Synthesis and Characterization of Tetrakis(carbonyl)platinum(II) Hexakis(fluorosulfato)platinate(IV), [Pt(CO)₄][Pt(SO₃F)₆]

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Carbonyl derivatives of platinum have both a rich and interesting chemistry and a long history.[1,2] Carbonyl platinum-(II) chlorides, reported by Schützenberger in 1870,[3] were the first metal carbonyl derivatives to be synthesized. They and their Br and I analogues now include mono and dinuclear, neutral or anionic complexes, with platinum in the +1, +2, and occasionally +4 oxidation state.[1,2] The neutral chloro derivatives, e.g. square planar *cis*- and *trans*-Pt(CO)₂Cl₂ and chloride-bridged [Pt(CO)-Cl₂]₂, exhibit CO-stretching frequencies[4] slightly below 2200 cm⁻¹, well above the value of 2143 cm⁻¹ reported for CO(g),[5] and reduced platinum to CO π-back-bonding has been postulated.[6]

We want to report here on the synthesis of a novel platinum carbonyl compound of the composition Pt(CO)₂(SO₃F)₃, which, based on ¹⁹F and ¹³C NMR, infrared, Raman and UV–vis spectra is formulated as [Pt(CO)₄][Pt(SO₃F)₆]. The compound differs from previously reported metal carbonyl derivatives in two respects: (i) The square planar cation, [Pt(CO)₄]²⁺, is the first binary cationic carbonyl platinum species. There are also no thermally stable, square planar, binary carbonyl species reported for other transition metals. (ii) The average CO stretching frequency (ν(CO$_{av}$)) is 2251 cm⁻¹, the highest reported so far.

The single step synthesis involves the interaction of carbon monoxide with the superacid system HSO₃F/Pt(SO₃F)₄[7] according to:

$$2Pt(SO_3F)_4 + 5CO \xrightarrow[\sim 2atm, 25\,°C]{HSO_3F}$$

$$[Pt(CO)_4][Pt(SO_3F)_6] + CO_2 + S_2O_5F_2$$
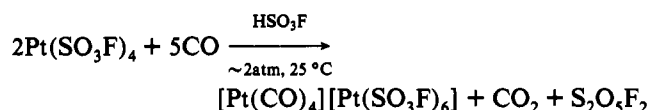
The yellow hygroscopic solid produced is isolated by filtration in approximately 80% yield . Reductive carbonylation occurs with similar ease here as in the superacid system HSO₃F/Au-(SO₃F)₃.[8,9] The volatile byproducts CO₂ and S₂O₅F₂ are separated by trap to trap distillation and identified by their vibrational spectra, and fluorosulfuric acid is again found to be a convenient and suitable reaction medium. The products differ however,

because gold is completely reduced to Au(I) and solid Au(CO)-SO₃F forms via the intermediate [Au(CO)₂]⁺(solv).[10,11]

[Pt(CO)₄][Pt(SO₃F)₆] is diamagnetic, sparingly soluble in HSO₃F, and insoluble in SO₂. Solutions in HSO₃F exhibit increased electrical conductivities, of the same order as solutions of other [Pt(SO₃F)₆]²⁻ salts,[7,12] suggesting ionic dissociation. The solutions permit characterization of the constituent ions by spectroscopic means. A resonance at 47.4 ppm in the ¹⁹F NMR spectrum, observed in addition to the HSO₃F resonance at 40.3 ppm, is attributed to the [Pt(SO₃F)₆]²⁻ anion in analogy to a previous report.[7] The ¹³C resonance is observed at 140.5 ppm on solutions of [Pt(¹³CO)₄]²⁺, with satellite bands due to coupling to ¹⁹⁵Pt ($I = {}^1/_2$), which yield $J({}^{195}Pt-{}^{13}C) = 1576 \pm 2$ Hz. While the J value compares well with published precedents for Pt(II)–carbonyl deriatives,[4] the chemical shift is about 11 ppm lower than values reported for Pt(CO)₂Cl₂ and Pt(CO)₂Br₂.[4] Attempts to record a ¹⁹⁵Pt NMR spectrum are unsuccesful, quite possibly on account of the limited solubility of [Pt(CO)₄][Pt(SO₃F)₆] in HSO₃F. The UV spectrum of the solutions in HSO₃F shows intense absorptions with λ$_{max}$ at 256 and 300 nm. The spectrum and the colour appear to be due to the [Pt(SO₃F)₆]²⁻ ion.[7] The solid melts at about 140 °C with gas evolution and noticeable decomposition. The gaseous products obtained upon heating are identified by their IR spectra as SiF₄ and SO₂F₂. The expected clean elimination of CO to give Pt^{II}[Pt^{IV}(SO₃F)₆] is not observed. Previously reported [Pt(SO₃F)₆]²⁻ derivatives with Cs⁺, ClO₂⁺, Br₃⁺, or Ba²⁺ as counter cations display similar thermal stabilities.[7] It is not really surprising that an anion like [Pt(SO₃F)₆]²⁻ should be capable of stabilizing highly electrophilic cations like Br₃⁺ [7] and [Pt(CO)₄]²⁺. According to criteria based on ¹¹⁹Sn Mössbauer spectra of their dimethyltin(IV) salts,[13] [Pt(SO₃F)₆]²⁻ is only surpassed by SbF₆⁻ and Sb₂F₁₁⁻ as a very weak nucleophile, and should have a similar ability to stabilize highly electrophilic cations in the solid state.

There are three related, previously reported species which should be mentioned: (i) A number of salts contain the square planar, isoelectronic anion [Pt(CN)₄]²⁻,[14] which provides a good structural analogue to [Pt(CO)₄]²⁺. (ii) Cocondensation of CO and Pt, studied from 4.2 to 10 K by matrix IR spectroscopy, has reportedly resulted in the formation of binary carbonyls of the composition Pt(CO)$_n$ ($n = 1$–4).[15] The low thermal stability of the products, the conventional mode of metal–CO bonding, with ν(CO) below 2060 cm⁻¹, and the suggested tetrahedral structure of Pt(CO)₄, differ from observations for [Pt(CO)₄]²⁺. (iii) Finally, the addition of gaseous CO to solutions of Cu₂O in strong protonic acids has produced carbonyl cations of the type [Cu(CO)$_n$]⁺($n = 1,3$, or 4), among them [Cu(CO)₄]⁺. However, no isolable products form, and evidence rests on CO uptake, IR and ¹³C NMR data.[16]

Structural conclusions and formulation of the new compound in the solid state as [Pt(CO)₄][Pt(SO₃F)₆] are based on the vibrational spectra, since so far all efforts to obtain suitable crystals for an X-ray diffraction study have failed. The Raman spectrum is shown in Figure 1. Raman shifts and IR band positions, together with estimated relative intensities, are summarized in Table I. They are compared to previously reported Raman data for Ba-[Pt(SO₃F)₆][7] and IR data for (ClO₂)₂[Pt(SO₃F)₆].[7] The band assignment for [Pt(SO₃F)₆]²⁻ has been suggested previously.[7]

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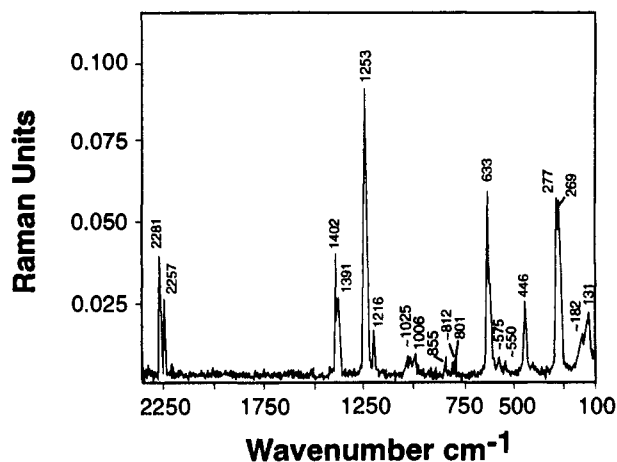(16) Souma, Y.; Iyoda, J.; Sano, H. *Inorg. Chem.* 1976, *15*, 968.

Figure 1. Raman spectrum of [Pt(CO)4][Pt(SO3F)6].

Table I. Vibrational Frequencies (ν (cm^{-1})) of [Pt(CO)4][Pt(SO3F)6], and Related Compounds

[Pt(CO)4][Pt(SO3F)6]		Ba[Pt-(SO3F)6]^a	(ClO2)2-[Pt(SO3F)6]^b	approx assignt^c
infrared	Raman	Raman	infrared	
	2281 vs			ν(CO)(A$_{1g}$)
	2257 s			ν(CO)(B$_{1g}$)
2235 ms				} ν^{12}(CO)(E$_u$)
2231 m,sh				
2190 vw,b				ν^{13}(CO)
1395 vs	1402 s	1397 vw	1415 vs	} ν_{as}(SO2)
1385 s,sh	1391 s	1386 m	1378 s,sh	
1230 m,sh	1253 vs	1258 vs	1245 m,sh	} ν_{sym}(SO2)
1200 vs	1216 m	1218 m	1215 vs,	
1190 s,sh			1192 s,sh	
	1025 w	1033 m		} ν(SO-M)
	1006 w	1012 w		
966 vs			968 vs	
928 s,sh			925 s	
835 ms	855 m	857 w	825 vs	} ν(SF)
815 s,sh	812 w	838 vw		
805 vs	801 m		805 s,sh	
660 m			662 m	} ν_{as}(Pt–O) + δ(SO3F)
650 m,sh			650 m	
	633 vs	629 vs		} ν_{sym}(Pt–O) + δ(SO3F)
	624 s,sh			
595 ms	575 vw	583 vw	587 s	δ_{as}(SO3)
560 m	550 vw	549 vw	546 s	δ_{sym}(SO3)
530 m				} Pt(CO)4 vibrations?
489 m				
468 w,sh	446 s	460 m	452 m,sh	ν_{as}(Pt–O) + def
	410 vw	422 vw		
		411 w		ρ(SO3F)
	277 vs	283 vs		} δ_{sym}(Pt–O) + δ(SO3F)
	269 vs,sh			
	182 m			} δ(Pt–CO)
	131 s			

^{a} Reference 7. ^{b} Reference 12, ClO2$^+$ bands at 1298, 1285, 1045 and 517 cm^{-1} are omitted. ^{c} Key: ν = stretch, δ = deformation, ρ = rocking mode, sym = symmetrical, as = asymmetrical, s = strong, m = medium, w = weak, v = very, b = broad, sh = shoulder, br = bridging, Int = estimated intensity, and ν = wave number.

In the vibrational spectra of [Pt(CO)4][Pt(SO3F)6], bands due to the anion are clearly identified by their positions and the relative intensities in comparison to precedents.[7,12] It is noted that some of these bands show partly resolved small splittings or shoulders which have not been observed previously and which may be caused by the molecular [Pt(CO)4]$^{2+}$ cation. In the SO3F stretching range very similar band positions are observed, and characteristic Raman bands, partially due to skeletal Pt–O$_6$ vibrations[7] at ~630, ~450 and ~290 cm^{-1}, are prominent in the lower frequency region.

Of the bands due to [Pt(CO)4]$^{2+}$, only the CO stretching modes are easily recognized. The assignment proposed in Table I

parallels that proposed for the CN stretching vibrations of [Pt(CN)4]$^{2-}$.[17,18] The noncoincidence of IR and Raman bands points to a centrosymmetrical cation. As found for linear [Au(CO)2]$^+$ [10] and [Pt(CN)4]$^{2-}$,[17,18] Raman bands in the intraligand stretching region are observed at higher wavenumbers than the IR bands. The small splitting of the IR-active E$_u$ mode at ~2230 cm^{-1} is only recognizable in a high-resolution spectrum. Of the remaining bands due to the cation, only Raman shifts between 182 and 131 cm^{-1} are recognizable, while the remaining bands can not be unambiguously identified. Similarly for [Au(CO)2]$^+$(solv), only νCO was initially identified,[10] while other peaks overlapped with intense HSO3F–SO3F$^-$ bands in the lower spectral region. For [Au(CO)2][Sb2F11],[11] where the complete assignment of all seven fundamentals due to the cation is possible, the metal–carbon and C–O deformation modes have relatively low intensities. This is also found for the corresponding bands of [Pt(CN)4]$^{2-}$,[17,18] which are all observed in the narrow range of ~400–100 cm^{-1}.

Additional support for the [Pt(CO)4]$^{2+}$ cation and the proposed assignment comes from very recent findings.[19,20] Under more forcing conditions (80 °C and 1–2 atm of CO) reductive carbonylation of Pt(SO3F)4 produces completely reduced *cis*-Pt(CO)2(SO3F)2, which can be isolated and solvolyzed in liquid SbF5 in a CO atmosphere, to allow the formation of [Pt(CO)4]-[Sb2F11]2.[20] This reaction is in complete analogy to the conversion of Au(CO)SO3F to [Au(CO)2][Sb2F11] reported by us.[11] The CO stretching vibrations for [Pt(CO)4][Sb2F11]2 are, at 2289 (A$_{1g}$), 2267 (B$_{1g}$), and 2244 (E$_u$) cm^{-1}, about 10 wavenumbers higher than reported here, a consequence of the more weakly basic anion.[13] The corresponding salt [Pd(CO)4][Sb2F11]2 is obtained in an identical manner, and the [Pd(CO)4]$^{2+}$ cation is found to be square planar as well.[20]

The very high CO stretching frequencies for [Pt(CO)4]$^{2+}$ with average values of 2251–2261 cm^{-1} are consistent with expectations for a cation. For neutral compounds like *cis*-Pt(CO)2Cl2, ν(CO$_{av}$) decreases to 2164.5 cm^{-1} while for [Pt(CO)Cl3]$^-$ an even lower ν(CO) value of 2083 cm^{-1} is reported.[4] The dependency of ν(CO) on the net ionic charge of the platinum carbonyl species observed here and hence on the effective nuclear charge on platinum suggests increasing Pt to CO π-back-donation in the series [Pt(CO)4]$^{2+}$ < *cis*-Pt(CO)2Cl2 < [Pt(CO)Cl3]$^-$. It is concluded that in [Au(CO)2]$^+$, with a ν(CO$_{av}$) value of 2231 cm^{-1}, and more so in [Pt(CO)4]$^{2+}$, with ν(CO$_{av}$) 2261–2251 cm^{-1}, π-back-donation is drastically reduced and not essential in view of the observed thermal stability of the cations. As suggested for [Au(CO)2]$^+$,[10,11] the ability of gold and platinum to form strong covalent bonds, aided by relativistic effects[21] and polar contributions to these bonds, is seemingly responsible for the observed thermal stability of the noble metal carbonyl cations.

Like the isoelectronic and isostructural anionic cyanide complexes of Au(I) and Pt(II),[17,18] both [Au(CO)2]$^+$ and [Pt(CO)4]$^{2+}$ are viewed as coordination complexes of Au(I) and Pt(II) with CO as ligand, which differ from classical organometallic transition metal carbonyls. Their generation in a strongly ionizing protonic acid like HSO3F, the positively charged central atoms, the effective atomic numbers of 16 for [Pt(CO)4]$^{2+}$ and 14 for [Au(CO)2]$^+$, and their geometries are in support of this view.

Experimental Section

(a) Chemicals. Platinum powder of 99.9% purity and 0.5–1.2 μm was obtained from Ventron Corp. (Alfa Inorganics). Bis-

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(fluorosulfuryl) peroxide, $S_2O_6F_2$,[22] and platinum tetrakis-(fluorosulfate), $Pt(SO_3F)_4$,[7] were prepared according to published methods. Carbon monoxide, CP grade (99.5%), obtained from Linde Gases, was dried by cooling to −196 °C and partly reevaporating. Technical grade fluorosulfuric acid, HSO_3F, was purified as described previously.[23]

(b) Instrumentation. Infrared spectra were recorded on a Perkin-Elmer 598 grating spectrometer. Higher resolved spectra were recorded on a Bomem DA3 series FT-IR. Solid samples were pressed as thin films between AgBr windows (Harshaw Chemicals). Gaseous samples were contained in a 10-cm cell fitted with a 4-mm Kontes stopcock and AgBr windows. FT-Raman spectra were obtained courtesy of Dr. H. Homborg and Prof. W. Preetz, University of Kiel, Germany.

Precipitates were filtered using an apparatus similar to that described by Shriver.[24] Chemical analyses were carried out by Mr. P. Borda of this department and Beller Laboratories, Göttingen, Germany.

Reactions of solutions in HSO_3F with CO and the handling and identification of volatile reaction products and of moisture sensitive solids have been described by us previously.[10]

(c) Preparation of $[Pt(CO)_4][Pt(SO_3F)_6]$. Platinum powder (0.495 g, 2.54 mmol) was reacted with ∼4 mL of $S_2O_6F_2$ and

∼5 mL of HSO_3F in a 50-mL round-bottom flask to give Pt-$(SO_3F)_4$ in solution.[7] After removal of all volatile materials (mainly excess $S_2O_6F_2$), carbon monoxide was condensed into the reactor to give an initial pressure of ∼2 atm, and the solution was left stirring at room temperature overnight. The volatile fractions at −196 °C, −78 °C, and room temperature were measured and identified by infrared spectroscopy as CO, CO_2, and $S_2O_5F_2$ respectively. All volatiles were removed *in vacuo*, and a second portion of CO was added to the solution, which had become slightly lighter in color. After CO additions over 2 days, a yellow precipitate appeared. The reaction was assumed complete when there was no further CO uptake, the color of the solution had changed from red-brown to bright yellow, and no more precipitate appeared to be formed. The mixture was filtered and dried *in vacuo* for 2 days at ambient temperature. Approximately 80% of the precipitate was recovered due to its slight solubility in HSO_3F.

Anal. Calcd for $C_2F_3O_{11}PtS_3$: C, 4.38; S, 17.48; F, 10.39; Pt, 35.58. Found: C, 4.60; S, 18.00; F, 9.7; Pt, 35.16.

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