

Scanning tunneling microscopy observation of giant palladium-561 clusters

J.C. Poulin^a, H.B. Kagan^{a,*}, M.N. Vargaftik^b, I.P. Stolarov^b, I.I. Moiseev^b

^a *Laboratoire de Synthèse Asymétrique (UA CNRS 1497), Institut de Chimie Moléculaire d'Orsay, Université de Paris Sud, 91405 Orsay cedex, France*

^b *N.S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 31 Leninski prospect, 117907 Moscow GSP-1, Russia*

Received 28 March 1994; accepted 26 September 1994

Abstract

STM observation showed giant palladium-561 clusters which are larger in size than observed earlier by TEM and HREM studies. The difference is presumably due to the ligand shell of the clusters, which is invisible to electron microscopy.

Keywords: Palladium-561 clusters; Giant clusters; Scanning tunneling microscopy; Ligand; Graphite substrate; Highly oriented pyrolytic graphite (HOPG)

1. Introduction

Giant palladium clusters of $\text{Pd}_{561}\text{L}_{60}(\text{OAc})_{180}$ ($\text{L} = 1,10$ -phenanthroline, phen (**1**) and α, α' -bipyridine) and $\text{Pd}_{561}\text{Phen}_{60}\text{O}_{60}\text{X}_{60}$ ($\text{X} = \text{PF}_6^-$ (**2**), ClO_4^- , BF_4^- , CF_3COO^-) idealized formulae have been found to be active homogeneous catalysts for various organic reactions, e.g. oxidative acetoxylation of alkenes and alkylarenes; oxidation of alkenes, formic acid and alcohols; acetal formation [1]. On the basis of elemental analysis data, TEM, SAXS and EXAFS studies [1–3], clusters **1** and **2** were found to contain a close-packed metal core and ligands L, O, X, that are located at the periphery of a cluster. Further support to this conclusion came recently from HREM and MALD MS studies [4,5]. The data mentioned, except that of elemental analysis, pertain

mainly to the cluster metal core and packing.

In this study, we used scanning tunneling microscopy, STM [6], to obtain more information on the shape and size of clusters **1** and **2**, including their ligand surrounding.

2. Experimental

Giant palladium cluster **1** was prepared by reduction of $\text{Pd}(\text{OAc})_2$ with dihydrogen in AcOH solution containing phen ($\text{Pd}/\text{phen} = 2/1$ molar ratio) followed by oxidation of the intermediate polyhydride cluster with O_2 , using the method described elsewhere [2]. Cluster **2** was obtained from aqueous solution of cluster **1** by precipitation with KPF_6 [1,7].

A Nanoscope II apparatus equipped with electrochemically etched tungsten tips was used for

* Corresponding author.

STM observations. Operating conditions were as follows: a tunnel current in the range 10 to 100 pA, voltage bias between -50 mV and 700 mV in the constant current mode, in air atmosphere and room temperature. Recorded images were 400×400 pixels. The scanning speed was in the range 100 to 250 nm/s, yielding 25×25 nm² images in a time of 40 to 90 s.

Samples were prepared using a solution of cluster 1 in acetic acid and cluster 2 in acetonitrile, concentrations were < 1 mg/ml of solution. A freshly cleaved piece of highly oriented pyrolytic graphite (HOPG) was coated by spreading of a few microliters of the solution on the surface.

After evaporation of the solvent under air, the sample was ready for STM examination.

3. Results and discussion

Clusters 1 and 2 are easily seen by STM when adsorbed (from a solution) on HOPG surface. In the STM images, the clusters are sphere shaped, no intramolecular details are seen. In these images, the molecular shape seems to be independent of the tunneling conditions, in the used range (Fig. 1).

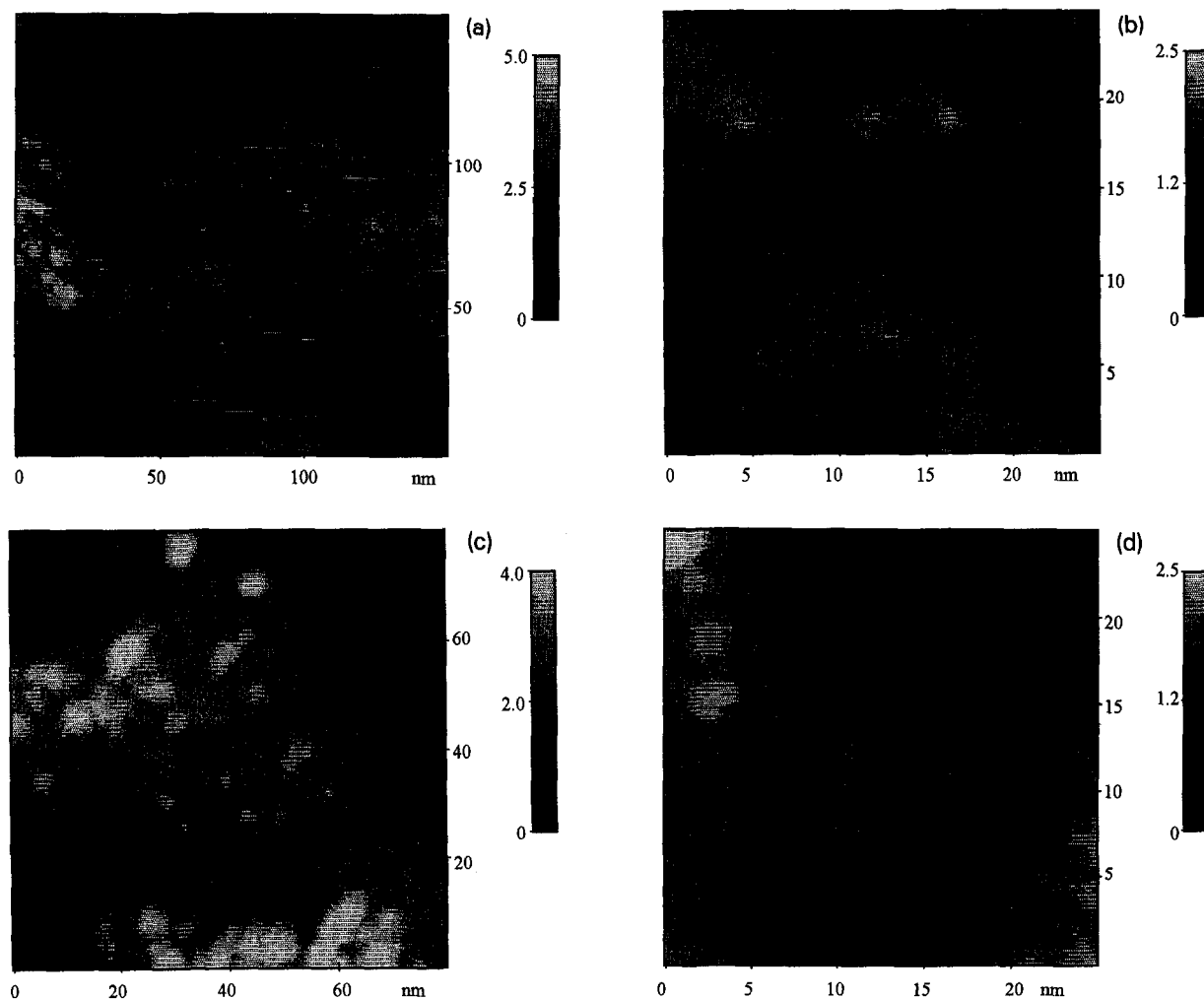


Fig. 1. STM images of giant clusters (a) cluster 1 150×150 nm², (b) cluster 1 25×25 nm², (c) cluster 2 80×80 nm², (d) cluster 2 25×25 nm².

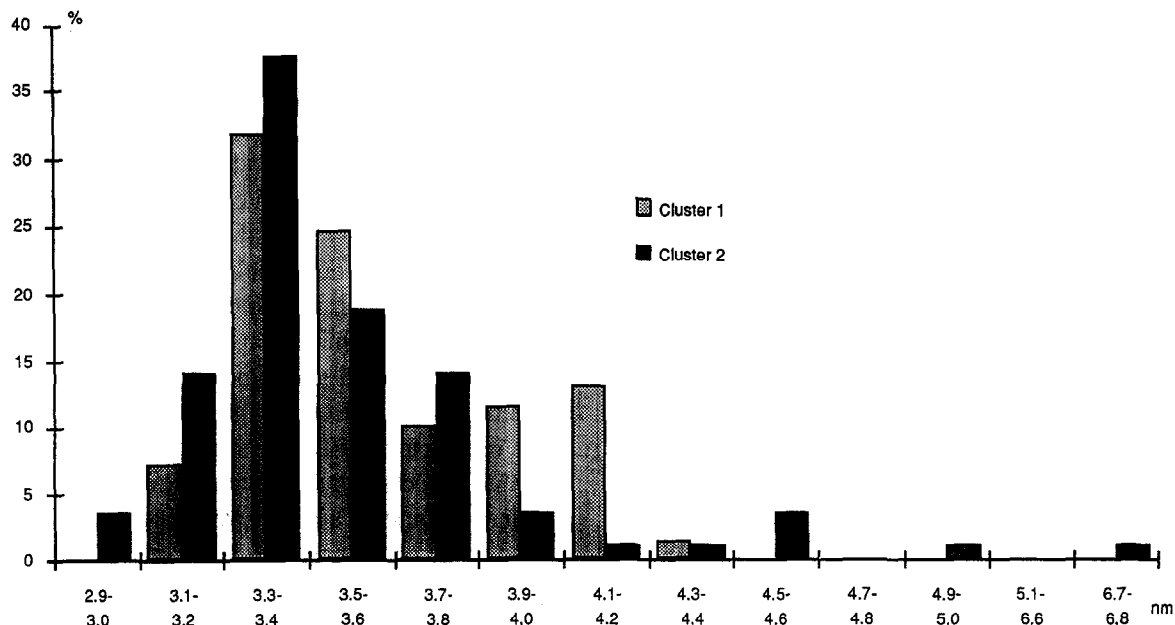


Fig. 2. Size distribution of clusters 1 and 2.

The size of molecules was measured on the samples of freshly prepared clusters on five different fields $25 \times 25 \text{ nm}^2$ STM images for each cluster. Due to reduced contrast, the smaller and 'rear plane' molecules are rejected from the measurements. The size distribution diagram (Fig. 2) was obtained by taking the diameter of individual molecules. Size measurements are consistent using three different modes: diameter of individual molecules, top-to-top distance of vicinal molecules, or frequency analysis in nearly crystalline areas. For molecules of the same level, the two latter techniques are not affected by tip convolution. Size measurements by frequency analysis are about 10% greater than measured by the two first methods. Cluster 2 appears to be rather organized in the large area observed for molecular size measurement (more than $50 \times 50 \text{ nm}^2$) (Fig. 1d). STM shows a tendency of clusters 1 or 2 to aggregate by contacting their outer spheres, with a beginning of two-direction crystallization in the case of cluster 2. However individual cluster molecules were clearly observed.

In earlier observations of the above clusters using TEM or HRTEM, the measurements of the palladium core was in the $2.6 \pm 0.35 \text{ nm}$ or

$2.2 \pm 0.4 \text{ nm}$ range [8]. The size distribution (Fig. 2) obtained by STM is centered at 3.3 to 3.6 nm, reflecting the composition spreading around the idealized formulae 1 and 2.

According to the idealized model, that is based upon previous TEM, SAXS, EXAFS and elemental analysis data [1–3], the expected van der Waals diameter of clusters 1 and 2, including ligand shell, is within 4–5 nm. From the point of view of tunneling microscopy, the boundary of ligand shell is apparently not the same as that of van der Waals. However, it is still unclear which part of the ligand shell is mapped in the tunneling microscopy experiment. Nevertheless, the difference between the size of the metal core ($\sim 2.5 \text{ nm}$ found by TEM and HREM experiments) and that found by STM ($\sim 3.5 \text{ nm}$) is reasonably pronounced, possibly being stemmed, at least partly, from a cluster ligand shell. Isolated cluster molecules were observed during a long time without any detectable motion (observation with tunnel current $\leq 50 \text{ pA}$) (Fig. 3). It is interesting to notice that the diameter of the four isolated molecules observed in Fig. 3 is approximately 4.5 nm, very close to the expected van der Waals actual size. That observation was done on a sample not

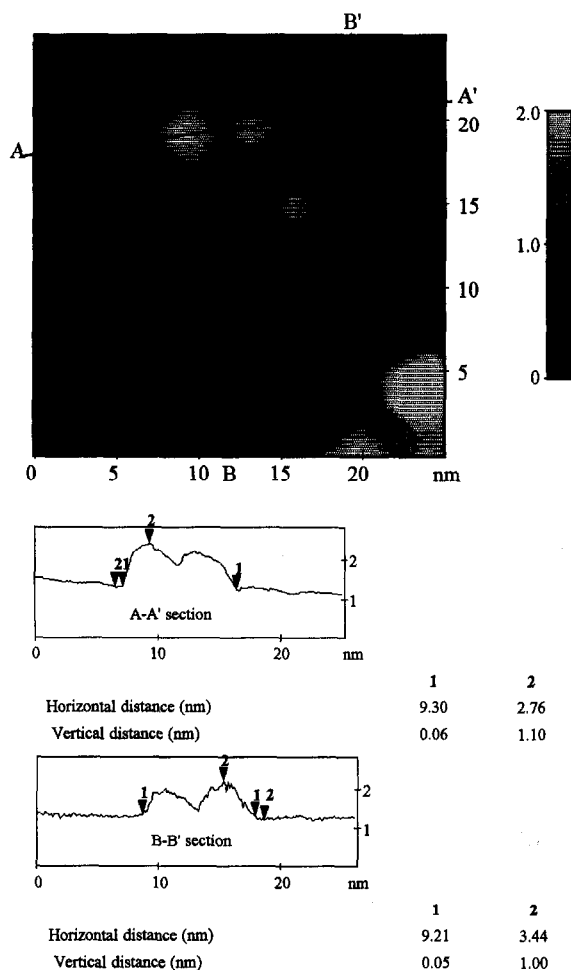


Fig. 3. Profile analysis of STM images of cluster 2.

so fresh as the ones used for size measurements (Fig. 2). That discrepancy may be due to a difference between the size of freshly prepared clusters and older ones. Another explanation may be a systematical difference in measurements between areas of isolated molecules and high density coverage of the support.

Height measurements showed the cluster altitude (1.0 to 1.1 nm) noticeably less than diameter size in the observation plane (Fig. 3). A similar effect of the 'missing height' in STM images of giants clusters $\text{Pd}_{561}\text{Phen}_{38}\text{O}_{\sim 200}$ was found previously by Schmid et al. [9–11]. However, unlike those results, we have no observation to confirm that clusters are easily picked up by STM tip [9,10].

It may be useful to remember that STM is not topologically sensitive, as obtained images are linked to tunneling probability between conductive substrate and tip. The electronic properties of such a junction are linked to parameters maintained constant during an experiment (as tip and substrate materials, direction of electron tunneling, bias voltage and tunneling current), and other ones depending on local electronic structure used to create images. In our experiments the sample is made of adsorbed molecules onto a support, the electronic properties are obviously not the same for chemically different areas of uncoated and coated support. For understanding and modeling tunneling on such a locally heterogeneous sample, a network of 'supramolecular' orbitals must be used for calculations of local tunneling probabilities. These orbitals can be seen as combinations of support ones and these of the molecules, localized in the adsorption sites. Calculations of STM images show the influence of adsorbate constitution. In such a prediction, an O atom appears as a dip and a S is seen as a bump on the same Re surface [12]. To simplify, the height measurement is only easy to interpret on a homogeneous sample, especially in the case of molecular steps.

Molecules must remain motionless during scanning to be visualized. Usually the molecules are immobilized onto the surface of substrate by a two dimensional arrangement [6]. The observed immobilization of the giant clusters may be a consequence of a strong adsorption, but such high density molecules may be held in position by inertia.

4. Conclusion

Comparison of the data obtained with TEM, HREM and STM gives support for the idealized model of palladium giant clusters 1 and 2 [1,2], in which the cluster molecule is composed of a metallic core surrounded by a ligand shell. Transmission electron microscopy shows the metal core while STM gives a reasonable evidence for ligand shell of the clusters.

Acknowledgements

Some of us are grateful for financial support from the Russian Foundation for Fundamental Science (to MV, IS and IM) under contract No. 93-03-4415. We thank the referees for valuable remarks.

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