

**[Pd(CH₃COO)₂]_n from X-ray powder
diffraction data**Sergei D. Kirik,* Ruslan F. Mulagaleev and Alexander I.
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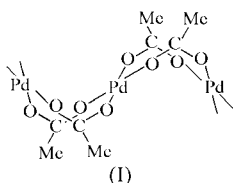
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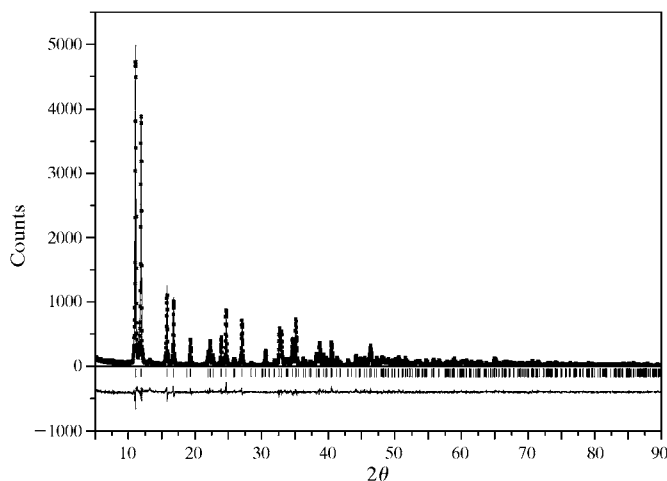
The water-insoluble title compound, *catena*-poly[palladium(II)-di- μ -acetato- $\kappa^4 O:O'$], [Pd(C₂H₃O₂)₂]_n, was obtained from a nitratopalladium solution and acetic acid as a pale-pink powder. *Ab initio* crystal structure determination was carried out using X-ray powder diffraction techniques. Patterson and Fourier syntheses were used for atom location and the Rietveld technique was applied for the final structure refinement. The structure consists of palladium acetate complexes connected into polymeric chains running along *b*, in which two Pd atoms are bridged by two acetate groups that are in a *cis* configuration with respect to one another. The unique Pd atom lies on a site with *2/m* symmetry and the acetate moieties have imposed *m* symmetry; these are joined into infinite chains running along the *b* direction. The shortest Pd...Pd distance in the row is 2.9192 (1) Å. The planes of adjacent palladium complexes are inclined towards each other, the angle between the planes being approximately 30°.

Comment

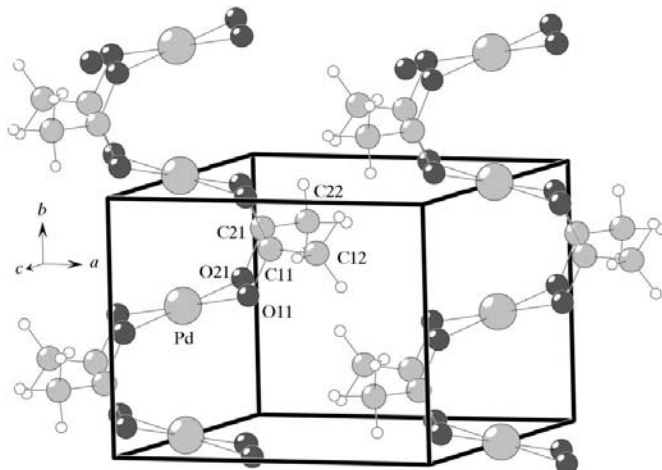
Palladium acetate complexes have been extensively investigated because they have some useful properties, especially for catalyst preparation (Stephenson *et al.*, 1965; Romm *et al.*, 1992; Pandey & Henry, 1974). Crystal data have been reported for palladium acetate and some adducts, for example, [Pd₃(CH₃COO)₆] (Lyalina *et al.*, 1993), [Pd₃(CH₃COO)₆]-0.5H₂O (Scapski & Smart, 1970), [Pd₃(CH₃COO)₆]-0.5CH₂Cl₂ (Cotton & Han, 1985) and [Pd₃(CH₃COO)₆]-0.5C₆H₆ (Cotton & Han, 1983). In all of these compounds, palladium forms a triangular cluster, with two acetate groups in bridging positions on each side of the triangle. In the present work, a



polymeric form of palladium acetate, (I), was investigated. We did not find any mention of this form in the literature,

**Figure 1**

Observed (dots), calculated (superimposed solid line) and difference profiles after Rietveld refinement. The reflection positions are marked by ticks.

**Figure 2**

The crystal structure of polymeric [Pd(CH₃COO)₂]_n.

including the Cambridge Structural Database (Allen, 2002). However, it seems to be the most easily obtained form, although it has not yet been characterized because of the absence of a single-crystal sample. We have obtained the structure solution using X-ray powder diffraction techniques.

The main structural units of (I) are the [Pd(CH₃COO)₂] complexes. Pd atoms occupy the special position (0, $\frac{1}{2}$, $\frac{1}{2}$) and form rows along *b*, with a Pd...Pd distance of 2.9192 (1) Å; this distance is less than those reported for the triangular clusters, in which the Pd...Pd distances range from 3.098 to 3.196 Å (Lyalina *et al.*, 1993). All acetate groups in (I) are of the bridging type. Each Pd...Pd contact is formed by two acetate groups in *cis* positions with respect to one another. In spite of the bridging character of the acetate groups, the palladium coordination is square planar, since the Pd atom is located on an inversion centre; by contrast, [Pd₃(CH₃COO)₆] (Lyalina *et al.*, 1993) is only approximately planar. Because of the tension in the chemical bonding, the coordination planes

of neighboring Pd atoms are not parallel, being inclined towards one another with an angle between the planes of approximately 30°. In contrast, the angle between the [PdO₄] planes in the trimer cluster is about 60° (Lyalina *et al.*, 1993). As noted above, the larger angle in the trimer is complemented by a longer Pd··Pd distance. The differences in these two geometric features can be attributed to the higher thermodynamic stability of the polymeric form of palladium acetate. A similar chain arrangement was found previously in some acetate-containing palladium compounds with additional donor ligands. In particular, [Pd₃(CH₃COO)₄]₂{[CH₂-CH(CH₃)₂]₂}(C₈H₁₀O₂) (Fuchita *et al.*, 1996), [Pd₃(CH₃COO)₄]₂{[SbPh₃]₂Ph₂}] (Barton *et al.*, 1990) and [Pd₃(CH₃COO)₄](C₁₃-H₂₁O₄)₂ (Ukhin *et al.*, 1981) demonstrate planar palladium coordination with acetate groups in *cis* positions; the Pd··Pd distances are 2.98 (2), 3.01 (8) and 2.9 (2) Å, respectively.

In summary, palladium acetate can form at least two isomers, *viz.* trimeric and polymeric. The Pd atoms in both forms have square-planar coordination. The higher thermodynamic stability of the polymeric form is related to the mutual orientation of the [PdO₄] planes of adjacent complexes, which provides stronger Pd··Pd interactions.

Experimental

The synthesis of (I) was carried out by adding acetic acid to a solution of palladium dissolved in nitric acid. The solution was heated at 393 K. The precipitated pale-pink product was filtered off, washed with water and dried in air.

Crystal data

[Pd(C ₂ H ₃ O ₂) ₂]	Cu Kα radiation
<i>M_r</i> = 224.51	λ = 1.5418 Å
Monoclinic, <i>P</i> 2 ₁ / <i>m</i>	μ = 21.21 mm ⁻¹
<i>a</i> = 7.4467 (1) Å	<i>T</i> = 293 K
<i>b</i> = 5.8383 (1) Å	Pale yellow
<i>c</i> = 7.9900 (1) Å	Specimen shape: circular flat plate
β = 93.46 (1)°	20.0 × 20.0 × 0.5 mm
<i>V</i> = 346.74 (1) Å ³	Specimen prepared at 101 kPa
<i>Z</i> = 2	Specimen prepared at 293 K
<i>D_x</i> = 2.15 Mg m ⁻³	Particle morphology: thin powder

Data collection

DRON-4 powder diffractometer	321 independent reflections
θ/2θ scans	θ _{max} = 45°
Specimen mounting: packed powder pellet	<i>h</i> = 0 → 6
Specimen mounted in reflection mode	<i>k</i> = 0 → 5
321 measured reflections	<i>l</i> = -6 → 7
	2θ _{min} = 5.0, 2θ _{max} = 90.0°
	Increment in 2θ = 0.02°

Refinement

Refinement on <i>F</i> ²	Profile function: Pearson VII
<i>R_p</i> = 0.108	41 parameters
<i>R_{wp}</i> = 0.152	H-atom parameters constrained
<i>R_{exp}</i> = 0.117	(Δ/σ) _{max} = 0.1
<i>R_B</i> = 0.047	Preferred orientation correction:
<i>S</i> = 1.38	March–Dollase correction

The sample was prepared by top-loading the standard quartz sample holder and removing the excess of the well grained substance. 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 by indexing and

Table 1

Selected geometric parameters (Å, °).

Pd—O11	2.050 (8)	C11—C12	1.44 (3)
Pd—O21	2.017 (8)	C21—C22	1.41 (3)
O11—C11	1.31 (2)	Pd—Pd ⁱ	2.9192 (1)
O21—C21	1.28 (2)		
O21—Pd—O11	89.9 (3)	O21—C21—O21 ⁱⁱ	111.5 (4)
O11—Pd—O21	90.1 (3)	Pd ⁱⁱⁱ —Pd—O11	80.3 (3)
O11 ⁱⁱ —C11—O11	116.6 (7)	Pd ⁱⁱⁱ —Pd—O21	78.5 (2)

Symmetry codes: (i) $-x, y - \frac{1}{2}, 1 - z$; (ii) $x, \frac{3}{2} - y, z$; (iii) $-x, \frac{1}{2} + y, 1 - z$.

refining using programs described by Visser (1969) and Kirik *et al.* (1979). The space group was determined from the analysis of systematic absences. The intensities of 120 reflections were estimated from the powder pattern by means of a full-profile fitting procedure (Le Bail *et al.*, 1988) and used in Patterson synthesis. Pd atoms were located directly from the Patterson map, and the positions of O and C atoms were defined from difference Fourier syntheses. H atoms were not located but were included in the refined structure model, rigidly connected to their C atoms and taking into account special positions of the 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: SK1735). Services for accessing these data are described at the back of the journal.

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