

approximately parallel to (100) as shown in Fig. 3. Two complex cations related by a twofold screw axis parallel to **b** are linked by weak hydrogen bonds: N(3)···O(3) = 2.98 (1), H(N3)···O(3) = 2.26 (5) Å; N(3)···O(4) = 3.01 (1), H(N3)···O(4) = 2.41 (5) Å.

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Bis(1,5-cyclooctadiene)platinum(0); X-ray Structure at 200 K

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Abstract. C₁₆H₂₄Pt, triclinic, $P\bar{1}$, $a = 10.605$ (10), $b = 9.370$ (12), $c = 7.382$ (6) Å, $\alpha = 110.33$ (8), $\beta = 89.43$ (7), $\gamma = 107.72$ (9)° (200 K), $Z = 2$, $D_m = 1.98$, $D_x = 2.03$ g cm⁻³. 3128 corrected intensities used in the final refinement of the structure, R (R') 0.031 (0.036), showed that the Pt atom is approximately tetrahedrally coordinated to two tub-shaped cyclooctadiene ligands. Mean Pt–C and C=C are 2.211 (7) and 1.398 (9) Å respectively.

Introduction. The title compound, [Pt(cod)₂], was first prepared by Müller & Göser (1967) but their two-stage synthesis *via* [Pt{Pr₂(cod)}] gave relatively low yields. A new synthesis was developed by Spencer (1979) in which the treatment of [PtCl₂(cod)] with Li₂(C₈H₈) in diethyl ether in the presence of cod gives substantially higher yields of [Pt(cod)₂].

[Pt(cod)₂] has since become a most useful and important entry point into zero-valent Pt chemistry (Stone, 1975, 1981; Green, Howard, Spencer & Stone, 1975), and in particular to the simple binary olefin complexes [Pt(olefin)₂] (Green, Howard, Spencer & Stone, 1977; Howard, 1978). The ease of displacement of cod from [Pt(cod)₂] by unstrained olefins,

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isocyanides and phosphines, for example (Green *et al.*, 1975; Green, Howard, Murray, Spencer & Stone, 1977), led us to investigate the exact geometry of this interesting molecule.

The crystals are not indefinitely stable and discolour quite rapidly in air. That chosen for data collection, of approximate dimensions 0.15 × 0.16 × 0.17 mm, was sealed in a Lindemann-glass capillary and cooled to 200 K [Syntex P2₁ four-circle automated diffractometer, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å]. 3128 diffracted intensities (from a total of 3439) which satisfied the criterion $I > 2\sigma(I)$ were corrected for absorption ($\mu = 109.6$ cm⁻¹) and used in the solution and refinement of the structure. All non-hydrogen atoms were refined with anisotropic thermal parameters, while the H atoms were refined isotropically. No phase change was observed nor any significant crystal degradation on cooling to 200 K. Scattering factors and corrections for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974) and all computations were carried out using the XRAY system of programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) at the University of London Computer Centre.

Discussion. The molecular structure is shown in Fig. 1, final atomic positional parameters are in Table 1,* and Table 2 shows bond lengths and angles involving the non-hydrogen atoms only.

The asymmetric unit comprises one molecule in which the Pt atom is bound to the four C=C double bonds in an approximately tetrahedral arrangement. The dihedral angle between the planes each containing the mid-point [C(*n*,*m*)] of the coordinated C=C bonds

* Lists of structure factors, H-atom parameters, all thermal parameters, the molecular geometry associated with the H atoms only and a table of least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36974 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

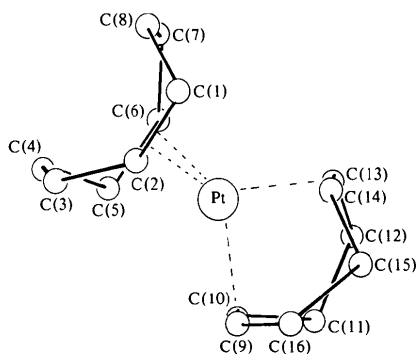


Fig. 1. A view of the molecular structure, with the atom-numbering scheme.

Table 1. Final atomic positional parameters (fractional coordinates) and equivalent isotropic thermal parameters, with estimated standard deviations in parentheses

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq} ($\text{\AA}^2 \times 10^3$)
Pt	0.25129 (2)	0.05697 (2)	0.25024 (2)	12.6
C(1)	0.4217 (7)	0.2708 (6)	0.2820 (8)	20.2
C(2)	0.3603 (6)	0.2863 (6)	0.4617 (7)	18.8
C(3)	0.2674 (7)	0.3880 (7)	0.5491 (8)	22.5
C(4)	0.1648 (7)	0.3691 (7)	0.4053 (9)	23.3
C(5)	0.1220 (6)	0.2045 (6)	0.2562 (8)	18.4
C(6)	0.1798 (7)	0.1629 (7)	0.0706 (8)	20.6
C(7)	0.2963 (8)	0.2737 (8)	0.0058 (8)	26.9
C(8)	0.4098 (7)	0.3637 (7)	0.1549 (8)	22.6
C(9)	0.1888 (7)	-0.0738 (7)	0.4575 (8)	22.6
C(10)	0.0926 (7)	-0.1362 (6)	0.3091 (8)	19.3
C(11)	0.0733 (7)	-0.2953 (6)	0.1462 (9)	21.0
C(12)	0.1528 (7)	-0.2849 (7)	-0.0351 (8)	23.3
C(13)	0.2795 (7)	-0.1477 (6)	0.0022 (7)	19.4
C(14)	0.3711 (7)	-0.1118 (6)	0.1467 (8)	19.3
C(15)	0.3571 (8)	-0.2155 (7)	0.2718 (9)	26.0
C(16)	0.2918 (8)	-0.1521 (7)	0.4674 (8)	28.0

Table 2. Bond lengths (\AA) and selected interbond angles ($^\circ$), with estimated standard deviations in parentheses

(i) Coordination around the Pt atom

Pt—C(1)	2.194 (7)	C(1)—Pt—C(2)	39.1 (2)
Pt—C(2)	2.141 (6)	C(5)—Pt—C(6)	39.2 (2)
Pt—C(5)	2.214 (8)	C(9)—Pt—C(10)	34.8 (2)
Pt—C(6)	2.171 (7)	C(13)—Pt—C(14)	34.4 (2)
Pt—C(9)	2.251 (7)	C(1,2)—Pt—C(5,6)	82.9 ^(a)
Pt—C(10)	2.230 (7)	C(1,2)—Pt—C(9,10)	130.1
Pt—C(13)	2.240 (6)	C(1,2)—Pt—C(13,14)	115.3
Pt—C(14)	2.250 (8)	C(9,10)—Pt—C(5,6)	87.6
Pt—C(1,2)	2.043 ^(a)	C(9,10)—Pt—C(13,14)	116.9
Pt—C(5,6)	2.066	C(13,14)—Pt—C(5,6)	129.7
Pt—C(9,10)	2.138		
Pt—C(13,14)	2.133		

(ii) 1,5-Cyclooctadiene ligands

C(1)—C(2)	1.453 (9)	C(1)—C(2)—C(3)	127.5 (6)
C(2)—C(3)	1.558 (10)	C(2)—C(3)—C(4)	112.7 (5)
C(3)—C(4)	1.455 (10)	C(3)—C(4)—C(5)	111.2 (6)
C(4)—C(5)	1.484 (7)	C(4)—C(5)—C(6)	122.8 (5)
C(5)—C(6)	1.470 (9)	C(5)—C(6)—C(7)	127.1 (4)
C(6)—C(7)	1.545 (9)	C(6)—C(7)—C(8)	113.2 (6)
C(7)—C(8)	1.461 (9)	C(7)—C(8)—C(1)	111.4 (5)
C(8)—C(1)	1.514 (11)	C(8)—C(1)—C(2)	123.3 (6)
C(9)—C(10)	1.340 (9)	C(9)—C(10)—C(11)	123.0 (7)
C(10)—C(11)	1.511 (8)	C(10)—C(11)—C(12)	115.1 (5)
C(11)—C(12)	1.591 (10)	C(11)—C(12)—C(13)	117.3 (5)
C(12)—C(13)	1.498 (8)	C(12)—C(13)—C(14)	120.9 (6)
C(13)—C(14)	1.329 (8)	C(13)—C(14)—C(15)	121.8 (5)
C(14)—C(15)	1.534 (11)	C(14)—C(15)—C(16)	113.3 (6)
C(15)—C(16)	1.597 (10)	C(15)—C(16)—C(9)	116.5 (6)
C(16)—C(9)	1.504 (12)	C(16)—C(9)—C(10)	122.2 (5)

(a) No e.s.d.'s are quoted since the midpoints C(*n*,*m*) of bond C(*n*)-C(*m*) were not refined.

and the Pt atom is 103° [*i.e.* Pt, C(1,2), C(5,6) and Pt, C(9,10), C(13,14)] and the mean 'angle of bite' [C(*n*,*m*)-Pt-C(*n'*,*m'*)] is 85° . There are obvious distortions from exact tetrahedral geometry around the metal and from the idealized *mm*2 symmetry of an uncoordinated, tub-shaped cod, both of which appear to minimize any H...H contacts. The closest contact between any two H atoms is 2.14 \AA and for non-hydrogen atoms is 2.5 \AA between non-adjacent C atoms in the rings.

Calculations have shown (Hoffmann & Rösch, 1974) that in the case of hypothetical tetrakis(ethylene)nickel the most favourable geometry to accommodate four ethylene ligands around the metal in a pseudo-tetrahedral arrangement would be the quasi-dodecahedral structure (scheme 1) rather than the quasi-cubic (scheme 2). In [Pt(cod)₂], however, we have found a distortion from (2) towards (1), but here we are concerned with a constrained, bidentate olefin and our results should better be compared with those published for other similar systems coordinated to Ni, namely [Ni(cod)(duroquinone)] (Glick & Dahl, 1965) and [Ni(duroquinone)₂] (Aleksandrov & Struchkov, 1973) where the quasi-cubic structures have also been observed. For the isoelectronic complexes [Ni(cod)₂]

(Dierks & Dietrich, 1965) and $[\text{Ag}(\text{cod})_2]\text{BF}_4$ (Albinati, Meille & Carturan, 1979), both of which show distortions of the cyclooctadiene ligands, again the geometry is essentially quasi-cubic.



Quasi-dodecahedral (1)



Quasi-cubic (2)

In the title and in the latter two compounds, the C=C double bonds are not constrained to lie parallel, as they are in duroquinone, and are seen to be twisted relative to one another by some 9° . A skewing of the C_8 ring is observed in the free ligand (Hedberg & Hedberg, 1964) with distortions at the non-olefinic C atoms being predominant.

It is noteworthy that in the solid state the eight olefinic C atoms of $[\text{Pt}(\text{cod})_2]$ are not symmetrically bound to the Pt atom, and the ligand which is more closely related to the metal [C(1)–C(8); Pt–C (mean) 2.180 (7) Å] shows correspondingly longer C=C separations [mean, 1.469 (9) Å] than does the other (cod) ligand [C(9)–C(16)] with Pt–C and C=C distances of 2.243 (7) and 1.334 (9) Å respectively. The ligand which lies closer to the Pt atom shows less variation of the remaining ring C–C distances than does C(9)–C(16) where the ligated C=C bonds are significantly shorter than all other C–C separations [1.334 (9) cf. 1.539 (10) Å]. These values all fall within the ranges we have observed previously for other 'Pt(cod)' complexes (Laguna, Green, Howard, Smart, Spencer & Stone, 1977; Boag, Green, Howard, Stone & Wadepohl, 1981; Christofides, Howard, Rattue, Spencer & Stone, 1980; Chetcuti, Howard, Pfeffer, Spencer & Stone, 1981). The variations in bond lengths observed within the molecule are assumed to be due in part to intramolecular forces and subsequent relief of strain energy by such distortions. The small angle of bite (mean 85°) compared to the idealized tetrahedral angle indicates considerable strain within the coordinated ligand and the displacement of cod from $[\text{Pt}(\text{cod})_2]$, which would be accompanied by relief of such strain energy, proceeds with ease under relatively mild conditions (Spencer, 1979).

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