

Articles

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Reaction of Carbon Monoxide in the Superacid $\text{HSO}_3\text{F}-\text{Au}(\text{SO}_3\text{F})_3$ and the Gold(I) Bis(carbonyl) Cation $[\text{Au}(\text{CO})_2]^+$. Isolation and Characterization of Gold(I) Carbonyl Fluorosulfate, $\text{Au}(\text{CO})\text{SO}_3\text{F}$

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Solutions of gold tris(fluorosulfate), $\text{Au}(\text{SO}_3\text{F})_3$, in fluorosulfuric acid, HSO_3F , behave as superacids and will dissolve up to ~ 3.5 mol of CO/mol of $\text{Au}(\text{SO}_3\text{F})_3$. During the CO uptake, Au(III) is reduced to Au(I), with $\text{Au}^+(\text{sol})$ stabilized by CO to give the cation $[(\text{OC})\text{Au}(\text{CO})]^+(\text{sol})$. The linear five-atom cation is characterized by its vibrational spectrum with CO stretching frequencies observed at 2251 (Raman) and 2211 (IR) cm^{-1} . The cation is stable in solution, but solvent removal in vacuo leads to the formation of a new gold(I) monocarbonyl derivative, $\text{Au}(\text{CO})\text{SO}_3\text{F}$, in quantitative yield as a white solid. $\text{Au}(\text{CO})\text{SO}_3\text{F}$ is thermally stable up to 190 °C. The CO stretch is found at 2198 and 2195 cm^{-1} in the Raman and IR spectra, respectively, well above the value of free CO.

Introduction

Solutions of gold tris(fluorosulfate), $\text{Au}(\text{SO}_3\text{F})_3$, in fluorosulfuric acid, HSO_3F , have been recognized previously¹ as strong, monoprotic superacids, with the weakly basic tetrakis(fluorosulfato)aurate(III) ion, $[\text{Au}(\text{SO}_3\text{F})_4]^-$, capable of stabilizing a number of strongly electrophilic cations.² The seemingly low oxidizing power of Au(III) in this system suggests a possible use: the protonation of weakly basic, readily oxidizable carbon monoxide, in the hope of forming the formyl cation, HCO^+ .

This formyl cation has been suggested as a primary ionic product formed in the combustion of hydrocarbons. It has also been observed as a reasonably abundant species in interstellar molecular clouds,³ and its microwave spectrum is known.⁴ In addition, the formyl cation is postulated as a reactive intermediate in acid- and superacid-catalyzed formylation reactions.⁵ However, attempts to observe the cation by NMR spectroscopy under stable ion conditions using ¹³C-enriched CO in superacid solution have been unsuccessful, on account of rapid proton exchange even at low temperatures.⁵ On the other hand, matrix isolation experiments have allowed detection of weakly bound molecular complexes of the type $\text{OC}\cdots\text{HF}$ and $\text{CO}\cdots\text{HF}$, with the former the more stable one.⁶

We want to report on the behavior of carbon monoxide in the superacid $\text{HSO}_3\text{F}-\text{Au}(\text{SO}_3\text{F})_3$, followed by PVT measurements, vibrational spectroscopy, and, to a limited extent, UV-visible and ¹⁹F NMR spectroscopy. While the interaction ultimately leads to gold(I) carbonyl fluorosulfate, $\text{Au}(\text{CO})\text{SO}_3\text{F}$, which is isolated and characterized, there is strong evidence for the formation of the novel, linear cation $[(\text{OC})\text{Au}(\text{CO})]^+$ in solution as a precursor to $\text{Au}(\text{CO})\text{SO}_3\text{F}$.

Experimental Section

Chemicals. Gold powder (20 mesh) of 99.99% purity was obtained from the Ventron Corp. HSO_3F technical grade (Orange County Chemicals) was doubly distilled before use.⁷ $\text{S}_2\text{O}_6\text{F}_2$ was obtained by the catalytic fluorination of SO_3 over AgF_2 ,⁸ and CO was produced from formic acid and H_2SO_4 in a 200-mL glass flask fitted with a Knotes valve. Removal of all less volatile impurities was accomplished by cooling the reaction products with liquid oxygen prior to use and removing the CO under vacuum. CsSO_3F is obtained from CsCl and HSO_3F as described.⁷ A sample of DSO_3F was obtained from Aldrich Chemicals, and AgSbF_6 was purchased from Ozark-Mahoning Pennwalt.

Instrumentation. UV-visible spectra were recorded on a Perkin-Elmer 124 spectrophotometer. Raman spectra were recorded on a Spex Ra-

malog 5 instrument, equipped with an Ar^+ (Spectra Physics) laser, with samples contained in 5 mm o.d. NMR tubes or 2 mm o.d. capillaries. The NMR tubes were equipped with a rotationally symmetrical, Teflon stem valve (Young, London, U.K.). ¹⁹F NMR spectra were measured on a Varian XL300 spectrometer. Gas-phase IR spectra were recorded on a Perkin-Elmer 598 grating spectrometer, while condensed-phase spectra were obtained on a Nicolet 5-DX FT-IR instrument. Solid or liquid samples were pressed as thin films between IR grade silicon disks (Wacker Chemie, Burghausen, FRG) of 45-mm diameter and 0.5-mm thickness, mounted in an airtight sample holder made from Teflon.

Amounts of gaseous reactants or reaction products were determined in a vacuum line of known volume with the aid of a Setra 280E capacity manometer. Synthetic reactions were performed in ~ 100 -mL glass bulbs equipped with 10-mm valves with Teflon stems (Young, London, U.K.).

Solid samples are manipulated inside a Vacuum Atmospheres Corp. Dri Lab, Model HE-493, filled with dry N_2 and equipped with a HE-493 Dri Train circulating unit.

Synthesis of Gold(I) Carbonyl Fluorosulfate, $\text{Au}(\text{CO})\text{SO}_3\text{F}$. $\text{Au}(\text{CO})\text{SO}_3\text{F}$ is conveniently prepared in a sublimation apparatus made from Pyrex glass with an internal volume of about 150 mL, fitted with a Teflon stem valve (Young) and a Teflon-coated spin bar. The apparatus is charged with 0.592 g (3.005 mmol) of gold powder. The cold finger is initially sealed with Halocarbon wax, and the apparatus is evacuated. About 4 g of HSO_3F (~ 40 mmol) and 2 g of $\text{S}_2\text{O}_6\text{F}_2$ (~ 10 mmol) are added by distillation in vacuo. The mixture is stirred at room temperature until all of the gold powder has dissolved. The excess $\text{S}_2\text{O}_6\text{F}_2$ is subsequently removed in vacuo. The resulting orange solution is stirred vigorously, and 10 mmol of CO is admitted to the reactor. The rapid CO uptake is monitored by measuring the vapor pressure above the liquid phase. The color of the liquid changes immediately to yellow and eventually fades completely, to become colorless when the reaction is completed. The volatile products, excess CO, as well as CO_2 , $\text{S}_2\text{O}_5\text{F}_2$, and HSO_3F , are removed in vacuo overnight, with the reactor at room temperature. At this stage the cold finger is cooled with running water and the solid residue is slowly warmed to 80 °C under a dynamic vacuum. A white solid sublimes from the light yellow melt onto the cold finger, and only a very small amount of a brown residue is left behind. Yield: 0.974 g of $\text{Au}(\text{CO})\text{SO}_3\text{F}$ (expected 0.9736 g). $\text{Au}(\text{CO})\text{SO}_3\text{F}$ melts at 49–50 °C to a slightly yellow liquid that begins to decompose

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Table I. Vibrational Frequencies and Assignments for Au(CO)SO₃F and Related Compounds^a

Au(CO)SO ₃ F					Au(CO)Cl ^b		KSO ₃ F ^c	
Raman (liq)		IR (solid)			IR (CH ₂ Cl ₂)		Raman (solid)	
$\Delta\nu$, cm ⁻¹	int	ν , cm ⁻¹	int	assgnt ^d	ν , cm ⁻¹	assgnt	$\Delta\nu$, cm ⁻¹	assgnt
2198	vs	2195	s	$\nu(^{12}\text{CO})$	2163	$\nu(^{12}\text{CO})$		
		2145	w, sh	$\nu(^{13}\text{CO})$	2114	$\nu(^{13}\text{CO})$		
1368	w	1360	vs	$\nu(\text{SO}_3)$ (A'')			1285	$\nu(\text{SO}_3)$ (E)
1200	m	1198	vs	$\nu(\text{SO}_3)$ (A')			1079	$\nu(\text{SO}_3)$ (A ₁)
1020	s	1020	vs	$\nu(\text{SO}_3)$ (A')			745	$\nu(\text{SF})$ (A ₁)
792	w, br	810	s	} $\nu(\text{SF})$				
		768	s					
640	m	641	m	$\nu(\text{AuO}) + \rho(\text{SO}_3)$ (A')			594	} $\delta(\text{SO}_3)$ (E)
578	m	577	s	$\delta(\text{SO}_3)$ (A')			586	
553	w	554	s	$\delta(\text{SO}_3)$ (A'')			570	$\delta(\text{SO}_3)$ (A ₁)
456	w	445	w	$\nu(\text{AuC})$	443	$\nu(\text{AuC})$		
435	w			$\delta(\text{AuCO})$	416	$\delta(\text{AuCO})$		
400	w	411	w	$\rho(\text{SO}_3\text{F})$ (A')	371	} $\nu(\text{AuCl})$	407	$\rho(\text{SO}_3\text{F})$ (E)
		390	w	$\rho(\text{SO}_3\text{F})$ (A'')	364			
268	m	251	m	Au(CO)SO ₃ F bend				
115	w			Au(CO)SO ₃ F tors	95	$\delta(\text{ClAuC})$		

^a Abbreviations: s = strong, m = medium, w = weak, v = very, br = broad, sh = shoulder, ν = stretch, δ = bend, ρ = rocking. ^b Reference 19a. ^c Reference 13b. ^d For the OSO₂F group. C_{3v} symmetry is assumed.

at 190 °C. Anal. Calcd for CAuFO₄S: C, 3.70; S, 9.88. Found: C, 3.81; S, 9.99.

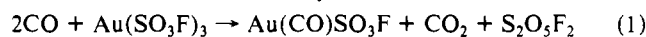
For a more detailed analysis of the volatile reaction products and their prior separation by trap to trap distillation, the following cool bath temperatures are recommended: -60 °C for HSO₃F, -120 °C for S₂O₆F₂ or S₂O₆F₂, and -196 °C for CO₂. CO remains volatile at -196 °C in vacuo.

Results and Discussion

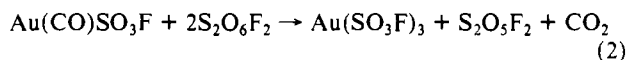
(a) Synthesis and Characterization of Au(CO)SO₃F. Gaseous carbon monoxide, CO, is found to be nearly insoluble in fluoro-sulfuric acid. Uptake from the gas phase with an initial CO pressure of ~1 atm is followed by a slight pressure decrease at 25 °C, suggesting a CO:HSO₃F mole ratio of <0.01. If however Au(SO₃F)₃ is generated by oxidation of gold with S₂O₆F₂¹ and the excess S₂O₆F₂ is removed in vacuo from the approximately 1.7 M (for a nonstandard definition of M, see footnote to Table II) solution in HSO₃F, CO is rapidly absorbed from the gas phase. Ultimately about 3.5 mol of CO/mol of Au(SO₃F)₃(soln) will dissolve at 25 °C.

During the CO uptake, two distinct color changes occur in the liquid phase. The initial orange color of the solution, which absorbs laser light (Ar^+ , $\lambda_0 = 514.5$ nm) and prevents the recording of a Raman spectrum, changes to yellow. Raman scattering is now observed. Continued CO dissolution produces a colorless solution. The assumption that reduction of Au(III) to Au(I) occurs is confirmed by the isolation (by trap to trap distillation), identification (by IR spectroscopy), and mass determination (by PVT measurements) of the volatile products. A 1-mol sample of Au(SO₃F)₃ generates 1 mol each of the volatile reduction products CO₂ and S₂O₅F₂.

When all volatile materials at room temperature are removed, a white solid crystallizes out and subsequently sublimes between 70 and 80 °C. This solid is identified as gold(I) carbonyl fluorosulfate, Au(CO)SO₃F. If the experiment is carried out in a sublimation apparatus, as described in the Experimental Section, the isolated yield of Au(CO)SO₃F is almost quantitative. The overall reaction is described by



Besides microanalysis of Au(CO)SO₃F and the quantitative material balance for the formation reaction, the composition is confirmed also by the reaction of Au(CO)SO₃F with excess S₂O₆F₂ and the material balance for the oxidation reaction



Gold(I) carbonyl fluorosulfate, Au(CO)SO₃F, is a white, moisture-sensitive solid, which melts at 49–50 °C to a pale yellow

liquid. The liquid is thermally stable to 190 °C and has at 60 °C a density of 3.65 g cm⁻³. Above 190 °C, CO evolution occurs, presumably resulting in the formation of the as yet unknown AuSO₃F, but at ~220 °C, gold metal and a yellow oil form. Metallic gold and a black oil are also produced when Au(CO)-SO₃F is exposed to moisture.

The molecular structure of Au(CO)SO₃F, with a terminal CO and a monodentate fluorosulfate group both bonded to Au, possibly in a collinear fashion, is evident from the vibrational spectra summarized in Table I. Exposure to laser light, with the sample at room temperature, causes the compound to melt, and only a Raman spectrum of the melt is obtained and compared to the infrared spectrum of the solid.

The most intriguing feature of the vibrational spectra is an unprecedentedly high CO stretching frequency, observed at 2198 cm⁻¹ in the Raman and at 2195 cm⁻¹ in the IR spectra. This is well above the value of 2143 cm⁻¹ reported for free CO.⁹ Similarly high $\nu(\text{CO})$ values have been reported previously for other mononuclear derivatives, e.g. for [Cu(CO)]⁺[AsF₆]⁻,¹⁰ where a value of 2180 cm⁻¹ is observed.

It appears that both Au(I) and Cu(I) act predominantly as σ -acceptors in both compounds, with possibly little or no π -back-donation. The observed increase in $\nu(\text{CO})$ on coordination reflects removal of electron density from the very slightly antibonding MO on carbon, designated as 5 σ p,¹¹ which is not compensated for by back-donation. As the two examples illustrate, the acceptor ability of the metal is increased by a weakly nucleophilic anionic ligand like AsF₆⁻ or SO₃F⁻.

Band positions found for the fluorosulfate vibrations, in particular in the stretching region, are not consistent with an ionic formulation as had been proposed for [Cu(CO)]⁺[AsF₆]⁻.¹⁰ A comparison to vibrational spectra of two other examples of metal carbonyl fluorosulfates, Mn(CO)₅SO₃F and Re(CO)₅SO₃F,¹² is helpful.

In ionic fluorosulfates like KSO₃F,¹³ where the anion has C_{3v} symmetry, two SO₃ and one SF stretching frequencies are found at 1285 (E), 1079 (A₁), and 745 (A₁) cm⁻¹, respectively. Anion coordination through oxygen in a monodentate fashion results in a lower symmetry, a splitting of the E mode into two components,

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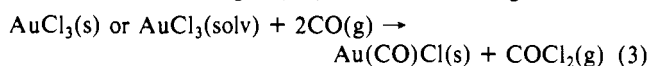
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a shift of the third SO_3 stretch to lower wavenumbers, and a frequency increase for $\nu(\text{SF})$. The E-mode splitting observed for $\text{Au}(\text{CO})\text{SO}_3\text{F}$ is $\sim 165\text{ cm}^{-1}$ larger than the 125- and 60-cm^{-1} splittings observed for $\text{Mn}(\text{CO})_5\text{SO}_3\text{F}$ and $\text{Re}(\text{CO})_5\text{SO}_3\text{F}$, respectively. The strength of the monodentate coordination to Au(I) is also reflected in the positions of the remaining two stretching vibrations, $\nu(\text{SO}_3)$ at ~ 1020 and $\nu(\text{SF})$ at 800 cm^{-1} . The vibrational data suggest the following acceptor order for the carbonyl fragments: $\text{Au}(\text{CO}) > \text{Mn}(\text{CO})_5 > \text{Re}(\text{CO})_5$.

Assignments consistent with a coordinated monodentate SO_3F group in $\text{Au}(\text{CO})\text{SO}_3\text{F}$ are fairly straightforward for the remaining bands. The observation of bands below 400 cm^{-1} , where neither SO_3F^- nor $\text{Au}(\text{CO})^+$ modes are expected, lends additional support for the proposed covalent interaction, and assignment as torsion or deformation modes is suggested for these bands. An additional, slightly unusual feature in the vibrational spectra of $\text{Au}(\text{CO})\text{SO}_3\text{F}$ is the occurrence of two $\nu(\text{SF})$ bands in the IR spectrum of the solid, at 810 and 768 cm^{-1} , probably due to two different rotameric forms of the SO_3F^- group. In the Raman spectrum of the melt, both vibrations have merged to give a broad band at 792 cm^{-1} . In addition, $\nu(\text{AuC})$ and $\nu(\text{AuCO})$ are not well resolved in the IR spectrum while the small splitting of the SO_3F rocking mode at $\sim 400\text{ cm}^{-1}$ is seen in the IR spectrum only.

Only a single, well-characterized mononuclear gold(I) carbonyl derivative has been reported previously:¹⁴ gold(I) carbonyl chloride, $\text{Au}(\text{CO})\text{Cl}$. This compound has been known for almost 65 years^{15,16} and has become a convenient starting material for the synthesis of other gold(I) complexes.¹⁴ There are a number of interesting similarities between $\text{Au}(\text{CO})\text{Cl}$ and $\text{Au}(\text{CO})\text{SO}_3\text{F}$ described here. The thermal stability is lower, and $\text{Au}(\text{CO})\text{Cl}$ decomposes between 110 and $114\text{ }^\circ\text{C}$ to AuCl and CO . The CO stretch is also somewhat lower and is observed at $2153\text{--}2162\text{ cm}^{-1}$ in the IR spectrum of solutions in various solvents^{17,18} and at 2183 cm^{-1} in the Raman spectrum of the solid.^{19a} The molecular structure is known, and a complete vibrational assignment and analysis of $\text{Au}(\text{CO})\text{Cl}$ as a linear four-atom molecule is available.¹⁹ Its vibrational spectral data are included in Table I for the purpose of comparison.

There are various methods of preparation reported for $\text{Au}(\text{C}-\text{O})\text{Cl}$. All involve gaseous CO and its reaction with either AuCl or AuCl_3 , as solids or in solution of several aprotic solvents. Reaction temperatures range from 25 to $140\text{ }^\circ\text{C}$, and the initial pressure of CO extends from atmospheric to fairly high.^{14-16,20} Reported yields range from poor to quantitative.^{16,17,20} The interaction of CO with gold(III) chloride according to

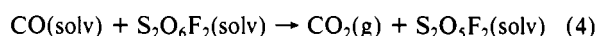


appears to show a direct analogy to the synthetic route reported here, if the known thermal instability of the phosgene analogue $\text{CO}(\text{SO}_3\text{F})_2$, resulting in the formation of CO_2 and $\text{S}_2\text{O}_5\text{F}_2$,²¹ is considered. However there are three interesting differences: (i) Formation of $\text{Au}(\text{CO})\text{SO}_3\text{F}$ occurs in a homogeneous reaction, with both CO and $\text{Au}(\text{SO}_3\text{F})_3$ seemingly dissolved in HSO_3F . (ii) The color changes mentioned at the outset indicate distinct phases in the reaction, with two occurring at room temperature. The most efficient routes to $\text{Au}(\text{CO})\text{Cl}$ require elevated temperatures.^{17,20} (iii) Unlike the stoichiometry suggested by eqs 1 and 3, $\text{Au}(\text{CO})\text{SO}_3\text{F}$ forms quantitatively only when at least 3 mol of CO/mol of $\text{Au}(\text{SO}_3\text{F})_3$ is used.

It is felt that the solvent HSO_3F may allow the stabilization of cationic intermediates in solution, and evidence for such an intermediate will be discussed next. The characterization of $\text{Au}(\text{CO})\text{SO}_3\text{F}$, described above, should allow its identification in solution, as soon as it is formed.

(b) **Solution Behavior of CO in $\text{HSO}_3\text{F}\text{--Au}(\text{SO}_3\text{F})_3$.** In order to study the behavior of carbon monoxide in the superacid $\text{HSO}_3\text{F}\text{--Au}(\text{SO}_3\text{F})_3$, or $\text{H}[\text{Au}(\text{SO}_3\text{F})_4](\text{soln})$, as argued previously,¹ and to gain some insight into the way in which $\text{Au}(\text{C}-\text{O})\text{SO}_3\text{F}$ forms, it is necessary (a) to measure accurately the amounts of gaseous CO that are initially taken up from the gas phase, (b) to determine the amounts of CO retained in solution after a vacuum is applied or the temperature of the solution is raised, and (c) to obtain spectroscopic information on the "dissolved" CO .

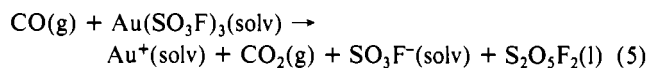
Pressure measurements in reactors and vacuum-line sections of known volume (*PVT* measurements) at constant temperature allow a reasonable estimate of the CO uptake from the gas phase, the approximate rate of uptake, and the stability toward gas release of the resulting solutions under vacuum. Dissolved CO is conveniently determined by the reaction of the solution with an excess of $\text{S}_2\text{O}_6\text{F}_2$ according to



The amount and purity of CO_2 obtained are determined by *PVT* and IR measurements, following separation of CO_2 from other volatile materials ($\text{S}_2\text{O}_6\text{F}_2$, $\text{S}_2\text{O}_5\text{F}_2$) by trap to trap distillation. As the reaction of $\text{Au}(\text{CO})\text{SO}_3\text{F}$ with $\text{S}_2\text{O}_6\text{F}_2$ indicates, metal-bound CO can be estimated in this manner but the amount of $\text{S}_2\text{O}_6\text{F}_2$ used should be large enough to allow the oxidation of $\text{Au}(\text{I})$ to $\text{Au}(\text{III})$. In addition, the reaction is conveniently followed by weighing the reactor, which allows an estimate of the gold concentration in solution and provides, together with *PVT* measurements, a quantitative material balance of the reaction.

The reported failure to detect the formyl cation, $\text{HCO}^+(\text{soln})$, in superacid solution by NMR methods because of rapid proton exchange even at $-80\text{ }^\circ\text{C}$ emphasizes the need for alternate spectroscopic techniques. Both IR and Raman spectroscopies are found to be useful. The initial orange color of the $\text{HSO}_3\text{F}\text{--Au}(\text{SO}_3\text{F})_3$ solution prevents Raman scattering by absorbing the excited laser line ($\lambda_0 = 514.5\text{ nm}$). Initial rapid CO uptake brings about a color change of the solution to yellow, and Raman spectra are subsequently obtained. Thin silicon disks contained in airtight Teflon sample holders are sufficiently acid resistant to permit the recording of IR spectra on thin films by using a FTIR instrument. The results of the CO uptake and retention measurements at various stages of the reaction will be discussed first.

As mentioned, an initial 0.17 M solution of $\text{Au}(\text{SO}_3\text{F})_3$ changes color to yellow on first CO uptake. In the UV-vis spectrum the absorption edge (optical density = 1, path length = 1 mm) shifts from 470 to 450 nm . About 2 mol of CO/mol of $\text{Au}(\text{SO}_3\text{F})_3$ is taken up rapidly, and the reduction of gold(III) to gold(I) is evident from the appearance of vibrational bands at 735 and $\sim 327\text{ cm}^{-1}$ in the Raman spectrum, which are attributed to disulfuryl difluoride, $\text{S}_2\text{O}_5\text{F}_2$.²² Continued uptake of CO by the solution, which is stirred vigorously, results in a colorless solution within a few hours. The absorption edge in the UV-vis spectrum has now shifted to 290 nm . Between 3.0 and 3.5 mol of CO/mol of gold species has been consumed at this point, and 1 mol is required for the reduction of $\text{Au}(\text{III})$ to $\text{Au}(\text{I})$ according to



Removal of excess CO in vacuo and subsequent trap to trap distillation of the volatile compounds, CO_2 , $\text{S}_2\text{O}_5\text{F}_2$, and some of the fluorosulfuric acid, with the reaction flask at room temperature result in a colorless, clear solution $\sim 1.0\text{ M}$ in $\text{Au}(\text{I})$, which has retained slightly less than $\sim 2\text{ mol}$ of CO/mol of $\text{Au}(\text{I})$. Continued removal of HSO_3F is accompanied by a slow release of

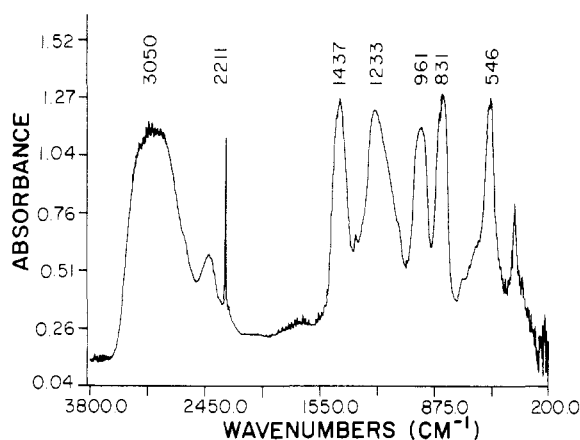
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Table II. Vibrational Spectra of CO Dissolved in HSO₃F–Au(SO₃F)₃ Solutions^a

HSO ₃ F		soln a: 0.8 M Au(III)/1.3 M CO				soln b: 1.0 M Au(I)/1.8 M CO				soln c: 2.5 M Au(I)/2.6 M CO					
IR		Raman		IR		Raman		IR		Raman		IR		Raman	
ν , cm ⁻¹	int	$\Delta\nu$, cm ⁻¹	int	ν , cm ⁻¹	int	$\Delta\nu$, cm ⁻¹	int	ν , cm ⁻¹	int	$\Delta\nu$, cm ⁻¹	int	ν , cm ⁻¹	int	$\Delta\nu$, cm ⁻¹	int
3075	s, br			3060	s, br			3050	s, br			3050	s, br		
2405	w, br			2395	w, br			2400	w, br			2370	m, br		
						2254	m			2251	s			2250	w
				2211	m			2211	s			2211	m		
				2200	sh					2200	m	2197	m	2195	vs
				2174	vw			2174	vw			2174	vw, sh		
												2148	vw		
1435	vs	1435	w	1443	s	1430	w	1437	s	1450	w	1437	m		
1238	s							1339	w			1345	m		
		1220	s, br	1215	s, br	1230	m	1233	s, br	1240	s, br	1238	s	1240	m, br
1209	sh														
						1020	m	1094	sh	1085	m	1050	m	1070	m
961	s	960	m	959	s	961	w, br	960	s	960	m, br	943	s	945	w
839	s	850	s	837	s	850	m	831	s	845	s	838	s	840	m
						650	s								
550	m	554	s	550	m	555	m	555	sh	553	s	555	sh	560	w
						460	m	546	s			546	s		
403	w	404	m	403	w	390	w	400	w	400	m			400	w
		395	m			280	vs								

^aM is defined in this study as mol/kg of solution.

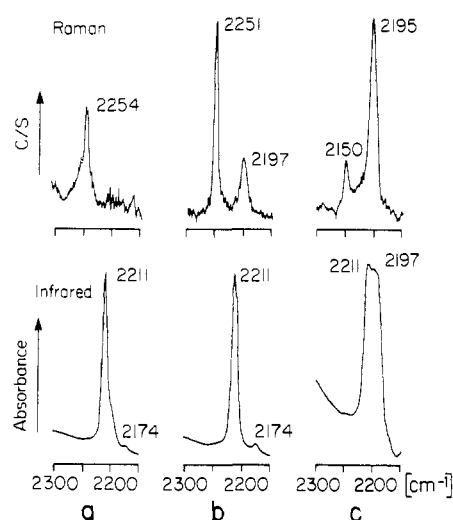
**Figure 1.** Infrared spectrum of 1 M [Au(CO)₂]⁺ in HSO₃F solution.

additional CO from solution. Finally, with concentrations of about 4.8 M Au(I) and about 5.05 M CO, white needles form and Au(CO)SO₃F is isolated in nearly quantitative yield by sublimation, as discussed.

The nature of the CO retention in solution is evident from the vibrational spectra of these solutions. The vibrational data for these solutions are summarized in Table II. An IR spectrum of a thin film of a gold(I) solution is shown in Figure 1. The CO stretching range only is featured in Figure 2 for IR and Raman spectra of various solutions.

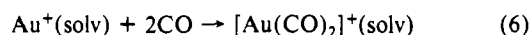
There are five interesting observations concerning the band position of $\nu(\text{CO})$ in these solutions: (i) The observed CO stretching frequencies are unusually high, 2211 and 2251 cm⁻¹ in the IR and Raman spectra, respectively. The measured frequencies are well above those of free CO or of Au(CO)SO₃F discussed above. (ii) Band positions of $\nu(\text{CO})$ are identical within limits of accuracy for yellow Au(III) solutions and colorless Au(I) solutions. (iii) A CO stretch at 2200 cm⁻¹, attributable to Au(CO)SO₃F, is observed in both IR and Raman spectra for concentrated gold(I) solutions only. The noted gain in intensity of this band occurs at the expense of the IR and Raman bands at 2211 and 2151 cm⁻¹, respectively. (iv) Replacement of the solvent HSO₃F by DSO₃F has no measurable effect on $\nu(\text{CO})$ at the various stages of the reaction. (v) The two $\nu(\text{CO})$ bands formed initially do not coincide in the IR and Raman spectra of the solutions. The band separation of ~40 wavenumbers is well outside the limits of accuracy.

The observations summarized above allow the following conclusions: (I) The principal absorbing species appears to be linear

**Figure 2.** Expanded Raman and infrared spectra in the range 2150–2300 cm⁻¹ for solutions a–c listed in Table II.

and centrosymmetrical. (II) The species will most likely have two CO groups. This conclusion is based in part on the observed Au:CO ratio of 1:2. (III) The absence of a measurable H/D shift for $\nu(\text{CO})$ argues against the presence of a protonated CO species causing the spectrum.

It hence appears that the formyl cation, HCO⁺, the object of this study, cannot be responsible for the observed spectrum and may not be present in detectable quantities. Centrosymmetrical [H(CO)₂]⁺(solv) with two CO groups bridged by a proton is unlikely to be responsible for the spectra in the CO region because this species should form to some extent in other superacids as well. Attempts to replace the HSO₃F–Au(SO₃F)₃ superacid by the recently reported HSO₃F–Ta(SO₃F)₅²³ system result in solutions that fail to show any substantial CO uptake. Since Ta(V) is resistant toward reduction, it appears that the reduction of Au(III) to Au(I) according to eq 5 plays an important role in the dissolution of CO, with reduction followed by stabilization or complexation of Au⁺(solv) by CO according to



The postulated centrosymmetric bis(carbonyl)gold(I) cation has two known analogous molecules, which allow some comparison.

Table III. CO or CN Stretching Modes for $[\text{Au}(\text{CO})_2]^+$, $\text{Au}(\text{CO})_2$, and $[\text{Au}(\text{CN})_2]^-$ (cm^{-1})

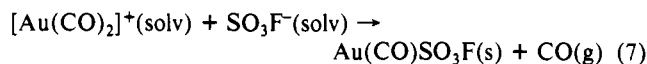
vibration	$[\text{Au}(\text{CO})_2]^+$	$\text{Au}(\text{CO})_2^a$	$[\text{Au}(\text{CN})_2]^-^b$
ν_1 in phase $\text{Au}^{(12\text{C}-^{16}\text{O})_2}$ or $\text{Au}^{(12\text{C}-^{14}\text{N})_2}$	2251	2072	2161
ν_3 out of phase $\text{Au}^{(12\text{C}-^{16}\text{O})_2}$ or $\text{Au}^{(12\text{C}-^{14}\text{N})_2}$	2211	1935.8	2142
ν_3' out of phase $\text{Au}^{(13\text{C}-^{16}\text{O})(^{12}\text{C}-^{16}\text{O})}$ or $\text{Au}^{(13\text{C}-^{14}\text{N})(^{12}\text{C}-^{14}\text{N})}$	2174	1905	2101

^a Reference 24; IR data only. ^b Reference 25; $\text{K}[\text{Au}(\text{CN})_2]$ in H_2O (Raman) or 1-methyl-2-pyrrolidinone (IR) solution.

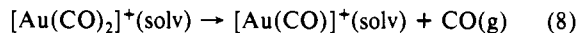
The neutral molecule $\text{Au}(\text{CO})_2$ has been obtained by codeposition of gold atoms and CO in inert-gas matrices and has been studied primarily by IR spectroscopy.²⁴ The isoelectronic anion $[\text{Au}(\text{CN})_2]^-$ is well-known and reportedly is one of the more stable Au(I) complexes.¹⁴ Its vibrational spectrum has been extensively studied²⁵ and provides a useful comparison to that of $[\text{Au}(\text{CO})_2]^+$.

Binary transition-metal carbonyl cations appear to be rare.²⁶ However octahedral cations of the type $[\text{M}(\text{CO})_6]^+$ with $\text{M} = \text{Mn}, \text{Tc},$ or Re are well-known and extensively characterized.²⁶ They obey the effective atomic number rule and require generally high CO pressures and elevated temperatures during synthesis. In contrast, $[\text{Au}(\text{CO})_2]^+$ forms under mild conditions and gold has 14 electrons in the valence shell.

The formation of $\text{Au}(\text{CO})\text{SO}_3\text{F}$ becomes a very facile substitution reaction



completely in accord with our observations. As the concentration increases, the solution becomes strongly basic and "salts" formation occurs. A stepwise substitution with initial dissociation of $[\text{Au}(\text{CO})_2]^+$ according to



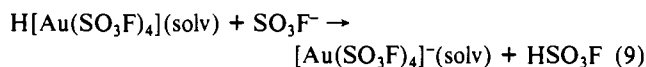
and subsequent reaction of $[\text{Au}(\text{CO})]^+$ with the fluorosulfate ion become a distinct possibility. As seen in Table II and Figures 1 and 2a, $\nu(\text{CO})$ of the newly formed species is observed at 2203–2200 cm^{-1} , slightly higher than in $\text{Au}(\text{CO})\text{SO}_3\text{F}$, which would be consistent with the intermediate formation of $[\text{Au}(\text{CO})]^+$.

Addition of CsSO_3F to the superacid and the in situ formation of $\text{Cs}[\text{Au}(\text{SO}_3\text{F})_4]$ have no effect on the overall reaction. Substitution of the remaining CO by SO_3F^- does not occur, and the complex salt $\text{Cs}[\text{Au}(\text{SO}_3\text{F})_2]$ is not obtained; $\text{Au}(\text{CO})\text{SO}_3\text{F}$ forms instead and is isolated by sublimation.

Support for the postulated $[\text{Au}(\text{CO})_2]^+$ and the stabilization of Au^+ by CO comes from two additional experiments. First, if $\text{Au}(\text{CO})\text{SO}_3\text{F}$ is redissolved in HSO_3F , the IR spectrum shows $\nu(\text{CO})$ at 2211 cm^{-1} , suggesting a reversal of reaction 7; however metallic gold is formed as well. The yellow color of the solution and formation of colloid gold indicate partial disproportionation of uncomplexed Au^+ to gold and Au(III). It seems that uncomplexed Au^+ is unstable and will undergo disproportionation in HSO_3F . Hence an addition 2 mol of CO is needed to stabilize Au(I) formed in the reduction process. Dissolution of $\text{Au}(\text{C}-\text{O})\text{SO}_3\text{F}$ will result in a deficiency of CO and partial disproportionation. Second, to demonstrate the stabilization of a d^{10} metal ion by CO, the more readily available and stable Ag^+ ion, solutions of AgSbF_6 in HSO_3F are studied in a CO uptake experiment. Initial rapid pressure-dependent uptake of ~ 0.9 mol of CO/mol of silver(I) at 1 atm of CO is observed; however the resulting solutions are unstable and CO is released when a vacuum is applied. The implication that Ag^+ is a weaker acceptor than Au^+ is evident from an early CO uptake study of Ag_2SO_4 dissolved

in concentrated H_2SO_4 or oleum,²⁷ where rapid pressure-dependent CO uptake is reported with subsequent release of CO in vacuo.

It appears that both the reduction of Au(III) to Au(I) according to eq 5 and complex formation to give $[\text{Au}(\text{CO})_2]^+$ (eq 6) are responsible for the initial rapid CO uptake. The reduction reaction generates SO_3F^- , which together with a gradually decreasing concentration of $\text{H}[\text{Au}(\text{SO}_3\text{F})_4]$ causes the color change from orange to yellow:



Solutions of $\text{M}[\text{Au}(\text{SO}_3\text{F})_4]$ in HSO_3F are reportedly^{1,2} lighter in color than solutions of $\text{Au}(\text{SO}_3\text{F})_3$. The resulting solutions of $[\text{Au}(\text{CO})_2]^+(\text{sol})$ are reasonably stable but decomposition, possibly via $[\text{Au}(\text{CO})]^+(\text{sol})$, eventually occurs, leading to the formation of $\text{Au}(\text{CO})\text{SO}_3\text{F}$.

A number of steps in the overall reaction leading to the formation of $\text{Au}(\text{CO})\text{SO}_3\text{F}$ have become clear during the course of this study, but the initial step, the interaction of gaseous CO with the superacid, remains unclear.

The protonation of CO to give a very reactive and hence undetectable formyl cation as a transient species and the direct addition of CO to the $[\text{Au}(\text{SO}_3\text{F})_4]$ species are both viable possibilities, but vibrational spectroscopy may not be able to shed further light on the problem.

A final comment remains to be made. This study has shown that the previously suggested^{1,2} resistance of $\text{Au}(\text{SO}_3\text{F})_3$ in HSO_3F toward reduction is lower than was initially assumed. It is in part this tendency of $\text{Au}(\text{SO}_3\text{F})_3$ to be reduced by CO that prevents isolation of a solid complex such as $[\text{Au}(\text{CO})_2]^+[\text{Au}(\text{SO}_3\text{F})_4]^-$. In addition, attempts to concentrate solutions of $[\text{Au}(\text{CO})_2]^+(\text{sol})$ lead to the formation of $\text{Au}(\text{CO})\text{SO}_3\text{F}$ rather than to $[\text{Au}(\text{CO})_2]^+\text{SO}_3\text{F}^-$.

(c) **Vibrational Spectra and Assignments of Solutions Containing $[\text{Au}(\text{CO})_2]^+$.** Besides $\text{Au}(\text{CO})_2$ ²⁴ and the anion $[\text{Au}(\text{CN})_2]^-$,²⁵ carbon suboxide, C_3O_2 , with two CO groups linked by a central carbon, provides another example for a five-atom centrosymmetrical molecule of point group $D_{\infty h}$. Again, a very detailed vibrational analysis is available for this molecule.²⁸

For $[\text{Au}(\text{CO})_2]^+$ and the three molecular species serving as precedents, the irreducible representation of the normal vibrations is

$$\Gamma_{\text{vib}} = 2\Sigma_g^+ [\nu_1, \nu_2 (\text{Raman pol})] + 2\Sigma_u^+ [\nu_3, \nu_4 (\text{IR})] + \Pi_g [\nu_5 (\text{Raman dep})] + 2\Pi_u [\nu_6, \nu_7 (\text{IR})]$$

Of the seven normal modes, the two CO stretching modes $\nu_1(\Sigma_g^+)$ at 2251 cm^{-1} and $\nu_3(\Sigma_u^+)$ at 2211 cm^{-1} are easily recognized and assigned. They may be viewed as "in-phase" and "out-of-phase" CO stretching vibrations. Both fundamentals are listed in Table III and compared to the corresponding bands for $\text{Au}(\text{CO})_2$ ²⁴ and $[\text{Au}(\text{CN})_2]^-$.²⁵ Due to the broad solvent bands (see e.g. Figure 1) none of the other fundamentals are clearly identifiable in either Raman or IR spectra; however the detailed study on various $[\text{Au}(\text{CN})_2]^-$ salts as solids or in solution²⁵ provides an approximate

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idea where they should occur. Of the fundamentals, the bending mode ν_7 is observed at $\sim 125\text{ cm}^{-1}$ and is clearly out of the range of our instrument, while the Raman-active mode ν_5 at $\sim 300\text{ cm}^{-1}$ is seemingly obscured by other bands. The anion $[\text{Au}(\text{SO}_3\text{F})_4]^-$ has a very intense Raman band at 280 cm^{-1} (1), while in Au(I) solutions the reduction product $\text{S}_2\text{O}_5\text{F}_2^{22}$ and also $\text{Au}(\text{CO})\text{SO}_3\text{F}$ have bands in this region. The remaining fundamentals ν_2 and ν_4 , the AuC_2 stretches, and ν_6 are expected in a narrow range between 400 and 450 cm^{-1} but are again obscured by solvent or solute bands. Disappointingly also, solutions in DSO_3F do not help to clarify the situation either.

As can be seen from Table III, the correspondence between the three sets of data is generally good. However, the position of ν_1 for neutral $\text{Au}(\text{CO})_2$ appears to be rather high. This band is only observed in the IR spectrum of the matrix molecule and assignment as "in-phase" CO stretch may be doubtful. In all three molecules, the in-phase stretching mode seems to occur at higher wavenumbers than does the out-of-phase stretch. Also ν_3' , the out-of-phase stretching mode for the singly ^{13}C -substituted species $(\text{X}-^{13}\text{C})\text{Au}(^{12}\text{C}-\text{X})$ with $\text{X} = \text{O}$ or N , is observed as a very weak band $30\text{--}40\text{ cm}^{-1}$ lower than ν_3 .

Both CO stretches for $[\text{Au}(\text{CO})_2]^+$ occur at considerably higher wavenumber than is suggested for the neutral species. It appears that CO is interacting more strongly with Au^+ than with Au atoms. The difference in C–O and Au–C bond strength is reflected also in the thermal stability. $[\text{Au}(\text{CO})_2]^+$ exists at room temperature in HSO_3F , while $\text{Au}(\text{CO})_2$ is found between 6 and 10 K in various matrices. In the matrix, $\nu(\text{CO})$ is reduced from the value of free CO at 2134 cm^{-1} while in the cation $\nu(\text{CO})$ is raised. In addition, $\text{Au}(\text{CO})_2$ is described as green²⁴ with λ_{max} at 520 nm while for $[\text{Au}(\text{CO})_2]^+$ no visible bands are observed and solutions in the absence of the intensely absorbing $[\text{Au}(\text{SO}_3\text{F})_4]^-$ ion are transparent in the visible region.

The isoelectronic anion $[\text{Au}(\text{CN})_2]^-$ seems to provide a better basis for comparison to $[\text{Au}(\text{CO})_2]^+$. Here $\nu(\text{CN})$ is raised above the value of 2080 cm^{-1} reported for CN^- in alkali-metal cyanides and their aqueous solutions²⁹ to an average value of 2151.5 cm^{-1} for the in- and out-of-phase stretch.²⁵ The bonding is viewed, on the basis of a detailed vibrational analysis of linear metal bis-(cyanides),³⁰ as involving a strong covalent Au–C σ -interaction with little or no π -back-donation. Metal–carbon force constants for $[\text{Au}(\text{CN})_2]^-$, $\text{Hg}(\text{CN})_2$, and $[\text{Ag}(\text{CN})_2]^-$ are reported as 2.81, 2.61, and 1.83 mdyn/\AA , respectively.³⁰

The same conclusion is possible for $[\text{Au}(\text{CO})_2]^+$, where the average $\nu(\text{CO})$ value is 2231 cm^{-1} , well above the value of 2143 cm^{-1} for free CO^9 and even higher than $\nu(\text{CO})$ in $\text{CO}^+(^2\Sigma^+)$, where a value of 2184 cm^{-1} is listed.⁹ Only for $\text{C}_3\text{O}_2^{28}$ are similarly high $\nu(\text{CO})$ vibrations observed, but here extensive π -conjugation is

anticipated. As in $\text{Au}(\text{CO})\text{SO}_3\text{F}$, it seems to be also more appropriate to view the bonding in $[\text{Au}(\text{CO})_2]^+$ in very simple terms, as involving strong covalent Au–C σ -bonds, with the C–O bond in essence viewed as a triple bond that is not weakened by π -back-donation. It is hoped that the $[\text{Au}(\text{CO})_2]^+$ ion can also be generated in other protonic solvents, e.g. anhydrous HF, so that the remaining part of the vibrational spectrum becomes clearly observable and a detailed force field calculation for this interesting ion can be obtained.

The remaining bands in the IR and Raman spectra, summarized in Table II, are generally of four types and are readily recognized: (i) Solvent bands are found in both Raman and IR spectra in close analogy to reported precedents.^{31,32} (ii) The $[\text{Au}(\text{SO}_3\text{F})_4]^-$ ion is identified by strong Raman bands at ~ 650 , 460 , and 280 cm^{-1} ,^{1,2} before complete reduction has taken place. (iii) After reduction of Au(III) to Au(I), bands attributable to $\text{S}_2\text{O}_5\text{F}_2^{22}$ are found and noticeable band broadening of HSO_3F bands with a shoulder at $\sim 1080\text{ cm}^{-1}$ indicates the presence of SO_3F^- ions dissolved in HSO_3F .³³ The ^{19}F NMR spectrum shows a single resonance at 41 ppm relative to CFCl_3 for these solutions. (iv) In concentrated solutions, bands at 1340 and 546 cm^{-1} in the IR spectrum are attributed to $\text{Au}(\text{CO})\text{SO}_3\text{F}$, as discussed above. All observations confirm the course of the reaction as discussed in the preceding section.

Conclusions

While the formyl cation, HCO^+ , has remained elusive, two interesting novel results have come out of this study: the isolation of $\text{Au}(\text{CO})\text{SO}_3\text{F}$ and the proposed identification of the cation $[\text{Au}(\text{CO})_2]^+$ in solution. The use of a strong protonic acid, HSO_3F , in the synthesis of transition-metal carbonyl derivatives appears to be unprecedented, and an extension of this method to the superacid system $\text{HSO}_3\text{F}\text{--Pt}(\text{SO}_3\text{F})_4^{35}$ in the hope of synthesizing Pt(II)CO derivatives appears to be fruitful. The unusually high CO stretching frequencies observed for both Au(I)–carbonyl derivatives suggests a strong σ -bond between Au and C that is not strengthened by appreciable π -back-donation, in contrast to the "normal" synergic bonding mode encountered in transition-metal carbonyls.

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