Palladium-561 Giant Clusters: Chemical Aspects of Self-organization on a Nano Level

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Three packing modes: FCC, nearly icosahedral (or multiply twinned) and random, for the cores of palladium-561 giant clusters, were evidenced by high resolution electron microscopy and electron diffraction data.

Palladium-561 giant clusters approximated by the idealized formula $Pd_{561}L_{60}(OAc)_{180}$ **1**, are known to consist of a densely-packed Pd metal nucleus and coordinated L (1,10-phenanthroline or 2,2′-bipyridine) and outer-sphere OAc^- ligands at its periphery.[1–3] The idealized formulation corresponds to the most abundant cluster species of ~ 25 A metal core diameter. In fact, the cluster cores of the material are characterized by some size distribution, ~ 5 A, around this value. The rest, more rare in occurrence, of the cluster species can be expected to differ from the abundant ones in their core size, chemical composition and properties.

As the first step of a more detailed study on the cluster species which constitute the whole range of core size distribution, we have attempted to separate a sample of cluster **1** into fractions of different solubility in acetic acid/benzene binary mixtures. For this purpose, a freshly prepared solution of cluster **1** in acetic acid was precipitated with successively increasing portions of benzene to give three fractions (the fraction number, AcOH:benzene ratio and yield of the fraction are listed below: 1, 1:1, 15%; 2, 1:2, 40%; 3, 1:3, 39%).

The fractionation was expected to separate the cluster sample primarily by the size of cluster cores. Contrary to this expectation, the core size distribution determined by transmission electron microscopy (TEM)[†] showed that the size of the cores of the most abundant cluster species varied only slightly (24, 24 and 27 A for fractions 1, 2 and 3, respectively, see Fig. 1). The shape of the size distribution varies along the fractional series more markedly. As seen in Fig. 1, fraction 1 exhibits a fairly narrow, near-unimodal size distribution. Fraction 2 is characterized by a broader but still unimodal distribution. Fraction 3 is the broadest size-distributed one and is close to a three-modal distribution with maxima around 16, 27 and 36 A, respectively.

The electron diffraction (ED) pattern for fraction 1 was found to consist of several rings which correspond exactly to a FCC packing mode of palladium atoms within a cluster metal core, see Fig. 2(*a*). High resolution electron microscopy (HREM) images of the cores also gave evidence for a FCC arrangement of metal atoms, as depicted by Fig. 3(*a*). In the case of fraction 2 the majority of cluster metal particles seem also to be packed in a FCC manner. However, within this fraction we encounter certain particles of quite another internal arrangement (a somewhat lesser number of such particles was also found in fraction 1). As seen from Fig. 4, particles of this kind exhibit a five-fold axis that allows us to refer to such a particle as an icosahedral one or, in other words, a multiply-twinned one with a five-fold axis. This observation is in reasonable agreement with our earlier EXAFS data on giant Pd-561 clusters,[1–3] as well as with recent HREM studies on giant clusters.[4,5]

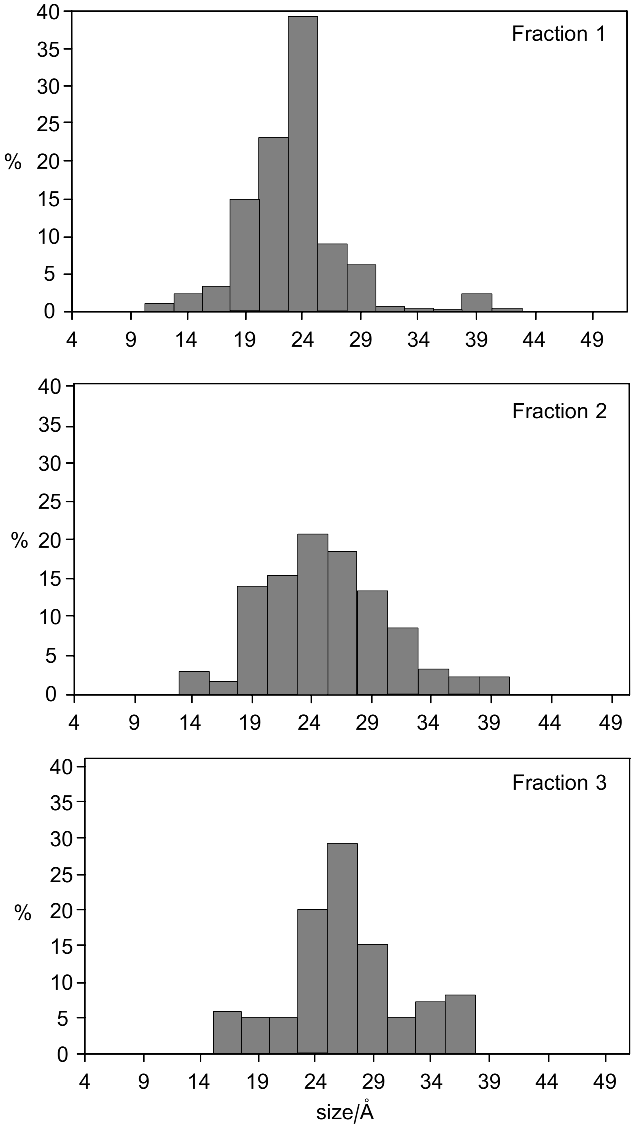

Fig. 1 Size distribution of the metal cores for the fractions 1–3 of giant cluster $Pd_{561}Phen_{60}(OAc)_{180}$ by electron microscopy data (Philips CM-30; cluster specimens were deposited onto small graphite crystals, 120 to 350 particles contributed to the histograms).

The most striking result was revealed by the electron microscopy data for the metal particles of fraction 3. Both ED pattern and HREM images shown in Figs. 2(*b*), 3(*b*) gave evidence for the lack of any arrangement but a close ordering of metal atoms within cluster metal cores. Therefore, this study has revealed at least three kinds of metal cores of Pd-561 giant clusters: i, those packed near-perfectly as FCC metal particles; ii, icosahedral or multiply-twinned particles

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[†] TEM micrographs and electron diffraction patterns were obtained with a Philips CM-30 (P. N. Lebedev Physical Institute, Moscow) and JEOL-4000EX (Novosibirsk) electron microscopes. Experimental details are described elsewhere.[2]

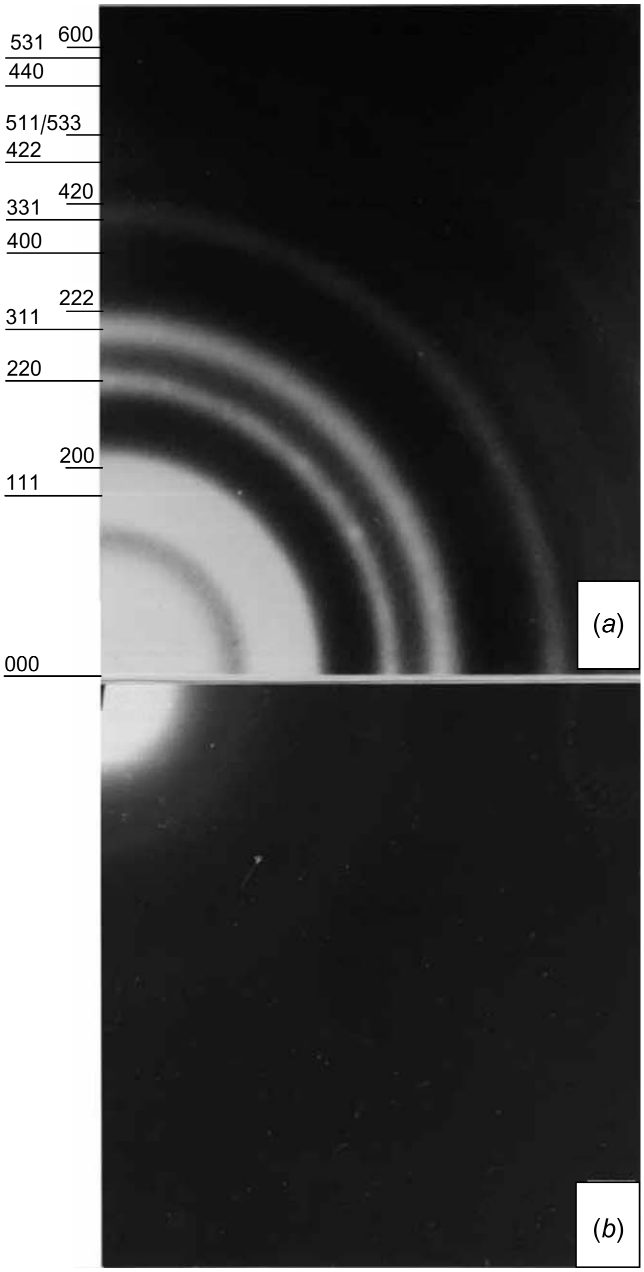

Fig. 2 Electron diffraction patterns for fractions 1 (*a*) and 3 (*b*) (Philips CM-30; cluster specimens were deposited onto an amorphous carbon film). The positions of (*h,k,l*) reflections which were calculated for bulk Pd metal are shown on the left of pattern (*a*).

and iii, metal particles with no close ordering. The last case seems to represent an example of a very small, 25 A in size, internally disordered metal particle.

The data obtained can be rationalized from the standpoint of chemical transformations occuring in the preparation of giant clusters. Cluster **1** is known to be prepared by a two-step synthesis:[1,2]

(1) Reduction of $Pd(OAc)_2$ with H_2 in AcOH solution containing a small amount of ligand L to give a high-molecular polyhydride Pd cluster of the composition $[Pd_4H_4(OAc)L]_n$ ($n = \sim 100$) **2**, reaction (1):[6]

$$\mathrm{Pd(OAc)_2 + L + H_2 \rightarrow 1/}n\underset{\mathbf{2}}{\mathrm{[Pd_4H_4(OAc)L]}_n}\mathrm{ + AcOH} \qquad (1)$$

(2) Oxidative treatment of polyhydride cluster **2** with dioxygen to form giant cluster **1**, reaction (2):

$$\mathrm{[Pd_4H_4(OAc)L]}_n\mathrm{ + O_2 + AcOH} \rightarrow \mathbf{1}\mathrm{ + Pd(OAc)_2 + L + H_2O} \qquad (2)$$

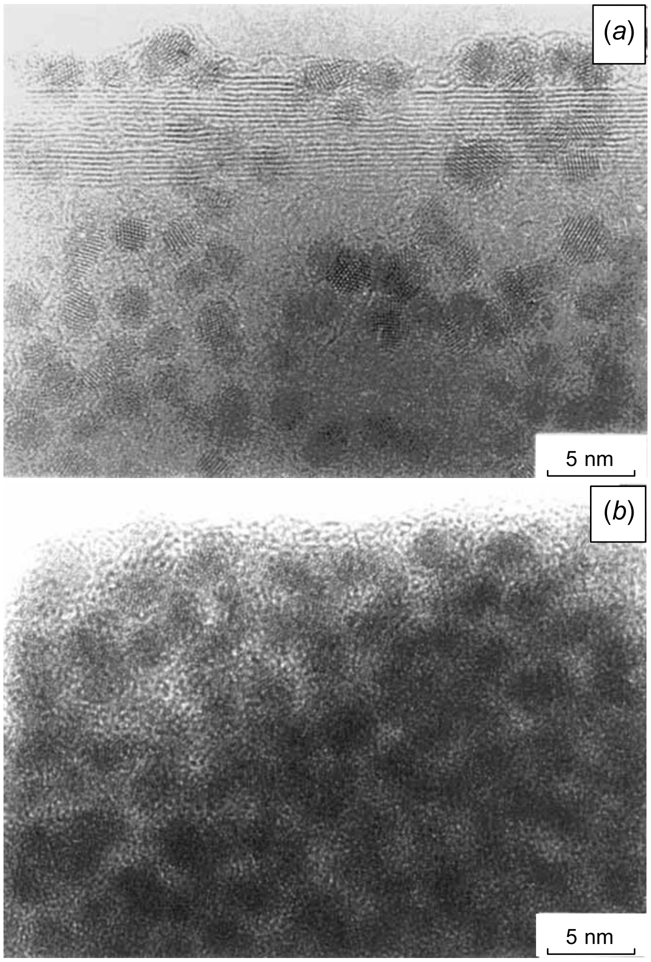

Fig. 3 HREM images of cluster cores for fraction 1 (*a*) and 3 (*b*) (JEOL-4000 EX, accelerating voltage 400 kV; cluster particles are seen against crystalline graphite plane).

According to EXAFS, NMR and TEM-ED data,[2,6] polyhydride cluster **2** which is formed in the first stage of the synthesis, reaction (1), is composed of small, most likely tetrahedral, Pd_4 cluster units connected together *via* H and/or OAc bridges to form a fractal or "curdled-chain" polymer. In the second step of the synthesis, reaction (2), polymer **2** loses all the hydride and some of the OAc^- ligands by the action of O_2 to form giant cluster **1**.

ED and HREM data showed FCC packing of Pd atoms in the metal core of cluster **1** and its analogues with various L and X ligands (OAc^-, PF_6^-, ClO_4^-, CF_3COO^-, *etc*).[3–5,7] Meanwhile, EXAFS data evidenced packing of an icosahedral type for a cluster **1** metal core.[4,5] An icosahedral (or multiply-twinned, containing a five-fold axis) metal core was also found for some larger specimens of cluster **1** by the HREM technique, whereas the rest of the **1** metal cores were observed as FCC packed ones.[4,5] The discrepancy between EXAFS and TEM-ED data is evident, being caused not only by non-uniformity of the material under study but also by the difference in the experimental conditions of the two techniques. Due to high-voltage electron irradiation under the conditions of electron microscopy experiments, the loss of the ligands, reduction of metal atoms with electron beam and relaxation of cluster metal core cannot be ruled out. The "naked" metal nuclei of the clusters can be expected to undergo relaxation to a FCC structure, typical of Pd bulk metal.

In this context, the observation of multiply-twinned, including icosahedral, particles in this work (see Fig. 4) and in our previous HREM studies[4,5] can be considered as evidence for icosahedral packing of at least part of the initial cluster molecules. Icosahedral particles can hardly be formed

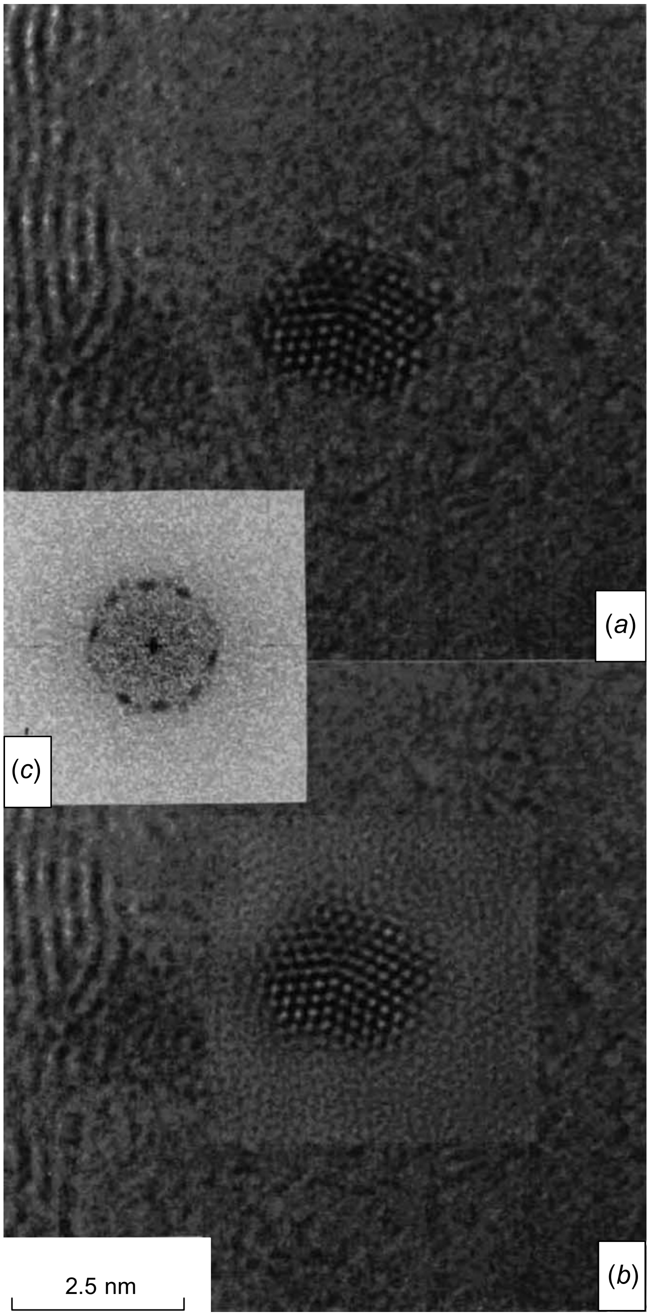

Fig. 4 HREM image of a single cluster particle with five-fold axis from fraction 2: direct image (*a*); the same image after computer refining (*b*); optical pattern for the same single particle (*c*) (JEOL-4000 EX, accelerating voltage 400 kV).

from FCC packed ones under the influence of the electron beam, whereas the probability of the reverse process seems to be fairly high.

The transformation of the fractal-like polyhydride cluster **2** into cluster **1,** containing a close-packed metal core, seems to be a rather involved multistep reaction. As an oversimplification, reaction (2) can be considered as the removal, by the action of dioxygen, of H ligands (and some of the L, OAc^- ligands) followed by combining of tetrahedral Pd_4 blocks into a polyhedral cluster resembling the final product. One would expect that a system consisting of more than a hundred Pd_4 blocks would take several different forms, with disordered packing of the Pd_4 blocks, in their passage from fractal to close packed shape. These intermediate forms can resemble the final compound in their size and even composition but differ in shape and packing. We believe that some of the non-removed ligands or unsuitable arrangements of the building blocks can prevent the proper final package being achieved on the way from cluster **2** to cluster **1**.

Table 1 Magnetic susceptibility of unresolved and fractionated samples of cluster **1**.[a]

Cluster sample	$\chi_g^{300}/10^{-6}$ CGSU	$\chi_g^{77}/10^{-6}$ CGSU
1, unresolved (total material)	$+1.3 \pm 0.2$	$+1.8 \pm 0.3$
fraction 1	$+1.6 \pm 0.3$	$+2.1 \pm 0.5$
fraction 2	$+1.0 \pm 0.2$	$+1.2 \pm 0.2$
fraction 3	$+0.6 \pm 0.2$	$+1.1 \pm 0.2$

[a] Specific susceptibility, χ_g, was measured with a Faraday balance within the 0–7.5 kOe field interval at 300–77 K, with ±10% experimental error.

Pd-561 clusters, both non-fractionated **1** and that of $Pd_{561}Phen_{60}O_{60}(PF_6)_{60}$ idealized formula, were previously found to be weak, metal-like paramagnetics whose susceptibility is almost temperature-independent.[2,8] In this context, it was of interest to study the magnetic properties of the fractionated clusters.

The data in Table 1 show that all the cluster samples, both unresolved, total **1** and its fractions 1–3, exhibit weak, only slightly temperature-dependent paramagnetism of Van Vleck type within the 77–300 K temperature interval. It is noteworthy that the fraction 3, containing disordered metal nuclei, revealed some smaller χ_g values (with some steeper temperature dependence) despite the substantial contribution of sizable particles which, if ordered like bulk metal would exhibit higher χ_g values than those inherent in smaller, more orderly-packed particles.

So the magnetic properties seem to be in an agreement with the speculation concerning the nature of the cluster core in fraction 3.

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References

1 M. N. Vargaftik, V. P. Zagorodnikov, I. P. Stolarov, I. I. Moiseev, V. A. Likholobov, D. I. Kochubey, A. L. Chuvilin, V. I. Zaikovsky, K. I. Zamaraev and G. I. Timofeeva, *J. Chem. Soc., Chem. Commun.*, 1985, 937.

2 M. N. Vargaftik, V. P. Zagorodnikov, I. P. Stolarov, I. I. Moiseev, D. I. Kochubey, V. A. Likholobov, A. L. Chuvilin and K. I. Zamaraev, *J. Mol. Catal.*, 1989, **53**, 315.

3 I. I. Moiseev and M. N. Vargaftik, in *Perspectives in Catalysis*, eds. J. A. Thomas and K. I. Zamaraev, Blackwell, London, 1992, p. 91.

4 V. V. Volkov, G. Van Tendeloo, M. N. Vargaftik, I. P. Stolarov and I. I. Moiseev, *Mendeleev Commun.*, 1993, 187.

5 V. V. Volkov, G. Van Tendeloo, M. N. Vargaftik and I. I. Moiseev, *J. Crystal Growth,* 1993, **132**, 359.

6 M. N. Vargaftik, V. P. Zagorodnikov, I. P. Stolarov, D. I. Kochubey, V. M. Nekipelov, V. M. Mastikhin, V. D. Chinakov, K. I. Zamaraev and I. I. Moiseev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 2381 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1985, 2206).

7 G. Schmid, *Chem. Rev.*, 1992, 1709.

8 V. P. Zagorodnikov, M. N. Vargaftik, D. I. Kochubey, V. A. Likholobov, V. N. Kolomiychuk, A. N. Naumochkin, A. L. Chuvilin, V. M. Novotortsev, O. G. Ellert and I. I. Moiseev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 849 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1989, 762).

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