Refinement of the crystal structure of μ -((1,2,5,6- η :3,4,7,8- η)-1,3,5,7-cyclooctatetraene)bis(dimethylplatinum(II)), $[\text{Pt}(\text{CH}_3)_2]_2(\text{C}_8\text{H}_8)$, at 243 K

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Abstract

$\text{C}_{12}\text{H}_{20}\text{Pt}_2$, monoclinic, $C12/c1$ (no. 15), $a = 10.881(1) \text{ \AA}$, $b = 11.128(1) \text{ \AA}$, $c = 10.758(1) \text{ \AA}$, $\beta = 111.687(2)^\circ$, $V = 1210.4 \text{ \AA}^3$, $Z = 4$, $R_{\text{gt}}(F) = 0.030$, $wR_{\text{ref}}(F^2) = 0.074$, $T = 243 \text{ K}$.

Source of material

To a suspension of dichlorocyclooctatetraeneplatinum(II) (0.5053 g, 1.37 mmol) in ether (30 ml) was added slowly methyllithium (1.6 M solution in ether, 5.07 ml, 8.11 mmol), and stirred for 4 h at -5°C . After methanolysis with 1 ml MeOH, the resulting mixture was diluted with pentane (20 ml), and then filtered directly through a plug of Al_2O_3 (3 cm $\times$ 2 cm) and eluted with pentane. The solvent was removed in vacuo, the dark brown residue was dissolved in pentane, and filtered once more through a new plug of Al_2O_3 (3 cm $\times$ 2 cm). Evaporation of the solvent gave a yellow powder (0.2601 g). ^1H NMR analysis reveals that the product is a mixture, containing mono- and dinuclear Pt(II) compounds, $[\text{Pt}(\text{CH}_3)_2(\text{C}_8\text{H}_8)]$ and $[\text{Pt}_2(\text{CH}_3)_4(\text{C}_8\text{H}_8)]$, with a molar ratio of 2.64:1. Yellow needle-shaped crystals of diplatinum complex suitable for X-ray structure analysis were obtained via slow evaporation from an acetone solution of the mixture. ^1H NMR and MS data are available in the CIF.

Experimental details

Three H atoms (H1, H2, H4) were located from Fourier difference maps and refined isotropically. The H3 atom was also found and refined, but the C3—H3 bond distance was restrained to the averaged value of the other bond lengths and an estimated standard deviation to achieve reasonable bond data. The methyl H atoms at C5 were positioned using AFIX 137 instruction ($d(\text{C—H}) = 0.97 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{C})$) [1]. The other methyl group with C6 appears to be disordered. Its H atoms were modeled as disordered over two sites rotated by 60° from one another using AFIX 123 instruction [1], with an occupancy ratio of 0.6(1)/0.4.

Discussion

The title compound was previously prepared by the reaction of cyclooctatetraenediiodoplatinum(II) with Grignard reagent, CH_3MgI [2]. The NMR spectrum of the compound was examined for potential long-range coupling by the ^{195}Pt nuclei [3], and X-ray structure analysis was also carried out [4]. The published and our crystal structures are essentially the same, however, the geometric properties and parameters here presented are slightly different and more accurate, respectively.

The complex consists of two dimethylplatinum groups bridged by an 1,3,5,7-cyclooctatetraene (cot) ligand, and is disposed about a twofold axis passing through the two Pt atoms and the center of the ligand along the b axis. Each Pt atom is essentially in a square-planar environment defined by the two C atoms of methyl groups and the two midpoints of the π -coordinated double bonds of the cot ligand. The Pt, C atoms and the midpoints form two coordination planes with the largest deviations 0.022 $\text{\AA}$ (C5) and 0.006 $\text{\AA}$ (C6), respectively, from the least-squares planes and with approximately 90° ($\angle \text{C5—Pt1—C5}^i = 86.7(5)^\circ$, $\angle \text{M1—Pt1—M1}^i = 85.9^\circ$, $\angle \text{C5—Pt1—M1}^i = 93.7^\circ$, $\angle \text{C6—Pt2—C6}^i = 86.3(5)^\circ$, $\angle \text{M2—Pt2—M2}^i = 86.4^\circ$, $\angle \text{C6—Pt2—M2} = 93.7^\circ$, symmetry code $i: 1-x, y, \frac{1}{2}-z$; M1 and M2 denote the midpoints of the olefinic bonds C1—C2 and C3—C4, respectively). The planes are perpendicular to each other (89.4°). The Pt—C(cot) bond lengths range from 2.227(8) $\text{\AA}$ to 2.240(8) $\text{\AA}$, and the distances between the Pt atom and the midpoints are 2.124 $\text{\AA}$ (M1) and 2.126 $\text{\AA}$ (M2), and slightly longer than the Pt—C(methyl) bond (2.053(8) $\text{\AA}$ and 2.044(8) $\text{\AA}$). The cot ligand coordinates the two Pt atoms very symmetrically in the tub conformation. The distance between the Pt atoms is 4.1267(4) $\text{\AA}$. The four C atoms (C1, C2, C1ⁱ and C2ⁱ) coordinated to Pt1 and the four C atoms (C3, C4, C3ⁱ and C4ⁱ) coordinated to Pt2 lie on a plane, respectively, with the torsion angles $\angle \text{C1—C2—C1}^i\text{—C2}^i = 1.0^\circ$ and $\angle \text{C3—C4—C3}^i\text{—C4}^i = 0.1^\circ$. The Pt atoms are displaced by 1.554(6) $\text{\AA}$ (Pt1) from the plane C1/ C2/C1ⁱ/C2ⁱ and 1.550(6) $\text{\AA}$ (Pt2) from the plane C3/C4ⁱ/C3ⁱ/C4. The planes are perfectly parallel to each other with a dihedral angle 0.00(1) $^\circ$. The cot ring angles lie in the range of $120.4(7)^\circ$ – $121.2(7)^\circ$ in the complex.

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Table 1. Data collection and handling.

Crystal:	yellow needle, size 0.195 × 0.198 × 0.205 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	230.50 cm ⁻¹
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{\max}$:	56.54°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	3710, 1400
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1318
$N(\text{param})_{\text{refined}}$:	84
Programs:	SHELXS-97 [5], SHELXL-97 [1], ORTEP-III [6]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	x	y	z	U_{iso}
H(1)	8f		0.28(1)	-0.018(9)	0.10(1)	0.03(2)
H(2)	8f		0.30(1)	-0.015(9)	0.312(9)	0.04(2)
H(3)	8f		0.419(8)	0.143(7)	0.424(7)	0.02(2)
H(4)	8f		0.35(1)	0.17(1)	0.02(1)	0.05(3)
H(5A)	8f		0.6660	-0.2773	0.3760	0.062
H(5B)	8f		0.7140	-0.2206	0.2666	0.062
H(5C)	8f		0.5996	-0.3179	0.2246	0.062
H(6A)	8f	0.6(1)	0.4852	0.4656	0.1571	0.062
H(6B)	8f	0.6	0.3923	0.3813	0.0421	0.062
H(6C)	8f	0.6	0.5470	0.3813	0.0767	0.062
H(6D)	8f	0.4	0.4644	0.3532	0.0268	0.062
H(6E)	8f	0.4	0.5574	0.4375	0.1418	0.062
H(6F)	8f	0.4	0.4027	0.4375	0.1072	0.062

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt(1)	4e	½	-0.11670(3)	¼	0.0251(2)	0.0218(2)	0.0311(2)	0	0.0082(2)	0
Pt(2)	4e	½	0.25413(3)	¼	0.0318(2)	0.0216(2)	0.0272(2)	0	0.0085(2)	0
C(1)	8f	0.3478(8)	0.0224(7)	0.1521(8)	0.025(3)	0.026(4)	0.035(4)	0.002(3)	0.005(3)	0.007(3)
C(2)	8f	0.3699(8)	0.0235(7)	0.2873(8)	0.028(4)	0.025(4)	0.044(4)	0.002(3)	0.015(3)	0.010(3)
C(3)	8f	0.4577(9)	0.1148(7)	0.3784(8)	0.040(4)	0.024(4)	0.030(4)	0.007(3)	0.018(4)	0.004(3)
C(4)	8f	0.4100(9)	0.1149(7)	0.0939(8)	0.041(4)	0.029(4)	0.023(3)	-0.001(3)	0.012(3)	0.002(3)
C(5)	8f	0.6381(9)	-0.2508(7)	0.284(1)	0.036(5)	0.025(4)	0.061(6)	0.009(3)	0.016(4)	-0.002(3)
C(6)	8f	0.478(1)	0.3882(8)	0.1135(9)	0.055(6)	0.027(4)	0.037(4)	-0.002(4)	0.011(4)	0.010(3)

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