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Synthesis, Molecular Structure, and Vibrational Spectra of *cyclo*-Bis(μ-carbonyl)dipalladium(I) Fluorosulfate, [*c*-$Pd_2(\mu\text{-}CO)_2](SO_3F)_2$

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The synthesis, molecular structure, and complete vibrational spectrum of *cyclo*-bis(μ-carbonyl)dipalladium(I) fluorosulfate, [*c*-$Pd_2(\mu\text{-}CO)_2](SO_3F)_2$, are reported. The synthesis is achieved by reductive decomposition of $Pd(CO)_2(SO_3F)_2$ in fluorosulfuric acid, HSO_3F; at 25 °C, long orange-red needles form over a period of about 3 weeks. The compound is stable up to 157 °C (the decomposition point). The molecular structure is solved by single-crystal X-ray diffraction. Crystals of $[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$ are monoclinic, $C2/c$; $a = 11.495(1)$, $b = 8.255(1)$, and $c = 9.556(1)$ Å; $\beta = 91.94(1)°$; $Z = 8$. The structure is solved by the Patterson method and is refined by full-matrix least-squares procedures to $R = 0.061$ and $R_w = 0.075$ for 2667 reflections with $I \geq 3\sigma(I)$. The structure reveals planar $[Pd_2(\mu\text{-}CO)_2]^{2+}$ cations formed by two nearly symmetrically CO-bridged palladium atoms, linked by bidentate-bridging fluorosulfate anions into a polymeric sheet. The vibrational spectrum using FT-IR and FT-Raman spectroscopy down to 50 cm^{-1} is interpreted in terms of D_{2h} symmetry for the molecular cation, and 10 of the expected 12 fundamental vibrations are detected and assigned. The vibrational spectrum features the highest CO stretching frequency ($\bar{\nu}(CO)_{av} = 2002$ cm^{-1}) so far reported for a bidentate-bridging CO ligand in metal–carbonyl chemistry.

Introduction

In the past,[1,2] several carbonyl derivatives of palladium have been reported with the metal in the formal oxidation state +2, +1, or 0; however, binary palladium carbonyls are rather rare. They include CO adsorbates on palladium surfaces of the compositions PdCO and $Pd_2(CO)$[3,4] and matrix-isolated molecules of the types $Pd(CO)_n$ with $n = 1$–4.[5–7] Both groups contain zerovalent palladium. The matrix-isolated molecules studied by vibrational spectroscopy are of very limited thermal stability.

We very recently reported the synthesis of the first example of a binary carbonyl cation, $[Pd(CO)_4]^{2+}$.[8] This cation, studied by vibrational spectroscopy, is thermally stable to ~150 °C, has a square-planar geometry, and exhibits unusually high CO-stretching vibrations with $\bar{\nu}(CO)_{av}$ at 2259 cm^{-1}, well above the value of 2143 cm^{-1} reported for gaseous CO.[9] The $[Pd(CO)_4]^{2+}$ cation is stabilized by the very weakly basic anion $Sb_2F_{11}^-$ [10] and formed by the solvolysis of $Pd(CO)_2(SO_3F)_2$ in liquid antimony(V) fluoride[11] in the presence of CO according to

$$Pd(CO)_2(SO_3F)_2 + 8SbF_5 + 2CO \xrightarrow[60\text{–}80\ °C]{SbF_5} [Pd(CO)_4][Sb_2F_{11}]_2 + 2Sb_2F_9SO_3F \quad (1)$$

The starting material for the above reaction, $Pd(CO)_2(SO_3F)_2$, is obtained by the reductive carbonylation of the mixed-valency compound $Pd^{II}Pd^{IV}(SO_3F)_6$[12] in HSO_3F:

$$Pd^{II}Pd^{IV}(SO_3F)_6 + 5CO \xrightarrow[\sim 0.5\ \text{atm of CO}]{25\ °C} 2Pd(CO)_2(SO_3F)_2 + CO_2 + S_2O_5F_2 \quad (2)$$

While the composition of the yellow solid product obtained via reaction 2 is established by microanalysis as $Pd(CO)_2(SO_3F)_2$, the vibrational spectra of the CO-stretching region suggest a mixture of several isomers. Subsequent attempts to separate this mixture by recrystallization from fluorosulfuric acid have resulted in the formation of orange-red crystals of the composition $Pd(CO)SO_3F$, which are found suitable for a single-crystal X-ray diffraction study.

The molecular structure of this novel palladium(I) carbonyl derivative reported here reveals a cyclic, completely planar $[Pd_2(\mu\text{-}CO)_2]^{2+}$ cation, linked by bidentate, symmetrically bridging fluorosulfate groups into a polymeric sheet. The CO groups are symmetrically bridging, and the molecular cation belongs to the point group D_{2h}.

Vibrational spectra consisting of IR and Raman spectra down to 50 cm^{-1} are reported here as well. A vibrational study is of interest on two accounts: (i) There are very few structurally characterized cyclic heteroatomic inorganic molecules of the point group D_{2h} known. Previously reported examples of six-atom cyclic systems have included hypothetical but plausible molecules like dimeric $(BeCl_2)_2$[13] or matrix isolated $(MgBr_2)_2$, studied by infrared spectroscopy.[14] In addition, for S_2N_2 the molecular structure,[15] a vibrational analysis, a Raman spectrum,[16] and a number of IR bands[17] are known. (ii) There have been a number of reports on

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carbonyl cations with unusual spectroscopic features formed by electron-rich metals, such as Ag(I),[18,19] Au(I),[20,21] and Pt(II) and Pd(II),[8] and stabilized by very weakly basic anions. Most notable among these features is $\bar{\nu}$(CO), found generally above 2200 cm^{-1}. The cyclic species $[Pd_2(\mu\text{-}CO)_2]^{2+}$ is the first binuclear cation that is thermally stable in this series. It will be interesting to see if the unusual spectroscopic features noted previously for cations of the noble metals with terminal CO groups[8,18–21] extend also to those with bridging carbonyl ligands.

There is a structural precedent for $[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$, dimethyltin(IV) bis(fluorosulfate), $(CH_3)_2Sn(SO_3F)_2$. It is also a sheetlike polymer with bidentate, symmetrically bridging fluorosulfate groups.[22] Both its infrared and Raman spectra are known[23,24] and should help in identifying the anion vibrations in the spectrum of $[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$.

Experimental Section

(a) Chemicals. Palladium powder was obtained from the Ventron Corp. (Alfa Inorganics). Fluorosulfuric acid, HSO_3F (technical grade), was obtained from Orange County Chemicals and purified by double distillation.[25] Bis(fluorosulfuryl) peroxide, $S_2O_6F_2$, was prepared by fluorination of SO_3 using AgF_2 as a catalyst.[26] Carbon monoxide (CP grade, 99.5% purity) was obtained from Linde Gases and dried by condensation in a trap cooled to −196 °C and partial evaporation. $Pd(SO_3F)_3$[12] was prepared as described by us previously.

(b) Instrumentation and Equipment. Infrared spectra down to 400 cm^{-1} were recorded on two instruments: A Perkin-Elmer 598 grating spectrometer and a Bomen MB 102 Fourier-transform infrared spectrometer (FTIR). Solid samples were finely ground and pressed as thin films between AgBr or AgCl windows (Harshaw Chemicals). Far-infrared spectra in the range 500–50 cm^{-1} were obtained with a Bruker IFS-66v spectrometer with the samples as polyethylene pellets. FT-Raman spectra were recorded with a Bruker FRA 106 FT Raman accessory mounted on an IFS-66v FTIR optical bench. Samples were contained in melting-point capillaries.

Volatile materials and gases were measured in a vacuum line of known volume. A Setra 280E pressure transducer with digital output was used to measure the pressure. Standard vacuum-line techniques were employed to manipulate air- and moisture-sensitive samples. Reactions were carried out inside Pyrex round-bottom flasks (50 or 100 mL) fitted with 4-mm Kontes stopcocks and B10 ground-glass cones. Since all products were hygroscopic, they were manipulated and stored inside a Vacuum Atmospheres Corp. Dri-Lab, Model HE 493, filled with dry nitrogen and equipped with an HE 493 Dri-Train.

(c) Synthesis of Single Crystals of $[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$. Approximately 150 mg of pale yellow solid $Pd(CO)_2(SO_3F)_2$, obtained by reductive carbonylation of $Pd(SO_3F)_3$ in HSO_3F, was placed in a round-bottom flask and redissolved in about 5 mL of HSO_3F. The color of the solution changed immediately from pale yellow to light orange. After the solution stood for 4 days at room temperature, small needlelike orange-red crystals were observed. An additional 2 weeks was needed to allow the crystals to grow to a size suitable for single-crystal X-ray diffraction. The crystals were isolated by pipetting the orange-red solution out of the flask and washing the crystals repeatedly with small amounts of HSO_3F. The fluorosulfuric acid was removed first by pipetting and then by vacuum transfer with the sample at room temperature. The needles, which had grown to a length of 10–12 mm, were cut into small pieces inside the drybox and fitted into Lindemann glass capillaries. Samples used for vibrational spectroscopy were ground into a fine powder, again inside the drybox. $[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$ is an orange-red, extremely hygroscopic crystalline material that melts at 157 °C with decomposition to give a black residue. Anal. Calc for CO_4SFPd: S, 13.73; C, 5.14. Found: S, 13.97; C, 5.09.

Table 1. Crystallographic Data[a]

compd	$[Pd(CO)(SO_3F)]_n$	V, Å^3	906.3(2)
formula	CFO_4PdS	Z	8
fw	233.47	ρ_{calc}, g/cm^3	3.422
cryst system	monoclinic	T, °C	21
space group	$C2/c$	μ, cm^{-1}	44.91
a, Å	11.495(1)	transm factors	0.75–1.00
b, Å	8.255(1)	$R(F)$	0.061
c, Å	9.556(1)	$R_w(F)$	0.075
β, deg	91.94(1)		

[a] Temperature 294 K, Rigaku AFC6S diffractometer, Mo Kα (λ = 0.710 69 Å) radiation, graphite monochromator, takeoff angle 6.0°, aperture 6.0 × 6.0 mm at a distance of 285 mm from the crystal, stationary-background counts at each end of the scan (scan:background time ratio 2:1), $\sigma^2(F^2) = [S^2(C + 4B) + (0.01F^2)^2]/L_p^2$ (S = scan rate, C = scan count, B = normalized background count), function minimized $\sum w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o^2)$, $R = \sum||F_o| - |F_c||/\sum|F_o$, $R_w = (\sum w(|F_o| - |F_c|^2)^{1/2}$, and gof $= [\sum w(F_o| - |F_c|)^2/(m - n)]^{1/2}$. Values given for R, R_w, and gof are based on those reflections with $I \geq 3\sigma(I)$.

Table 2. Atomic Coordinates and B_{eq} Values

atom	x	y	z	B_{eq},[a] Å^2
Pd(1)	0.41737(3)	0.02552(4)	0.09417(3)	1.789(6)
S(1)	0.28837(9)	0.3681(1)	0.2017(1)	1.93(2)
F(1)	0.3654(4)	0.4972(4)	0.2763(4)	2.99(7)
O(1)	0.3556(3)	0.2210(5)	0.2221(4)	2.60(7)
O(2)	0.1839(4)	0.3642(5)	0.2814(5)	3.35(8)
O(3)	0.2747(4)	0.4127(7)	0.0609(5)	3.19(8)
O(4)	0.4733(4)	−0.3082(5)	0.0272(5)	3.35(8)
C(1)	0.4857(4)	−0.1730(5)	0.0136(5)	2.07(7)

[a] $B_{eq} = (8/3)\pi^2\sum\sum U_{ij}a_i^*a_j^*(\mathbf{a}_i\cdot\mathbf{a}_j)$.

Table 3. Bond Lengths (Å)[a]

Pd(1)–Pd(1)^1	3.4777(7)	Pd(1)–Pd(1)^2	2.6939(6)
Pd(1)–O(1)	2.159(3)	Pd(1)–O(2)^3	2.153(4)
Pd(1)–O(3)^4	2.653(4)	Pd(1)–C(1)	1.984(4)
Pd(1)–C(1)^2	1.966(4)	S(1)–F(1)	1.545(4)
S(1)–O(1)	1.449(4)	S(1)–O(2)	1.444(4)
S(1)–O(3)	1.420(5)	O(4)–C(1)	1.133(6)

[a] Superscripts refer to symmetry operations: (1) $1 - x, y, {}^1/_2 - z$; (2) $1 - x, -y, -z$; (3) ${}^1/_2 - x, y - {}^1/_2, {}^1/_2 - z$; (4) ${}^1/_2 - x, {}^1/_2 - y, -z$; (5) ${}^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z$.

(d) X-ray Crystallographic Analysis of $[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$. Crystallographic data appear in Table 1. The final unit-cell parameters were obtained by least-squares calculations on the setting angles for 25 reflections with 2θ = 67.8–73.0°. The intensities of three standard reflections, measured every 200 reflections throughout the data collection, remained constant. The data were processed[27] and corrected for Lorentz and polarization effects and for absorption (empirical; based on azimuthal scans for three reflections).

The structure was solved by conventional heavy-atom methods, the coordinates of the Pd and S atoms being determined from the Patterson function and those of the remaining atoms from subsequent difference Fourier syntheses. All atoms were refined with anisotropic thermal parameters. A secondary extinction correction was applied, the final value of the exctinction coefficient being 1.35(8) × 10^{-6}. Neutral-atom scattering factors and anomalous-dispersion corrections were taken from ref 28. Final atomic coordinates and equivalent isotropic thermal parameters and selected bond lengths and bond angles appear in Tables 2–4, respectively. Complete tables of crystallographic data, anisotropic thermal parameters, torsion angles, and intermolecular contacts are included as supplementary material.

Results and Discussion

(a) Synthetic Aspects. The reductive carbonylation of the solid, mixed-oxidation-state compound $Pd^{II}Pd^{IV}(SO_3F)_6$[12] at 25 °C

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Table 4. Bond Angles (deg)[a]

Pd(1)^1–Pd(1)–Pd(1)	101.25(2)	Pd(1)^1–Pd(1)–O(1)	72.3(1)
Pd(1)^1–Pd(1)–O(2)^3	79.4(2)	Pd(1)^1–Pd(1)–O(3)^4	153.94(10)
Pd(1)^1–Pd(1)–C(1)	96.9(2)	Pd(1)^1–Pd(1)–C(1)^2	98.4(2)
Pd(1)^2–Pd(1)–O(1)	138.4(1)	Pd(1)^2–Pd(1)–O(2)^3	87.4(2)
Pd(1)^2–Pd(1)–O(3)^4	104.18(10)	Pd(1)^2–Pd(1)–C(1)	46.7(1)
Pd(1)^2–Pd(1)–C(1)^2	47.3(1)	O(1)–Pd(1)–O(2)^3	87.4(2)
O(1)–Pd(1)–O(3)^4	84.8(2)	O(1)–Pd(1)–C(1)	168.3(2)
O(1)–Pd(1)–C(1)^2	92.1(2)	O(2)^3–Pd(1)–O(3)^4	87.4(2)
O(2)^3–Pd(1)–C(1)	86.1(2)	O(2)^3–Pd(1)–C(1)^2	177.8(2)
O(3)^4–Pd(1)–C(1)	104.6(2)	O(3)^4–Pd(1)–C(1)^2	94.7(2)
C(1)–Pd(1)–C(1)^2	94.0(2)	F(1)–S(1)–O(1)	102.8(2)
F(1)–S(1)–O(2)	104.2(3)	F(1)–S(1)–O(3)	105.4(3)
O(1)–S(1)–O(2)	111.1(3)	O(1)–S(1)–O(3)	115.5(3)
O(2)–S(1)–O(3)	116.1(3)	Pd(1)–O(1)–S(1)	137.3(3)
Pd(1)^5–O(2)–S(1)	138.8(3)	Pd(1)^4–O(3)–S(1)	130.0(3)
Pd(1)–C(1)–Pd(1)^2	86.0(2)	Pd(1)–C(1)–O(4)	135.8(4)
Pd(1)^2–C(1)–O(4)	138.2(4)		

[a] Superscripts refer to symmetry operations: (1) $1 - x, y, {}^1/_2 - z$; (2) $1 - x, -y, -z$; (3) ${}^1/_2 - x, y - {}^1/_2, {}^1/_2 - z$; (4) ${}^1/_2 - x, {}^1/_2 - y, -z$; (5) ${}^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z$.

produces almost exclusively *cis*-$Pd(CO)_2(SO_3F)_2$ with $\bar{\nu}$(CO) at 2208 and 2228 cm^{-1} [11] (see eq 2). If the reaction is carried out in fluorosulfuric acid, the composition of the pale yellow product is again $Pd(CO)_2(SO_3F)_2$ (Anal. Calc: C, 6.66; S, 17.78. Found: C, 6.67; S, 17.97). However, the vibrational spectrum shows greater complexity in the SO_3F-stretching and -deformation regions. There are also now four bands in the CO-stretching region. Besides bands of medium intensity at 2208 and 2228 cm^{-1}, attributed to *cis*-$Pd(CO)_2(SO_3F)_2$,[11] two strong bands at 2179 and 1967 cm^{-1} are observed. The band positions suggest the presence of both a bridging and a terminal CO group,[29-31] which in turn is possibly evidence for an oligomeric, CO-bridged isomeric species.

To separate the apparent isomer mixture, recrystallization from fluorosulfuric acid was undertaken. Indeed, a needlelike crystalline material formed from solution over a period of about 3 weeks. However, there were indications of substantial changes: The color of the solution changed from pale yellow to orange. The IR spectrum of this solution in HSO_3F shows three bands in the CO-stretching region. Bands at 2213 and 2233 cm^{-1} have previously been observed for solutions of *cis*-$Pd(CO)_2(SO_3F)_2$ in HSO_3F,[11] as well as a band at 1982 cm^{-1} due to partly ionized $[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$ (*vide infra*). The bands at 2179 and 1967 cm^{-1}, attributed to the oligomeric isomer, are no longer observed, which in turn may suggest that only this form is involved in the formation of $[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$. However, we noticed recently that on standing at room temperature the solid isomer mixture or its solution in HSO_3F will convert slowly to *cis*-$Pd(CO)_2(SO_3F)_2$. It is therefore unclear whether the oligomeric form has undergone conversion to the *cis* isomer or decomposition to $[Pd(CO)SO_3F]_n$. The crystals obtained as precipiate are red-orange, and the CO band is observed at 1977 cm^{-1} in the IR spectrum of the solid compound. In addition, the decomposition point of the product (157 °C) is now higher and the composition, determined by microanalysis, is found to correspond closely to the formula $Pd(CO)SO_3F$.

It appears that reductive elimination of SO_3F radicals, their dimerization to $S_2O_6F_2$, and the simultaneous loss of 1 mol of carbon monoxide have occurred according to

$$2Pd(CO)_2(SO_3F)_2 \xrightarrow{HSO_3F} 2Pd(CO)SO_3F + 2CO + S_2O_6F_2 \tag{3}$$

which is possibly followed by oxidation of CO to CO_2

$$CO + S_2O_6F_2 \xrightarrow{HSO_3F} CO_2 + S_2O_5F_2 \tag{4}$$

as observed recently.[20]

Even though the quantity of material used was too small to permit an unambiguous identification of the gaseous byproducts, the ^{19}F-NMR spectrum of the solution clearly shows the resonance of $S_2O_5F_2$ at 47.5 ppm. As a relevant precedent, the rather uncommon reductive elimination of $S_2O_6F_2$ has been observed previously for palladium fluorosulfates:[12,32]

$$Pd^{II}Pd^{IV}(SO_3F)_6 \xrightarrow{160\ °C} 2Pd(SO_3F)_2 + S_2O_6F \tag{5}$$

However, the process involves reduction of Pd(IV) to Pd(II) and requires elevated temperatures. In addition, bis(carbonyl) derivatives of palladium are rare and are considered to be thermally unstable.[1,2] Hence CO elimination is probable because the only other $Pd(CO)_2$ compounds known, organometallic derivatives of the type *cis*-$Pd(CO)_2R_2$ (R = C_6F_5, C_6Cl_5),[33] are stable only below −30 °C under CO pressure and will lose CO readily. In addition, the displacement of CO by SO_3F^- in HSO_3F according to

$$[Au(CO)_2]^+ + SO_3F^- \xrightarrow{70\ °C} Au(CO)SO_3F + CO \tag{6}$$

is known.[20] It appears that the formation of $Pd(CO)SO_3F$ in HSO_3F is a rather slow process, which in turn produces single crystals sufficient to permit the structural and spectroscopic studies reported here.

There are a number of seemingly polymeric or oligomeric precedents of diamagnetic palladium(I) carbonyl derivatives of the type $[Pd(CO)X]_n$, with X = Cl, Br, or O_2CR.[1,2] The first member of this group, $[Pd(CO)Cl]_n$, appears to have been reported by Manchot and König in 1926,[34] and the molecular structure of an acetate derivative of the composition $[Pd(CO)CH_3CO_2]_4{\cdot}2CH_3CO_2H$ is known[35,36] and will be discussed below. The most common synthetic route to these compounds is the reaction of CO with PdX_2 (X = Cl, Br, O_2CR) in various solvents.[1,2] The conversion of dimeric $[Pd(CO)Cl_2]_2$, with bridging Cl and terminal CO, to $[Pd(CO)Cl]_n$ in the presence of CO and with acetic anhydride as solvent is also reported,[30] but the route discovered here inadvertently is novel and confirms again that HSO_3F is a very suitable medium for the generation of noble-metal carbonyl cations[20,21] and their derivatives.

(b) Molecular Structure of $[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$. Selected bond distances and bond angles are listed in Tables 3 and 4, respectively. The packing within a polymeric sheet is shown in Figure 1, and the coordination environment of palladium, including selected interlayer contacts, is depicted in Figure 2.

The molecular structure consists of cyclic, completely planar four-membered $[Pd_2(\mu\text{-}CO)_2]$ units (point group D_{2h}) with essentially symmetrical carbonyl bridges and a cross-ring Pd–Pd distance of 2.6929(6) Å. Individual metallacycles are connected by symmetrically bridging, O-bidentate fluorosulfate groups, to give rise to polymeric sheets. The coordination environment of palladium, ignoring the Pd–Pd crossring interaction, may be described as approximately cis square planar, with bond angles between 94 and 86.1° and average Pd–C and Pd–O distances of 1.975 and 2.156 Å, respectively.

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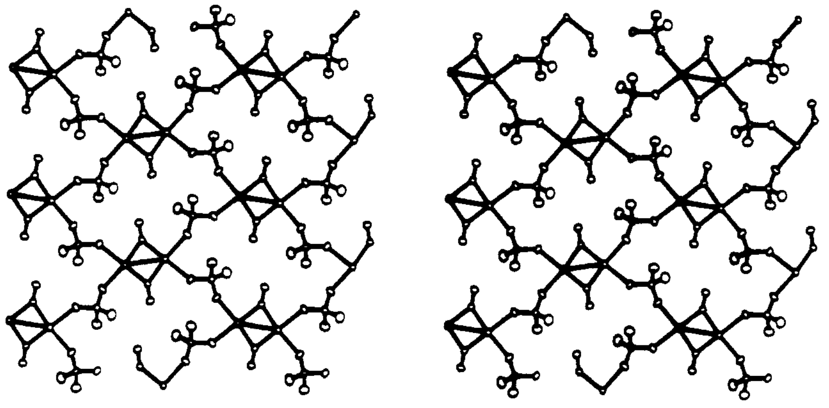

Figure 1. Stereoview of a single layer of the polymeric sheet structure of $[Pd(CO)(SO_3F)]_n$.

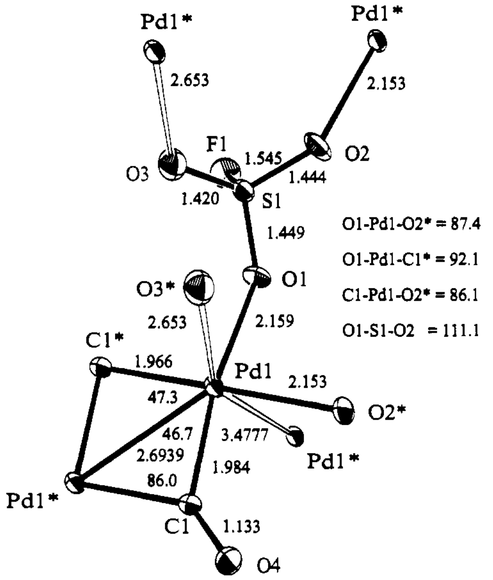

Figure 2. Perspective view of $[Pd(CO)(SO_3F)]_n$ showing the asymmetric unit and the nearest neighbors. 33% probability thermal ellipsoids are shown. Asterisks denote symmetry-related atoms (see footnote to Table 3 for more detailed information). Bond lengths are given in angstroms, and angles are in degrees.

Table 5. Relevant Bond Distances and Angles for Various Fluorosulfate Derivatives[a]

	$Me_2Sn(SO_3F)_2$[b]	$[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$	$[Au(SO_3F)_3]_2$[c]	NH_4SO_3F[d]
d(SO(1)), Å	1.472(8)	1.449(4)	1.467(6)	1.45(2)
d(SO(2)), Å	1.473(11)	1.444(4)	1.471(7)	1.45(2)
d(SO(3)), Å	1.454(7)	1.420(5)	1.384(7)	1.45(2)
d(SF), Å	1.561(8)	1.545(4)	1.507(7)	1.55(2)
∠O(1)SO(2), deg	110.5(5)	111.1(3)	111.3	113
$\angle MOS_{av}$, deg	148	138	130.5	
$d(MO)_{av}$, Å	2.24(1)	2.156(4)	2.018	

[a] O(1) and O(2) denote the two coordinated oxygen atoms. [b] Reference 22. [c] Reference 37; only bond parameters for the bidentate bridging fluorosulfate group are listed. [d] Reference 38.

There are, in addition, interlayer contacts: a Pd···Pd contact of 3.4777(7) Å and a Pd···O(3) interaction of 2.653(4) Å involving the third oxygen atom of the fluorosulfate group, which results in a rather distorted octahedral environment for each palladium. The observed 4:2 coordination is commonly observed in primarily square planar solid-state structures.

A very similar molecular structure type is found for dimethyltin(IV) bis(fluorosulfate), $(CH_3)_2Sn(SO_3F)_2$.[22] Again, a sheetlike polymer is present with bidentate, symmetrically bridging fluorosulfate groups and a regular square planar environment for tin consisting of four weakly coordinated oxygen atoms. Octahedral coordination for tin is completed, however, by the two methyl groups, and the third oxygen atom of the fluorosulfate group does not appear to be involved in any significant interaction with the tin atom.

Even though there are additional obvious differences (the $[Pd_2(\mu\text{-}CO)_2]$ ring is coplanar with the polymeric sheet, while the linear dimethyltin(IV) moiety is aligned perpendicular to it), there are two strong similarities, as can be seen in Table 5, where the essential bond distances and angles are listed and compared to structural data for the bridging fluorosulfate group of dimeric $[Au(SO_3F)_3]_2$[37] and for NH_4SO_3F,[38] where an ionic SO_3F^- group is present: (i) Metal–oxygen bonds are long and weak for both $(CH_3)_2Sn(SO_3F)_2$[22] and $[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$. The longer Sn–O distances of 2.24 Å compared to 2.156 Å for Pd–O can be attributed to a slightly larger covalent radius for tin. (ii) The sulfur–oxygen bond lengths for the two fluorosulfate groups in the polymers, labeled S–O(1) and S–O(2), differ only slightly from that of S–O(3), where O(3) indicates the third oxygen not involved in direct coordination to Sn or Pd. The bond length difference for both types of S–O groups is only ~0.025 Å, compared to 0.085 Å for $[Au(SO_3F)_3]_2$.[37] It is concluded that departure from C_{3v} symmetry is very slight in both cases. In addition, all S–O and S–F bond lengths are identical to those reported for NH_4SO_3F[38] within error limits.

The assumption that molecular, dipositive cations, linear $(CH_3)_2Sn^{2+}$,[22] and cyclic $[Pd_2(\mu\text{-}CO)_2]^{2+}$ are linked by SO_3F^- ions, packed in a bidentate fashion to give layered structures, is, in the dimethyltin(IV) compound, consistent with the reported ^{119}Sn Mössbauer data[23,24] for this and other dimethyltin(IV) salts of very strong protonic acids and superacids.[10]

The discussion will now turn to the cyclic $[Pd_2(\mu\text{-}CO)_2]^{2+}$ cation. While several molecular structures of palladium(I) carbonyl derivatives with bridging CO groups have become known, one of these, that of a tetranuclear cluster found in a complex of the composition $[Pd_4(\mu\text{-}CO)_4(\mu\text{-}CH_3CO_2)_4]\cdot 2CH_3CO_2H$,[35,36] is of particular relevancy. The cluster consists of two $[Pd_2(\mu\text{-}CO)_2]^{2+}$ cations with symmetrically bridging CO groups and bond distances and angles very similar to the ones reported here, as the summary in Table 6 indicates. However, in the case of the tetranuclear cluster, a pair of these $[Pd_2(\mu\text{-}CO)_2]^{2+}$ cations is linked by symmetrically bridging acetate ions into dimers, giving rise to a planar, nearly rectangular arrangement of four Pd(I) centers alternately bridged by two CO and two $CH_3CO_2^-$ groups. In addition, hydrogen-bonded acetic acid dimers are found in lattice spaces between the metal clusters.

As can be seen in Table 6, there is in general very good correspondence between the two sets of data, with only minor

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Table 6. Selected Bond Parameters for the Cyclic $[Pd_2(\mu\text{-}CO)_2]^{2+}$ Cation

	$[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$	$[Pd_4(\mu\text{-}CO)_4(\mu\text{-}CH_3CO_2)_4]\cdot 2CH_3CO_2H$[a]
d(Pd–Pd), Å	2.6929(6)	2.663(1)
d(Pd···Pd),[b] Å	3.4777(7)	2.909(1)
d(Pd(1)–C(1)), Å	1.966(4)	1.97
d(Pd(2)–C(11)), Å	1.984(4)	2.01
d(PdO)$_{av}$, Å	2.156(4)	2.12
d(CO), Å	1.133(6)	1.15
∠Pd(1)C(1)Pd(2), deg	86.0	84.2

[a] Reference 35; esd's are only quoted where they could be found in the reference. [b] Denotes, in the case of $[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$, the interlayer Pd–Pd contact and, for $[Pd_4(\mu\text{-}CO)_4(\mu\text{-}CH_3CO_2)_4]\cdot CH_3CO_2H$, the Pd–Pd bonds with two acetate bridges.

exceptions. The rather long Pd···Pd contact of 2.909(1) Å for $[Pd_4(\mu\text{-}CO)_4(\mu\text{-}CH_3CO_2)_4]\cdot 2CH_3CO_2H$, supported by two bridging acetate groups, is compared in the case of $[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$ to an interlayer contact of 3.4777(7) Å. The shorter Pd–O bond lengths of 2.12 Å are a reflection of the greater basicity of the acetate group compared to that of the fluorosulfate group.

On the other hand, the short Pd–Pd bond distances, supported by two bridging CO groups in each case, are almost identical to previously reported[39–42] Pd–Pd single bonds for Pd(I) complexes, which are commonly found in the range 2.53–2.69 Å. The two Pd–C distances are in each case not completely identical in length, but the differences are almost within the estimated standard deviations.

The C–O bond distance for the $[Pd_2(\mu\text{-}CO)_2]^{2+}$ cation is rather short for a bridging carbonyl ligands. The distance is 1.133(6) Å, only slightly longer than in CO, 1.1281 Å.[43] For the acetate derivative a value of 1.15 Å is quoted,[35] and no conclusions are possible. It is anticipated that the CO-stretching frequencies for both compounds, to be discussed subsequently, allow a better comparison.

There is less agreement with structural data reported for other Pd(I)–carbonyl derivatives where other π-acceptor ligands are present as well in the molecule. Frequently, as in $Pd_2(\mu\text{-}CO)Cl_2\cdot 3PEt_2Ph$[42] or $[Pd(dppm)O_2CCF_3](\mu\text{-}CO)$[44] (dppm = bis(diphenylphosphino)methane), asymmetric carbonyl bridges are present with C–O distances of 1.156(4)[42] and 1.20(3) Å,[44] respectively. In the case of (μ-carbonyl)(μ-(bis(diphenylarsino)methane)dichlorodipalladium(I), a symmetric carbonyl bridge is claimed;[45] however, the Pd–C distances of 1.84(5) and 1.95(6) Å are not sufficiently accurate to be completely certain on this point.

In all of these structurally characterized palladium(I) carbonyl derivatives,[34,35,42,44,45] only bridging CO groups are encountered. There is, however, one exception—bis[(μ-chloro)dicarbonylpalladium(I)], $[Pd(CO)_2(\mu\text{-}Cl)]_2$,[46] where bridging chlorides and only terminal CO ligands are found. While there is no precedent for both composition and structure among other palladium carbonyl derivatives,[1,2] close inspection of the reported unit-cell parameters, internuclear distances, and IR stretching frequencies of $[Pd(CO)_2(\mu\text{-}Cl)]_2$[46] results in the disturbing observation that these data are identical within error limits to previously reported parameters for the well-known complex $[Rh(CO)_2(\mu\text{-}Cl)]_2$.[47,48]

In summary, the cyclic $[Pd_2(\mu\text{-}CO)_2]^{2+}$ reported here departs from previously characterized palladium(I) carbonyl derivatives on three accounts: (i) it is the first structurally characterized binary carbonyl cation formed by a group-10 metal; (ii) the molecular cation is a rare case of a thermally stable, inorganic cyclic molecule of D_{2h} symmetry; and (iii) the C–O distance is very short for a symmetrically bridging carbonyl ligand. The last two points provide an incentive for a vibrational study, which will be discussed in the next section.

(c) Vibrational Spectra. Vibrational spectroscopy has played a very useful role in studies of metal carbonyl compounds[49,50] for three reasons: (i) CO-stretching vibrations are usually observed between 2100 and 1600 cm^{-1}, where they are easily identified and where vibrational coupling to other fundamentals is usually not observed. (ii) The band position of $\bar{\nu}$(CO) is very sensitive to subtle changes in coordination and bonding of the CO ligand to the metal center. Hence information regarding the molecular geometry of metal carbonyl compounds as well as the bonding characteristics of the CO ligand has become readily available in the past[49,50] from the study of the CO-stretching vibrations. (iii) In areas of high C–O bond order (between 2 and 3), small changes in bond order are more clearly manifested in shifts of $\bar{\nu}$(CO) (cm^{-1}) than in the internuclear distance of C–O (Å), where estimated standard deviations and, in case of terminal CO groups, thermal motion cause uncertainties.

In spite of these advantages, a detailed vibrational analysis, beyond the CO-stretching range, of transition-metal carbonyl derivatives is rarely attempted. This is largely due to experimental limitations. Equipment to record far-IR spectra is commonly not available. Raman spectra are difficult to obtain because many metal–carbonyl derivatives are intensely colored and photolytically labile. In addition, necessary structural information is often either not available, or the molecular structures are far too complex for a meaningful vibrational analysis of the molecules.

All the above-mentioned limitations do not apply here. The molecular structure of $[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$ reveals two weakly interacting ions, and the molecular structure of $(CH_3)_2Sn(SO_3F)_2$[22] (where the complete vibrational spectrum is known[23,24]) provides a useful precedent.

The cyclic $[Pd_2(\mu\text{-}CO)_2]^{2+}$ cation has D_{2h} symmetry. Since there is no preferred rotational axis, arbitrary choices have to be made. The 2-fold axis with both CO groups placed on it is designated as the *z* axis, and the Pd–Pd bond axis becomes the *y* axis. The irreducible representations of normal vibrations for the cation $[Pd_2(\mu\text{-}CO)_2]^{2+}$ are

$$\Gamma_{vib} = 3A_g[\nu_1,\nu_2,\nu_3(Ra,p)] + 1B_{2g}[\nu_4(Ra,dp)] + 2B_{3g}[\nu_5,\nu_6(Ra,dp)] + 2B_{1u}[\nu_7,\nu_8(IR)] + 2B_{2u}[\nu_9,\nu_{10}(IR)] + 2B_{3u}[\nu_{11},\nu_{12}(IR)]$$

for a total of twelve nondegenerate fundamentals. Six are observed only in the Raman, and the other six, only in the IR spectrum.

Even though it has been argued in the preceding section that the fluorosulfate ion, on the basis of bond distances and angles, approaches C_{3v} symmetry, the weak interaction with the cyclic $[Pd_2(\mu\text{-}CO)_2]^{2+}$ cation results in a symmetry reduction to C_s. The irreducible representations for this point group applied to a five-atom molecule are

$$\Gamma_{vig} = 6A'[\nu_1\text{–}\nu_6(Ra,p,IR)] + 3A''[\nu_7\text{–}\nu_9(Ra,dp,IR)]$$

With all 9 fundamentals due to the anion both Raman and IR

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Table 7. Vibrational Spectral Data for $[Pd_2(CO)_2](SO_3F)_n$ and $(CH_3)_2Sn(SO_3F)_2$[a]

IR: ν (cm^{-1}) intens		Raman: Δ^- (cm^{-1}) intens	
$[Pd_2(CO)_2]$-$(SO_3F)_2$	$(CH_3)_2$-$Sn(SO_3F)_2$	$[Pd_2(CO)_2]$-$(SO_3F)_2$	$(CH_3)_2$-$Sn(SO_3F)_2$
1977 s		*2027* vs	
~*1940* vw, sh		1330 m	
1311 s	1351 vs, br		1354 s
		1303	
		1215 vw	
1202 vs	1189 vs, br		1231 w
		1189 w	
1083 s	1088 m	1086 vs	1088 s
	1072 s, br		
827 ms	827 m, sh	823 m	826 ms
682 ms			
638 m, sh			
603 m	600 m, sh	600 w	610 w
585 m, s	581 ms	586 m	584 m
567 s	556 ms	572	551 mw
435 m	417 s	435 m	420 w
424 m		426 m	
		416 m s	
406 m		409 s	
395 ms			
	360 w		367 mw
	304 w		320 mw
		265 ms	
		256 ms	
243 vs			
		118 w	
112 ms			
		97 vw	
76 m		85 w	

[a] SO_3F modes only.

active, while the 12 fundamentals due to the cation are subject to the mutual exclusion rule, a differentiation between both sets of fundamentals and hence an unambiguous identification of the bands due to the cation should in principle be possible.

The vibrational bands for $[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$ down to 50 wavenumbers are listed in Table 7 and compared to the bands due to the fluorosulfate group in $(CH_3)_2Sn(SO_3F)_2$[23,24] down to 300 cm^{-1}. Of the Raman bands of the latter compound, a weak SO_3 stretch at 1231 cm^{-1} had previously not been observed but was detected in the FT-Raman spectrum obtained in this study. The FT-Raman spectrum of $[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$ is shown in Figure 3.

The bands attributed in both compounds to the fluorosulfate group show reasonable correspondence. The SO_3-stretching vibrations of $[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$ found at 1310 and 1200 cm^{-1} are both split by ~25 cm^{-1} in the Raman spectrum only. This splitting may be attributed to factor group effects. The two SO_3 bands arise from a splitting of the asymmetric SO_3-stretching mode (E) for ionic fluorosulfates, usually found at ~1280 cm^{-1},[50] due to a symmetry reduction from C_{3v} to C_s. The extent of this splitting may be taken as a measure of the covalent anion–cation interaction and the departure from C_{3v} symmetry for the fluorosulfate group. The actual band separations are 110 cm^{-1} for $[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$ and ~170 cm^{-1} for $(CH_3)_2Sn(SO_3F)_2$, consistent with observations in regard to S–O bond lengths for both compounds, as summarized in Table 5 and discussed in the preceding section. Finally it is noted that the SF-stretching vibrations at ~825 cm^{-1} are intermediate between $\bar{\nu}$(SF) values for ionic alkali metal fluorosulfates at ~750–780 cm^{-1} [51] and covalent fluorosulfates at ~880 cm^{-1}.[52]

In summary, the internal vibrations of the fluorosulfate groups in $[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$ are consistent with weakly interacting fluorosulfate ions, arranged in a bidentate fashion. It hence appears justified to partition the observed vibrational bands into those due to the anion, as done in the section above, and to attribute the remaining bands, which must follow the mutual exclusion rule, to the cation. In view of the rather weak covalent anion–cation interaction and interlayer contacts revealed by the molecular structure determination, vibrations involving both the cation and anion should be observable only at very low wavenumbers.

Consistent with this view of weak covalent anion–cation interaction, only single bands due to the CO-stretching vibrations are observed in both the Raman, at 2027 cm^{-1}, and the IR spectrum, at 1977 cm^{-1}, of $[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$. A very weak shoulder at ~1940 cm^{-1} in the IR spectrum is assigned as $\bar{\nu}$(^{13}C–O). For $[Pd_4(\mu\text{-}CO)_4(\mu\text{-}O_2CCH_3)_4]$ two intense IR bands are found at 1940 and 1975 cm^{-1},[35] and for the solvate with acetic acid, where a molecular structure is known,[35,36] the IR bands are shifted to 1934 and 1968 cm^{-1}. It appears that vibrational coupling within the tetranuclear cluster is a likely cause for the intense doublets in the CO-stretching region. Unfortunately, Raman spectra do not seem to have been reported for both cluster compounds.

For seemingly polymeric $[Pd(CO)X]_n$ (X = Cl, Br),[53] intense IR bands at 1978 and 1953 cm^{-1}, respectively, are reported, but for both compounds several bands of lower intensity are observed in the CO-stretching region, at both slightly lower and slightly higher wavenumbers. Bands at lower wavenumbers, two for each compound, may be interpreted either as ^{13}C-satellite bands or as bands due to vibrational coupling. The bands at higher wavenumbers, at 2023 and 2002 cm^{-1} for the chloro and at 2008 and 1996 cm^{-1} for the bromo derivative, may be symmetric CO-stretching vibrations, which should be only Raman active for point group D_{2h} and which are split by vibrational coupling. Their observation in the IR spectrum implies that the symmetry in the suggested $[Pd_2(\mu\text{-}CO)_2]$ units[53,54] is lower than D_{2h}. Due to thermal instability of the two Pd(I)–carbonyl derivatives, a Raman spectrum, which would confirm our interpretation, is again not reported.

A common feature of all Pd(μ-CO) derivatives discussed here[35,53] and of $[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$ is the unusual band position of $\bar{\nu}$(CO), which is about 200 cm^{-1} higher than for bidentate bridging groups in transition-metal carbonyl compounds.[49,50] For neutral, polynuclear Pd(I) derivatives, the situation is different. In addition to the derivatives cited above, which are of the general type $[Pd(CO)X]_n$ with X = Cl, Br, CH_3CO_2, or SO_3F,[35,36,53,54] where π-donation appears to be reduced, there are examples among the complexes with reported crystal structures where the CO-stretching vibrations are considerably lower and fall into a more normal range for bridging carbonyls.[49,50,54] However, here other π-acid ligands are present in the molecule in addition to CO. In $[Pd(dppm)(O_2CCF_3)]_2(\mu\text{-}CO)$[44] (dppm = bis((diphenylphosphino)methane), an asymmetric CO bridge is observed and $\bar{\nu}$(CO) is reported at 1720 cm^{-1}. For the analogous dpam derivative (dpam = bis(diphenylarsino)methane), $[Pd(dpam)Cl]_2(\mu\text{-}CO)$,[45] the CO bridge is symmetric within experimental error (Pd–C = 1.84(5) and 1.95(6) Å), and $\bar{\nu}$(CO) is again observed at 1720 cm^{-1}, which is well within the range 1700–1860 cm^{-1} quoted for bidentate bridging CO ligands in classical transition-metal carbonyl derivatives.[53] The latter examples allow the comment that, at least formally, addition of a bidentate π-acceptor ligand like dpam to polymeric $[Pd(CO)Cl]_n$ with the principal $\bar{\nu}$(CO) band at 1978 cm^{-1},[53,54] has reduced $\bar{\nu}$(CO) by 258 cm^{-1}. Besides structural changes, the CO–Pd bond type is altered by increasing the metal to CO π-back-donation in the resulting complex.

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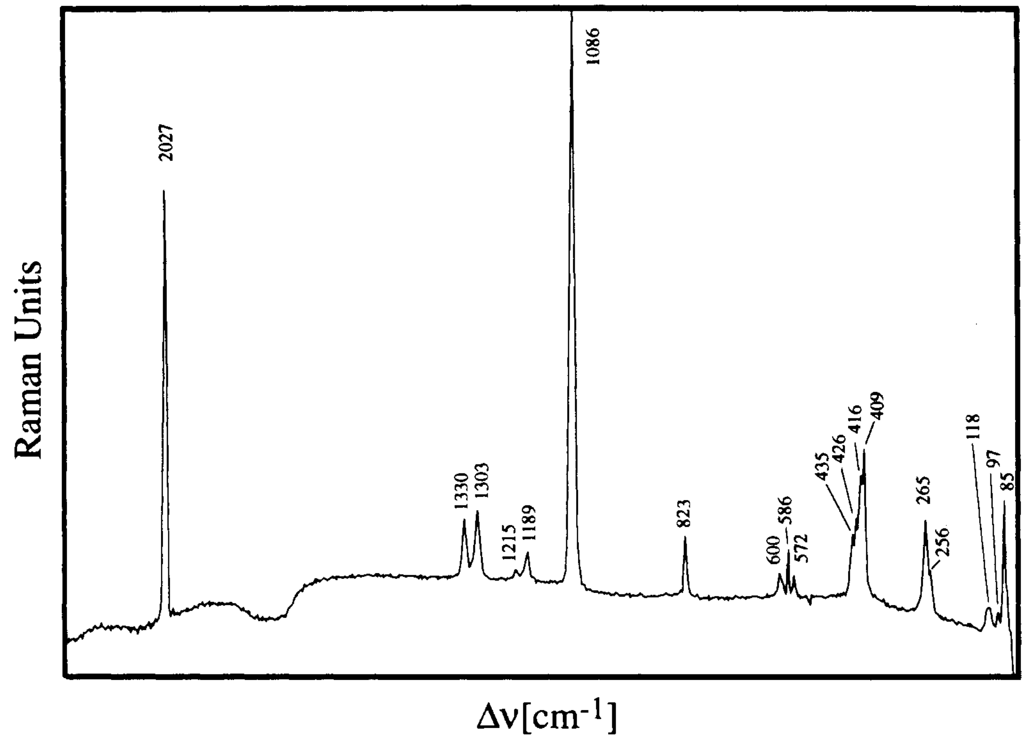


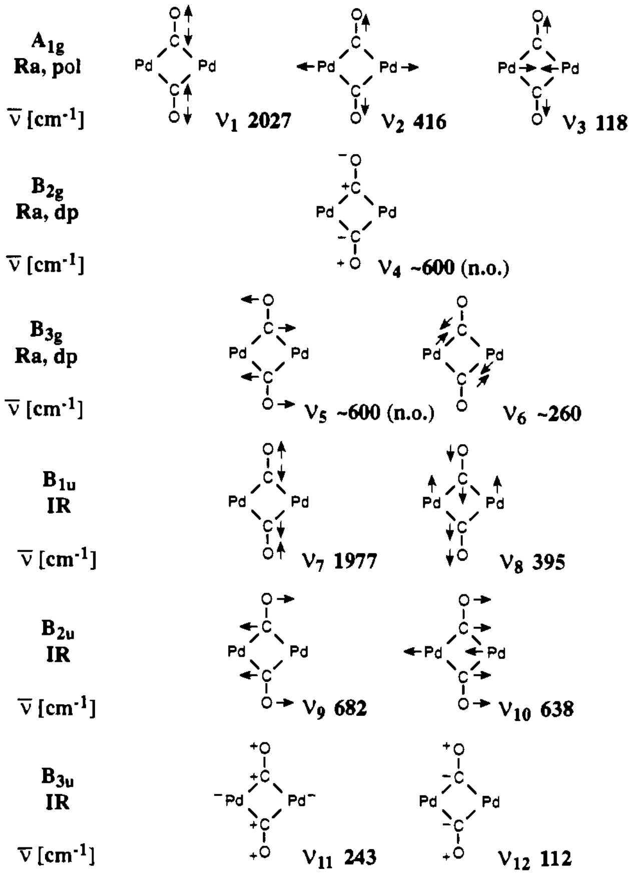
Figure 3. FT-Raman spectrum of $[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$.

For the cation $[Pd_2(\mu\text{-}CO)_2]^{2+}$ the identification and assignment of $\bar{\nu}$(CO) and the identification of the remaining fundamentals are easily accomplished. As seen from Table 7, a total of 10 vibrational bands (6 IR active, 4 Raman active), listed in italics, are attributed to the cation. The 12 fundamental vibrations of the $[Pd_2(\mu\text{-}CO)_2]^{2+}$ ring are depicted in Figure 4 together with a tentative assignment. This assignment is, in the absence of relevant precedents, based largely on the relative masses of atoms involved in various vibrational motions.

It appears that two of the six Raman-active vibrations are not found. The two missing bands are $\nu_4(B_{2g})$, a symmetric, out-of-plane CO deformation, and $\nu_5(B_{3g})$, a symmetric in-plane CO deformation mode. Both vibrations are very similar and may even coincide, due to accidental degeneracy. They are expected in the region of ~600 cm^{-1}, where overlap with anion bands can occur. In addition, as in the case of $[Au(CO)_2]^+$,[21] the bands due to deformation modes may be of very low intensity. It is hoped that continued synthetic efforts will lead to $[Pd_2(\mu\text{-}CO)_2]^{2+}$ salts with different counteranions, e.g., SbF_6^- or $Sb_2F_{11}^-$. This will hopefully permit an unrestricted view of the spectral region at ~600 cm^{-1}. A similar approach has been successful in the case of $[Au(CO)_2][Sb_2F_{11}]$, where a complete vibrational assignment is reported.[21]

In summary, the cyclic $Pd_2(\mu\text{-}CO)_2$ unit appears to be present in all Pd(I)–monocarbonyl derivatives of the type $[Pd(\mu\text{-}CO)X]_n$ (X = Cl, Br, CH_3CO_2, SO_3F) know so far. Structural differences appear to be caused by the bridging anion X. Strong, effective bridging by the halide anions appears to be leading to, alternately, CO- and Cl- or Br-bridged polymers, according to their vibrational spectra.[53,54] Less effective bridging by bidentate acetate groups results in the pairing of two $[Pd_2(\mu\text{-}CO)_2]$ units according to the molecular structure[35,36] and consistent with the vibrational spectra. The weakly nucleophilic, poorly bridging fluorosulfate anions, arranged in a bidentate mode, isolate individual $[Pd_2(\mu\text{-}CO)_2]^{2+}$ cations sufficiently to permit a vibrational treatment in terms of point group D_{2h}.

Common to all palladium(I) carbonyl derivatives of the $[Pd(\mu\text{-}CO)X]_n$ type is the unusually high CO stretching frequency, which for $[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$ averages out to 2002 cm^{-1}, about 200–300 cm^{-1} higher than observed for transition-metal carbonyls.[49,50,55] The bonding situation hence parallels very recent observations made by us for various cationic Pd(II)–carbonyl derivatives with terminal CO groups,[8,11] most notably among them $[Pd(CO)_4][Sb_2F_{11}]_2$[8] with $\bar{\nu}(CO)_{av}$ of 2259 cm^{-1}, again 200–400 cm^{-1} higher than in the corresponding classical transition-



(n.o.) denotes not observed.

Figure 4. Fundamental vibrations of $[Pd_2(\mu\text{-}CO)_2]^{2+}$.

metal carbonyls.[49,50,55] In both instances extensively reduced π-back-donation from Pd to CO is suggested.

Summary and Conclusions

On the basis of the molecular structure and the complete vibrational spectrum of $[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$ reported here, a strong case can be made for the presence of a planar, binuclear carbonyl-bridged cation $[Pd_2(\mu\text{-}CO)_2]^{2+}$ of point group D_{2h}. This is the fourth in a series of highly symmetric and thermally stable carbonyl cations like $[Au(CO)_2]$ $(D_{\infty h})$,[20,21] $[Pt(CO)_4]^{2+}$, and $[Pd(CO)_4]^{2+}$ (both D_{4h}),[8] reported by us very recently, but the first with bridging CO ligands and the first structurally characterized cation in this group. In all, four cations with unusually high CO-stretching frequencies are observed on account of the substantially reduced π-back-donation. The classical synergetic bonding scheme does not apply and the effective atomic number rule is irrelevant for the noble-metal carbonyl cations.

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Supplementary Material Available: Complete tables of crystallographic data, anisotropic thermal parameters, torsion angles, and nonbonded contacts out to 3.60 Å for $[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$ (6 pages). Ordering information is given on any current masthead page.

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[55] Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; John Wiley & Sons: New York, 1988; p 1034.