

[Pd₈(CH₃COO)₈(NO)₈]: solution from X-ray powder diffraction data

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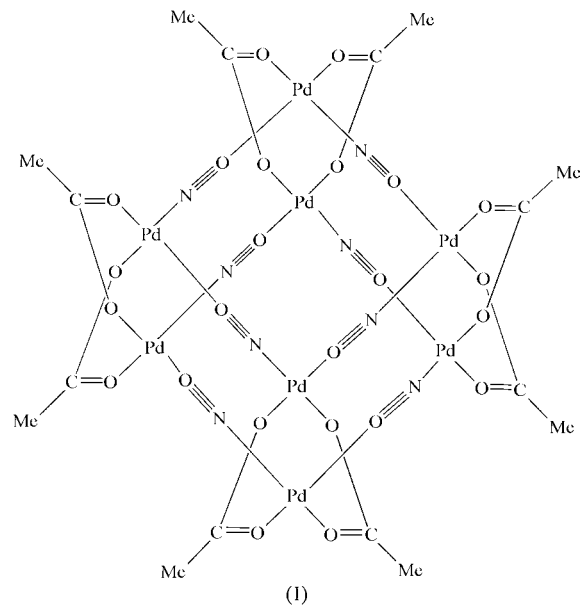
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The water-insoluble title compound, octakis(μ -acetato- $\kappa^2O:O$)octakis(μ -nitroso- $\kappa^2N:O$)octapalladium(II), [Pd₈(CH₃COO)₈(NO)₈], was precipitated as a yellow powder from a solution of palladium nitrate in nitric acid by adding acetic acid. *Ab initio* crystal structure determination was carried out using X-ray powder diffraction techniques. Patterson and Fourier syntheses were used for atom locations, and the Rietveld technique was used for the final structure refinement. The crystal structure is of a molecular type. The skeleton of the [Pd₈(CH₃COO)₈(NO)₈] molecule is constructed as a tetragonal prism with Pd atoms at the vertices. The eight NO⁻ groups are in bridging positions along the horizontal edges of the prism. The N and O atoms of each nitroso group coordinate two different Pd atoms. The vertical edges present Pd···Pd contacts with a short distance of 2.865 (1) Å. These Pd atoms are bridged by a pair of acetate groups in a *cis* orientation with respect to each other. The complex has crystallographically imposed *4/m* symmetry; all C atoms of the acetate groups are on mirror planes. The unique Pd atom lies in a general position and has square-planar coordination, consisting of three O and one N atom.

Comment

Nitroso–acetate and nitrite–acetate complexes of palladium are, frequently, intermediate compounds in the synthesis of palladium acetate, which is an important industrial catalyst. These complexes can be obtained at various ratios of acetate and nitroso groups, and present an example of stable cluster complexes with various palladium nucleation numbers. Therefore, these compounds are rather interesting models for studying polynuclear complexes. A search of the Cambridge Structural Database (Allen, 2002) for palladium–acetate compounds with NO⁻ or NO₂⁻ ligands revealed structures for [Pd₃(CH₃COO)₅(NO₂)] (Chiesa *et al.*, 1990), [Pd₆(CH₃COO)₈(NO)₂] (Chiesa *et al.*, 1990) and [Pd₄(CH₃COO)₆(NO)₂]·CH₂Cl₂ (Podberzskaya *et al.*, 1981), as well as one nitroso–acetate compound of

platinum, *viz.* [Pt₄(CH₃COO)₆(NO)₂]·2CH₃COOH (Meester & Skapski, 1973). In the present paper, the crystal structure of the novel octanuclear complex compound [Pd₈(CH₃COO)₈(NO)₈], (I), as determined from powder diffraction data (Fig. 1), is reported.



The complex has crystallographically imposed *4/m* symmetry; all C atoms of the acetate groups are on mirror planes. The unique Pd atom lies in a general position and has square-planar coordination, consisting of three O and one N atom. The [Pd₈(CH₃COO)₈(NO)₈] structure is of molecular type with relatively large molecules consisting of 48 non-H atoms (Fig. 2). The skeleton of the molecule is constructed as a tetragonal prism with Pd atoms at the vertices. However, the eight Pd atoms are not directly bonded in a single cluster unit. Rather, there are four Pd₂ fragments on vertical edges of the prism. The Pd···Pd contacts of 2.865 (1) Å in the fragments can be considered as metal–metal bonds. These Pd₂ groups are

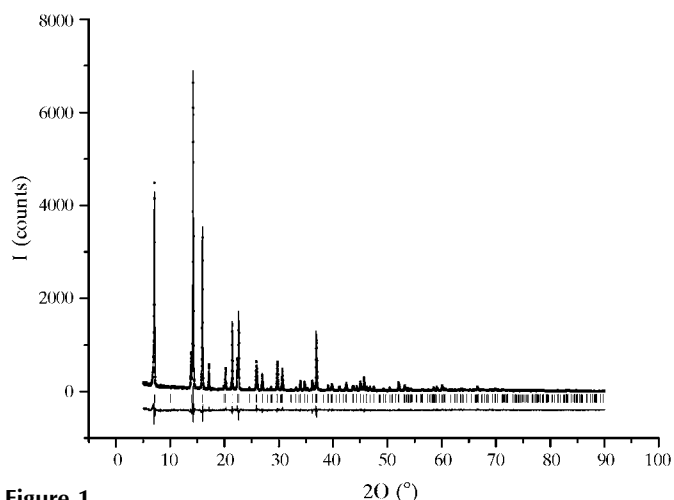


Figure 1
The observed (dots), calculated (superimposed solid) and difference profiles after the Rietveld refinement. The reflection positions are marked by ticks.

connected *via* NO⁻ ligands, which form the eight horizontal edges of the prism. The Pd···Pd contacts are enforced by two acetate groups positioned across the bond in a bridging mode and *cis* oriented with respect to each other.

The nitroso groups exhibit a bidentate bonding mode in the compound, coordinating one Pd atom by the O atom and another by the N atom. The exact positions of the NO⁻ ligands are not coincident with the lines connecting the Pd atoms. Rather, the ligands lie a little higher or lower than this line, allowing the Pd coordination geometry to remain very close to

ideal square planar (Table 1). The very short N≡O distance, 1.06 (3) Å, is consistent with the triple bond expected in a negatively charged NO⁻ anion. The packing arrangement in the crystal conforms to an *I*-centered cell with the centers of the [Pd₈(CH₃COO)₈(NO)₈] molecules situated on the lattice points and the molecules rotated approximately 60° around the *z* axis with respect to the Pd₈ cages (Fig. 3). This packing results in the formation of columns from stacked complexes, with intermolecular Pd···Pdⁱⁱⁱ distances of 3.9856 (10) Å along the *z* direction [symmetry code: (iii) *x*, *y*, -*z*].

The known nitroso–acetate compounds of palladium and platinum can be separated into two groups in terms of the number of metal atoms in the cluster. The compounds [Pd₂(CH₃COO)₂(NO)₂], [Pd₄(CH₃COO)₆(NO)₂]·CH₂Cl₂ and [Pt₄(CH₃COO)₆(NO)₂]·2CH₃COOH have two atoms in clusters with a Pd···Pd distance shorter than 2.92 Å. [Pd₃(CH₃COO)₅NO₂] and [Pd₆(CH₃COO)₈(NO)₂] have triangular clusters with Pd···Pd contacts in the range 3.03–3.20 Å. In this respect, (I) can be related to the first group. Another point of classification is the coordination of the NO⁻ groups. Bidentate bonding of NO⁻ is a specific feature of the studied structure. The title compound is the first example of such coordination in the family of nitroso–acetate compounds of palladium and platinum.

Experimental

The synthesis of (I) was carried out by adding acetic acid to a solution of palladium nitrate in nitric acid. The solution was heated at 378 K. The precipitated yellow product was filtered off, washed with water and dried in air.

Crystal data

[Pd(C₂H₃O₂)₈(NO)₈]
M_r = 1563.79
 Tetragonal, *I4/m*
a = 17.5504 (3) Å
c = 6.8504 (2) Å
V = 2110.04 (8) Å³
Z = 2
D_x = 2.461 Mg m⁻³
 Cu Kα radiation
μ = 27.65 mm⁻¹
T = 293 K
 Yellow
 Specimen shape: circular flat plate
 20.0 × 20.0 × 0.5 mm
 Specimen prepared at 101 kPa
 Specimen prepared at 293 K
 Particle morphology: thin powder

Data collection

DRON-4 powder diffractometer
θ/2θ scans
 Specimen mounting: packed powder pellet
 Specimen mounted in reflection mode
 478 measured reflections
 478 independent reflections
*θ*_{max} = 45°
h = 0 → 16
k = 0 → 16
l = 0 → 6
 2*θ*_{min} = 5.0, 2*θ*_{max} = 90.0°
 Increment in 2*θ* = 0.02°

Table 1

Selected geometric parameters (Å, °).

Pd–O1	1.99 (2)	O2–C21	1.31 (2)
Pd–O2	2.01 (2)	C11–C12	1.41 (3)
Pd–O3	1.98 (2)	C21–C22	1.41 (3)
Pd–N	1.92 (2)	O3 ⁱ –N	1.06 (3)
O1–C11	1.29 (2)	Pd–Pd ⁱⁱ	2.865 (1)
O2–Pd–O1	88.9 (6)	O1–Pd–N	91.3 (7)
O2–Pd–O3	89.2 (6)	O1–C11–O1 ⁱⁱ	123.2 (2)
O3–Pd–N	90.5 (6)	O2–C21–O2 ⁱⁱ	113.8 (3)

Symmetry codes: (i) *y*, -*x*, *z*; (ii) *x*, *y*, 1 - *z*.

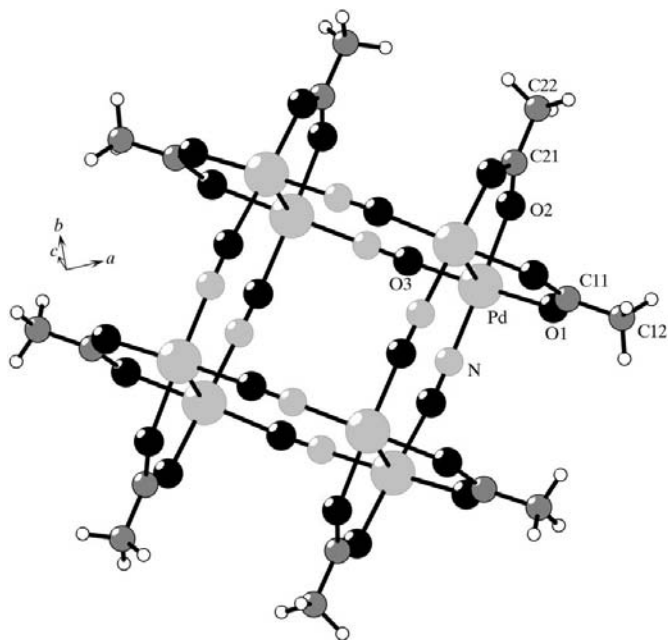


Figure 2
The molecular complex [Pd₈(NO)₈(CH₃COO)₈].

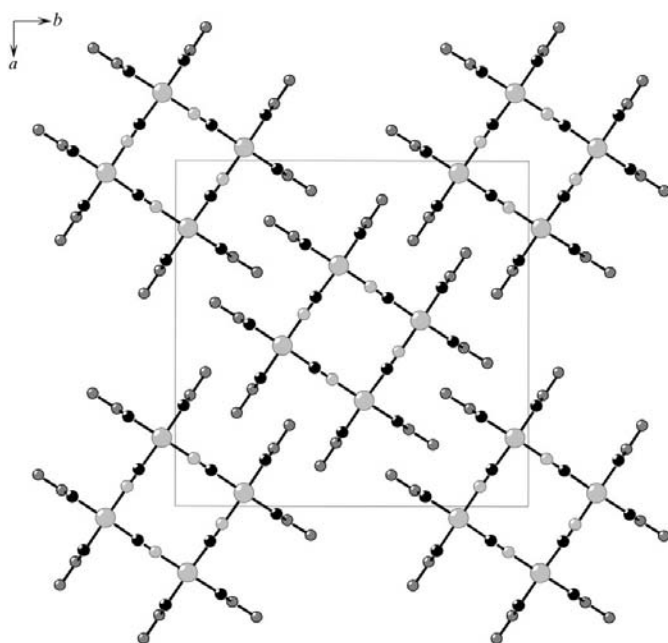


Figure 3
The arrangement of complex molecules in the crystal structure.

*Refinement*Refinement on F^2 $R_p = 0.106$ $R_{wp} = 0.146$ $R_{exp} = 0.105$ $R_B = 0.053$ $S = 1.39$

Excluded region(s): none

Profile function: Pearson VII

45 parameters

H-atom parameters constrained

 $(\Delta/\sigma)_{max} = 0.05$

Preferred orientation correction:

March–Dollase correction

The sample was prepared by top-loading a standard quartz sample holder. Corundum was used as the external standard. X-ray powder diffraction data are deposited in the JCPDS–ICDD PDF2 database (ICDD, 2003). Cell parameters were obtained from d -spaces by indexing and refining using programs described by Visser (1969) and Kirik *et al.* (1979). The space group was determined from an analysis of systematic absences. The intensities of 85 reflections were estimated from the powder pattern by means of the full-profile fitting procedure (Le Bail *et al.*, 1988) and used in the Patterson synthesis. The Pd atoms were located directly from the Patterson map. The positions of light atoms (O, N and C) were obtained from a difference Fourier synthesis. H atoms were not located, but they were included in the refined structure models and rigidly connected to their C atoms, keeping in mind the special positions of C atoms. The final refinement was carried out by the Rietveld (1969) method.

Data collection: DRON-4 data collection software; cell refinement: *POWDER* (Kirik *et al.*, 1979); program(s) used to solve structure: modified version of *DBWM* (Wiles & Young, 1981); program(s) used

to refine structure: modified version of *DBWM*; molecular graphics: *XP* (Siemens, 1989).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1216). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Chiesa, A., Ugo, R., Sironi, A. & Yatsimirski, A. (1990). *Chem. Commun.* pp. 350–351.
- ICDD (2003). Powder Diffraction File. PDF-2. International Centre for Diffraction Data, Newtown Square, PA 19073-3273, USA.
- Kirik, S. D., Borisov, S. V. & Fedorov, V. E. (1979). *Zh. Strukt. Khim.* **20**, 359–364. (In Russian.)
- Le Bail, A., Duroy, H. & Fourquet, J. L. (1988). *Mater. Res. Bull.* **23**, 447–452.
- Meester, P. de & Skapski, A. C. (1973). *J. Chem. Soc. Dalton Trans.* pp. 1194–1198.
- Podberezskaya, N. V., Bakakin, V. V., Kuznetsova, N. I., Danilyuk, A. F. & Likholobov, V. A. (1981). *Dokl. Akad. Nauk SSSR (Proc. Natl Acad. Sci. USSR)*, **256**, 870–874.
- Rietveld, H. M. (1969). *J. Appl. Cryst.* **2**, 65–71.
- Siemens (1989). *XP*. Version 4.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Visser, J. W. (1969). *J. Appl. Cryst.* **2**, 89–95.
- Wiles, D. B. & Young, R. A. (1981). *J. Appl. Cryst.* **14**, 149–151.