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Crystal structures of dichloro((1,2,5,6-η)-1,3,5,7-cyclooctatetraene)-platinum(II), $PtCl_2(C_8H_8)$, and diiodo((1,2,5,6-η)-1,3,5,7-cycloocta-tetraene)platinum(II), $PtI_2(C_8H_8)$

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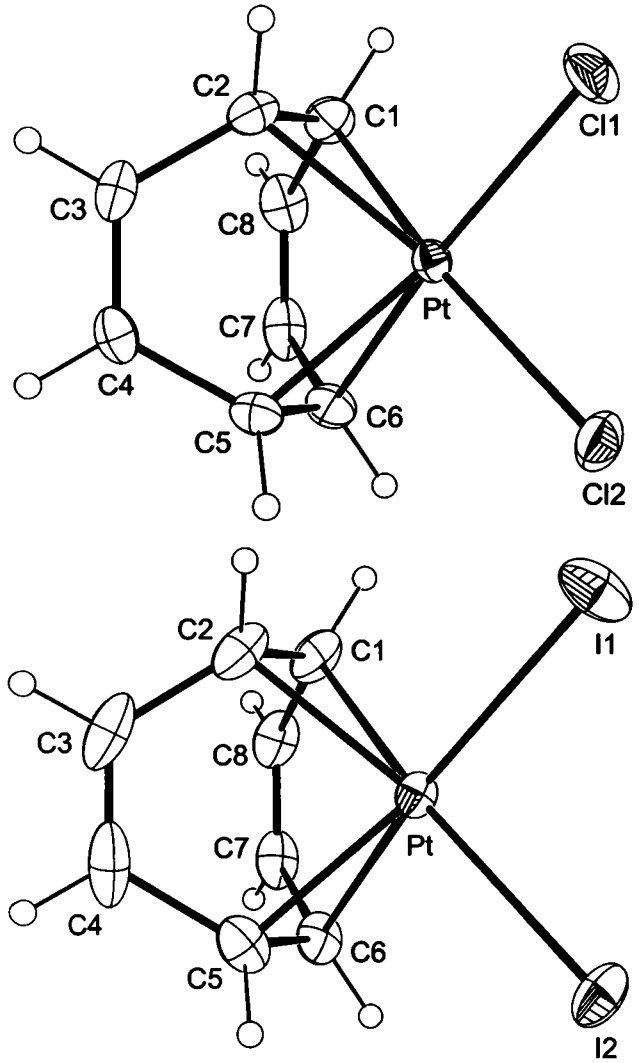

Abstract

$C_8H_8Cl_2Pt$, monoclinic, $P12_1/n1$ (no. 14), a = 7.846(5) Å, b = 9.668(6) Å, c = 11.530(7) Å, β = 98.31(1)°, V = 865.4 Å^3, Z = 4, $R_{gt}(F)$ = 0.039, $wR_{ref}(F^2)$ = 0.099, T = 293 K.

$C_8H_8I_2Pt$, monoclinic, $P12_1/n1$ (no. 14), a = 8.4261(9) Å, b = 10.741(1) Å, c = 11.600(1) Å, β = 99.586(2)°, V = 1035.2 Å^3, Z = 4, $R_{gt}(F)$ = 0.033, $wR_{ref}(F^2)$ = 0.091, T = 293 K.

Source of material

The title complexes were synthesized according to the literature procedure [1]. Crystals suitable for X-ray structure analysis were obtained via slow evaporation from a CH_2Cl_2 solution of $[PtCl_2(C_8H_8)]$ (PTC) and from a $CDCl_3$ solution of $[PtI_2(C_8H_8)]$ (PTI), respectively.

Discussion

The title compounds $[PtX_2(C_8H_8)]$ with X = Cl and I are isomorphous with the analogous Pd(II) compound $[PdCl_2(C_8H_8)]$ [2]. In the complexes, the central Pt atoms are in a square-planar environment defined by the two X atoms and the two midpoints ($M1$, $M2$) of the π-coordinated double bonds of the 1,3,5,7-cyclooctatetraene (cot) ligand ($M1$ and $M2$ denote the midpoints of the olefinic bonds C1—C2 and C5—C6, respectively). The Pt, X atoms and the midpoints lie in a coordination plane with the largest deviations of 0.013 Å ($M2$) and 0.009 Å (Pt) from the least-squares planes for PTC and PTI, respectively. The bond angles are approximately 90° (∠Cl1–Pt–Cl2 = 90.53(8)°, ∠$M1$–Pt–$M2$ = 87.2°, ∠$M1$–Pt–Cl1 = 90.9°, ∠$M2$–Pt–Cl2 = 91.4° in PTC and ∠I1–Pt–I2 = 90.41(2)°, ∠$M1$–Pt–$M2$ = 86.9°, ∠$M1$–Pt–I1 = 91.6°, ∠$M2$–Pt–I2 = 91.1° in PTI).

The four Pt—C bond lengths in both complexes are nearly equal (2.152(6) Å – 2.164(8) Å in PTC and 2.179(8) Å – 2.189(7) Å in PTI), and the distances between the Pt atom and the midpoints are 2.041 Å ($M1$), 2.047 Å ($M2$) for PTC and 2.069 Å ($M1$), 2.071 Å ($M2$) for PTI. The cot ligands coordinate the Pt atoms very symmetrically in the tub conformation, and display a some increase in the double-bond distances (1.39(1) Å, 1.39(1) Å in PTC and 1.40(1) Å, 1.40(1) Å in PTI) compared with the non-coordinating double bonds (1.33(1) Å, 1.31(1) Å in PTC and 1.27(2) Å, 1.30(1) Å in PTI). The four coordinating C atoms (C1, C2, C5 and C6) and the four non-coordinating C atoms (C3, C4, C7 and C8) lie on a plane each, with the torsion angles ∠C1–C2–C5–C6 = –0.5(7)° (PTC), –0.2(6)° (PTI) and ∠C3–C4–C7–C8 = 0.2(6)° (PTC), –0.2(8)° (PTI). The Pt atoms are displaced by 1.480(4) Å (PTC) and 1.502(4) Å (PTI) from the plane C1/C2/C5/C6, and by 2.478(4) Å (PTC) and 2.492(4) Å (PTI) from the plane C3/C4/C7/C8. The dihedral angles between these least-squares planes are 0.6(6)° (PTC) and 0.3(5)° (PTI). In the complexes, the cot ring angles lie in the range of 120.1(7)° – 123.8(7)° for PTC and 121.0(8)° – 123.4(8)° for PTI.

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1. Dichloro[(1,2,5,6-η)-1,3,5,7-cyclooctatetraene]platinum(II), $PtCl_2(C_8H_8)$

Table 1. Data collection and handling.

Crystal:	yellow prism, size 0.08 × 0.10 × 0.10 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	167.56 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{max}$:	56.92°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5297, 2030
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1843
$N(param)_{refined}$:	100
Programs:	SHELXS-97 [3], SHELXL-97 [4], ORTEP-III [5]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(1)	4e	0.3193	−0.0668	0.2972	0.046
H(2)	4e	0.1585	0.0856	0.1845	0.040
H(3)	4e	−0.0878	0.1560	0.2719	0.045
H(4)	4e	−0.0415	0.3214	0.4114	0.043
H(5)	4e	0.2523	0.4025	0.4630	0.043
H(6)	4e	0.4136	0.2522	0.5785	0.048
H(7)	4e	0.2456	0.0496	0.6192	0.054
H(8)	4e	0.1975	−0.1096	0.4781	0.054

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	4e	0.40334(3)	0.20432(2)	0.34378(2)	0.0228(2)	0.0263(2)	0.0250(2)	−0.00018(7)	0.0069(1)	0.00137(8)
Cl(1)	4e	0.5335(3)	0.1415(2)	0.1858(2)	0.049(1)	0.065(1)	0.0375(9)	0.0024(9)	0.0254(8)	−0.0023(9)
Cl(2)	4e	0.6075(2)	0.3727(2)	0.3930(2)	0.0295(8)	0.0374(9)	0.076(1)	−0.0084(7)	0.0084(9)	−0.0053(9)
C(1)	4e	0.2699(9)	0.0085(7)	0.3386(7)	0.042(4)	0.026(3)	0.047(4)	−0.009(3)	0.012(3)	−0.002(3)
C(2)	4e	0.1689(9)	0.1030(7)	0.2689(6)	0.037(3)	0.034(3)	0.029(3)	−0.008(3)	0.001(3)	−0.003(3)
C(3)	4e	0.0240(9)	0.1766(8)	0.3061(7)	0.023(3)	0.049(4)	0.039(4)	−0.003(3)	0.001(3)	0.012(3)
C(4)	4e	0.051(1)	0.2734(7)	0.3890(7)	0.030(3)	0.039(4)	0.041(4)	0.004(3)	0.015(3)	0.007(3)
C(5)	4e	0.228(1)	0.3046(6)	0.4454(7)	0.042(4)	0.031(4)	0.035(4)	0.004(3)	0.006(3)	−0.005(3)
C(6)	4e	0.329(1)	0.2111(7)	0.5173(7)	0.045(4)	0.055(5)	0.021(3)	−0.004(3)	0.011(3)	−0.008(3)
C(7)	4e	0.2655(9)	0.0709(9)	0.5436(7)	0.036(4)	0.066(5)	0.035(4)	0.006(4)	0.011(3)	0.026(4)
C(8)	4e	0.238(1)	−0.0226(8)	0.4608(8)	0.045(4)	0.037(4)	0.056(5)	0.003(3)	0.017(4)	0.016(4)

2. Diiodo[(1,2,5,6-η)-1,3,5,7-cyclooctatetraene]platinum(II), $PtI_2(C_8H_8)$

Table 4. Data collection and handling.

Crystal:	orange-red prism, size 0.15 × 0.15 × 0.17 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	194.59 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{max}$:	56.48°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6335, 2388
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2209
$N(param)_{refined}$:	101
Programs:	SHELXS-97 [3], SHELXL-97 [4], ORTEP-III [5]

Table 5. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(1)	4e	0.2512	0.3599	0.4498	0.053
H(2)	4e	0.3961	0.2217	0.5696	0.056
H(3)	4e	0.2338	0.0457	0.6072	0.073
H(4)	4e	0.1907	−0.0992	0.4746	0.079
H(5)	4e	0.3094	−0.0716	0.2979	0.052
H(6)	4e	0.1628	0.0619	0.1726	0.047
H(7)	4e	−0.0682	0.1396	0.2535	0.052
H(8)	4e	−0.0246	0.2855	0.3887	0.053

Table 6. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	4e	0.39381(3)	0.17434(2)	0.33691(2)	0.0171(2)	0.0350(2)	0.0283(2)	0.00304(8)	0.0037(1)	0.00205(8)
I(1)	4e	0.61081(6)	0.34528(5)	0.39324(7)	0.0243(3)	0.0450(3)	0.0943(5)	−0.0024(2)	−0.0011(3)	−0.0103(3)
I(2)	4e	0.53596(6)	0.10239(6)	0.16665(4)	0.0380(3)	0.0741(4)	0.0417(3)	0.0079(2)	0.0193(2)	−0.0011(2)
C(1)	4e	0.2283(9)	0.2718(9)	0.4324(7)	0.030(4)	0.066(5)	0.040(4)	0.010(4)	0.019(3)	−0.005(3)
C(2)	4e	0.317(1)	0.1857(9)	0.5070(7)	0.034(4)	0.079(6)	0.028(4)	0.005(4)	0.005(3)	−0.001(3)
C(3)	4e	0.255(1)	0.062(1)	0.5325(8)	0.054(5)	0.097(7)	0.034(4)	0.018(5)	0.014(4)	0.027(5)
C(4)	4e	0.230(1)	−0.022(1)	0.4553(9)	0.058(6)	0.068(6)	0.078(7)	0.014(5)	0.031(5)	0.045(5)
C(5)	4e	0.2622(9)	−0.0011(7)	0.3338(8)	0.030(4)	0.038(4)	0.063(5)	0.001(3)	0.010(3)	0.003(3)
C(6)	4e	0.1716(8)	0.0818(7)	0.2559(6)	0.020(3)	0.054(4)	0.041(4)	−0.010(3)	0.001(3)	0.002(3)
C(7)	4e	0.0367(9)	0.1555(8)	0.2901(7)	0.019(3)	0.062(5)	0.048(4)	−0.003(3)	0.000(3)	0.017(4)
C(8)	4e	0.0626(9)	0.2414(8)	0.3698(7)	0.028(4)	0.059(5)	0.048(4)	0.015(3)	0.013(3)	0.012(4)

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