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Note

Synthesis and the structure of mixed carboxylatoplatinum(IV) complexes involving one trifluoroacetate ligand

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Abstract

Mono(trifluoroacetato)platinum(IV) complexes of the formula $[Pt^{IV}(dach)L_3(TFAc)]$ (dach = *trans*-(±)-1,2-diaminocyclohexane, TFAc = trifluoroacetate, L = acetate or propionate) could be prepared from the reaction of $[Pt^{IV}(dach)L_3(OH)]$ with trifluoroacetic anhydride in the presence of a base and the crystal structure of compound **4** was determined by X-ray crystallography. In vitro antitumor activity of complex **4** (ED_{50} = 3.1 μM) was found to be much higher than carboplatin (ED_{50} = 10.2 μM).
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Keywords: Platinum(IV); Antitumor drug; Electrophilic substitution

1. Introduction

Platinum(IV) complexes have been extensively studied for the past two decades to improve the toxicity and severe side effects of the platinum(II)-based anticancer drugs [1–3]. Platinum(IV) complexes have shown the possibility as an orally active anticancer drug, which may be greatly improved both in toxicity and the acquired drug resistance caused by cisplatin or carboplatin [4–7]. The lipophilicity of the Pt(IV) complexes has been regarded as one of the most important factors in structure–activity relationship [8,9]. We reported previously a new series of platinum(IV) complexes of the formula $[Pt^{IV}(dach)L_3(OH)]$ (dach = *trans*-(±)-1,2-diaminocyclohexane, L = acetate or propionate) obtained by selective nucleophilic substitution of tetrahydroxoplatinum(IV) complexes by carboxylic acids with appropriate pK_a values (pK_a = 4–5) [10]. These Pt(IV) complexes were further derivatized by the well-known electrophilic substitution of the remaining hydroxo ligand with different carboxylic anhydrides to tune further their lipophilicity and water solubility [11]. This synthetic method afforded various mixed carboxylatoplatinum(IV) complexes, $[Pt^{IV}(dach)L_3L']$ (L′ = acetate, propionate, valerate, and pivalate), but resulted in unexpected products involving two trifluoroacetate (TFAc) ligands instead of one TFAc of the formula $[Pt^{IV}(dach)L_2(TFAc)_2]$, when the reaction was carried out with trifluoroacetic anhydride. Here, we report a new method to obtain pure complexes involving only one TFAc ligand of the formula $[Pt^{IV}(dach)L_3(TFAc)]$, and the crystal structure and in vitro antitumor activity of the complexes will be briefly discussed.

2. Experimental

2.1. Materials and measurements

Potassium tetrachloroplatinate(II) purchased from Kojima, *trans*-(±)-1,2-diaminocyclohexane (dach),

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acetic anhydride (Ac_2O), propionic anhydride (Pr_2O) and trifluoroacetic anhydride ($TFAc_2O$) from Aldrich were used without further purification. Elemental analyses were carried out in the Organic Chemistry Research Center of Sogang University. IR spectra were recorded as KBr pellets on a Perkin Elmer 16FPC FT-IR spectrophotometer. ^{1}H NMR spectra were measured with Bruker 250 MHz spectrometer. ESI-Mass measurements were performed by HP5989A equipped with HP59987A as an electron-spray source. A mixture of methanol and water (80:20) containing 1% formic acid was used as solvent for the mass analysis. The starting platinum(IV) complexes, [Pt^{IV}(dach)$(OAc)_3$(OH)] (**1**) and [Pt^{IV}(dach)$(OPr)_3$(OH)] (**2**) were prepared according to the previous method as depicted in Scheme 1 [10].

2.2. Synthesis

Trifluoroacetic anhydride (0.5 mmol) and triethylamine (0.75 mmol) were added to a solution of tris(carboxylato)monohydroxoplatinum(IV) complexes (0.2 mmol) in CH_2Cl_2(4 ml). After the reaction mixture was stirred for 4 h at room temperature, the solution was evaporated to dryness. The crude solid was dissolved in methanol and precipitated with ether, and purified by column chromatography (silica gel, CH_2Cl_2: methanol = 10:1, v/v). The crystals suitable for X-ray crystallography were obtained by slow evaporation of the methanolic solution.

2.2.1. [Pt^{IV}(dach)$(OAc)_3$(OTFAc)] (**3**)

Yield, 59%. *Anal.* Calc. for $C_{14}H_{23}F_3N_2O_8Pt$: C, 28.05; H, 3.87; N, 4.67. Found: C, 28.03; H, 3.61; N, 4.68%. ^{1}H NMR (D_2O): 2.72 (m, 2H, NCH), 2.25 (m, 2H, CH_2), 2.07 (s, 6H, eq-CH_3CO_2), 2.04 (s, 3H, ax-CH_3CO_2), 1.55 (m, 4H, CH_2), 1.19 (m, 2H, CH_2). IR (KBr, cm^{-1}): ν_{max} 3052, 2968, 1721, 1642, 1360, 1306, 1192. MS (ESI): *m/z* 598.8 [M^+].

2.2.2. [Pt^{IV}(dach)$(OPr)_3$(OTFAc)] (**4**)

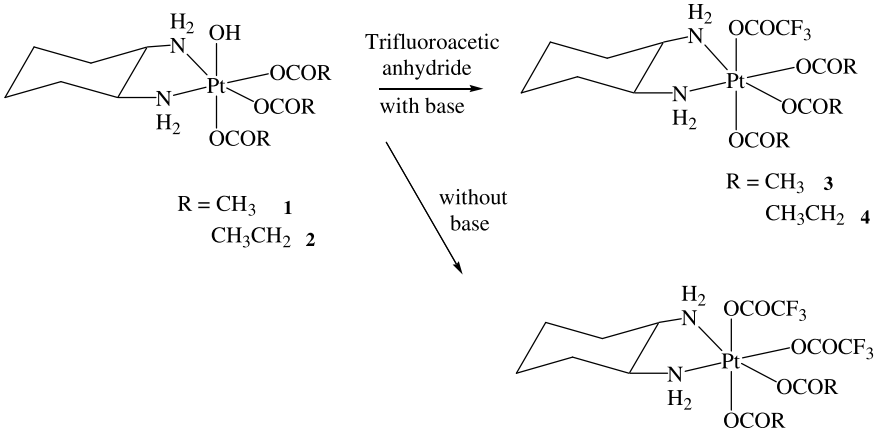
Yield, 68%. *Anal.* Calc. for $C_{17}H_{29}F_3N_2O_8Pt$: C, 31.83; H, 4.56; N, 4.37. Found: C, 31.83; H, 4.56; N, 4.37; Found: C, 31.84; H, 4.59; N, 4.34%. ^{1}H NMR (D_2O, δ): 2.80 (m, 2H, NCH), 2.32 (m, 8H, OPr-CH_2 and CH_2), 1.61 (m, 4H, CH_2), 1.23 (m, 2H, CH_2), 1.03 (q, 9H, OPr-CH_3). IR (KBr, cm^{-1}): ν_{max}2984, 2942, 1722, 1632, 1462, 1350, 1210. MS (ESI): *m/z* 664.0 [$M + Na^+$].

2.3. Assay of in vitro cytotoxicity

The new present complexes **3** and **4** were subjected to bioassay according to the previous method [12].

2.4. X-ray structure determination

All the X-ray data were collected on an Enraf-Nonius CAD4 automated diffractometer equipped with a Mo X-ray tube and a graphite crystal monochromator. The orientation matrix and unit cell dimensions were determined from 25 machine centered reflections in the 2θ range of 15–25°. The variation of intensities was monitored by repeated check of intensities of three reflections every 1 h during the data collection period. Absorption corrections were applied by empirical psi scan on three reflection planes with a χ value of near 90°. A direct or Patterson method (SHELXS-97) [13] was employed to locate the platinum atom. Subsequent cycles of Fourier map and least square refinements located other atoms (SHELXL-97) [14]. All the nonhydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation using a riding model. All the calculations were carried out using VAX and PC computers. The crystallographic data for complex **4** are listed in Table 1.



Scheme 1. The synthetic route to Pt(IV) complexes of mixed carboxylates.

Table 1
Crystallographic data for $[Pt^{IV}(dach)(OPr)_3(TFAc)]$

Empirical formula	$C_{17}H_{29}F_3N_2O_8Pt$
Formula weight	641.51
Crystal system	monoclinic
Space group	$P2_1/c$ (No. 14)
Unit cell dimensions	
a (Å)	10.891(2)
b (Å)	17.343(4)
c (Å)	12.143(4)
α (°)	90
β (°)	95.33(2)
γ (°)	90
Volume (Å^3)	2283.5(9)
Z	4
$D_{calc.}$ (mg/m^3)	1.866
Absorption coefficient (mm^{-1})	6.213
$F(000)$	1256
Crystal size (mm)	$0.12 \times 0.20 \times 0.22$
θ range for data collection	1.68–25.16°
Reflections collected/unique	4313/4080 [R_{int} = 0.0582]
Completeness to θ = 25.16	99.3%
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	4080/10/280
Goodness-of-fit on F^2	1.055
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0662, wR_2 = 0.1645
R indices (all data)	R_1 = 0.1522, wR_2 = 0.2015
Largest difference peak and hole (e Å^{-3})	1.526 and −1.661

$R_1 = \sum ||F_o| - |F_c|| / \sum |F_0|$, $wR_2 = \{\sum (F_o^2 - F_c^2)^2 / \sum wF_o^4\}^{1/2}$, where $w = 1/\{\sum^2 F_o^2 + (0.0197P)^2 + 0.00P\}$, and where $P = \{\max(F_o^2, 0) + 2F_c^2\}/3$.

3. Results and discussion

The reaction of the tetrahydroxoplatinum(IV) complex with acetic or propionic acid afforded tricarboxylatomonohydroxoplatinum(IV) complexes by proton mediated nucleophilic substitution as reported previously [10]. The remaining hydroxo ligand was further derivatized by electrophilic substitution with various carboxylic anhydrides. Generally, the electrophilic substitution reaction of the axial hydroxo ligand of (diamine)platinum(IV) complexes was easily carried out without side reaction [15], particularly in the case of the complexes bearing the chelating equatorial dicarboxylate ligand. The alternative electrophilic substitution reaction with acyl chloride needs the presence of a base, such as triethylamine or pyridine, to remove hydrochloric acid formed [16]. When $[Pt^{IV}(dach)L_3(OH)]$ was reacted with acetic or propionic anhydride, the reaction proceeded cleanly, leading to $[Pt^{IV}(dach)L_3L']$ (L′ = acetate, propionate) because the generated acid is weak acid (pK_a = 4–5) and their conjugate base is not so strong to replace the carboxylate ligand coordinated to the platinum(IV) atom [17]. However, in the reaction with trifluoroacetic anhydride, bis(trifluoroacetato)Pt(IV) complexes of the formula $[Pt^{IV}(dach)L_2(TFAc)_2]$ were obtained probably because the trifluoroacyl group (CF_3CO^+) was presumed to attack the hydroxo ligand, forming a trifluoroacetate ligand, but the strong trifluoroacetic acid resultant from the anhydride was subjected to nucleophilic substitution to replace one of the three carboxylate ligands coordinated to the platinum(IV) atom. In other words, the strong trifluoroacetic acid seems to weaken and labilize the Pt–O bond of other carboxylate ligands so that the nucleophilic substitution by the trifluoroacetate ion may easily take place. Therefore, the elimination of the resultant trifluoroacetic acid may be necessary to avoid the formation of the unexpected product substituted with the second trifluoroacetate. In fact, the addition of an equivalent amount of a base afforded the pure reaction product involving only one trifluoroacetate and three intact carboxylate ligands.

The electrophilic substitution of the axial hydroxo ligand by trifluoroacetic anhydride did not change considerably the ^{1}H NMR spectra of the complexes compared with that of the starting $[Pt^{IV}(dach)L_3(OH)]$. The ^{1}H NMR spectra taken in D_2O showed characteristic multiplet pattern of the two protons near the amine group of dach, probably due to the asymmetrically substituted trifluoroacetate ligand at axial position. Three acetate ligands in equatorial and axial position gave the distinct signals at 2.08 and 2.05 ppm, respectively, although the difference of the chemical shift of propionate in $[Pt^{IV}(dach)(OPr)_3(OH)]$ is less evident.

The ORTEP drawing of complex **4** is drawn in Fig. 1 and its relevant distances and angles is listed in Table 2. The crystal structure of complex **4** is almost the same as that found in other platinum(IV) complexes reported previously [17]. All compounds derived from tetrahydroxoplatinum(IV) complexes exhibited similar structural characteristics. The local geometry around the

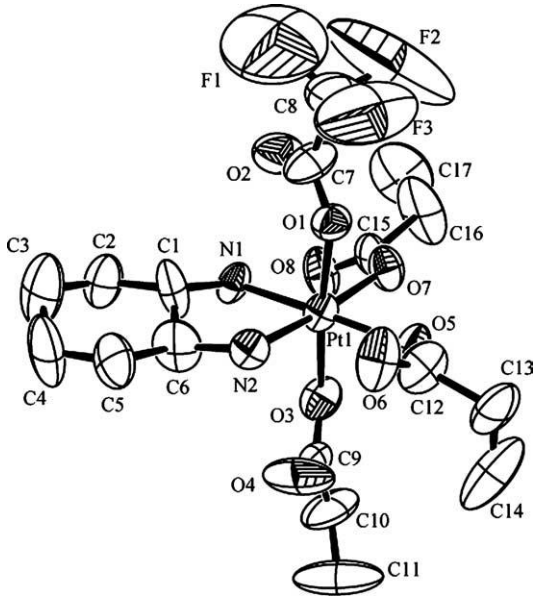


Fig. 1. ORTEP drawing with an atomic labeling scheme for $[Pt^{IV}(dach)(OPr)_3(TFAc)]$.

Table 2
Selected bond lengths (Å), intramolecular hydrogen bond length (Å) and angles (°) for $[Pt^{IV}(dach)(OPr)_3(TFAc)]$

Pt(1)–O(7)	2.004(14)	Pt(1)–O(5)	2.006(13)
Pt(1)–O(3)	2.008(14)	Pt(1)–N(1)	2.016(14)
Pt(1)–O(1)	2.033(13)	Pt(1)–N(2)	2.056(16)
O(1)–C(7)	1.29(2)	C(8)–F(1)	1.482(13)
N(1)–O(2)	2.701	N(2)–O(6)	2.788
N(2)–O(4)	2.724	N(1)–O(8)	2.738
O(7)–Pt(1)–O(5)	80.7(6)	O(7)–Pt(1)–O(3)	90.8(6)
O(7)–Pt(1)–N(1)	97.4(6)	O(5)–Pt(1)–O(1)	87.7(6)
O(3)–Pt(1)–O(1)	174.4(6)	N(1)–Pt(1)–O(1)	95.7(7)
O(5)–Pt(1)–N(2)	100.0(6)	N(1)–Pt(1)–N(2)	82.4(6)

Table 3
In vitro antitumor activity of platinum(IV) complexes of mixed carboxylates

Complex	Cytotoxicity
	ED_{50} (μM)
$[Pt^{IV}(dach)(OAc)_3(OH)]^{10}$ (**1**)	>40
$[Pt^{IV}(dach)(OPr)_3(OH)]^{10}$ (**2**)	27.6
$[Pt^{IV}(dach)(OAc)_2(OTFAc)_2]^{10}$	7.2
$[Pt^{IV}(dach)(OPr)_2(OTFAc)_2]^{10}$	1.3
$[Pt^{IV}(dach)(OAc)_3(OTFAc)]$(**3**)	9.5
$[Pt^{IV}(dach)(OPr)_3(OTFAc)]$(**4**)	3.1
JM216	1.2
Carboplatin	10.2

platinum(IV) is a distorted octahedral arrangement with three propionate and one trifluoroacetate groups (O(5)–Pt–O(7) = 80.7° and O(1)–Pt–O(3) = 174.4(6)°). The four carboxylate ligands occupy their positions with intramolecular hydrogen bonds by the carbonyl groups with two amine groups (N(1)–O(2) = 2.701, N(2)–O(6) = 2.788, N(2)–O(4) = 2.724 and N(1)–O(8) = 2.738 Å).

The in vitro antitumor activity of the present Pt(IV) complexes are listed along with reference complexes in Table 3. The present complexes were designed to have the optimal range of partition coefficient (log*P*) between those of $[Pt^{IV}(dach)(OPr)_4]$ (log*P* = 0.18) and of $[Pt^{IV}(dach)(OBu)_4]$ (OBu = butanoyl, log*P* = 1.54) [8,11]. The in vitro cytotoxicity against the murine leukemia L1210 cell line shows that the present complexes exhibit higher activity than carboplatin and comparable activity to JM216.

In conclusion, we have prepared mono(trifluoroacetato)platinum(IV) complexes in the presence of a base, and the structure was confirmed by various physicochemical analyses including X-ray crystallography. Their in vitro antitumor activity was found to be higher than carboplatin and their in vivo activity is to be assayed. The methodology to obtain a variety of the platinum(IV) complexes with a wide range of lipophilicity or water solubility was further extended and conformed to the previously proposed mechanism involving proton assisted nucleophilic substitution of the platinum(IV) complexes.

Acknowledgement

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Appendix A. Supporting information

Tables of crystallographic details, non-hydrogen positional parameters, bond distances and angles, anisotropic thermal parameters of non-hydrogen atoms, and hydrogen coordinates and isotropic thermal parameters for complex **4** (8 pages). Ordering information is given on any current masthead page. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2004.07.037.

References

[1] B.K. Keppler, Metal Complexes in Cancer Therapy, VCH, Weinheim, 1993.
[2] D.D. Von Hoff, R. Schilsky, C.M. Reichert, R.L. Reddick, M. Rozencweig, R.C. Young, F.M. Muggia, Cancer Treat. Rep. 63 (1979) 1527.
[3] W.B. Pratt, R.W. Ruddon, W.D. Ensminger, J. Maybaum, The Anticancer Drugs, second ed., Oxford University Press, New York, 1994, pp. 133–168.
[4] Z.H. Siddik, G.S. Hagopian, G. Thai, Tomisaki, S. Toyomasu, T.A.R. Khokhar, J. Inor. Chem. 77 (1999) 65.
[5] L. Cai, K. Lim, S. Ren, R.S. Cadena, W.T. Beck, J. Med. Chem. 44 (2001) 2959.
[6] M.D. Hall, T.W. Hambley, Coord. Chem. Rev. 232 (2002) 49.
[7] C.F.J. Barnard, J.F. Vollano, P.A. Chaloner, S.Z. Dewa, Inorg. Chem. 35 (1996) 3280.
[8] Y.A. Lee, S.S. Lee, K.M. Kim, C.O. Lee, Y.S. Sohn, J. Med. Chem. 43 (7) (2000) 1409.
[9] R. Kizu, T. Nakanishi, M. Miyazaki, T. Tashiro, M. Noji, A. Matsuzawa, M. Eriguchi, Y. Takeda, N. Akiyama, Y. Kidani, Anti-Cancer Drugs 7 (1996) 248.
[10] R. Song, K.M. Kim, Y.S. Sohn, Inorg. Chimica. Acta 338 (2002).
[11] R. Song, S.Y. Park, Y.–S. Kim, Y.M. Kim, S.J. Kim, B.T. Ahn, Y.S. Sohn, J. Inorg. Biochem. 96 (2003) 339.
[12] Y.S. Sohn, H. Baek, Y.H. Cho, Y.A. Lee, O.S. Jung, C.O. Lee, Y.S. Kim, Int. J. Pharm. 153 (1997) 79.
[13] G.M. Sheldrick, SHELXS-97: A Program for Structure Determination, University of Göttingen, Germany, 1997.
[14] G.M. Sheldrick, SHELXL-97: A Program for Structure Refinement, University of Göttingen, Germany, 1997.
[15] S. Shamsuddin, C.C. Santillan, J.L. Stark, K.H. Whitmire, Z.H. Siddik, A.R. Khokhar, J. Inorg. Biochem. 71 (1998) 29.
[16] M. Galanski, B.K. Keppler, Inorg. Chim. Acta 265 (1997) 271.
[17] K.M. Kim, Y.A. Lee, S.S. Lee, Y.S. Sohn, Inorg. Chim. Acta 292 (1999) 52.

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Pt(1) O(3) 2.008(14)
Pt(1) N(1) 2.016(14)
Pt(1) O(1) 2.033(13)
Pt(1) N(2) 2.056(16)
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N(2) C(6) 1.52(3)
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O(2) C(7) 1.23(3)
O(3) C(9) 1.30(2)
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O(5) C(12) 1.28(3)
O(6) C(12) 1.24(3)
O(7) C(15) 1.25(2)
O(8) C(15) 1.22(3)
C(1) C(6) 1.35(3)
C(1) C(2) 1.52(3)
C(2) C(3) 1.47(3)
C(3) C(4) 1.40(4)
C(4) C(5) 1.49(4)
C(5) C(6) 1.54(3)
C(7) C(8) 1.5021(13)
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C(8) F(1) 1.4820(13)
C(8) F(2) 1.4821(13)
C(9) C(10) 1.59(3)
C(10) C(11) 1.43(4)
C(12) C(13) 1.52(3)
C(13) C(14) 1.40(4)
C(15) C(16) 1.54(3)
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_atom_site_aniso_U_23
_atom_site_aniso_U_13
_atom_site_aniso_U_12
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N(1) 0.065(10) 0.036(9) 0.049(9) 0.006(7) -0.020(8) 0.004(8)
N(2) 0.056(10) 0.056(10) 0.043(9) 0.001(8) -0.004(8) 0.001(8)
O(1) 0.060(8) 0.054(8) 0.059(9) 0.002(7) 0.019(7) 0.008(7)
O(2) 0.074(11) 0.107(15) 0.095(14) 0.041(11) 0.019(10) 0.025(10)
O(3) 0.087(11) 0.056(9) 0.055(9) -0.020(7) 0.010(8) 0.005(8)
O(4) 0.053(9) 0.170(20) 0.091(13) -0.044(14) -0.037(9) 0.037(11)
O(5) 0.080(9) 0.040(8) 0.065(9) 0.013(7) 0.000(8) 0.004(7)
O(6) 0.134(16) 0.064(11) 0.058(10) 0.004(9) -0.010(10) -0.017(10)
O(7) 0.070(9) 0.064(10) 0.051(9) 0.012(7) 0.006(7) -0.015(8)
O(8) 0.082(11) 0.080(12) 0.067(10) 0.010(9) -0.015(9) -0.036(10)
C(1) 0.090(17) 0.077(18) 0.078(16) 0.017(14) -0.003(13) -0.051(15)
C(2) 0.110(20) 0.057(14) 0.071(16) 0.009(12) -0.012(14) -0.009(14)
C(3) 0.170(30) 0.080(20) 0.100(20) -0.008(16) -0.060(20) -0.030(20)
C(4) 0.130(30) 0.100(20) 0.120(20) 0.020(20) -0.050(20) -0.070(20)
C(5) 0.089(17) 0.076(17) 0.080(17) -0.025(14) -0.004(14) -0.029(15)
C(6) 0.073(16) 0.099(19) 0.078(16) 0.017(16) -0.047(14) -0.009(15)
C(7) 0.110(20) 0.073(17) 0.059(14) -0.015(13) 0.022(14) 0.033(15)
C(8) 0.090(20) 0.140(30) 0.140(30) 0.060(30) 0.040(20) 0.030(20)
C(9) 0.049(12) 0.039(12) 0.110(20) 0.007(12) -0.012(13) 0.003(10)
C(10) 0.120(20) 0.090(20) 0.120(20) -0.006(18) 0.050(20) 0.058(19)
C(11) 0.090(20) 0.260(50) 0.075(18) -0.060(20) -0.011(16) 0.100(30)
C(12) 0.110(20) 0.075(17) 0.044(13) 0.018(12) 0.001(13) 0.016(15)
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C(13) 0.110(20) 0.059(16) 0.100(20) 0.017(15) -0.029(17) 0.023(15)
C(14) 0.250(50) 0.070(20) 0.140(30) 0.020(20) -0.020(30) 0.060(30)
C(15) 0.057(13) 0.055(12) 0.060(14) -0.005(11) -0.007(11) -0.018(11)
C(16) 0.088(19) 0.180(30) 0.120(20) 0.070(20) -0.081(19) -0.070(20)
C(17) 0.120(30) 0.210(40) 0.120(30) -0.010(30) -0.050(20) -0.030(30)
F(1) 0.410(70) 0.370(60) 0.380(60) 0.030(50) 0.300(60) 0.090(50)
F(2) 0.110(20) 0.800(110) 0.220(40) 0.180(60) 0.050(20) -0.020(40)
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O(7) Pt(1) N(2) 173.7(6)
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O(2) C(7) C(8) 117.0(17)
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F(3) C(8) F(1) 108.5(14)
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F(1) C(8) F(2) 109.1(14)
F(3) C(8) C(7) 111.2(12)
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F(2) C(8) C(7) 108.8(13)
O(4) C(9) O(3) 127(2)
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