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The Platinum Catalyst [bpyrPtCl$_2$] in Superacidic Solution

Stefan Seidel and Konrad Seppelt*

Institut für Chemie, Freie Universität, 14195 Berlin, Germany

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The methane oxidation catalyst [bpyrPtCl$_2$] (bpyr = bis-pyrimidine) dissolves in superacidic HF/SbF$_5$ solution under formation of a dinuclear cation [H$_2$bpyrPt(μ-Cl)$_2$PtbpyrH$_2$]$^{6+}$. Two crystal forms are isolated, [Pt$_2$Cl$_2$bpyr$_2$H$_4$]$^{6+}$(SbF$_6^-$)$_4$-(Sb$_2$F$_{11}^-$)$_2$·2HF (**I**) (triclinic, $P\bar{1}$, $a = 814.8(2)$ pm, $b = 1444.8(3)$ pm, $c = 2300.5(5)$ pm, $\alpha = 89.627(4)°$, $\beta = 84.285(4)°$, $\gamma = 84.665(4)°$, $Z = 2$) and [Pt$_2$Cl$_2$bpyrH$_4$]$^{6+}$(Sb$_2$F$_{11}^-$)$_6$·4HF (**II**) (triclinic, $P\bar{1}$, $a = 879.4(2)$ pm, $b = 1170.4(3)$ pm, $c = 1789.9(5)$ pm, $\alpha = 95.37(2)°$, $\beta = 99.97(2)°$, $\gamma = 100.41(2)°$, $Z = 1$). The cation in **I** has an angle of 148.4(1)° between the two square plane platinum environments, while the cation in **II** is fully planar. The non-platinum-bound nitrogen atoms are all protonated in the superacidic medium.

Introduction

Platinum(II)diimine complexes have been known for some time. These and related platinum compounds are under continuing investigations because of their complex photo behavior,[1,2] their physiological behavior in connection with platinum based tumor therapy,[3] and their potential as catalysts for C−H bond activation, especially the oxidation of methane to methanol.[4] By using [Pt(bpyr)Cl$_2$] (bpyr = bis-pyrimidine) as a catalyst, dissolved in concentrated sulfuric acid at 220 °C, methane is converted into methylbisulfate in approximately 90% conversion and 81% selectivity. Methylbisulfate can readily be hydrolyzed to methanol. The reason this procedure has not yet entered industrial scale is due to the problems of removal of water and methanol from the concentrated sulfuric acid solvent. This work has inspired the search for related catalysts in related solvent systems: For example, N-heterocyclic biscarbene palladium dichlorides oxidize methane to methyltrifluoroacetate in CF$_3$COOH solution at 80−90 °C.[5]

The reaction mechanism of the methane oxidation particularly at the [Pt(bpyr)Cl$_2$] catalyst has been the subject of theoretical analyses.[6,7] Electrophilic substitution, oxidative addition, and σ-bond metathesis have been considered as a mechanism. The calculations disagree also over the question of whether the non-platinum-bonded nitrogen atoms in the bis-pyrimidine ligand are protonated.

To the best of our knowledge, it has not been possible to isolate a Pt−bpyr complex once it is dissolved in concentrated H$_2$SO$_4$, possibly because the viscosity of H$_2$SO$_4$ makes crystallizations very difficult. Our approach has been to look for reaction products of [Pt(bpyr)Cl$_2$] in another strong protonic acid, namely HF/SbF$_5$, which has been successfully been used for many crystallizations in past years.[8]

Experimental Section

Material and Apparatus. Bipyrimidyl is commercially available and has been used without further purification. [Pt(bpyr)Cl$_2$] was prepared by reaction of (NH$_4$)$_2$[PtCl$_4$] and 2,2-bipyrimidine in CH$_2$Cl$_2$, according to ref 9.

Synthetic work and sample handing were performed using Teflon-PFA ((poly)perfluoroether-tetrafluoroethylene copolimerisate) tubes that are sealed at one end and equipped at the other end with a metal valve, and thus connectable to a metal vacuum line. HF was dried by performing several trap-to-trap condensations and by discarding the less volatile fractions. SbF$_5$ (Merck) was purified similarly by discarding the highly volatile fractions.

Raman spectra were recorded on a Bruker RFS 100 S instrument with Nd:YAG laser excitation, $\lambda = 1064$ nm. Samples were kept in the Teflon-PFA tubes, and the Raman scattering from the tubes was digitally subtracted.

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* To whom correspondence should be addressed. E-mail address: seppelt@chemie.fu-berlin.de.

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Table 1. Crystal Data and Structure Refinement for $[Pt_2Cl_2bpyr_2H_4]^{6+}(SbF_6^-)_4(Sb_2F_{11}^-)_2 \cdot 2HF$ (**I**) and $[Pt_2Cl_2bpyr_2H_4]^{6+}(Sb_2F_{11}^-)_6 \cdot 4HF$ (**II**)

	I	**II**
empirical formula[a]	$C_{16}H_{16}Cl_2F_{48}N_8Pt_2Sb_8$	$C_{16}H_{16}Cl_2F_{70}N_8Pt_2Sb_{12}$
fw	2667.5	3572.4
temp, K	173	173
space group	$P\bar{1}$	$P\bar{1}$
a, pm	814.8(2)	879.4(2)
b, pm	1444.8(3)	1170.4(3)
c, pm	2300.5(5)	1789.9(5)
α, deg	89.627(4)	95.37(2)
β, deg	84.285(4)	99.97(2)
γ, deg	84.665(4)	100.41(2)
V, 10^6 pm^3	2683.28	1769.7
Z	2	1
d(calcd) Mg/m^3	3.301	3.352
abs coeff, mm^{-1}	9.45	8.72
cryst size, mm^3	0.2 × 0.1 × 0.05	0.2 × 0.5 × 0.05 × 0.02
final R indices ($I > 4\sigma(I)$)	$R = 0.0408$[b]	$R = 0.0327$[b]
all data	$R = 0.0568$,[b] wR2 = 0.1028[c]	$R = 0.0435$,[b] wR2 = 0.0789[c]

[a] Only crystallographically located hydrogen atoms are counted. [b] $R = \Sigma(|F_o| - |F_o|)/\Sigma|F_o|$. [c] $wR2 = \{\Sigma[(wF_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Single crystals were handled in a special device, cut to an appropriate size, and mounted on a Bruker SMART CCD 1000 TU diffractometer, using Mo Kα irradiation, a graphite monochromator, a scan width of 0.3° in ω, and a measuring time of 20 s per frame. After semiempirical absorption corrections (SADABS) by equalizing symmetry-equivalent reflections, the SHELX programs were used for solution and refinement.[10] All atoms except hydrogen are refined anisotropically. Hydrogen atoms bound to N have been located by difference Fourier maps and refined independently from other atomic positions, however, with a single isotropic displacement parameter for all hydrogen atoms. Hydrogen atoms bound to C have been treated similarly in **II**, while in **I** these hydrogen atoms are fixed in calculated positions. Hydrogen atoms of the HF molecules could not be located.

[Pt(bpyr)Cl$_2$] [270 mg (0.6 mmol)] is weighed into an PFA tube (8 mm outer diameter, equipped with a stainless steel valve). On the metal vacuum line, 2 mL of anhydrous HF is added at −196 °C. Upon warming to room temperature, gas evolution is observed, and a brown, clear solution is formed. By addition of 1.1 g of SbF$_5$, a yellow brown precipitate is formed. This dissolves upon heating to 70 °C in the sealed tube. Slow cooling to room temperature affords yellow crystals.

Two kinds of crystals are found, both triclinic, see Table 1.

Raman spectrum of **II** (cm^{-1}, cryst − 160 °C): 3128(1), 1660(10), 1647(7), 1576(70), 1543(25), 1446(30), 1402(55), 1312(20), 1287(15), 1220(15), 1211(10), 1121(8), 1040(5), 1061(100), 1044(12), 778(8), 683(25), 651(70), 600(5), 384(10), 345(14), 295(23), 280(5), 264(20), 229(10), 212(10), 109(100). Raman (HF/SbF$_5$, 30 °C, cm^{-1}): 3126(1), 1659(8), 1648(4), 1575(50), 1542(20), 1446(30, 1402(55), 1312(20), 1290(20), 1220(30), 1121(15), 1068(2), 1060(100), 1044(8), 779(15), 683(20), 675(sh), 650(8), 600(10), 384(20), 345(8), 296(50), 264(sh), 231(15), 213(sh), 108(100). 1312(10). Ir spectra of **II** (cm^{-1}, Nujol): 1648 m, 1587 m, 1533 m, 1293 w, 1203 w, 1121 w, 1070 w, 1039 m, 805 m, 632 br,s, 492 m. Mp 186 °C. Elemental analysis of **II**: Pt calcd 11.0%, found 10.8%.

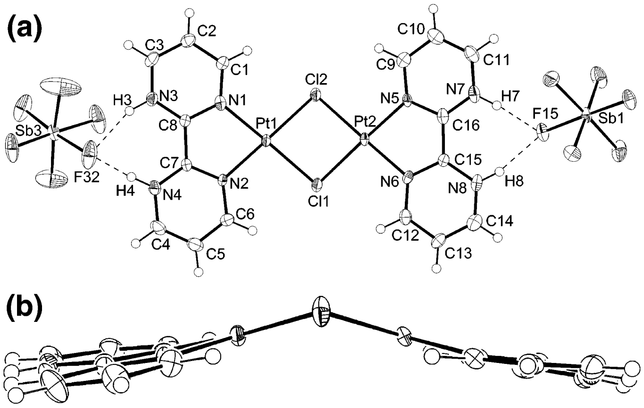

Figure 1. Crystal structure of the cation including the hydrogen bridged SbF$_6^-$ anions in **I** with displacement ellipsoids at the 50% probability level. (a) View perpendicular to the major plane. (b) View of the cation showing the angle of 148.4(1)° between the two square planar platinum environments.

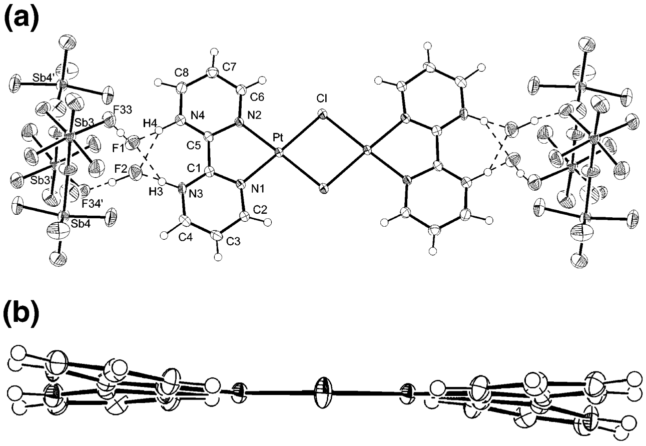

Figure 2. Crystal structure of the cation including the N−H···F−H···F−Sb$_2$F$_{10}^-$ bridging in **II** with displacement ellipsoids at the 50% probability level. (a) View perpendicular to the molecular plane. (b) View of the cation parallel to the plane.

Results and Discussion

[Pt(bpyr)Cl$_2$] dissolves readily in anhydrous HF under HCl gas evolution at temperatures slightly above room temperature forming a yellow solution upon addition of SbF$_5$, and cooling to room temperature affords yellow brown crystals. These have been structurally characterized by single crystal structure determinations. Two kinds of crystals have been observed: $[Pt_2Cl_2bpyr_2H_4]^{6+}(SbF_6)_4^-(Sb_2F_{11}^-)_2 \cdot 2HF$ (**I**) and $[Pt_2Cl_2bpyr_2H_4]^{6+}(Sb_2F_{11}^-)_6 \cdot 4HF$ (**II**). Both crystals behave quite similarly. Details of the crystallographic experiments are summarized in Table 1.

The crystals, both triclinic, differ in the compositions of the anions. Obviously, higher concentrations of SbF$_5$ in HF direct the formation toward **II**, which thus can be regularly obtained, whereas we consider **I** as an accidental crystallization. The SbF$_6^-$ and Sb$_2$F$_{11}^-$ anion show the well-known bond distances and angles. The angle of the Sb−F−Sb bridge in the five different Sb$_2$F$_{11}^-$ anions varies between 151.2° and 155.8°, values that are observed quite often for this anion.

The cations are the focus of this work. Loss of HCl results in dimerization into a double chlorine bridged dimer in both crystals, see Figures 1 and 2 and Table 2. The cations in both crystals are very similar; in particular, the Pt−Cl and

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Table 2. Important Bond Lengths (pm) and Angles (deg) of I

Pt(1)−N(1)	200.3(6)	Pt(2)−N(5)	200.0(5)
Pt(1)−N(2)	200.1(5)	Pt(2)−N(6)	199.8(5)
Pt(1)−Cl(1)	230.4(2)	Pt(2)−Cl(1)	230.7(2)
Pt(1)−Cl(2)	230.2(2)	Pt(2)−Cl(2)	230.1(2)
N(1)−C(8)	133.7(8)	N(5)−C(16)	133.3(8)
N(2)−C(7)	131.9(8)	N(6)−C(15)	133.8(8)
N(3)−C(8)	133.3(8)	N(7)−C(16)	132.1(9)
N(4)−C(7)	133.2(8)	N(8)−C(15)	135.7(6)
C(7)−C(8)	148.4(9)	C(15)−C(16)	147.2(9)
N(3)−H(3)	39(9)	N(3)···F(32)	293.2(8)
N(4)−H(4)	92(8)	N(4)···F(32)	266.0(8)
N(7)−H(7)	86(9)	N(7)···F(15)	266.2(7)
N(8)−H(8)	93(8)	N(8)···F(15)	284.8(8)
N(1)−Pt(1)−N(2)	80.7(2)	N(5)−Pt(2)−N(6)	80.7(2)
Cl(1)−Pt(1)−Cl(2)	82.35(6)	Cl(1)−Pt(2)−Cl(2)	82.09(6)
N(1)−Pt(1)−Cl(1)	176.3(2)	Cl(5)−Pt(2)−Cl(1)	177.7(2)
N(2)−Pt(1)−Cl(2)	179.3(2)	N(6)−Pt(2)−Cl(2)	177.7(1)
F(1)···F(24)	257.9(7)	F(2)···F(54)	294.9(8)
F(2)···F(26)	294.9(8)		

Table 3. Important Bond Lengths (pm) and Angles (deg) of **II**

Pt−N(1)	199.9(4)	Pt−N(2)	200.8(4)
Pt−Cl	230.8(1)	Pt−Cl#	230.7(1)
N(1)−C(1)	132.8(6)	N(2)−C(5)	135.2(6)
N(3)−C(1)	133.0(6)	N(4)−C(5)	133.4(7)
C(1)−C(5)	147.4(7)	N(1)−Pt−N(2)	80.1(2)
Cl−Pt−Cl#	82.51(5)	Pt−Cl−Pt#	97.49(5)
Cl−Pt−N(1)	176.7(1)	Cl#−Pt−N(2)	178.4(1)
N(3)−H(3)	84(4)	N(4)−H(4)	94(6)
N(3)···F(1)	271.8(6)	N(3)···F(2)	270.9(6)
N(4)···F(1)	281.3(7)	N(4)···F(2)	277.7(6)
F(1)···F(33)	256.8(6)	F(2)···F(34)	254.4(7)

Pt−N distances are the same within the estimated standard deviations. The numbers also do not differ much from those found in the various crystallographic forms of the precursor [bpyr $PtCl_2$].[11−13]

One striking difference is the nonplanarity in **I** and planarity in **II** of the Pt_2Cl_2 ring, see Figures 1 and 2. Planarity is observed also in the only other dimeric cationic nitrogen chlorine complexes [(tmeda)$PtCl_2$Pt(tmeda)]$^{2+}$[14] and [CH_3C(*p*-tol)N)$_2$][$PtCl_2$Pt (N(*p*-tol)CCH_3)$_2$]$^{2+}$.[15]

In **I**, however, the two N_2PtCl_2 best planes have an angle of 148.4(1)° with each other. In a theoretical investigation, the planarity or nonplanarity of such binuclear d^8 complexes with Ni(II), Pd(II), Pt(II), Rh(I), and Ir(I) has been investigated.[16] The majority of the more than 300 known structures are planar, but there remains a large number of exceptions. The interplanar angle can have values below 110°. Pt(II) complexes with unsubstituted bridges are almost always planar. With [bpyrH_2Pt(μ-Cl)$_2$PtbpyrH$_2$]$^{6+}$, we observe a rare case of such a structural isomerism.

Another structural problem is how much the non-platinum-bound nitrogen atoms are protonated. In the superacidic medium HF/SbF_5, it can be anticipated that full (4-fold) protonation might occur.

Indeed, in both **I** and **II** these nitrogen bonded hydrogen atoms have been located in electron density maps and are refined independently of the positions of other atoms. The resulting N−H bond distances and corresponding bond angles agree with anticipated values (with a single exception of the N(3)−H(3) bond length of 38 pm in **I**; this crystal strucure is anyhow the less precise one); see Figures 1a and 2a and Tables 2 and 3.These four nitrogen bonded hydrogen atoms have the closest contacts of all the atoms of the cations to fluorine atoms. As indicated in Figure 1a, in **I** each of these hydrogen atoms is part of a N−H···F−SbF_5^- bridge bond with N···F distances between 266.0 and 293.2 pm, see Table 2. This does not come as a surprise. Of the two anions SbF_6^- and $Sb_2F_{11}^-$ and the solvent HF, SbF_6^- is the most basic component. The two solvent HF molecules have only bridges to SbF_6^- and $Sb_2F_{11}^-$ units and are of no interest here.

In **II**, however, it is the HF molecules that bridge to the nitrogen bonded hydrogen atoms, see Figure 2a. Further bridging occurs between the HF molecules and $Sb_2F_{11}^-$ anions. In other words, the HF molecules act as spacer between cations and anions, suggesting that in such SbF_5-rich solution **II** is fully ionized. Raman spectra of solid **II** and those in HF/SbF_5 solution are very similar suggesting that the dimer is also present in solution.

The question of whether a double chlorine bridged dimer is a part in the catalytic cycle of the methane oxygenation reaction cannot be answered by these findings. But, at the high temperatures employed in the H_2SO_4 medium, an equilibrium between a double square planar dimer and trigonal monomer could exist.

The [Pt(bpyr)Cl$^+$]$_2$ in HF/SbF_5 is in itself not a reasonable system for the methane oxygenation. First, one would expect fluorination rather than oxidation of methane, and second, up to about 80° there is no reaction with CH_4. Higher temperatures are difficult to handle due to the vapor pressure of HF.

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Supporting Information Available: Listings of crystal data and intensity collection parameters, anisotropic thermal parameters, and all bond lengths and angles and drawings of the molecular units. This material is available free of charge via the Internet at http://pubs.acs.org.

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