Inorg. Chem.*, 1998, 813.
9 U. Simon, *Adv. Mater.*, 1998, **10**, 1487.
10 G. Schmid, *Inorg. Synth.*, 1990, **7**, 214.

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