

Crystal Structure of the Organometallic Polymer $[\text{Pd}\{\text{CH}_2\text{C}(\text{O})\text{Me}\}\text{Cl}]_n$, Determined by X-ray Powder Diffraction Methods

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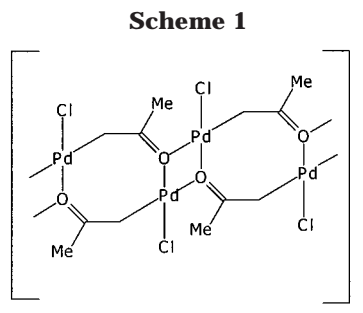
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Summary: The crystal and molecular structure of the recently synthesized organometallic $[\text{Pd}\{\text{CH}_2\text{C}(\text{O})\text{Me}\}\text{Cl}]_n$ polymer (*Organometallics* 2001, 20, 2767) has been unravelled by *ab initio* powder diffraction methods and shown to possess a different stereochemistry from the model proposed on the basis of IR spectral data.

Transition metal enolates (also called ketonyls or 2-oxoalkyls) have been proposed as intermediates in numerous organic transformations, and some of them have been isolated and characterized.¹ In a recent issue of *Organometallics*, the $[\text{Pd}\{\text{CH}_2\text{C}(\text{O})\text{Me}\}\text{Cl}]_n$ polymer, **1**, "a key product for the synthesis of acetyl/palladium-(II) complexes", was reported.² In that paper, several acetyl derivatives obtained from **1** by reaction with different Lewis bases (I^- , tmeda, phen, bipy, PPh_3 , dmsO, tht, etc.) were also described, mostly characterized by IR, NMR, and, for a few, standard single-crystal X-ray diffraction methods. In addition, also the mercury-(II) precursor, $[\text{Hg}\{\text{CH}_2\text{C}(\text{O})\text{Me}\}_2]$, was structurally characterized by this technique.²

However, owing to their poor solubility in weak donor solvents and to depolymerization reactions occurring in acetonitrile, for **1** and its $[\text{Pd}\{\text{CH}_2\text{C}(\text{O})\text{Me}\}\text{I}]_n$ congener, **2**, only analytical and IR data were available, which led to the structural model presented in Scheme 1, which contains terminal Cl^- ligands and $\mu_3(\kappa^1\text{-C}, \kappa^2\text{-O})$ acetyl fragments.

This kind of coordination of the acetyl ligand is unprecedented and attracted our attention. Since we have recently demonstrated that the structures of simple organometallic polymers,³ even in the absence of single crystals, can be successfully determined by *ab*



initio X-ray powder diffraction (XRPD) methods,⁴ we decided to investigate the structural chemistry of these species, aiming to confirm, or dismiss, the model presented in ref 2 on the basis of a thorough analysis of the low-frequency IR absorption bands. The notion that insoluble species of this kind are necessarily polymeric has been recently dismissed by the successful, complete XRPD characterization of the polycrystalline cyclic oligomers of general formula $[\text{EM}(\text{CO})_4]_n$ ($n = 6$, $\text{E} = \text{H}$, $\text{M} = \text{Re}^{3b}$; $n = 2$, $\text{E} = \text{Hg}$, $\text{M} = \text{Ru}^5$). However, our *ab initio* XRPD study (see Experimental Section) confirmed the polymeric nature of **1** and led to the structural model described in the following.

Crystals of **1** contain infinite chains of the one-dimensional $[\text{Pd}\{\text{CH}_2\text{C}(\text{O})\text{Me}\}\text{Cl}]_n$ polymer, running parallel to **b** (and generated by the glide plane normal to **a**), with the metal atoms following each other at 3.85-(1) Å distances ($\approx b/2$). The chloride ion and the acetyl fragment bridge $\text{Pd}\cdots\text{Pd}$ vectors in the μ_2^- and $\mu_2(\kappa^1\text{-C}, \kappa^1\text{-O})$ coordination modes, respectively, leading to square-planar *trans*- PdCl_2CO chromophores,⁶ whose best planes (along the chain) are not parallel, but nearly 40° off. A drawing of a portion of the polymer is shown in Figure 1.

The structural model derived for **1** does not match the proposed connectivity pattern shown in Scheme 1; rather, it is better represented by that drawn in Scheme 2, where both chloride and acetyl act as "conventional" bridging fragments ($\text{Pd}-\text{Cl}$ 2.36(3) and 2.39(3)

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(1) Ruiz, J.; Rodríguez, V.; Cutillas, N.; Pardo, M.; Pérez, J.; López, G.; Chaloner, P.; Hitchcock, P. B. *Organometallics* 2001, 20, 1973, and references therein. (b) Gallo, E.; Ragaini, F.; Cenini, S.; Demartin, F. *J. Organomet. Chem.* 1999, 586, 190. (c) Veya, P.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* 1993, 12, 4899.

(2) Vicente, J.; Arcas, A.; Fernández-Hernández, J. M.; Bautista, D. *Organometallics* 2001, 20, 2767.

(3) $[\text{Ru}(\text{CO})_4]_n$: Masciocchi, N.; Moret, M.; Cairati, P.; Ragaini, F.; Sironi, A. *J. Chem. Soc., Dalton Trans.* 1993, 471. (b) $[\text{HRe}(\text{CO})_4]_n$: Masciocchi, N.; D'Alfonso, G.; Garavaglia, L.; Sironi, A. *Angew. Chem., Int. Ed.* 2000, 39, 4477.

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(5) Masciocchi, N.; Cairati, P.; Ragaini, F.; Sironi, A. *Organometallics* 1993, 12, 4499.

(6) XRPD cannot exclude the presence of PdCl_2O_2 or PdCl_2C_2 chromophores, which are however unlikely on chemical grounds.

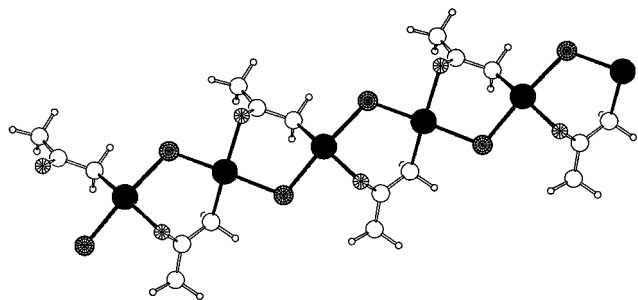
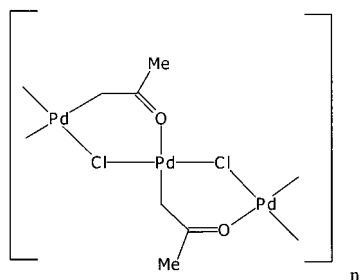


Figure 1. Schematic drawing of a fragment of the $[\text{Pd}\{\text{CH}_2\text{C}(\text{O})\text{Me}\}\text{Cl}]_n$ polymer; Pd atoms in black. H atoms (small empty circles) in idealized positions. Relevant bond distances and angles: Pd...Pd 3.85(1) Å, Pd...Pd...Pd 180°; Pd-Cl 2.36(3) and 2.39(3) Å; Pd-Cl-Pd 108.9°; Pd-O 2.40(5), Pd-C2 2.16(6) Å; *trans*-Cl-Pd-Cl 161.4(4)°, *trans*-O-Pd-C2 161(2)°.

Scheme 2



Å; Pd-Cl-Pd 108.2(5)°. Additional bond lengths and angles can be found in the caption of Figure 1.

Such a structural model, unexpected on the basis of the analysis of the spectroscopic data available in ref 2, should not be surprising, since its structural features were already present in $[\text{Pd}_2\{\text{CH}_2\text{C}(\text{O})\text{Me}\}_2\text{Cl}_2(\text{dmsO})_2]$, obtained by reacting **1** with excess dmsO. Comparison of the few relevant bond distances and angles demonstrates the strict similarity of these fragments (Pd-Cl 2.35 and 2.42 Å, Pd-Cl-Pd 110°, and Pd...Pd 3.90 Å in $[\text{Pd}_2\{\text{CH}_2\text{C}(\text{O})\text{Me}\}_2\text{Cl}_2(\text{dmsO})_2]$).

The question is now why a different structure was proposed based on the IR data. The key point in assigning the structure in Scheme 1 was the observation of only *one* absorption (at 354 cm^{-1}) in the 200–400 cm^{-1} region of the IR spectrum of **1**. This absorption was attributed to the Pd-Cl stretching based on the fact that it is absent in the spectrum of the corresponding iodine compound. Under this assumption, such a frequency clearly indicates a terminal chloride group, thus leading in a straightforward way to the proposed structure. We have recorded the IR spectrum in Nujol of **1** and also observed the absorption at 354 cm^{-1} as the only clearly emerging feature when a standard sample amount was employed. However, when a very concentrated sample was prepared (such that the 354 cm^{-1} absorption went out of scale), a second, weaker absorption emerged at 268 cm^{-1} (see Figure 2), which nicely falls in the spectral region where bridging chloride ligands absorb, as also shown by the data for other complexes reported in ref 2. Since this band is very weak and falls in a noisy part of the spectrum, it was probably not observed or neglected in the original work. To understand the origin of the 354 cm^{-1} absorption, we synthesized the $[\text{Pd}\{\text{CH}_2\text{C}(\text{O})\text{Me}\}\text{I}]_n$ analogue and re-

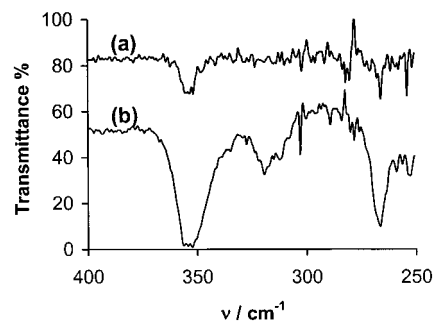


Figure 2. IR spectra (Nujol mull) of compound **1** in the 400–250 cm^{-1} region: (a) normal concentration, (b) very concentrated sample. The transmittance scale is common to both spectra.

corded XRPD patterns for a number of samples prepared following the published procedure. Unfortunately, only amorphous powders were obtained, thus hampering any further structural study.

At this stage, the exact attribution of the 354 cm^{-1} band cannot be given, although it must be connected to the acetyl moiety. The fact that it is not present in the spectrum of the palladium-iodide complex is surprising, but, since the structure of the latter is not known, it is possible that the two complexes are not isostructural. In any case, the results here reported indicate that spectroscopic data alone can be very misleading, and much caution should be used in employing them to attribute the structure of inorganic and organometallic species.⁷

This paper briefly demonstrates, once again, that if organometallic and coordination polymers can be obtained as polycrystalline samples, then they are optimal candidates for *ab initio* XRPD characterization, their molecular complexity being deeply buried within the crystal lattice and its symmetry operations. Obviously, the presence of heavy scatterers, such as transition metal atoms, greatly simplifies the solution of the phase problem, thus leaving the correct determination of the *true* unit cell the difficult step in the whole *ab initio* procedure. Interestingly, the location of the metal atoms alone, in the most critical cases, can afford significant information on the structural chemistry of the polymers, even in the absence of “well-resolved” Bragg peaks. Work can be anticipated in the direction of extracting such (otherwise inaccessible) information even from amorphous or poorly crystalline samples, such as the $[\text{Pd}\{\text{CH}_2\text{C}(\text{O})\text{Me}\}\text{I}]_n$ analogue or the still elusive β -phase of the $[\text{HRe}(\text{CO})_4]_n$ polymer.^{3b}

Experimental Section

Synthesis of the Complexes. $[\text{Pd}\{\text{CH}_2\text{C}(\text{O})\text{Me}\}\text{Cl}]_n$ (1**).** The complex was prepared as reported in the literature.² The initially obtained polymer, however, was poorly crystalline and showed wide peaks in the XRPD diffraction pattern, consistent with diffraction domains not larger than 250 Å. In an attempt to grow suitable single crystals, a CH_3CN /hexane suspension of the polymer was left to stand for two months under a dinitrogen atmosphere. After this time, no single crystal was obtained, but, contrary to the original sample, the solid had become markedly insoluble in CH_3CN . Since the IR spectrum of the sample was unchanged, the lower solubility suggested

(7) Masciocchi, N.; Moret, M.; Sironi, A.; Ardizzoia, G. A.; Cenini, S.; La Monica, G. *J. Chem. Soc., Chem. Commun.* **1995**, 1955.

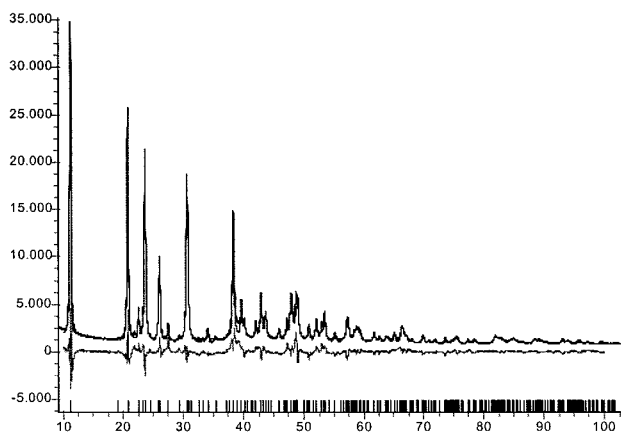


Figure 3. Rietveld refinement plot for $[\text{Pd}\{\text{CH}_2\text{C}(\text{O})\text{Me}\}\text{Cl}]_n$, with peak markers and difference plot at the bottom. Horizontal scale: 2θ , deg; vertical scale: I, cts.

that the polymer chains had grown and/or the average domain size had increased during that time. In agreement with this expectation, the new sample showed much sharper peaks in the XRPD pattern, which was then used for structure solution and refinement (see below), leading to a structural model showing an excellent matching between the experimental and calculated diffraction patterns.

$[\text{Pd}\{\text{CH}_2\text{C}(\text{O})\text{Me}\}\text{I}]_n$. Initial attempts to obtain the iodide complex by exchange with NaI from **1** were frustrated by the formation of large amounts of a dark insoluble material. Since NaI is hygroscopic and easily oxidizable, samples held in the air for long times are contaminated by I_2 and NaOH. Simply removing I_2 by placing contaminated NaI in vacuo until it became colorless did not solve the problem. To have a pure sample of NaI, the solid was first dissolved in the minimal amount of water, then treated with excess concentrated HI, and the solution evaporated over a Bunsen. The resulting solid was further heated until most of the present I_2 had sublimed, then it was placed under vacuum at room temperature for several hours until it was completely colorless. The purified NaI was stored under N_2 before use and quickly weighed in the air. By employing the so obtained salt, the reported synthesis could be reproduced, although a small amount of a dark solid, rather than a white precipitate (as reported), was anyway obtained, which was eliminated by filtration over Celite. The IR spectrum of the obtained compound matched that reported in ref 2.

Crystal data: $\text{C}_3\text{H}_5\text{ClOPd}$, fw 199.03, orthorhombic $Ibca$, $a = 15.790(1)$ Å, $b = 7.6928(8)$ Å, $c = 8.5851(9)$ Å, $V = 1043.31(2)$ Å³, $Z = 8$, $\rho_{\text{calc}} = 2.534$ g cm⁻³. Data collection was on a conventional vertical-scan Philips powder diffractometer (graphite-monochromatized $\text{Cu K}\alpha_{1,2}$ radiation, $\lambda_{\text{av}} = 1.5418$ Å, θ - 2θ scan, $\Delta 2\theta$ 0.02° step⁻¹, $t = 10$ s); indexing was by TREOR-90⁸ [$M(11) = 15$; $F(11) = 37$ (0.017, 18)⁹]; structure solution and refinement were by simulated annealing and the Rietveld method, respectively, using TOPAS-R.¹⁰ $\text{C}\cdots\text{C}$ anti-bumping restraints and a rigid group for the acetyl moiety were employed. Final agreement factors were R_p , R_{wp} , and $R_{\text{Bragg}} = 0.128, 0.096, 0.089$, respectively, for 4500 data points collected in the $10^\circ < 2\theta < 100^\circ$ range. Final Rietveld refinement plot is shown in Figure 3. The satisfactory, but still imperfect match between observed and calculated data is mostly attributed to anisotropic peak shapes (tentatively accounted for by a spherical harmonic model) and high angle tails, probably due to the disorder described below and,

(8) Werner, P. E.; Eriksson, L.; Westdahl, M. *J. Appl. Crystallogr.* **1985**, *18*, 367.

(9) After correction for space group reflection conditions.

(10) Kern, A.; Coelho, A. *TOPAS-R*; Bruker AXS GmbH: Karlsruhe, Germany, 2001.

Table 1. Fractional Atomic Coordinates for Non-H Atoms (esd's in parentheses^a)

atom	x/a	y/b	z/c	occ
Pd	0.75	0.63090(103)	0.50	1
Cl	0.33564(79)	0.88318(477)	0.03816(135)	0.5 ^b
O	0.12174(302)	0.51816(547)	0.43086(569)	0.5
C1	0.10864(381)	0.57456(1106)	0.56653(688)	0.5
C2	0.16116(373)	0.71240(762)	0.62904(613)	0.5
C3	0.04105(263)	0.50164(663)	0.66014(427)	0.5

^a The acetyl ligand has been treated as a rigorously rigid ligand. The coordinates have been taken from the final "restrained" refinement, while the *rather large* esd's have been obtained by the independent atom model upon freeing all restraints and computing an *additional* least-squares refinement cycle with zero coordinate shifts. ^b See text.

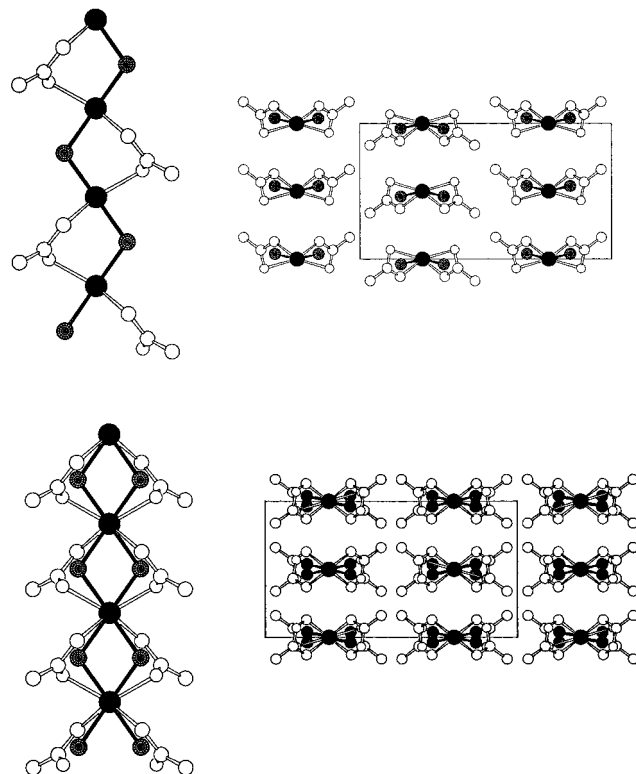


Figure 4. Fragment of the $[\text{Pd}\{\text{CH}_2\text{C}(\text{O})\text{Me}\}\text{Cl}]_n$ polymer (left) and its crystalline packing (viewed down $[010]$, right) for an *ideally* ordered phase in $Pbca$ (top) and the *real* polymer (disordered by a crystallographic 2-fold axis) in $Ibca$ (bottom).

consequently, to the discotic shape of several reciprocal lattice nodes. Table 1 contains the final refined fractional coordinates for non-H atoms.

Crystallochemical Analysis. **1** crystallizes in the $Ibca$ space group, with a rectangular packing of chains (if viewed down the chain axis, **b**). The space group symmetry implies the presence of chains disordered by a 2-fold axis parallel to **b** (see Figure 4, left). However, the ligand organization along the chain is *ordered* since the presence of *cis*-coordinated Pd atoms can be easily excluded on steric grounds. An ordered crystal structure can be drawn upon using the $Pbca$ ¹¹ symmetry operations, which maintains exactly the same packing features of $Ibca$ (see Figure 4, top), but removes the short, implausible, intermolecular C–C contacts of the latter. It is the loss of correlation between neighboring (ordered) chains that eventually leads to the *apparent* "molecular" disorder, thanks to the weakness of the intermolecular (van der Waals) contacts.

(11) A proper subgroup of $Ibca$; no reflections violating the body-centered lattice were, however, observed.

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