

Crystal and molecular structure of cycloocta-1,5-dionato acetylacetonato platinum tetrafluoroborate

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Abstract. Crystals of cycloocta-1,5-dionato acetylacetonato platinum tetrafluoroborate are orthorhombic and the space group is $Pca2_1$. The structure was solved by the heavy atom method and refined by full-matrix least-squares. The coordination of platinum is square-planar; the metal is coordinated to the π -orbitals of the double bonds of the cycloocta-1,5-diene ring and the oxygen functions of the planar acetylacetonone ligand. The cycloocta-1,5-diene occurs as a tub-shaped ring. The tetrafluoroborate group may be disordered. The molecules are held in space by van der Waals' forces only.

Keywords. Crystal structure; cycloocta-1,5-dienyl platinum; organometallic compound.

1. Introduction

Structural studies have been carried out extensively on organometallic compounds due to their role as catalysts and the growing interest in understanding metal-carbon bonding. Though a few cycloocta-1,5-diene (hereafterwards referred to as COD) complexes have been studied, no anionic complex of this type has so far been investigated, and the present study was aimed at such a study. The compound was supplied by Dr D A White of Monsanto Company, St. Louis, Missouri, U.S.A. A preliminary account of this work has already been published (Venkatasubramanian 1982), and the present communication gives details of this study.

2. Experimental

The compound crystallizes as colourless needles from acetone/alcohol mixtures. Approximate cell dimensions, obtained by photographic methods, were accurately redetermined on an automated diffractometer using a least-squares fit of arbitrarily chosen higher order reflections. The density was measured by flotation method using benzene-iodoform solutions.

The cell data are $a = 26.270$ (2), $b = 7.851$ (2), $c = 7.341$ (1) Å, $Z = 4$, space group: $Pca2_1$ (supported by successful structure solution and refinement). $D_{\text{mea}} = 2.08 \text{ g cm}^{-3}$, $D_{\text{cal}} = 2.12 \text{ g cm}^{-3}$.

A crystal ($0.09 \times 0.14 \times 0.14$ mm) was used to collect intensity data using a Siemens automated three-circle diffractometer. Of the 1565 reflections measured in the copper sphere ($2\theta_{\text{max}} = 120^\circ$), 282 had $I \leq 2\sigma(I)$ and were considered unobserved. The rest of the data were placed on a common relative scale by a periodically measured reflection and corrected for Lorentz and polarization factors. Because of the small size of the

crystal ($t = 1.61$) and the nearly cylindrical shape, no absorption corrections were considered necessary. It was felt that the absorption effects may reflect only the thermal parameters and may not very much affect the final atomic positions of the non-hydrogen atoms.

3. Determination and refinement of the structure

The extinction conditions $0kl$, l -odd; $h0l$, h -odd and $00l$, l -odd were consistent with the space groups $Pca2_1$ and $Pcam$. The Patterson map showed that the space group was probably $Pca2_1$. The heavy atom positions, determined from the three-dimensional unsharpened Patterson, were used to phase an initial electron density map, which clearly revealed the rest of the molecule. Isotropic refinement of the positions led to convergence at an R of 0.107. Inspection of the model showed that the z -coordinate of one of the oxygens has to be reversed. Four cycles of full-matrix isotropic refinement, omitting the tetrafluoroborate moiety, were carried out with the new model and R converged to 0.076; a difference map was now constructed.

During the refinement, the z -coordinates of the atoms C_1 and C_5 of the COB ring and C_{12} of the acetylacetonate ligand (hereafter referred to as $Acac$) oscillated around 0.5, while all the other atoms converged properly.

The coordinates of the atoms belonging to the tetrafluoroborate ion were located from the difference map. A mixed-mode refinement, with tetrafluoroborate ion in isotropic mode and all the other non-hydrogens in the anisotropic mode, resulted in convergence and an R of 0.067 after 3 cycles. The structure factor list showed that 5 of the intense low-order reflections suffered from extinction. These reflections were, therefore, removed from the data deck and refinement continued with 4 cycles of anisotropic ORFLS. R converged to 0.036.

The bond length and bond angle calculation at this stage showed that C_1 , C_5 and C_{12} were slightly misplaced from their true positions. It was difficult to refine these atomic coordinates by least-squares because whenever an attempt was made, it had a tendency to put them slightly out of position. It was therefore decided to accept the positions for these atoms as derived from the difference map and to vary the thermal parameters only. These coordinates gave rise to acceptable molecular geometry. Three cycles of anisotropic refinement reduced R to 0.043 and the shifts in coordinates were less than one-third of the standard deviations. It was decided to introduce a weighting scheme of Hughes' type, but an analysis of the data showed that the unit-weighting scheme could not be improved upon. An inspection of the difference map showed that the excursions of the density in the F map were random and hence the hydrogens could not be located. It was found that, at this stage, there were 22 reflections for which the structure factor agreement was not good. A remeasurement of these reflections did not alter their intensity estimates. An attempt to correct for dispersion effect increased the R value for both the original and mirror-image structures, even with the application of the effective scattering factor, f_e , where $f_e = [(f_0 - f')^2 + (f'')^2]^{1/2}$. The failure to reduce R even with the allowance of effective scattering factor may be because of the omission of absorption corrections. It was decided to terminate the refinement at this stage.

The scattering factors for platinum, oxygen, carbon and oxygen were taken from International Tables (1962). The final positional parameters of the non-hydrogen atoms along with their estimated standard deviations are given in table 1. Since full

Table 1. Final atomic coordinates.

Atom	x	y	z
Pt	0.3605 (0)	0.1760 (1)	0.5000 (0)
O ₁	0.3327 (5)	-0.0595 (17)	0.6007 (19)
O ₂	0.2924 (4)	0.2761 (15)	0.4449 (16)
C ₁ *	0.4356	0.0510	0.5000
C ₂	0.4263 (9)	0.1230 (38)	0.6585 (39)
C ₃	0.4431 (8)	0.3270 (42)	0.7368 (41)
C ₄	0.4410 (10)	0.4673 (33)	0.6027 (37)
C ₅ ‡	0.3957	0.4413	0.5000
C ₆	0.3904 (7)	0.3768 (28)	0.3326 (30)
C ₇	0.4363 (11)	0.2985 (23)	0.2561 (25)
C ₈	0.4652 (9)	0.1522 (42)	0.3472 (41)
C ₉	0.2875 (7)	-0.0934 (24)	0.6073 (27)
C ₁₀	0.2757 (8)	-0.2806 (28)	0.6888 (39)
C ₁₁	0.2462 (6)	0.0174 (23)	0.5605 (24)
C ₁₂ *	0.2502	0.1870	0.4659
C ₁₃	0.2038 (6)	0.2955 (29)	0.4326 (29)
B	0.3917 (11)	-0.2313 (50)	0.9206 (48)
F ₁	0.3864 (7)	0.0672 (22)	1.0219 (68)
F ₂	0.3685 (19)	-0.3530 (45)	0.9770 (81)
F ₃	0.4295 (7)	-0.2645 (29)	0.8419 (43)
F ₄	0.3547 (10)	-0.2177 (57)	0.7840 (62)

* denotes atoms held fixed in the final stages of refinement; values in parenthesis denotes standard deviation.

matrix methods are used in the refinement, the standard deviations quoted are only slight underestimates. A list of anisotropic thermal parameters as well as observed and calculated structure factors can be obtained from the author on request.

4. Discussion

4.1 Results

The bond lengths and bond angles, along with their estimated standard deviations and those of the dihedral angles are listed in table 2. Tables of mean planes and short contacts in the structure can also be obtained from the author.

The structure analysis shows that the platinum is square-planar and is virtually coplanar with the best plane through the oxygens of the Acac ligand and the mid-points of the double bonds of the COD ring. The COD ring occurs in the usual distorted tub conformation. The BF₄ ion is somewhat disordered.

4.2 The coordination of platinum

The coordination of platinum is a slightly distorted square-plane; the metal is coordinated to the two oxygens of the planar Acac ligand (2.016 Å, 2.040 Å) and to the

Table 2. Bond lengths (Å), bond angles and dihedral angles (degree) (ESDs in parenthesis).

Pt-O ₁	2.040 (13)	Pt-O ₂	2.016 (11)	Pt-C ₁	2.198 (1)	Pt-C ₂	2.183 (27)
Pt-C ₅	2.127 (1)	Pt-C ₆	2.129 (21)	Pt-C ₁₄	2.080	Pt-C ₁₅	2.027
C ₁ -C ₂	1.354 (30)	C ₂ -C ₃	1.531 (42)	C ₃ -C ₄	1.578 (41)	C ₄ -C ₅	1.570 (28)
C ₅ -C ₆	1.421 (29)	C ₆ -C ₇	1.466 (37)	C ₇ -C ₈	1.526 (41)	C ₈ -C ₁	1.616 (30)
C ₉ -C ₁₀	1.548 (29)	C ₉ -C ₁₁	1.417 (26)	C ₁₁ -C ₁₂	1.433 (17)	C ₁₂ -C ₁₃	1.498 (10)
C ₉ -O ₁	1.229 (22)	C ₁₂ -O ₂	1.312 (11)	B-F ₁	1.478 (48)	B-F ₂	1.175 (56)
B-F ₃	1.204 (40)	B-F ₄	1.458 (53)				
O ₁ PtO ₂	95.8 (5)	O ₁ PtC ₁	88.6 (3)	O ₁ PtC ₂	85.3 (8)	O ₁ PtC ₅	157.1 (4)
O ₁ PtC ₆	164.1 (7)	O ₂ PtC ₁	167.3 (3)	O ₂ PtC ₂	156.1 (5)	O ₂ PtC ₅	93.5 (3)
O ₂ PtC ₆	87.1 (6)	O ₁ PtC ₁₅	174.3	O ₂ PtC ₁₄	174.4	O ₁ PtC ₁₄	86.9
O ₂ PtC ₁₅	90.3	C ₁₄ PtC ₁₅	88.8	C ₁ C ₂ C ₃	128.9 (18)	C ₂ C ₃ C ₄	110.6 (23)
C ₃ C ₄ C ₅	109.5 (18)	C ₄ C ₅ C ₆	130.0 (13)	C ₅ C ₆ C ₇	110.1 (28)	C ₆ C ₇ C ₈	128.8 (33)
C ₇ C ₈ C ₁	119.7 (29)	C ₈ C ₁ C ₂	125.7 (17)	O ₁ C ₉ C ₁₀	113.3 (17)	O ₁ C ₉ C ₁₁	129.3 (17)
C ₁₀ C ₉ C ₁₁	117.5 (16)	C ₉ C ₁₁ C ₁₂	124.5 (15)	C ₁₁ C ₁₂ O ₂	123.7 (9)	C ₁₃ C ₁₂ O ₂	114.9 (9)
C ₁₁ C ₁₂ C ₁₃	119.1 (11)	PtO ₁ C ₉	122.9 (11)	PtO ₂ C ₁₂	124.5 (7)	F ₁ BF ₂	112.7 (39)
F ₁ BF ₃	121.7 (29)	F ₁ BF ₄	105.9 (31)	F ₂ BF ₃	118.6 (39)	F ₂ BF ₄	88.6 (38)
F ₃ BF ₄	101.5 (33)						
C ₁ (C ₂ C ₃)C ₄	38.9			C ₂ (C ₃ C ₄)C ₅	-39.7	C ₃ (C ₄ C ₅)C ₆	75.4
C ₄ (C ₅ C ₆)C ₇	-11.7			C ₅ (C ₆ C ₇)C ₈	45.4	C ₆ (C ₇ C ₈)C ₁	-23.6
C ₇ (C ₈ C ₁)C ₂	77.3			C ₈ (C ₁ C ₂)C ₃	3.6		

π -orbitals of the double bonds in COD (2.027 Å, 2.080 Å). Literature values for Pt–O distances vary from 1.968 Å (Mason *et al* 1969) to 2.25 Å (Leyden and Truter 1965) and for Pt–C bonds, the range is 1.97 Å (Roper and MacDonald 1973) to 2.39 Å (Cheung *et al* 1971). Our values of Pt–C vary from 2.127 to 2.198 Å. These observations show that Pt–oxygen and Pt–olefin bonding are relatively strong.

Views of the molecule projected on to (a) the plane perpendicular to PtO₁O₂ through Pt $-\frac{1}{2}(O_1 + O_2)$ and (b) the plane perpendicular to Pt $-\frac{1}{2}(O_1 + O_2)$ through the plane perpendicular to PtO₁O₂ are shown in figures 1 and 2 respectively. Both the midpoints of the double bonds, denoted as C₁₄ and C₁₅ lie on the same side of the PtO₁O₂ plane. As a result, the plane PtC₁₄C₁₅ lies at an angle of 6.4° to the plane containing platinum and oxygen. This may be due to packing forces and/or may represent dis-symmetry in the binding of platinum with the two ends of the double bonds.

4.3 Cycloocta-1,5-diene ring

The cycloocta-1,5-diene ring in this structure adapts a slightly distorted tub conformation, which is the usual form for this ring in free COD and its derivatives (Hedberg and Hedberg 1962; Dierks and Dietrich 1965; Churchill and Bezman 1972; van der Hinde and Baird 1963; Glick and Dahl 1965; Porta *et al* 1971; Koda *et al* 1971; Churchill and Bezman 1975; Goetzer and Gafner 1970; Ibers and Snider 1962; Jecny and Huml 1974). A chair shaped COD ring is, however, found to occur in the structure of *bis* (iron tetracarbonyl) COD (Kruger 1970) where the conformation is attributed to the inability of a single bulky iron tetracarbonyl group to bridge the gap in a tub-shaped ring.

The distorted tub form of COD is the only form that allows both the double bonds of the COD ring to be π -bonded to a single metal atom and introduces skewing in the ring.

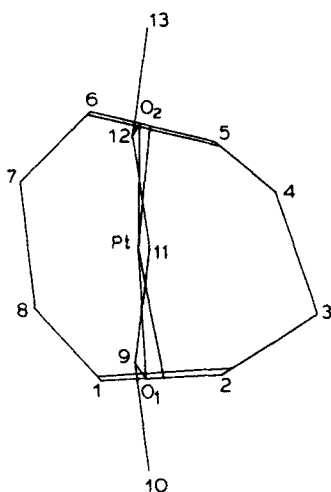


Figure 1. View of the molecule projected on to the plane perpendicular to PtO_1O_2 through $\text{Pt} - \frac{1}{2}(\text{O}_1 + \text{O}_2)$.

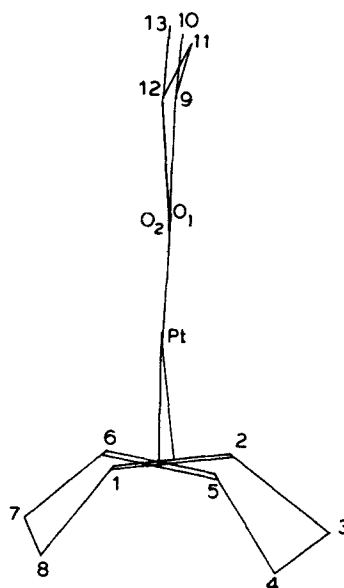


Figure 2. View of the molecule projected on to the plane perpendicular to $\text{Pt} - \frac{1}{2}(\text{O}_1 + \text{O}_2)$ through the plane perpendicular to PtO_1O_2 .

The extent to which this skewing can reduce Pitzer strain and non-bonded interactions in the ring is evidently limited and is possibly susceptible to packing forces, whereas a chair ring is free at least of Pitzer strain. Dunitz (1968) has suggested that tubs may nevertheless be more common than chairs because some attractive interaction may occur between the highly polarizable double bonds, which lie only at 3 Å apart (separation between midpoints in our structure = 2.88 Å).

The skewing makes the double bond no longer parallel, a similar situation exists for the bonds $\text{C}_3\text{--C}_4$ and $\text{C}_7\text{--C}_8$. The dihedral angle between the planes $\text{C}_3\text{C}_4\text{C}_8$ and $\text{C}_4\text{C}_7\text{C}_8$ is 33.7° and that between $\text{C}_2\text{C}_3\text{C}_6$ and $\text{C}_1\text{C}_2\text{C}_6$ is only 14.3° , showing thereby that skewing is more marked for $\text{C}(sp^3)\text{--C}(sp^3)$ bonds than for double bonds. Measure of this skewing can be seen by computing the inter-molecular distances, $\text{C}_3 \dots \text{C}_7$ (3.54 Å) and $\text{C}_4 \dots \text{C}_8$ (3.13 Å). (cf 3.26 Å for an ideal tub) and $\text{C}_1 \dots \text{C}_5$ (3.06 Å) and $\text{C}_2 \dots \text{C}_6$ (3.29 Å) (cf 2.88 Å for an ideal tub). The model shows that this distortion from $\text{mm}2$ symmetry avoids a complete eclipsing of both $\text{C}_3\text{--C}_4$ and $\text{C}_7\text{--C}_8$ bonds. The torsion angles $\text{C}_1(\text{C}_8\text{C}_7)\text{C}_6$ and $\text{C}_2(\text{C}_3\text{C}_4)\text{C}_5$ are 23.5° and 35.7° respectively showing that the skewing is not symmetrical and the COD ring does not have the non-crystallographic C_2 symmetry. The observed asymmetry may be partly due to inaccuracies in the location of atoms C_1 and C_5 , but it is also expected to be due to packing forces.

The angle between the mean molecular planes containing the olefinic bonds is 70.3° , a normal value. The torsion angles around these bonds are 3.6° ($\text{C}_8(\text{C}_1\text{C}_2)\text{C}_3$) and 11.7° ($\text{C}_7(\text{C}_6\text{C}_5)\text{C}_4$) respectively.

One of the characteristic features of all the known COD rings complexed to the metals

is the lengthening of the olefinic bonds to 1.40 Å (*cf* 1.34 Å in free COD), a phenomenon commonly found for all metal-olefin complexes. In our case, the lengths C₁–C₂ (1.35 Å) and C₅–C₆ (1.42 Å). The difference is barely significant for the first bond and this may be due to difficulties in locating C₁.

4.4 Acetylacetonate ligand

The bond lengths and bond angles of the Acac ligand agree well with similar values reported in literature. The ligand is virtually planar, and maximum deviation occurs for C₁₂ (0.07 Å); this is not significant when one considers the difficulties in the refinement of C₁₂. The C–O lengths are unequal, but this difference again could be partly due to the inability to refine C₁₂. It is noteworthy that the longer of the two Pt–O bonds (2.040 Å) is joined to the shorter of the C–O bonds (1.229 Å), a situation encountered in similar structures.

4.5 The tetrafluoroborate ion

The peaks for the atoms in the BF₄ group were broad and diffused in the difference map, which indicate exceptionally large thermal movements. However, there was no evidence for a disorder in the difference map. The fluorine atoms of the group have high

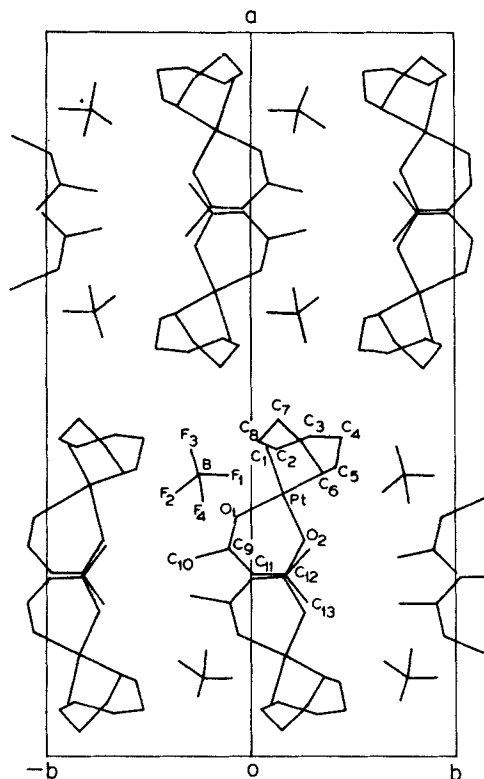


Figure 3. Molecular packing viewed along the *c* axis.

B values and B-F distances range from 1.19 to 1.49 Å. Distortion and disorder of the BF_4 ions are also found in other structures, but they are much more common and severe for ClO_4^- ions.

4.6 Crystal structure and packing

View of the structure projected along the 'c' axis is shown in figure 3. There are no abnormally short intramolecular contacts in the structure and the molecules are held in space by van der Waals' forces only. However, the CoD ring and to a much less extent the Acac ligand are deformable by these forces.

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References

- Cheung K K, Cross R J, Forrest K P, Wardle R and Mercer M 1971 *Chem. Commun.* 875
Churchill M R and Bezman S A 1972 *Inorg. Chem.* **11** 2243
Churchill M R and Bezman S A 1973 *Inorg. Chem.* **12** 531
Dierke H and Dietrich H 1965 *Zeit. fur. Krist.* **122** 1
Dunitz J D 1968 in *Perspectives in structural chemistry* (eds) J D Dunitz and J A Ibers, (New York: Wiley) Vol II
Hedberg L and Hedberg K 1964 *American crystallographers* Bozeman, Montana, U.S.A. Association Meeting
Glick M D and Dahl L F 1965 *J. Organomet. Chem.* **3** 207
Goetzer J and Gafner G 1970 *Acta Crystallogr.* **B26** 1985
Ibers J A and Snider R G 1962 *Acta Crystallogr.* **15** 923
International Tables for Crystallography 1962 (Birmingham, England: Kynoch Press) Vol III
Jecny J and Huml K 1974 *Acta Crystallogr.* **B30** 1105
Koda S, Takanaka A and Watanabe T 1971 *Bull. Chem. Soc. Jpn.* **44** 653
Kruger J 1970 *J. Organomet. Chem.* **22** 697
Leyden J E and Truter M R 1965 *J. Chem. Soc.* 6899
Mackenzie R K, MacNicol D D, Mills H H, Rappiel R A, Wilson F B and Zebkiewicz J A 1972 *J. Chem. Soc., Perkin. Trans. II* 1632
Mason R, Robertson G B and Pauling P 1969 *J. Chem. Soc. A.* 485
Porta P, Powell H M, Mawby G R and Venanzi G N 1971 *J. Chem. Soc. A* 485
Roper G and McDonald W S 1973 *J. Chem. Soc. Dalton. Trans.* 265
Van der Hinde J H Jr and Baird Jr W C 1963 *J. Am. Chem. Soc.* **85** 1009
Venkatasubramanian K 1982 *Indian. J. Phys.* **A56** 200