A Novel Giant Palladium Cluster

Michail N. Vargaftik,[a] Victor P. Zagorodnikov,[a] Igor P. Stolyarov,[a] Ilya I. Moiseev,*[a] Vladimir A. Likholobov,[b] Dmitry I. Kochubey,[b] Andrew L. Chuvilin,[b] Vladimir I. Zaikovsky,[b] Kirill I. Zamaraev,[b] and Galina I. Timofeeva[c]

[a] *N. S. Kurnakov Institute of General and Inorganic Chemistry, Academy of Science, 117071 Moscow V-71, U.S.S.R.*
[b] *Institute of Catalysis, Academy of Sciences, Siberian Department, Novosibirsk, U.S.S.R.*
[c] *A. N. Nesmeyanov Institute of Organo-Element Chemistry, Academy of Science, Moscow, U.S.S.R.*

Electron microscopy, electron diffraction, EXAFS, and ultracentrifuging data show that a new catalytically active cluster prepared by reduction of $Pd(OAc)_2$ by H_2 in the presence of L = 1,10-phenanthroline, or 2,2′-bipyridine, followed by O_2 treatment, contains a close-packed metal nucleus (570 ± 30 Pd atoms) bearing 60 ± 3 co-ordinated L and 180 ± 10 OAc^- in the outer sphere of the cluster.

Reduction of platinum metal salts by suitable reagents in the presence of stabilising ligands is a known method of preparation of clusters.[1] We have found that the products of reduction of $Pd(OAc)_2$ by H_2 in the presence of small quantities of L = 1,10-phenanthroline, phen, or 2,2′-bipyridine, bipy, followed by O_2 treatment, are non-crystalline Pd-containing substances soluble in H_2O and polar organic solvents, of a constant stoicheiometry $[Pd_9L(O)_3(OAc)_3]_m$ (**1**).

High resolution electron microscope (EM) studies (JEM-100 CX, 250 000 × direct magnification) of samples deposited on carbon or graphite supports from MeCN solutions (Figure 1) reveal that the Pd skeleton of (**1**) has almost spherical

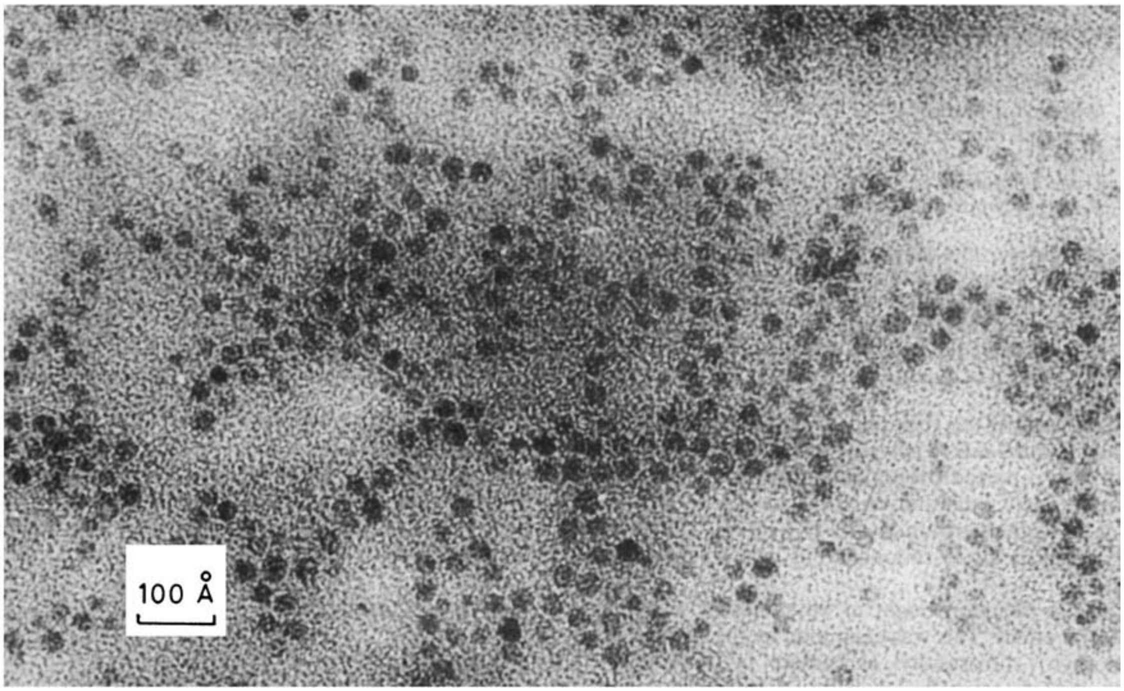

Figure 1. Electron micrograph of particles of (**1**) deposited on a carbon support.

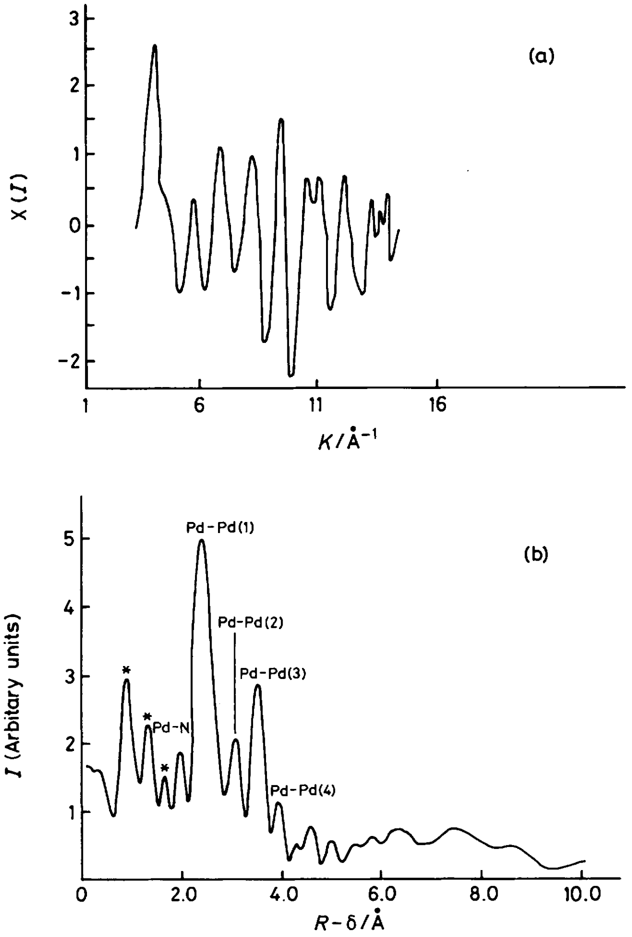

Figure 2. Extended *X*-ray absorption fine structure (EXAFS) of Pd *K*-edge of cluster (**1**) (a) and radial distribution function of atoms (b). * False maxima.

particles with a narrow size distribution: the average diameter is 26 Å, the standard dispersion (3.5 Å) slightly exceeds the microscope's resolution. From the rates of sedimentation of aqueous 0.05—0.30% wt. solutions of (**1**) on ultracentrifuging (MOM-3801, Hungary, 58 000 min^{-1}, moving frontier method) the molecular weight of (**1**), L = phen, was calculated, using Stock's formula for spherical particles, to be 89 500 ± 4 500. Therefore, for compound (**1**) $m = 63.5 \pm 3.5$, and the cluster contains 570 ± 30 Pd atoms.

$$[Pd_9L(O)_3(OAc)_3]_m$$

(**1**)

The samples of (**1**) revealed EM dark-field images (in 111 and 200 reflexes) and the electron diffraction pattern with 5—6 rings showed the crystalline nature of (**1**). The size of the particles responsible for the diffraction pattern was evaluated by the half-width of the rings as *ca.* 25 Å, in a good agreement with the EM data. The mean atomic volume of Pd in the observed particles of (**1**) calculated from these data is 16 Å^3, only slightly exceeding that of Pd metal (14.7 Å^3). This result excludes the possibility of co-ordination of the ligands by the inner Pd atoms. Therefore, the L and OAc groups must be situated at the periphery of the metal core of cluster (**1**).

EXAFS data (Figure 2) for a solid sample of (**1**), L = phen, showed four maxima for Pd–Pd distances (Table 1). Phase shifts were determined by simulating the spectra of model diatomic molecules using the phase and the amplitude functions calculated in reference 2. The four interatomic Pd–Pd distances found are compatible with a model of Pd atoms arranged in an icosahedron. Owing to lower packing density, this arrangement[3] may give a higher atomic volume for Pd in (**1**) than that in the f.c.c. packed metal, though the shortest Pd–Pd distance in (**1**) (2.60 Å) is lower than that in the metal by 0.14 Å.

A complete polyhedron of this type is formed by '*n*' monoatomic Pd layers packed around a central Pd atom, each layer consisting of $10n^2 + 2$ metal atoms.[3] Using this model, the nearest value to the experimental value of 570 ± 30, for the

Table 1. A comparison of experimental (EXAFS) Pd–Pd distances in (**1**), L = phen, with those calculated for various packings of the Pd core.[a]

	Pd–Pd Distances, Å				
EXAFS data	2.60 ± 0.04	3.10 ± 0.10	3.66 ± 0.10	4.08 ± 0.10	—
Packings[b]					
F.c.c.	2.60	—	3.66	—	—
H.c.p.	2.60	—	3.66	—	4.5
Icosahedron	2.60	3.10	3.66	4.1	—

[a] 2.60 Å is taken to be the shortest Pd–Pd distance. [b] F.c.c. = face centred cubic packing; h.c.p. = hexagonal cubic packing.

number of Pd atoms is 561, corresponding to a five-layer icosahedron with 252 Pd atoms in the outer shell.

The structure of the cluster (**1**) may be realized on the basis of this polyhedron, and using the Chini hypothesis.[4] By analogy with 13-atomic ($n = 1$)[4,5] and 55-atomic ($n = 2$)[6,7] clusters of Au and Rh, the cluster (**1**) may be regarded as a 'peach-like' giant molecule consisting of a regular-packed metal nucleus and ligands co-ordinated by Pd atoms in the outer layer. It follows from the stoicheiometry that the idealized 561-atomic palladium icosahedron bears 60 ± 3 L molecules and 180 ± 10 OAc groups. The nature of other O atoms is at present unclear.

Analysis of molecular models shows that the maximum number of L ligands on the surface of the icosahedron allowed sterically is 60. This number is only scarcely influenced by deviations from the idealised outer layer (as in truncated or capped polyhedra). Direct co-ordination of OAc seems to be interfered with, because of the bulky phen or bipy ligands. A similar steric situation has been observed in the tetrahedral $[Pd_4(CO)_2phen_4]^{4+}(OAc^-)_4$ cluster, where the OAc groups were found by *X*-ray analysis[8] to be outer-sphere anions. Therefore most, though probably not all, of the OAc^- anions in (**1**) are located in the outer sphere of the positively charged cluster and held there electrostatically.

The clusters (**1**), L = phen, bipy, are catalytically active in the oxidative acetoxylation of ethylene by O_2 to form vinyl acetate.[9] From steric considerations, only *ca.* 20 Pd atoms of (**1**) seem to be available for co-ordination of substrate molecules.

Received, 10th December 1984; Com. 1733

References

1 I. I. Moiseev, *Sov. Scientific Revs., Sect. B,* 1982, **4**, 140.
2 B. K. Teo and P. A. Lee, *J. Am. Chem. Soc.*, 1979, **101**, 2815.
3 A. L. Mackay, *Acta Crystallogr.*, 1962, **15**, 916.
4 P. Chini, *Gazz. Chim. Ital.*, 1979, **109**, 225.
5 J. W. A. van der Velden, F. A. Vollenbroek, J. J. Bour, P. T. Beurskens, J. M. M. Smiths, and W. P. Bosman, *Recl. Trav. Chim. Pay-Bas*, 1981, **100**, 148.
6 G. Schmid, R. Pfeil, R. Boese, F. Bandermann, S. Meyer, G. H. M. Calis, and J. W. A. van der Velden, *Chem. Ber.*, 1981, **B114**, 3634.
7 G. Schmid, U. Giebel, W. Huster, and A. Schwenk, *Inorg. Chim. Acta*, 1984, **85**, 97.
8 M. N. Vargaftik, T. A. Stromnova, T. S. Khodashova, M. A. Porai-Koshitz, and I. I. Moiseev, *Koord. Khim.*, 1981, **7**, 132.
9 M. N. Vargaftik, V. P. Zagorodnikov, and I. I. Moiseev, *Izv. Akad. Nauk SSR, Ser. Khim.*, 1983, 1209.