

## New Palladium Carbonyl Clusters: X-Ray Crystal Structure of [Pd<sub>4</sub>(CO)<sub>4</sub>(OAc)<sub>4</sub>](AcOH)<sub>2</sub>†

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**Summary** According to X-ray study the complex of stoichiometry AcO·Pd·CO, prepared from Pd(OAc)<sub>2</sub> and CO, consists of tetranuclear clusters with two short and two long Pd-Pd bonds.

BINARY palladium carbonyls are rather unstable,<sup>1</sup> Pd<sup>0</sup> carbonyls with phosphine ligands<sup>2</sup> and Pd<sup>I</sup> or Pd<sup>II</sup> carbonyl halides<sup>3</sup> being relatively more stable.

Our interest in the reactivity of palladium carboxylates towards CO prompted us to investigate carboxylate-substituted palladium carbonyl complexes. When Pd(CO<sub>2</sub>R)<sub>2</sub> (R = Me, CD<sub>3</sub>, Et, or Ph) dissolved in various solvents is brought in contact with CO, the reduction of Pd<sup>II</sup> to the metal usually occurs. However, in carboxylic acids or carboxylic acids-benzene mixtures as solvents, we have

succeeded in preparing relatively stable complexes of stoichiometry RCO<sub>2</sub>·Pd·CO·*n*RCO<sub>2</sub>H where *n* = 0 or 0.5.

Thus stirring Pd(OAc)<sub>2</sub> (4.4 mmol) in glacial acetic acid (100 ml) under CO for 1.5 h at 50 °C affords AcO·Pd·CO·0.5 AcOH (I) as a yellow, crystalline precipitate (80%). Single crystals of (I) were obtained directly from the reaction mixture by carrying out the reaction using dry air-CO (1:1) mixture instead of CO and slightly reduced initial concentration of Pd(OAc)<sub>2</sub>. After allowing the reaction mixture to stand for 3 h at 50 °C without stirring, the temperature was lowered at the rate of 2.5 °C h<sup>-1</sup> and the solution was allowed to stand at 20 °C for 3-4 days. The composition‡ and i.r. spectrum of the light-brown crystals (0.3-0.5 mm in dimension) obtained were identical to those of the fine-crystalline compound (I). Both fine and large crystals of

† No reprints available.

‡ All new complexes gave satisfactory elemental analyses.

(I) lose 0.5 mol of AcOH per Pd atom when kept *in vacuo* over KOH at 20 °C for about 10 days affording AcO·Pd·CO (II) as a yellow powder.

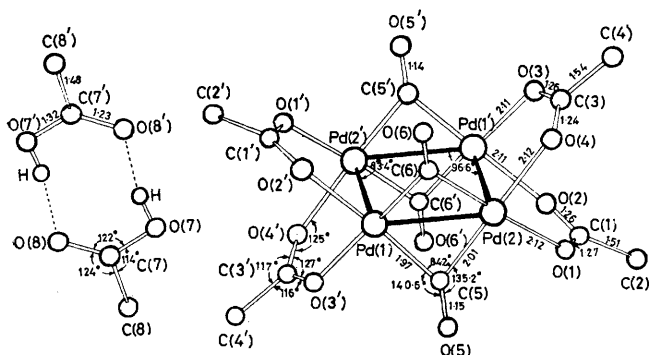


FIGURE. The structure of  $[\text{Pd}_4(\text{CO})_4(\text{OAc})_4] \cdot (\text{AcOH})_2$ .

The i.r. spectra of (I) and (II) show two strong absorption bands in the C–O stretching region at 1934 and 1975  $\text{cm}^{-1}$  for (I) and at 1940 and 1975  $\text{cm}^{-1}$  for (II). The  $\nu(\text{CO})$  bands for the deuterio-analogue of (I) appear at 1931 and 1965  $\text{cm}^{-1}$ . The i.r. spectra of  $\text{EtCO}_2\text{Pd}\cdot\text{CO}$  and  $\text{PhCO}_2\text{Pd}\cdot\text{CO}\cdot 0.5 \text{ PhCO}_2\text{H}$ , prepared by a similar method, exhibit carbonyl vibrations at 1935 and 1968, and 1958 and 1980  $\text{cm}^{-1}$ , respectively. The assignment of the frequencies for (I) [ $\nu(\text{CH})$ , 2994, 2945, and 2920;  $\nu(\text{CO}_2)$ , 1555 and 1518;  $\delta_{\text{as}}(\text{Me})$ , 1420;  $\delta_{\text{s}}(\text{Me})$ , 1350;  $\delta_{\text{s}}(\text{HCC})$ , 1045;  $\delta_{\text{as}}(\text{HCC})$ , 1028;  $\nu(\text{CC})$ , 939;  $\delta(\text{OCO})$ , 665;  $\gamma(\text{Me})$ , 620;  $\nu_{\text{as}}(\text{PdO})$ , 305 and 301; and  $\nu_{\text{s}}(\text{PdO})$ , 281  $\text{cm}^{-1}$ ] was made by a comparison with the i.r. spectrum of its deuterio-analogue.

The complexes (I) and (II) are quite stable in dry air at room temperature but rapidly decompose on contact with  $\text{H}_2\text{O}$  or alcohols resulting in Pd, CO, and  $\text{CO}_2$ ; in case of alcohols the reaction also produces dialkyl carbonates. A solution of  $\text{AcONa}$  in AcOH decomposes (I) into Pd, CO,  $\text{CO}_2$ , and acetic anhydride at 90 °C. The structure of (I) has been established by X-ray crystallography.

*Crystal data:*  $\text{C}_{16}\text{H}_{20}\text{O}_{16}\text{Pd}_4$ ,  $M = 893.8$ , triclinic,  $a = 7.597(3)$ ,  $b = 9.927(4)$ ,  $c = 10.066(4)$  Å,  $\alpha = 62.43(3)$ ,  $\beta = 69.89(3)$ ,  $\gamma = 74.42(3)^\circ$ ,  $Z = 2$ , space group  $P\bar{1}$ . Single-crystal X-ray diffraction data were collected with a Syntex P2<sub>1</sub> four-circle automatic diffractometer at  $-120$  °C [ $\lambda(\text{Mo-K}\alpha)$ , graphite monochromator,  $\theta$ - $2\theta$  scan,  $2\theta_{\text{max}} = 58^\circ$ ]. 2596 reflections were collected with  $I_{\text{obs}} > 2\sigma(I_{\text{obs}})$ . The structure was solved using the heavy-atom method and refined by full-matrix anisotropic least-squares to  $R = 0.043$ . The structure of the molecule is shown in the Figure. §

§ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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The H-atom of the  $\text{CO}_2\text{H}$  group of AcOH of crystallization was located in the difference synthesis as well as in the 6–7 diffuse maxima associated with each of C(2), C(4), and C(8) atoms revealing a rotational disorder of the Me groups. Standard deviations for the Pd–Pd, Pd–O, C–O, and C–C bond lengths are 0.001, 0.007, 0.012, and 0.015 Å, respectively.

Crystals of (I) consist of tetranuclear clusters  $\text{Pd}_4(\text{CO})_4(\text{OAc})_4$  and hydrogen-bonded dimeric molecules of AcOH of crystallization which occupy the symmetry centres  $(\frac{1}{2}, \frac{1}{2}, 0)$  and  $(\frac{1}{2}, 0, \frac{1}{2})$ , respectively. The  $\text{Pd}_4$  framework of the cluster is a parallelogram, its angles differing markedly from perpendicular (Figure). Atoms Pd(1), Pd(2') and Pd(1'), Pd(2) are connected by acetate bridges, Pd(1'), Pd(2') and Pd(1), Pd(2) are connected by CO bridges. The bridges of both types are symmetrical within error limits.

The Pd(1)–Pd(2) bond distance [2.663(1) Å] lies well within the range reported for Pd–Pd bonds (2.53–2.70 Å) in Pd<sup>I</sup> complexes.<sup>4</sup> The Pd(1)–Pd(2') distance (2.909 Å) is longer than the Pd–Pd bond length (2.751 Å) in the metal<sup>5</sup> but is noticeably shorter than twice the covalent radius of Pd (2.98 Å<sup>6</sup>). A similar Pd–Pd distance (2.94 Å) was found in  $[\pi\text{-C}_3\text{H}_5]_2\text{Pd}_2(\mu\text{-OAc})_2$ <sup>7</sup> where  $[\text{C}_3\text{H}_5\text{Pd}]^+$  fragments are connected by acetate-anion bridges. Thus complex (I) consists of  $[\text{Pd}_2(\text{CO})_2]^{2+}$  fragments connected in pairs with carboxylate bridges.  $\text{Pd}_2(\text{OAc})$  fragments are planar and form dihedral angle of 32° for Pd(1')O(3)O(4)C(3)C(4)Pd(2) and  $-41^\circ$  for Pd(1')O(1)O(2)C(1)C(2)Pd(2) with the  $\text{Pd}_4$  plane so that the dihedral angle between the planar fragments Pd(1)C(5)O(5)Pd(2) and Pd(1)C(6)O(6)Pd(2) (including carbonyl bridges) is 159°, both fragments being equally inclined to the  $\text{Pd}_4$  plane. Molecules of AcOH of crystallization form centrosymmetrical dimers owing to the strong hydrogen bonds O(7)–H...O(8') with distances O(7)...O(8'), 2.64; O(7)–H, 1.0(1); and H...O(8'), 1.7(1) Å, and the angle O(7)–H...O(8'), 156(6)°. Formation of such dimers is typical of carboxylic acid crystals.<sup>8</sup>

The band due to O–H stretching vibrations is likely to be weak because of hydrogen-bonding, and is presumably masked by the group of weak C–H bands in the region 2900  $\text{cm}^{-1}$ .

The results of X-ray study show that the four i.r. bands which disappear during the transformation of (I) into (II) [ $\nu(\text{C}=\text{O})$ , 1710;  $\delta(\text{Me})$ , 1018;  $\gamma(\text{OH})$ , 934 and  $\delta(\text{CCO})$ , 497  $\text{cm}^{-1}$ ] derive from the dimer  $(\text{AcOH})_2$ . All other bands in the 40–4000  $\text{cm}^{-1}$  region are comparable for the complexes (I) and (II). Therefore X-ray and i.r. data lead to the conclusion that the cluster units of (I) and (II) are nearly identical, the sole difference between these compounds being the presence of  $(\text{AcOH})_2$  molecules in (I).

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