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Methyl[hydrotris(1-pyrazolyl)borato]tetrafluoroethyleneplatinum

By Nicholas C. Rice and Joel D. Oliver

Department of Chemistry and the Killgore Research Center, West Texas State University, Canyon, Texas 79015, *USA*

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Abstract. $(CH_3)[HB(C_3H_3N_2)_3](C_2F_4)Pt$, $C_{12}H_{13}BF_4N_6Pt$, $M_r = 523·2$, orthorhombic, $P2_12_12_1$ (No. 19), $a = 12·993$ (2), $b = 9·156$ (1), $c = 13·372$ (2) Å, $V = 1590·8$ Å^3, $Z = 4$, $\mu = 173·7$ cm^{-1}, $D_x = 2·18$, $D_m = 2·14$ (1) g cm^{-3}. Full-matrix least-squares refinement of 1801 reflections yielded a final R of 0·037. The structure consists of a trigonal-bipyramidal arrangement of the three pyrazolyl N atoms, the methyl group and the C_2F_4 ligand about the Pt atom. Short intramolecular contacts involving one methyl H atom and two of the F atoms of the C_2F_4 ligand are observed.

Introduction. Suitable crystals of the title compound, MTFPT, were obtained by slow evaporation of a hexane solution. All X-ray measurements were made using a Diano XRD-700 diffractometer equipped with a single-crystal orienter with Cu $K\alpha$ radiation and at ambient room temperature (~22 °C). Least-squares refinement of 37 independent reflections with $K\alpha_1$ (1·54051 Å) and $K\alpha_2$ (1·54433 Å) well resolved yielded the unit-cell dimensions. The data crystal was bounded by $\{011\}$, 0·17 mm apart; $\{001\}$, 0·18 mm apart; $\{0\bar{1}1\}$, 0·21 mm apart and was cut perpendicular to these faces to a height of 0·36 mm. The crystal was mounted with [100] parallel to the φ axis of the goniostat. Intensity-weighted plots of the reciprocal lattice were used to determine the space group. Measurements of ω scans along the principal axes indicated suitable quality for data collection by the stationary-crystal/stationary-counter technique using a balanced Ni–Co filter pair. A total of 1826 unique reflections accessible within the range $3° \leq 2\theta \leq 145°$ were measured.

Analysis of the intensities of the six check reflections indicated a 6% isotropic decay during the 5 d of data collection. The data were broken into five blocks of approximately equal size and the appropriate decay factors were applied. Additional corrections to the net intensities were applied to account for Lorentz and polarization effects, α_1–α_2 splitting (Tulinsky, Worthington & Pignataro, 1959) and absorption as a function of crystal shape (J. M. Williams, Argonne National Laboratory program *MET* 176*X*). Standard deviations in the structure factor amplitudes, $\sigma(|F_o|)$, were calculated on the basis of counting statistics (Oliver, Henslee & Rush, 1976).

The coordinates of the Pt atom, derived from a sharpened, three-dimensional Patterson map, were used to phase an electron density calculation which revealed the remaining nonhydrogen atoms of the structure. The two equatorial pyrazolyl rings were refined as rigid groups with idealized geometry (Oliver & Rice, 1976). Four cycles of full-matrix least-squares refinement of this model employing isotropic temperature factors for all nonhydrogen atoms yielded $R = \sum||F_o| - |F_c||/\sum|F_o| = 0·083$ and $R_w = [\sum(w||F_o| - |F_c||^2)/\sum w(|F_o|)^2]^{1/2} = 0·082$ where $w = \sigma^{-2}(|F_o|)$. The function minimized in the least-squares calculations was $\sum w||F_o| - |F_c||^2$.

After three additional cycles of least-squares refinement employing anisotropic temperature factors for the 14 nongroup, nonhydrogen atoms were completed, a difference electron density map was calculated which revealed the remaining H atoms of the structure. The approximate coordinates for the methyl H atoms were used to calculate idealized coordinates (C—H distance = 1·04 Å and H—C—H angle = 109·5°) for these atoms. An isotropic temperature factor of 5·0 Å^2 was assigned to each methyl H atom and their atomic parameters were not subsequently refined. An additional five cycles of least-squares refinement varying the overall scale factor, the positional and anisotropic thermal parameters of the 14 nongroup, nonhydrogen atoms, the positional and isotropic thermal parameters of the four nongroup H atoms, the six orientational and positional parameters for each of the rigid groups and the isotropic thermal parameters of the nonhydrogen atoms of the rigid-body pyrazolyl rings produced convergence at $R = 0·046$ and $R_w = 0·045$.

At this point the sign of the imaginary component of the anomalous scattering correction of Pt was reversed prior to an additional two cycles of refinement to determine the correct choice of enantiomorph. The values of R and R_w decreased significantly to 0·037 and 0·036, respectively, implying that the appropriate isomer had now been chosen. Thus the atomic parameters and metrical details presented are those of the latter isomer.

A final difference electron density map contained only one large peak with a density −1·0 e Å^{-3} within

1·0 Å of the Pt atom and several smaller peaks with densities 0·25–0·60 e $Å^{-3}$ scattered throughout the unit cell. Atomic parameters are listed in Tables 1 and 2.[*]

Scattering factors for the B, C, F, N and Pt atoms were taken from Cromer & Waber (1965), while those for the H atoms were taken from Stewart, Davidson & Simpson (1965). The anomalous-dispersion correction factors for the Pt atoms were applied (Cromer & Liberman, 1970).

Discussion. Anomalous couplings in the NMR spectra of a series of five-coordinate complexes of methyl[hydrotris(1-pyrazolyl)borato]platinum with various polyfluoroolefin ligands have been interpreted in terms of novel through-space couplings of the F atoms of the olefins to both the axial pyrazolyl 3-H atom and the methyl H atoms (Clark & Manzer, 1973*a*,*b*, 1974). In order to acquire accurate stereochemical information about this type of complex the crystal structure of MTFPT was determined.

A stereoview of the molecule illustrating the atom-numbering scheme is given in Fig. 1. Bond lengths and bond angles are contained in Tables 3 and 4. The geometry of the $CH_3[HB(C_3H_3N_2)_3]Pt$ moiety observed in this work is very similar to that found by Davies & Payne (1974) in $(CH_3)[HB(C_3H_3N_2)_3]Pt(CF_3C{\equiv}CCF_3)$. The crystallographic mirror plane defined by the Pt atom, the methyl C atom and the axial pyrazolyl ring in the hexafluoro-2-butyne complex corresponds to a local mirror plane in MTFPT. As predicted by Clark & Manzer (1973*a*,*b*) the C=C lies in the trigonal plane.

Table 1. *Atomic parameters, with e.s.d.'s in parentheses*

Atomic fractional coordinates for the N, C, F, and B atoms are $\times 10^4$; those for Pt are $\times 10^5$: those for H are $\times 10^3$.

	x	*y*	*z*	*B* ($Å^2$)
Pt	−18451 (4)	−1425 (4)	4500 (3)	
N(1)	−1099 (7)	1274 (10)	−587 (8)	
N(2)	−1533 (7)	2633 (10)	−759 (7)	
C(1)	−1248 (13)	−1992 (16)	−58 (10)	
C(2)	−619 (11)	−1387 (13)	762 (10)	
C(3)	−2673 (10)	−1317 (15)	1486 (11)	
C(4)	−227 (10)	1252 (17)	−1134 (11)	
C(5)	−87 (11)	2560 (22)	−1631 (12)	
C(6)	−897 (12)	3425 (16)	−1354 (11)	
F(1)	−1698 (7)	−3303 (7)	50 (6)	
F(2)	−810 (8)	−2012 (10)	−973 (6)	
F(3)	−538 (8)	−2185 (9)	1597 (6)	
F(4)	331 (6)	−897 (8)	544 (7)	
B	−2546 (10)	3078 (14)	−239 (10)	
H(B)	−279 (6)	423 (8)	−49 (6)	1 (2)
H(4)	19 (7)	48 (10)	−114 (7)	2 (2)
H(5)	35 (10)	261 (14)	−203 (8)	4 (3)
H(6)	−98 (10)	447 (13)	−158 (8)	6 (4)
H(31)	−232	−232	161	5
H(32)	−342	−149	122	5
H(33)	−270	−74	216	5

Table 2. *Group parameters*

A description of these group parameters is provided elsewhere (Eisenberg & Ibers, 1965). Angular coordinates are in radians. The internal coordinate system of a coordinated pyrazolyl ring was as follows: The ring was defined to lie in the *xy* plane with atom N(2) at the origin, the vector N(2)—N(1) was coincident with the positive *x* axis, and the vector from the midpoint of N(1)—N(2) to atom C(4) was parallel to the *y* axis.

Group	x_0	y_0	z_0	φ	θ	ρ
PZ(1)	−0·3229 (5)	0·0552 (7)	−0·0249 (5)	−1·315 (5)	−2·720 (6)	−2·823 (6)
PZ(2)	−0·2058 (6)	0·1774 (6)	0·1324 (5)	3·129 (13)	2·038 (5)	−1·277 (13)

Derived pyrazolyl group C and N atoms*

	x	*y*	*z*	*B* ($Å^2$)
				PZ(1)
N(4)	−3229 (5)	552 (7)	−249 (5)	3·8 (2)
N(3)	−3351 (5)	1965 (6)	−539 (5)	3·4 (2)
C(7)	−4250 (6)	2114 (7)	−1022 (6)	4·4 (3)
C(8)	−4733 (5)	780 (10)	−1053 (6)	5·4 (3)
C(9)	−4069 (6)	−168 (6)	−561 (6)	4·4 (2)
				PZ(2)
N(6)	−2058 (6)	1774 (6)	1324 (5)	3·3 (2)
N(5)	−2350 (6)	3049 (7)	886 (4)	3·2 (2)
C(10)	−2441 (6)	4091 (6)	1584 (6)	4·1 (2)
C(11)	−2206 (6)	3501 (8)	2501 (4)	4·9 (3)
C(12)	−1971 (6)	2049 (8)	2306 (4)	3·9 (2)

Derived pyrazolyl group H atoms*†

	x	*y*	*z*
H(7)	−4544 (9)	3072 (10)	−1327 (9)
H(8)	−5445 (6)	550 (15)	−1379 (10)
H(9)	−4212 (10)	−1271 (6)	−456 (10)
H(10)	−2653 (10)	5173 (7)	1466 (9)
H(11)	−2209 (11)	4044 (12)	3188 (6)
H(12)	−1760 (10)	1297 (11)	2848 (6)

* Positional parameters of the rigid-group atoms are presented $\times 10^4$.

† H atoms were assigned isotropic thermal parameters equal to those of the C atoms to which they are bonded.

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[*] Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33807 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The C_2F_4 ligand is symmetrically bonded to the metal atom, as evidenced by the equality of the Pt—C(1) and the Pt—C(2) bond lengths. As observed in other structures the olefin becomes quite non-planar upon coordination to the metal with the four carbon-bound substituent atoms being folded away from the metal atom. Stalick & Ibers (1970) have defined an angle α to describe the extent of this folding back of the substituents on coordinated olefins. For MTFPT the angle α, defined by the intersection of the normal to the plane defined by the atoms C(1), F(1), and F(2) with that of the plane defined by the atoms C(2), F(3) and F(4), is 77·4°. Similar values for α in C_2F_4 ligands have been observed by Guggenberger & Cramer (1972), 74·3°, and Browning & Penfold (1973), 84°.

The four F atoms are coplanar, the atoms C(1) and C(2) being displaced 0·504 and 0·496 Å from that plane toward Pt. The C=C bond length of the C_2F_4 ligand is marginally longer than its value in other structures (Browning & Penfold, 1973; Evans & Russell, 1971; Green, Howard, Spencer & Stone, 1975*a*,*b*; Hitchcock, McPartlin & Mason, 1969; Guggenberger & Cramer, 1972) which ranges from 1·37 (3) to 1·44 (4) Å. In view of the large e.s.d.'s of these values, the difference is not significant.

One methyl H atom is 2·40 Å from F(1) and 2·31 Å from F(3). These distances are slightly shorter than the sum of their respective van der Waals radii (Pauling, 1960), 2·55 Å, and suggest that, in solution, rotation of the methyl group about the Pt—C(3) bond would bring these atoms into closer proximity and allow for a significant spin–spin interaction among these atoms. The 3-H atom of the axial pyrazolyl ring is 2·64 Å from F(2) and 2·59 Å from F(4).

Table 3. *Bond lengths* (Å) *with their standard deviations in parentheses*

Pt—C(1)	1·984 (14)	C(1)—C(2)	1·48 (2)
Pt—C(2)	2·003 (14)	C(1)—F(1)	1·34 (2)
Pt—C(3)	2·058 (14)	C(1)—F(2)	1·35 (2)
Pt—N(1)	2·133 (10)	C(2)—F(3)	1·34 (2)
Pt—N(4)	2·125 (7)	C(2)—F(4)	1·35 (2)
Pt—N(6)	2·127 (6)	N(1)—N(2)	1·39 (1)
B—N(2)	1·544 (16)	N(1)—C(4)	1·35 (2)
B—N(3)	1·516 (14)	N(2)—C(6)	1·36 (2)
B—N(5)	1·526 (15)	C(4)—C(5)	1·38 (2)
B—H	1·15 (8)	C(5)—C(6)	1·37 (2)

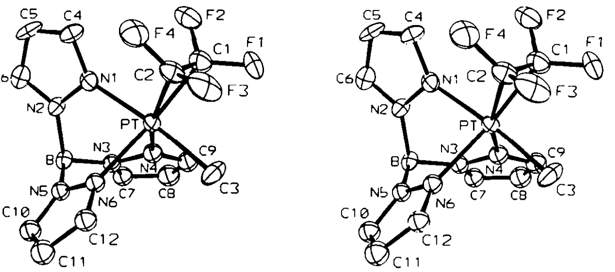

Fig. 1. Stereoview of the molecule, illustrating the atom-numbering scheme. Ellipsoids of 30% probability are shown.

Table 4. *Bond angles* (°) *with their standard deviations in parentheses*

C(1)—Pt—C(2)	43·5 (6)	Pt—C(2)—F(3)	123 (1)
C(1)—Pt—N(1)	96·8 (5)	Pt—C(2)—F(4)	120 (1)
C(1)—Pt—N(4)	115·9 (5)	F(1)—C(1)—F(2)	106 (1)
C(1)—Pt—N(6)	160·7 (5)	F(3)—C(2)—F(4)	107 (1)
C(1)—Pt—C(3)	89·4 (6)	F(1)—C(1)—C(2)	120 (1)
C(2)—Pt—C(3)	88·7 (5)	F(2)—C(1)—C(2)	117 (1)
C(2)—Pt—N(1)	96·9 (5)	F(3)—C(2)—C(1)	117 (1)
C(2)—Pt—N(4)	159·3 (4)	F(4)—C(2)—C(1)	118 (1)
C(2)—Pt—N(6)	117·3 (4)	N(2)—N(1)—C(4)	105 (1)
C(3)—Pt—N(1)	173·6 (5)	N(1)—N(2)—C(6)	109 (1)
C(3)—Pt—N(4)	90·6 (4)	N(1)—C(4)—C(5)	111 (1)
C(3)—Pt—N(6)	89·6 (4)	C(4)—C(5)—C(6)	106 (1)
N(1)—Pt—N(4)	85·2 (3)	C(5)—C(6)—N(2)	108 (1)
N(1)—Pt—N(6)	85·1 (3)	N(1)—N(2)—B	121 (1)
N(4)—Pt—N(6)	83·4 (3)	C(6)—N(2)—B	130 (1)
Pt—N(1)—N(2)	117·9 (7)	N(4)—N(3)—B	119 (1)
Pt—N(1)—C(4)	136·5 (9)	C(7)—N(3)—B	131 (1)
Pt—N(4)—N(3)	120·6 (5)	N(6)—N(5)—B	119 (1)
Pt—N(4)—C(9)	132·7 (5)	C(10)—N(5)—B	131 (1)
Pt—N(6)—N(5)	120·5 (5)	N(2)—B—N(3)	107 (1)
Pt—N(6)—C(12)	133·0 (5)	N(2)—B—N(5)	107 (1)
Pt—C(1)—C(2)	69·0 (7)	N(3)—B—N(5)	111 (1)
Pt—C(2)—C(1)	67·6 (8)	N(2)—B—H	110 (4)
Pt—C(1)—F(1)	124 (1)	N(3)—B—H	110 (4)
Pt—C(1)—F(2)	119 (1)	N(5)—B—H	110 (4)

No intermolecular contact distances shorter than the sum of the respective van der Waals radii of the atoms were observed.

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Barium μ-*N*,*N'*-Ethylenediaminetetraacetato-di-μ-oxo-dioxoditungstate(V) Hydrate

BY S. KHALIL AND B. SHELDRICK

Astbury Department of Biophysics, University of Leeds, Leeds LS2 9JT, England

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Abstract. Ba[$W_2^VO_4$(EDTA)]. 3·5H_2O, $C_{10}H_{12}BaN_2O_{12}W_2$.3·5$H_2O$, orthorhombic, *Ima*2 from the systematic absences *h*0*l*: $l = 2n + 1$, $h = 2n + 1$; *hkl*: $h + k + l = 2n + 1$. a = 19·241 (4), b = 14·852 (2), c = 14·091 (2) Å, Z = 8, F(000) = 3368, V = 4026·8 Å^3, D_c = 3·04 g cm^{-3}, λ(Cu $K\alpha$, Ni-filtered) = 1·5418 Å, μ(linear absorption coefficient) = 349·7 cm^{-1}, R = 0·054. Each asymmetric unit consists of two halves of independent molecules, each lying on the mirror plane. The two molecules differ in orientation; one molecule has both W atoms in the mirror plane with an O atom and its mirror image forming the double bridge, while the second molecule has the bridging O atoms in the mirror plane joining an off-plane W and its mirror image. The W–W distances are 2·557 and 2·542 Å respectively.

Introduction. Mo is an essential component of several redox enzymes, including nitrogenase, nitrate reductase, xanthine oxidase, sulphite oxidase and formate reductase. Recent reports (Johnson, Cohen & Rajagopalan, 1974; Ljungdahl, 1976) indicate that W is present and has a redox function in some enzymes. A substantial increase in the activity of formate dehydrogenase has been observed when W was substituted for Mo in various experiments (Ljungdahl, 1976). A large number of oxo-Mo^V complexes have been reported (Spivak & Dori, 1975*a*) but stronger reductants are generally required to reduce $W^{VI} \rightarrow W^V$ (Soares, 1976) and the structure of an oxo-W^V complex containing a W_2O_4 subunit, which is reported in this paper, appears to be the only well-characterized compound of this type.

The crystals were prepared and supplied by A. B. Soares and A. G. Sykes, Department of Inorganic and Structural Chemistry, University of Leeds, as part of aquation and redox studies on a dimeric W^V complex and the Mo analogue.

Analysis of the crystals showed: calculated for Ba[W_2O_4(EDTA)].2H_2O, W 41·2, C 13·5, N 3·14%, found, W 40·0, C 13·1, N 3·25%. A crystal (0·17 × 0·12 × 0·10 mm) was used to collect 1702 unique reflections on an Enraf–Nonius CAD-4 diffractometer with the ω–2θ scan technique and Cu $K\alpha$ (Ni-filtered) radiation (λ = 1·5418 Å). Orientation and standard-intensity checks were made at fixed intervals. Corrections were made for the Lorentz and polarization effects but no correction was made for absorption.

The space group, *Ima*2, was confirmed from the interatomic vectors on a three-dimensional Patterson synthesis and positions were derived for three heavy atoms, which were assumed to be two W atoms and one Ba atom. These positions were also obtained by direct methods using *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974). Structure factors were calculated and a three-dimensional Fourier synthesis was produced from the calculated phase angles and observed amplitudes. This showed an additional heavy peak, with sufficient electron density to be taken as a Ba atom, and hence all of the first three heavy-atom positions were now identified as W. At this stage none of the light-atom positions could be clearly