# Crystal Structure of Chiral Acetato-bridged Binuclear Cyclopalladated Complex $[Pd(\mu\text{-}O_2CMe)(S\text{-}C_6H_4CHMeNH_2)]_2$

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**Reaction of (*S*)-α-methylbenzylamine with $Pd(OAc)_2$ in anhydrous HOAc produced the chiral complex $[Pd(\mu\text{-}O_2CMe)(S\text{-}C_6H_4CHMeNH_2)]_2$ (1). The complex was characterized by $^1H$ NMR spectroscopy, elemental analysis and a single-crystal X-ray analysis. The X-ray crystal structure analysis revealed that complex 1 has four isomers: two outer and two inner isomers.**

**Keywords** chiral cyclopalladated complex, crystal structure, α-methylbenzylamine

## Introduction

Since Kleiman, Cope and coworkers described the first example of cyclopalladated complex,[1,2] it has aroused chemists' great interests in the structures and properties. Many crystal structures of monomeric cyclopalladated complexes have been investigated.[3,4] However, structures of acetato-bridged binuclear cyclopalladated complexes are rarely reported.[5] In this paper, we obtained the single crystal of chiral acetato-bridged binuclear cyclopalladated complex $[Pd(\mu\text{-}(O_2CMe)(S\text{-}C_6H_4CHMeNH_2)]_2$ (**1**) which was determined by a single crystal X-ray analysis.

## Experimental

*Synthesis of* $[Pd(\mu\text{-}O_2CMe)(S\text{-}C_6H_4CHMeNH_2)]_2$

(*S*)-α-Methylbenzylamine (2.23 mmol, 270 mg) and $Pd(OAc)_2$ (2.23 mmol, 500 mg) were dissolved in anhydrous HOAc (30 mL). The mixture was stirred for 4 d at room temperature under $N_2$ protection. The resulting orange solution was filtered, and solvent was removed to yield red solid. The solid was purified by chromatography on silica gel (100∶1 chloroform-methanol, *V*/*V*) (310 mg, yield 49%). The crystal was grown by slow diffusion of hexane into the dichloromethane solution at 298 K. $^1H$ NMR (400 MHz, $CDCl_3$) δ: 0.70 (inner isomer), 1.30 (outer isomer) (d, 6H, inner∶outer = 2∶3, $CH_3$), 2.10 (s, 6H, $CH_3CO$), 2.90—3.40 (br, 4H, $NH_2$), 4.00—4.30 (br, 2H, CHN), 6.45—6.60 (dd, 2H, aromatic), 6.75—7.90 (m, 6H, aromatic). Anal. calcd for $C_{20}H_{26}O_4N_2Pd_2$: C 42.20, H 4.25, N 4.92; found C 41.83, H 4.82, N 4.37.

X-*Ray structure determination*

A green prismatic crystal of dimensions 0.2 mm × 0.2 mm × 0.3 mm was chosen for the measurement. Diffraction data were collected on a Rigaku AFC7R diffractometer with graphite monochromated Mo Kα radation (λ = 0.071069 nm) at 293 K.

A total of 5874 reflections were collected within the range of $1.15° \leqslant \theta \leqslant 25.5°$ using $\omega\text{-}2\theta$ scan technique, of which 5276 reflections were observed with $I > 2\sigma(I)$. Intensities were corrected for Lorenz-polarization factors and empirical absorption based on Ψ scan technique. The structure was solved using direct methods, and refined by full-matrix least-squares method. The final cycle of refinement included 757 variable parameters and converged to $R = 0.030$ and $wR = 0.036$. The largest peak and deepest hole in the final difference Fourier map were $0.71 \times 10^{-3}$ and $-0.74 \times 10^{-3}$ e/nm$^3$, respectively. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.[6,7] The atomic coordinates and thermal parameters of non-hydrogen atoms are listed in Table 1. Details of crystal data and structure refinement are listed in Table 2. Selected bond lengths and angles are given in Table 3.

## Results and discussion

The title complex $[Pd(\mu\text{-}O_2CMe)(S\text{-}C_6H_4CHMeNH_2)]_2$ (**1**) was synthesized by reaction of (*S*)-α-

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methylbenzylamine with $Pd(OAc)_2$ in anhydrous HOAc in modest yield. The crystal structure of **1** was established by X-ray diffraction analysis. As expected, four isomers have been found, as shown by the ORTEP plots in Fig. 1 (**I**, **II**, **III**, **IV**).

**Table 1** Atomic coordinates and thermal parameters ($nm^2 \times 10^2$) of non-hydrogen atoms

| Atom | *x* | *y* | *z* | $B_{eq}$[a] | Atom | *x* | *y* | *z* | $B_{eq}$[a] |
|---|---|---|---|---|---|---|---|---|---|
| Pd(1) | 0.29366(2) | 0.3347 | 0.02248(3) | 3.81(1) | C(19) | 0.1839(4) | 0.4534(7) | 0.0880(7) | 6.2(3) |
| Pd(2) | 0.22431(2) | 0.48941(7) | 0.02589(4) | 4.60(1) | C(20) | 0.2611(5) | 0.618(1) | 0.2389(6) | 8.8(4) |
| Pd(3) | 0.21575(2) | 0.15413(5) | 0.48053(3) | 3.67(1) | C(21) | 0.1967(3) | -0.0151(8) | 0.5675(4) | 4.1(2) |
| Pd(4) | 0.28198(2) | -0.01152(7) | 0.49894(3) | 4.12(1) | C(22) | 0.1693(3) | -0.0638(8) | 0.6126(5) | 5.7(2) |
| Pd(5) | 0.45603(2) | 0.45666(7) | -0.05838(4) | 4.82(2) | C(23) | 0.3111(3) | 0.1521(8) | 0.6070(4) | 4.4(2) |
| Pd(6) | 0.04486(2) | 0.03569(8) | 0.55664(4) | 5.19(2) | C(24) | 0.3482(4) | 0.1969(9) | 0.6733(5) | 6.5(3) |
| O(1) | 0.3186(2) | 0.4261(5) | -0.0437(3) | 4.6(1) | C(25) | 0.2056(3) | 0.2451(6) | 0.3371(4) | 4.4(2) |
| O(2) | 0.2682(2) | 0.5524(5) | -0.0382(3) | 4.8(1) | C(26) | 0.1673(3) | 0.1652(7) | 0.3285(4) | 4.5(2) |
| O(3) | 0.2340(2) | 0.2873(5) | -0.0698(3) | 4.8(1) | C(27) | 0.1341(3) | 0.1390(9) | 0.2621(4) | 5.5(2) |
| O(4) | 0.1820(2) | 0.4087(5) | -0.0616(4) | 6.0(2) | C(28) | 0.1021(3) | 0.059(1) | 0.2571(5) | 6.7(3) |
| O(5) | 0.1848(2) | 0.0751(5) | 0.5471(3) | 4.5(1) | C(29) | 0.1019(3) | 0.0085(9) | 0.3180(5) | 5.8(2) |
| O(6) | 0.2303(2) | -0.0630(5) | 0.5544(3) | 4.9(1) | C(30) | 0.1334(3) | 0.0328(8) | 0.3847(4) | 5.0(2) |
| O(7) | 0.2746(2) | 0.2047(5) | 0.5746(3) | 4.8(1) | C(31) | 0.1662(3) | 0.1130(6) | 0.3921(4) | 3.9(2) |
| O(8) | 0.3206(2) | 0.0646(5) | 0.5906(3) | 5.2(1) | C(32) | 0.2313(4) | 0.2458(7) | 0.2785(5) | 5.7(2) |
| O(9) | 0.4916(2) | 0.5639(7) | -0.0996(3) | 6.9(2) | C(33) | 0.2764(3) | -0.0918(7) | 0.3530(5) | 5.4(2) |
| O(10) | 0.5598(2) | 0.5741(5) | -0.0077(4) | 6.3(2) | C(34) | 0.3144(3) | -0.0102(8) | 0.3723(4) | 5.0(2) |
| O(11) | -0.0103(3) | -0.0729(7) | 0.3997(4) | 7.5(2) | C(35) | 0.3413(4) | 0.0209(8) | 0.3279(5) | 6.4(3) |
| O(12) | 0.0584(2) | -0.0834(6) | 0.4894(4) | 6.8(2) | C(36) | 0.3764(4) | 0.093(1) | 0.3475(6) | 7.1(3) |
| N(1) | 0.2740(2) | 0.2432(5) | 0.0943(4) | 4.3(2) | C(37) | 0.3858(4) | 0.1349(10) | 0.4155(6) | 7.0(3) |
| N(2) | 0.2614(3) | 0.5710(6) | 0.1142(4) | 5.1(2) | C(38) | 0.3063(3) | 0.1061(8) | 0.4617(5) | 5.6(2) |
| N(3) | 0.2424(3) | 0.2306(5) | 0.4099(4) | 4.1(2) | C(39) | 0.3240(3) | 0.0324(7) | 0.4420(5) | 5.0(2) |
| N(4) | 0.2477(3) | -0.0852(5) | 0.4058(4) | 4.7(2) | C(40) | 0.2412(4) | -0.087(1) | 0.2764(5) | 7.8(3) |
| N(5) | 0.4198(3) | 0.3482(6) | -0.0210(4) | 5.1(2) | C(41) | 0.5307(4) | 0.6060(8) | -0.0650(5) | 5.4(2) |
| N(6) | 0.0815(3) | 0.1416(7) | 0.5173(4) | 5.5(2) | C(42) | 0.5427(5) | 0.703(1) | -0.0941(6) | 9.2(4) |
| C(1) | 0.3023(3) | 0.5142(7) | -0.0590(4) | 4.2(2) | C(43) | 0.4201(4) | 0.2470(8) | -0.0531(6) | 6.4(3) |
| C(2) | 0.3264(3) | 0.5770(8) | -0.1034(5) | 5.8(2) | C(44) | 0.4524(3) | 0.2501(8) | -0.1008(5) | 5.3(2) |
| C(3) | 0.1952(3) | 0.3315(8) | -0.0902(5) | 4.8(2) | C(45) | 0.4632(4) | 0.165(1) | -0.1347(7) | 8.1(4) |
| C(4) | 0.1566(4) | 0.2955(9) | -0.1575(6) | 6.5(3) | C(46) | 0.4939(5) | 0.171(1) | -0.1782(8) | 9.3(5) |
| C(5) | 0.3174(3) | 0.2242(6) | 0.1578(4) | 4.6(2) | C(47) | 0.5107(5) | 0.263(1) | -0.1918(8) | 9.1(4) |
| C(6) | 0.3456(3) | 0.3213(7) | 0.1722(4) | 4.2(2) | C(48) | 0.4988(4) | 0.349(1) | -0.1611(6) | 6.8(3) |
| C(7) | 0.3746(3) | 0.3518(8) | 0.2411(4) | 5.2(2) | C(49) | 0.4698(3) | 0.344(1) | -0.1144(5) | 5.1(2) |
| C(8) | 0.4011(3) | 0.4401(9) | 0.2486(5) | 5.9(2) | C(50) | 0.3683(6) | 0.220(1) | -0.095(1) | 14.2(7) |
| C(9) | 0.3988(3) | 0.4992(8) | 0.1889(5) | 5.4(2) | C(51) | 0.0297(4) | -0.1130(8) | 0.4314(5) | 5.8(3) |
| C(10) | 0.3708(3) | 0.4684(7) | 0.1196(5) | 4.8(2) | C(52) | 0.0415(5) | -0.207(1) | 0.3982(7) | 8.6(4) |
| C(11) | 0.3429(3) | 0.3803(7) | 0.1099(4) | 4.0(2) | C(53) | 0.0896(4) | 0.2365(9) | 0.5604(6) | 6.9(3) |
| C(12) | 0.3476(4) | 0.1381(7) | 0.1402(5) | 6.3(3) | C(54) | 0.0574(3) | 0.2371(10) | 0.6088(6) | 6.3(3) |
| C(13) | 0.2519(4) | 0.5341(8) | 0.1832(5) | 6.2(3) | C(55) | 0.0497(4) | 0.324(1) | 0.6451(8) | 8.9(4) |
| C(14) | 0.2016(4) | 0.4860(8) | 0.1590(5) | 5.9(2) | C(56) | 0.0194(6) | 0.317(2) | 0.6880(8) | 10.6(5) |
| C(15) | 0.1753(5) | 0.4708(10) | 0.2093(7) | 7.9(3) | C(57) | -0.0037(5) | 0.228(2) | 0.6952(7) | 9.7(5) |
| C(16) | 0.1320(6) | 0.424(1) | 0.1872(9) | 10.3(6) | C(58) | 0.0036(4) | 0.144(1) | 0.6600(6) | 7.4(3) |
| C(17) | 0.1141(5) | 0.388(1) | 0.120(1) | 10.7(6) | C(59) | 0.0344(3) | 0.1468(9) | 0.6158(5) | 5.6(2) |
| C(18) | 0.1397(4) | 0.404(1) | 0.0662(8) | 8.7(4) | C(60) | 0.0854(5) | 0.327(1) | 0.5108(7) | 9.6(4) |

[a] $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^* a_j^* a_i a_j$

**Table 2** Crystal data for compound $[Pd(\mu\text{-}O_2CMe)(S\text{-}C_6H_4CHMeNH_2)]_2$

| | | | |
|---|---|---|---|
| Empirical formula | $C_{60}H_{78}O_{12}N_6Pd_6$ | $D_{calc.}$ ($Mg \cdot m^{-3}$) | 1616 |
| Formula weight | 1713.71 | $F(000)$ | 3408 |
| Crystal color, Habit | Green, prismatic | $\mu$ (Mo K$\alpha$) ($cm^{-1}$) | 15.57 |
| Crystal dimensions (mm) | $0.20 \times 0.20 \times 0.30$ | Temperature (℃) | 20.0 |
| Crystal system | Monoclinic | Scan type | $\omega$-$2\theta$ |
| Lattice type | C-centred | No. observations [$I > 2.00\sigma(I)$] | 5276 |
| Space group | $C_2$( # 5) | No. variables | 757 |
| $a$ (nm) | 2.8549(4) | Reflection/parameter | 6.97 |
| $b$ (nm) | 1.3303(2) | Residuals: $R$; $R_w$ | 0.030; 0.036 |
| $c$ (nm) | 1.9425(4) | Goodness of fit indicator | 1.41 |
| $\beta$ (°) | 107.27(1) | Max shift/error in final cycle | 0.03 |
| $V$ ($nm^3$) | 7.044(2) | Maximum peak in final diff. Map ($e/nm^3$) | $0.71 \times 10^{-3}$ |
| $Z$ | 4 | Minimum peak in final diff. Map ($e/nm^3$) | $-0.74 \times 10^{-3}$ |

**Table 3** Selected bond lengths (nm) and angles (°) for molecular cyclopalladated complex **1**

| | | | |
|---|---|---|---|
| Pd(1)—Pd(2) | 0.2870(1) | Pd(3)—Pd(4) | 0.2856(1) |
| Pd(1)—O(1) | 0.2045(6) | Pd(3)—O(5) | 0.2058(6) |
| Pd(1)—O(3) | 0.2168(6) | Pd(3)—O(7) | 0.2189(6) |
| Pd(1)—N(1) | 0.2051(7) | Pd(3)—N(3) | 0.2029(7) |
| Pd(2)—O(2) | 0.2179(5) | Pd(4)—O(6) | 0.2180(6) |
| Pd(2)—O(4) | 0.2070(7) | Pd(4)—O(8) | 0.2061(6) |
| Pd(2)—N(2) | 0.2041(8) | Pd(4)—N(4) | 0.2035(7) |
| Pd(5)—Pd(5) | 0.2840(1) | Pd(6)—Pd(6) | 0.2838(1) |
| Pd(5)—O(9) | 0.2047(8) | Pd(6)—O(11) | 0.2067(8) |
| Pd(5)—O(10) | 0.2154(7) | Pd(6)—O(12) | 0.2160(7) |
| Pd(5)—N(5) | 0.2031(8) | Pd(6)—N(6) | 0.2034(8) |
| O(1)-Pd(1)-O(3) | 89.3(2) | O(5)-Pd(3)-O(7) | 89.9(2) |
| O(3)-Pd(1)-N(1) | 94.8(3) | O(7)-Pd(3)-N(3) | 93.6(3) |
| N(1)-Pd(1)-C(11) | 82.2(3) | N(3)-Pd(3)-C(31) | 82.2(3) |
| O(1)-Pd(1)-C(11) | 93.9(3) | O(5)-Pd(3)-C(31) | 94.4(3) |
| O(2)-Pd(2)-O(4) | 91.4(2) | O(6)-Pd(4)-O(8) | 89.7(2) |
| O(4)-Pd(2)-C(19) | 94.1(4) | O(8)-Pd(4)-C(39) | 94.7(3) |
| N(2)-Pd(2)-C(19) | 82.3(4) | N(4)-Pd(4)-C(39) | 81.6(4) |
| O(2)-Pd(2)-N(2) | 91.8(3) | O(6)-Pd(4)-N(4) | 94.0(3) |
| O(9)-Pd(5)-O(10) | 86.8(3) | O(11)-Pd(6)-O(12) | 85.9(3) |
| O(9)-Pd(5)-C(49) | 96.5(4) | O(11)-Pd(6)-C(59) | 96.5(4) |
| N(5)-Pd(5)-C(49) | 82.0(4) | N(6)-Pd(6)-C(59) | 83.2(4) |
| O(10)-Pd(5)-N(5) | 94.8(3) | O(12)-Pd(6)-N(6) | 94.4(3) |

The molecule consists of two Pd atoms, tetra-coordinated by two oxygen atoms of the acetate groups, and one C and one N in a square-planar environment. Each of the two Pd atoms has two different coordinated modes: chelating and bridging. The N and C of $\alpha$-methylbenzylamine coordinate to Pd in a chelating mode forming a five-member ring (N—Pd—C—C—C*), which enforces a *cis* arrangement upon two bridging acetates.

The acetato-bridged dinuclear complex exists in two configurations: outer isomers (**I** and **III**) and inner isomers (**II** and **IV**). The methyl groups of the chiral carbon atoms orientated outside the U-shape molecules for the outer isomers, while for the inner ones the methyl groups orientated inside the U-shape molecules. The $^1H$ NMR spectrum displays that the ratio of outer to inner isomers is 3:2. The inner methyl is shielded by the aromatic ring, which leads to the chemical shift of the protons appearing at 0.7.

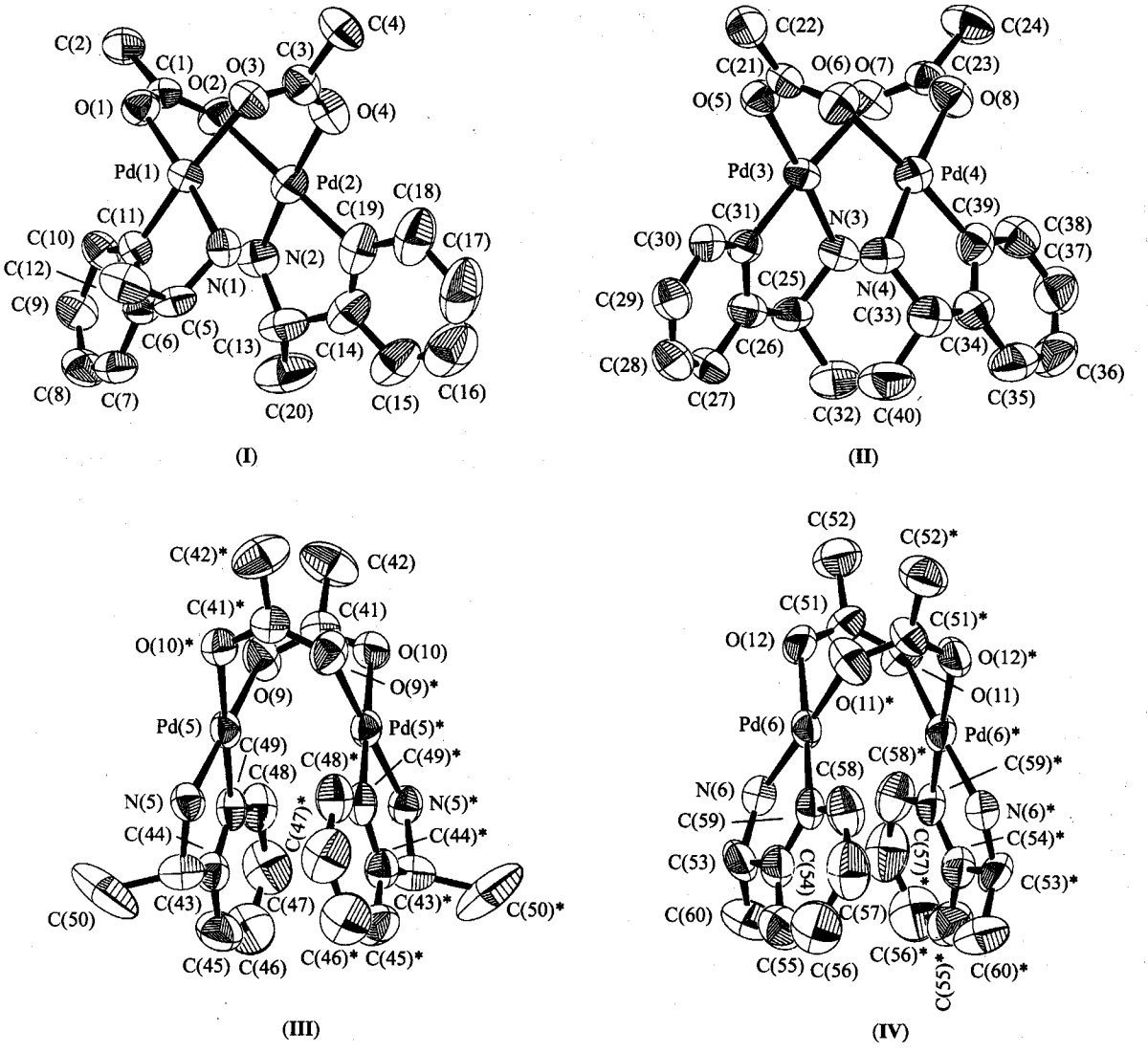


**Fig. 1** ORTEP of cyclopalladated complex **1**.

The isomer **I** structure displays eclipsed geometry of two five-member chelating rings, while **III** with eclipsed geometry of aromatic rings, which is consistent with the change of the bond angles around Pd. The O(1)-Pd(1)-C(11) bond angle of **I** is 93.9(3)°, while the O(9)-Pd(5)-C(49) bond angle of **III** is 96.5(4)°. So isomers **I** and **III** are mutually conformational isomers. Similar was that of isomers **II** and **IV**.

The distance of 0.28 nm displays that weak interreaction exists between two Pd atoms, but no significant Pd—Pd bond.

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