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Normal Phase Liquid Chromatographic Separation and Structure Determination of Palladium-2,2,7-trimethyloctane-3,5-dionate

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Abstract

The two geometrical isomers of Pd(tod)$_2$ have been separated by normal phase liquid chromatography. The major (*cis*) isomer has been characterized by X-ray crystallography. $C_{22}H_{38}PdO_4$, monoclinic, space group $P2_1/n$, $a = 11.585(4)$, $b = 10.567(5)$, $c = 20.262(5)$ Å, $\beta = 90.41(3)°$, $Z = 4$, $D_c = 1.27$ g cm^{-1}, $R = 0.056$, $R_w = 0.079$ for 2152 'observed' reflections.

Introduction

High pressure liquid chromatographic separation (HPLC) of metal chelates is an established analytical technique [1]. Metal chelates with unsymmetrical ligands can form geometrical isomers [2, 3]. For example, trifluoroacetylacetone (tfa) or 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-octane-3,5-dione (fod) are β-diketones with large differences in the substituent groups. In contrast, 2,2,7-trimethyl-octane-3,5-dione (tod) has only the very similar t-butyl and s-butyl substituents. The meridian and facial isomers of trivalent Cr(tod)$_3$ have been separated with normal and reversed phase HPLC [4]. Gas chromatography (GC) of Cr(tod)$_3$ yields only one peak [4] while the isomers of Cr(tfa)$_3$ and Cr(fod)$_3$ are thermally stable and can be separated [4, 5].

In an extension of our previous work, we have attempted to separate the geometrical isomers of the bivalent Pd(tod)$_2$. Pd(tod)$_2$ shows sufficient thermal stability to be eluted from a short capillary GC column after on column injection [6], but like Cr(tod)$_3$, yields only one peak [4].

It has been reported that the proton NMR spectrum of Pd(tod)$_2$ exhibits distinctive resonances for both geometrical isomers, with one of the isomers predominating [7] and we have confirmed this. We have now successfully separated the two isomers by HPLC and shown that the major component is the *cis* isomer by X-ray crystallography. We report our results herein.

Experimental

Pd(tod)$_2$ was synthesized by procedures reported by Wenzel *et al.* [8] and by Jahn and Wenclawiak [9]. For LC separations a few crystals were dissolved in hexane or dichloromethane or chloroform. The HPLC system was comprised of a Beckmann 110 B pump, a Rheodyne 7125 injection valve with 20 μl sample loop, an Altex Ultrasphere-Si, 5 μm, 250 × 2 mm diameter column, a Knauer fixed wavelength detector (254 nm) with 8 μl cuvette and a Shimadzu Chromatopac CR-3A recorder/integrator.

Crystals grown from evaporation of a dichloromethane solution were seen to be a mixture under the microscope. The major component formed yellow square or rectangular plates. One of these with dimensions 0.25 × 0.25 × 0.05 mm was chosen for X-ray examination. Crystal data: $C_{22}H_{38}PdO_4$, monoclinic, space group $P2_1/n$, $a = 11.585(4)$, $b = 10.567(5)$, $c = 20.262(5)$ Å, $\beta = 90.41(3)°$, $Z = 4$, $D_c = 1.27$ g cm^{-1}, Mo Kα ($\lambda = 0.71073$ Å), $T = 294$ K. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer to $2\theta_{max} = 52°$.

The structure was solved using Patterson and Fourier techniques and refined using full-matrix least-squares to $R = 0.056$. Atomic scattering factors

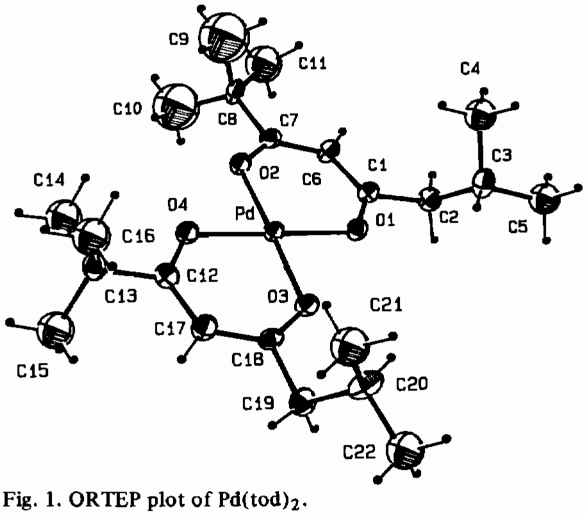

Fig. 1. ORTEP plot of Pd(tod)$_2$.

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were taken from standard sources [10, 11] and all calculations were carried out with SDP/VAX [12]. A summary of data collection, structure solution and refinement is given in Table I, final atomic parameters in Table II and selected bond lengths and angles are reported in the Table III. A perspective view of the molecule is shown in Fig. 1.

TABLE I. Experimental Details

A. Crystal data	
$C_{22}H_{38}PdO_4$	
Formula weight	472.95, $F(000) = 992$
Crystal dimensions	0.25 × 0.25 × 0.05 mm
Peak width at half-height	0.18°
Mo Kα radiation	$\lambda = 0.71073$ Å
Temperature	21 ± 1°
Monoclinic space group	$P2_1/n$
$a = 11.585(4)$ Å	
$b = 10.567(5)$ Å	
$c = 20.262(5)$ Å	
$\beta = 90.41(3)°$	
$V = 2480.3$ Å^3	
$Z = 4$ $\rho = 1.27$ g/cm^3	
$\mu = 7.6$ cm^{-1}	
B. Intensity measurements	
Instrument	Enraf-Nonius CAD4 diffractometer
Monochromator	graphite crystal, incident beam
Attenuator	Zr foil, factor 19.5
Take-off angle	2.8°
Detector aperture	2.0 to 2.1 mm horizontal 4.0 mm vertical
Crystal-detector distance	21 cm
Scan type	$\omega-2\theta$
Scan rate	1–7°/min (in omega)
Scan width (°)	$0.8 + 0.34 \tan \theta$
Maximum 2θ	52.0°
No. reflections measured	4117 total, 2901 unique
Corrections	Lorentz polarization linear decay (from 0.954 to 1.053 on I) reflection averaging (agreement on I = 2.9%) empirical absorption (from 0.68 to 0.99 on I)
C. Structure solution and refinement	
Solution	Patterson method
Hydrogen atoms	refined as riding atoms
Refinement	full-matrix least-squares
Minimization function	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
Least-squares weights	$4F_o^2/\sigma^2(F_o^2)$
Anomalous dispersion	all non-hydrogen atoms
Reflections included	2152 with $F_o^2 > 3.0\sigma(F_o^2)$
Parameters refined	194
Unweighted agreement factor	0.056
Weighted agreement factor	0.079
e.s.d. of obs. of unit weight	2.37
Convergence, largest shift	0.62σ
High peak in final difference map	1.11(11) e/A^3
Low peak in final difference map	−0.48(5) e/A^3
Computer hardware	VAX11/750
Computer software	SDP/VAX (Enraf-Nonius & B. A. Frenz & Associates, Inc.)

TABLE II. Positional Parameters[a]

Atom	x	y	z	$B(A^2)$[b]
Pd	0.02856(7)	0.08712(7)	0.25111(4)	3.27(1)
O1	0.1591(6)	0.1693(6)	0.2984(3)	3.8(2)
O2	0.0287(6)	0.2056(6)	0.1766(3)	3.8(2)
O3	0.0289(5)	−0.0374(6)	0.3243(3)	4.0(2)
O4	−0.1007(6)	0.0068(6)	0.2030(3)	4.2(2)
C1	0.2126(8)	0.2659(9)	0.2739(5)	3.6(2)
C2	0.3082(9)	0.311(1)	0.3159(5)	4.5(3)
C3	0.270(1)	0.362(1)	0.3840(6)	5.7(3)
C4	0.192(1)	0.478(1)	0.3747(7)	8.4(4)*
C5	0.373(1)	0.392(1)	0.4276(7)	8.2(4)*
C6	0.1897(9)	0.325(1)	0.2136(5)	4.0(2)
C7	0.1037(9)	0.2953(9)	0.1699(5)	3.7(2)
C8	0.0871(9)	0.371(1)	0.1067(5)	4.5(2)
C9	−0.020(2)	0.445(3)	0.111(1)	23(1)*
C10	0.049(2)	0.296(3)	0.056(1)	20(1)*
C11	0.170(2)	0.472(2)	0.0926(9)	12.6(6)*
C12	−0.1469(8)	−0.0971(9)	0.2202(5)	4.1(2)
C13	−0.2439(9)	−0.140(1)	0.1734(6)	5.0(3)
C14	−0.243(1)	−0.065(1)	0.1111(8)	10.1(5)*
C15	−0.241(1)	−0.281(1)	0.1590(8)	10.6(5)*
C16	−0.358(1)	−0.108(1)	0.2067(8)	10.3(5)*
C17	−0.116(1)	−0.166(1)	0.2752(5)	5.2(3)
C18	−0.0341(9)	−0.1344(9)	0.3234(5)	3.9(2)
C19	−0.012(1)	−0.228(1)	0.3789(5)	5.5(3)
C20	−0.031(1)	−0.163(1)	0.4453(6)	6.8(3)
C21	−0.157(1)	−0.125(2)	0.4568(8)	10.3(5)*
C22	0.003(2)	−0.252(1)	0.5024(9)	9.8(4)*

[a] e.s.d.s given in parentheses. [b] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

Results and Discussion

In reversed phase (RP) LC the resolution for geometrical isomers of $Cr(tod)_3$ and $Co(tod)_3$ is less than in normal phase (NP) LC. Therefore NPLC was chosen for $Pd(tod)_2$ [4, 6]. Previous experiments had shown that methylene chloride/hexane mixtures

TABLE III. Bond Distances (Å) and Angles (°)[a]

(a) Distances

Pd	O1	1.984(6)	C2	C3	1.55(2)	C13	C14	1.49(2)
Pd	O2	1.961(6)	C3	C4	1.53(2)	C13	C15	1.52(2)
Pd	O3	1.982(6)	C3	C5	1.52(2)	C13	C16	1.52(2)
Pd	O4	1.973(6)	C6	C7	1.36(1)	C17	C18	1.39(1)
O1	C1	1.29(1)	C7	C8	1.52(1)	C18	C19	1.52(1)
O2	C7	1.29(1)	C8	C9	1.47(3)	C19	C20	1.53(2)
O3	C18	1.26(1)	C8	C10	1.36(3)	C20	C21	1.53(2)
O4	C12	1.27(1)	C8	C11	1.47(2)	C20	C22	1.54(2)
C1	C2	1.47(1)	C12	C13	1.53(1)			
C1	C6	1.39(1)	C12	C17	1.38(1)			

(b) Angles

O1	Pd	O2	95.0(3)	C2	C3	C5	111(1)	C12	C13	C14	111(1)
O1	Pd	O3	86.1(3)	C4	C3	C5	111(1)	C12	C13	C15	113(1)
O1	Pd	O4	179.2(2)	C1	C6	C7	127.0(9)	C12	C13	C16	107(1)
O2	Pd	O3	178.1(3)	O2	C7	C6	125.9(9)	C14	C13	C15	111(1)
O2	Pd	O4	84.2(3)	O2	C7	C8	113.1(8)	C14	C13	C16	106(1)
O3	Pd	O4	94.6(3)	C6	C7	C8	121.0(9)	C15	C13	C16	109(1)
Pd	O1	C1	121.7(5)	C7	C8	C9	109(1)	C12	C17	C18	127.5(9)
Pd	O2	C7	123.6(6)	C7	C8	C10	112(1)	O3	C18	C17	126.7(9)
Pd	O3	C18	122.1(6)	C7	C8	C11	118(1)	O3	C18	C19	115.4(8)
Pd	O4	C12	123.8(6)	C9	C8	C10	95(2)	C17	C18	C19	117.8(9)
O1	C1	C2	113.3(8)	C9	C8	C11	101(1)	C18	C19	C20	109.4(9)
O1	C1	C6	126.7(9)	C10	C8	C11	119(1)	C19	C20	C21	113(1)
C2	C1	C6	120.0(9)	O4	C12	C13	113.1(9)	C19	C20	C22	110(1)
C1	C2	C3	114.2(9)	O4	C12	C17	124.8(9)	C21	C20	C22	107(1)
C2	C3	C4	110(1)	C13	C12	C17	122.1(9)				

[a] Numbers in parentheses are e.s.d.s in the least significant digits.

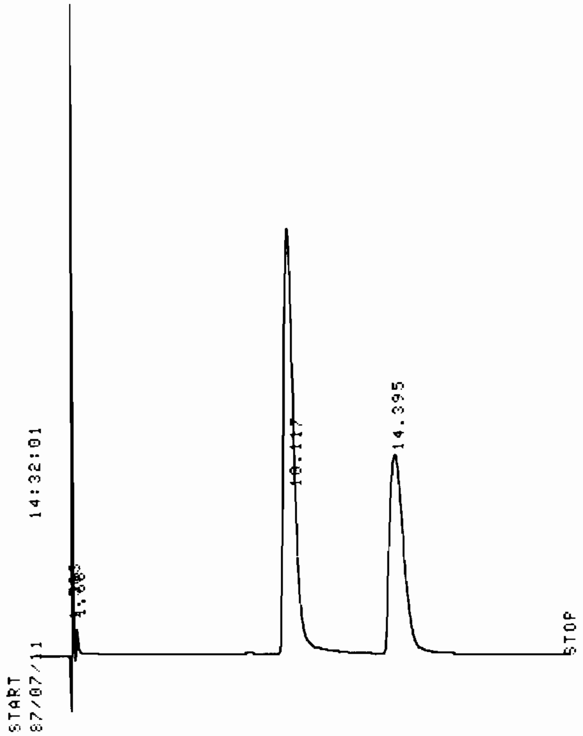

Fig. 2. HPLC separation of geometrical Pd(tod)$_2$ isomers (for conditions see text).

are the most useful for the separation of geometrical isomers of tod chelates on normal phase chromatography [6]. Other mixtures, which had also been tested were selected from Snyder's solvent triangle [13] but were not as suitable. For the separation of the Pd(tod)$_2$ geometrical isomers the eluent polarity (P′) had to be smaller ($P' < 1.6$) than for the separation of Cr(tod)$_3$ or Co(tod)$_3$ geometrical isomers ($P' = 2.5$).

Pd(tod)$_2$ was dissolved in hexane and injected onto the silica gel column with a mobile phase of hexane:methylene chloride (80:20). The chromatogram shows two peaks (Fig. 2). The ratio of these two peaks does not change over a 24-hour period and is the same for both preparation methods. At different flow rates the ratio of the two peaks did not change. An isomerization effect due to the time spent in the eluent can thus be excluded. In order to exclude solvent effects for the isomerization, two more solvents, methylene chloride and chloroform, were used to dissolve the Pd(tod)$_2$. No major differences for the chromatography were observed and solvent effects can therefore be excluded.

The X-ray structure determination showed that in the major component, the palladium is coordinated in the expected square planar fashion by two bidentate β-diketonate ligands. The maximum deviation from the least squares plane (Pt, O1, O2, O3, O4) is 0.012 Å. The geometry is clearly *cis* with respect to the t-butyl and s-butyl groups. The Pd–O bond lengths (average 1.975 Å) are all similar and comparable to known similar structures [14]. The intraligand O–Pd–O angles here are significantly greater than the interligand O–Pd–O angles. The present structure is in fact isomorphous with Cu(tod)$_2$ if a and c are inverted [8].

Supplementary Material

Tables of structure factors and anisotropic thermal parameters are available from the authors on request.

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