energy considerations may be important. It is also possible, however, that the diadducts are kinetic products and that the rate of conversion to the thermodynamic products is small under the conditions of the experiment. We plan further studies of this question.

Acknowledgment. The authors gratefully acknowledge the support of this investigation by The Robert A. Welch Foundation under Grant E-439. We are indebted to a reviewer for suggesting the comparison between our compounds and the $R_2SnM(CO)_n$·donor species described in ref 6–8. Special thanks go to Professor Mary Good for providing pertinent results prior to publication.

Registry No. $BF_3\cdot SnCl_2\cdot N(CH_3)_3$, 71928-91-1; $BF_3\cdot SnBr_2\cdot N(CH_3)_3$, 71974-94-2; $BF_3\cdot SnI_2\cdot N(CH_3)_3$, 71928-92-2; $BF_3\cdot SnCl_2\cdot OS(CH_3)_2$, 71928-93-3; $BF_3\cdot SnCl_2\cdot$TMED, 71928-94-4; $BF_3\cdot SnBr_2\cdot$TMED, 71928-95-5; $BF_3\cdot SnI_2\cdot$TMED, 71928-96-6; $BF_3\cdot$TMED$\cdot SnCl_2$, 71928-98-8; $BF_3\cdot SnCl_2\cdot$DP, 71928-99-9; $BF_3\cdot SnBr_2\cdot$DP, 71929-00-5; $BF_3\cdot SnI_2\cdot$DP, 71928-85-3; $BF_3\cdot$DP$\cdot SnCl_2$, 71928-87-5; $SnCl_2\cdot N(CH_3)_3$, 63528-08-5; $SnBr_2\cdot N(CH_3)_3$, 63528-09-6; $SnI_2\cdot N(CH_3)_3$, 63528-10-9; $SnCl_2\cdot OS(CH_3)_2$, 30822-84-5; $SnCl_2\cdot$TMED, 71928-88-6; $SnBr_2\cdot$TMED, 71928-89-7; $SnI_2\cdot$TMED, 71928-90-0; $SnCl_2\cdot$DP, 14872-79-8; $SnBr_2\cdot$DP, 31806-30-1; $SnI_2\cdot$DP, 46389-53-1; $BF_3\cdot$DP, 71913-06-9; $BF_3\cdot OS(CH_3)_2$, 865-41-8; $(CH_3)_2SO$, 67-68-5; $BF_3\cdot O(CH_2CH_3)_2$, 60-29-7; TMED, 110-18-9; 2,2′-dipyridyl, 366-18-7; $BF_3\cdot N(CH_3)_3$, 420-20-2; $(CH_3)_3N$, 75-50-3; $SnBr_2\cdot Me_2SO$, 71928-78-4; $SnI_2\cdot Me_2SO$, 71928-79-5; $SnF_2\cdot Me_2SO$, 26586-93-6; $SnCl_2\cdot$py, 14872-78-7; $BF_3\cdot SnBr_2\cdot Me_2SO$, 71928-80-8; $BF_3\cdot SnI_2\cdot Me_2SO$, 71928-81-9; $BF_3\cdot SnCl_2\cdot$py, 71974-96-4; $BF_3\cdot$TMED, 71963-95-6; BF_3, 7637-07-2.

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Gold(III) Fluorosulfate as Fluorosulfate Ion Acceptor. 2.[1] Compounds Containing Halogen and Halogeno(fluorosulfato) Cations

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Received July 26, 1979

Gold(III) fluorosulfate, $Au(SO_3F)_3$, is an excellent fluorosulfate ion acceptor, giving the tetrakis(fluorosulfato)aurate(III) ion, $[Au(SO_3F)_4]^-$. This ability is exploited in the synthesis of a number of $[Au(SO_3F)_4]^-$ complexes containing the cations Br_3^+, Br_5^+, $[Br(SO_3F)_2]^+$, and $[I(SO_3F)_2]^+$. All compounds are characterized by their vibrational spectra.

Introduction

We have recently found gold(III) fluorosulfate, $Au(SO_3F)_3$, to be a very good fluorosulfate ion acceptor,[1] forming readily the tetrakis(fluorosulfato)aurate(III) anion. Salts of the type $M[Au(SO_3F)_4]$, with $M^+ = Li^+, K^+, Cs^+, NO^+$, or ClO_2^+, are readily synthesized and characterized by their vibrational spectra; and the acid $H[Au(SO_3F)_4]$, formed when $Au(SO_3F)_3$ is dissolved in fluorosulfuric acid, is able to protonate HSO_3F.[1]

This strong tendency to form the $[Au(SO_3F)_4]^-$ ion and the high thermal stability of the salts suggest that SO_3F^- abstraction from halogen tris(fluorosulfates) such as $I(SO_3F)_3$ and $Br(SO_3F)_3$ should be feasible, and stable reaction products may be obtainable. Support for this view comes from the original synthesis of $Au(SO_3F)_3$,[2] by oxidation of gold with an excess of bromine(I) fluorosulfate, $BrSO_3F$, where a crystalline intermediate of the approximate composition $Au(SO_3F)_3\cdot 2BrSO_3F$ was reported. A formulation of this intermediate as $[Br_2SO_3F]^+[Au(SO_3F)_4]^-$ seems reasonable in view of the aforementioned SO_3F^- ion acceptor ability of $Au(SO_3F)_3$.

The purpose of this study is to characterize the intermediate more fully, to attempt the SO_3F^- abstraction from $I(SO_3F)_3$ and $Br(SO_3F)_3$, and to extend the investigation to tetrakis(fluorosulfato)aurate(III) complexes with polybromine cations.

Experimental Section

(A) Chemicals. Bromine (BDH, reagent grade) was stored over KBr and P_2O_5 and distilled in vacuo before use. Gold powder (100 mesh of 99.995% purity) was obtained from the Ventron Corp. Resublimed iodine (analytical reagent) was purchased from Fisher Scientific.

The following compounds were synthesized according to published methods: bis(fluorosulfuryl) peroxide, $S_2O_6F_2$,[3] and bromine(I) fluorosulfate, $BrSO_3F$.[4]

(B) Instrumentation. Raman spectra were obtained with either a Cary 81 or a Spex Ramalog 5 spectrophotometer equipped with a helium–neon laser (Spectra Physics Model 125) at λ 632.8 nm or an argon ion laser (Spectra Physics Model 164) at λ 514.5 nm respectively. A cell, suitable to record Raman spectra with the Spex Ramalog at 80 K, has been described by us.[6]

Infrared spectra were recorded on either a Perkin-Elmer 457 or 225 grating spectrophotometer. The latter was equipped with a low-temperature cell, also described earlier by us[7] together with suitable sampling techniques. Spectra at room temperature were obtained on thin films between silver chloride or bromide windows (Harshaw Chemicals).

All reactions were performed in Pyrex reaction vials of about 40-mL capacity, fitted with Kontes Teflon stem valves. Volatile materials were handled by using vacuum-line techniques. Solids were handled in a Vacuum Atmospheres Corp. "Dri Lab" Model No. HE-43-2, filled with purified dry nitrogen and equipped with a "Dri-Train" Model No. HE-93-B circulating unit.

Electrical conductance measurements were carried out with a Wayne–Kerr universal bridge, Type B221. The measuring temperature of 25.00 ± 0.01 °C was maintained in an oil bath equipped with a Sargent Thermonitor Model ST temperature control unit. The conductivity cell was similar in design to the one described by Barr et al.[8]

(C) Synthetic Reactions. (i) Preparation of $Br_3[Au(SO_3F)_4]$. About 5 g of $BrSO_3F$ was distilled in vacuo into a Pyrex reactor containing 293 mg (1.488 mmol) of gold powder. A vigorous, exothermic reaction occurred as soon as the reactor was warmed to room temperature. To ensure complete reaction, we heated the mixture to 60 °C for 6 h. Removal of all volatiles at room temperature yielded 1239 mg (1.488 mmol) of a dark brown solid which was analyzed as $Br_3[Au(SO_3F)_4]$.

(ii) Preparation of $Br_5[Au(SO_3F)_4]$. In a typical reaction, 175 mg (0.888 mmol) of gold powder was converted into $Br_3[Au(SO_3F)_4]$ as described above. After removal of all volatiles, approximately 5

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(1) Part 1: K. C. Lee and F. Aubke, *Inorg. Chem.*, **18**, 389 (1979).
(2) W. M. Johnson, R. Dev, and G. H. Cady, *Inorg. Chem.*, **11**, 2260 (1972).
(3) G. H. Cady and J. M. Shreeve, *Inorg. Synth.*, **7**, 124 (1963).
(4) F. Aubke and R. J. Gillespie, *Inorg. Chem.*, **7**, 559 (1968).
(5) O. Glemser and A. Smalc, *Angew. Chem., Int. Ed. Engl.*, **8**, 517 (1969).
(6) K. C. Lee and F. Aubke, *Can. J. Chem.*, **57**, 2058 (1979).
(7) W. W. Wilson, J. M. Winfield, and F. Aubke, *J. Fluorine Chem.*, **7**, 245 (1976).
(8) J. Barr, R. J. Gillespie, and R. C. Thompson, *Inorg. Chem.*, **3**, 1149 (1964).

0020-1669/80/1319-0119\$01.00/0

mL of Br_2 was distilled onto the brown solid. The reaction mixture was then warmed to 70 °C for 6 h. Removal of all excess bromine in vacuo yielded 875 mg (0.882 mmol) of a dark brown solid, suggesting the composition $Br_5[Au(SO_3F)_4]$.

(iii) Preparation of $[Br(SO_3F)_2][Au(SO_3F)_4]$. In a typical reaction, 37 mg of Br_2 (0.231 mmol) and 90 mg of gold powder (0.457 mmol) were reacted with approximately 5 g of bis(fluorosulfuryl) peroxide at 70 °C for 12 h. During the reaction two immiscible, light yellow layers formed, and, when the mixture was left for 3 days at ~0 °C, the bottom layer crystallized, to yield 408 mg (0.468 mmol) of a yellow solid after all volatiles had been removed at room temperature.

(iv) Preparation of $[I(SO_3F)_2][Au(SO_3F)_4]$. In a manner similar to the previous preparation, 92 mg (0.363 mmol) of I_2 and 143 mg (0.726 mmol) of gold powder were allowed to react with about 5 g of bis(fluorosulfuryl) peroxide at 80 °C for 12 h. After all the metal had reacted, light orange crystals formed on cooling. Removal of all excess $S_2O_6F_2$ yielded 650 mg (0.708 mmol) of $[I(SO_3F)_2][Au(SO_3F)_4]$.

(D) Analytical Data and Physical Properties. Quantitative analyses were performed by A. Bernhardt Microanalytical Laboratories, Elbach, West Germany. All analytical data quoted are in percentages.

(i) $Br_3[Au(SO_3F)_4]$ is a dark brown, polycrystalline, diamagnetic, and hygroscopic solid, dec pt ~105 °C. Thermal decomposition in vacuo affords $Au(SO_3F)_3$. Anal. Calcd for $Br_3[Au(SO_3F)_4]$: Au, 23.65; Br, 28.78; F, 9.12. Found: Au, 23.89; Br, 28.64; F, 9.15.

(ii) $Br_5[Au(SO_3F)_4]$ is a dark brown, polycrystalline, diamagnetic, and hygroscopic solid, mp +65 °C dec. The compound shows a slight decomposition pressure at 25 °C in vacuo but is stable at this temperature in a N_2 atmosphere. Anal. Calcd for $Br_5[Au(SO_3F)_4]$: Au, 19.84; Br, 40.25; F, 7.66. Found: Au, 20.07; Br, 40.20; F, 7.79.

(iii) $[Br(SO_3F)_2][Au(SO_3F)_4]$ is a light yellow, very hygroscopic crystalline solid, mp 52–55 °C. Anal. Calcd for $[Br(SO_3F)_2][Au(SO_3F)_4]$: Au, 22.61; Br, 9.17; S, 22.08; F, 13.08. Found: Au, 22.45; Br, 9.26; S, 21.84; F, 13.13.

(iv) $[I(SO_3F)_2][Au(SO_3F)_4]$ is a light orange to yellow, hygroscopic, crystalline solid, mp 70–73 °C. Anal. Calcd for $[I(SO_3F)_2][Au(SO_3F)_4]$: Au, 21.45; I, 13.82; F, 12.41. Found: Au, 21.61; I, 14.04; F, 12.67.

Results and Discussion

Synthesis. For isolation and characterization of the intermediate $Au(SO_3F)_3{\cdot}2BrSO_3F$, thought to contain a $Br_2SO_3F^+$ ion, the published[2] formation reactions were reinvestigated. The oxidation of gold by an excess of bromine(I) fluorosulfate did indeed yield a dark brown crystalline material; however, chemical analysis revealed its composition as $Br_3Au(SO_3F)_4$, suggesting a formulation as $Br_3^+[Au(SO_3F)_4]^-$.

The Br_3^+ cation has been described before;[9] e.g., in solid $Br_3^+AsF_6^-$ [5] or in solution of strong protonic acids.[10] The mode of formation during the reaction of gold with bromine(I) fluorosulfate is suggested in eq 1–3. Evidence for the oxidative

oxidation:

$$\mathrm{Au(s) + 3BrSO_3F(l) \xrightarrow{BrSO_3F} Au(SO_3F)_3(solv) + {}^3/_2Br_2(l)} \tag{1}$$

complexation:

$$\mathrm{Au(SO_3F)_3(solv) + BrSO_3F(l) + Br_2(l) \xrightarrow{BrSO_3F} Br_3[Au(SO_3F)_4](s)} \tag{2}$$

overall reaction:

$$\mathrm{Au(s) + 4BrSO_3F(l) \xrightarrow{BrSO_3F} Br_3[Au(SO_3F)_4](s) + {}^1/_2Br_2(l)} \tag{3}$$

addition of Br_2 to $BrSO_3F$ was recently[7] obtained from low-temperature infrared spectra. Fluorosulfate abstraction by $Au(SO_3F)_3$ seemingly leads to a thermally stable product.

The addition of $BrSO_3F$ to pure $Au(SO_3F)_3$ did not result in thermally stable, well-defined compounds. The resulting dark brown materials gradually lost $BrSO_3F$, and chemical analysis provided no evidence for $Au(SO_3F)_3{\cdot}2BrSO_3F$.

Further addition of bromine to $Br_3[Au(SO_3F)_4]$ according to (4) resulted in material of relatively low thermal stability.

$$\mathrm{Br_2 + Br_3[Au(SO_3F)_4] \xrightarrow{Br_2(l)} Br_5[Au(SO_3F)_4]} \tag{4}$$

Again a formulation invoking the Br_5^+ ion is possible. There is, however, no published precedent for such an ion,[9] while I_5^+ has been reported in solid I_5AlCl_4[11] as well as in fluorosulfuric acid solution.[12]

The observed low thermal stability of $Br_5Au(SO_3F)_4$ is not really surprising and extends also to its solutions in fluorosulfuric acid at 25 °C. While $Br_3Au(SO_3F)_4$ behaves like a basic solute, giving rise to very similar specific conductance values as $K[Au(SO_3F)_4]$ up to concentrations of 0.04 *m*, dissolution of $Br_5Au(SO_3F)_4$ in HSO_3F at 25 °C results in the evolution of Br_2 and the resulting conductivities suggest dissociation according to

$$\mathrm{Br_5^+(solv) \rightleftarrows Br_3^+(solv) + Br_2} \tag{5}$$

An alternate route to $Br_5Au(SO_3F)_4$ is found in the reaction of $[Br(SO_3F)_2][Au(SO_3F)_4]$ with an excess of bromine according to

$$\mathrm{[Br(SO_3F)_2][Au(SO_3F)_4] + 3Br_2 \rightleftarrows Br_5Au(SO_3F)_4 + 2BrSO_3F} \tag{6}$$

The course of this reaction is consistent with the formation of $Br_3[Au(SO_3F)_4]$ in the oxidation of gold by bromine(I) fluorosulfate discussed above.

A number of unsuccessful attempts were made to obtain a compound of the composition $Br[Au(SO_3F)_4]$ by reacting stoichiometric amounts of Br_2, $BrSO_3F$, and $Au(SO_3F)_3$ according to

$$\mathrm{{}^1/_2Br_2 + BrSO_3F + Au(SO_3F)_3 \rightarrow Br_2[Au(SO_3F)_4]} \tag{7}$$

Due to the lack of a suitable solvent only rather inhomogeneous products were obtained. The observation of a resonance Raman spectrum with the principal band at 360 cm^{-1} indicates that the dibromine cation Br_2^+ was present[9,10] but analytically pure products were not isolable.

Finally, the reaction of stoichiometric amounts of bromine or iodine and gold with a large excess of bis(fluorosulfuryl) peroxide according to

$$\mathrm{{}^1/_2X_2 + Au + 3S_2O_6F_2 \rightarrow [X(SO_3F)_2][Au(SO_3F)_4]} \tag{8}$$

with X = Br or I, resulted in the formation of two new tetrakis(fluorosulfato)aurate(III) compounds. The cations $[I(SO_3F)_2]^+$ and $[Br(SO_3F)_2]^+$ have been reported before[13] in compounds of the type $[X(SO_3F)_2]_2[Sn(SO_3F)_6]$ with X = Br or I, where ^{119}Sn Mössbauer spectra supported the ionic formulation.

Vibrational Spectra. Both $[X(SO_3F)_2][Au(SO_3F)_4]$ compounds with X = Br or I are excellent Raman scatters, and very well-resolved Raman spectra were obtained, in particular, when the spectra were recorded at 80 K. In contrast, both $Br_nAu(SO_3F)_4$ compounds, by virtue of their dark colors, give rather poorly resolved spectra.

The reactivity of all compounds discussed here precluded the use of mulling agents and restricted the useful infrared windows to AgCl, AgBr, and BaF_2. Low-temperature infrared spectra using CsI windows allowed extension of the transmission range down to 200 cm^{-1}.

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(9) R. J. Gillespie and J. Passmore, *Adv. Inorg. Chem. Radiochem.*, **17**, 49 (1975).

(10) R. J. Gillespie and M. J. Morton, *Inorg. Chem.*, **11**, 586 (1972).

(11) D. J. Merryman, P. A. Edwards, J. D. Corbett, and R. E. MacCarley, *J. Chem. Soc., Chem. Commun.*, 779 (1972).

(12) R. J. Gillespie and J. B. Milne, *Inorg. Chem.*, **5**, 1577 (1966).

(13) P. A. Yeats, B. Landa, J. R. Sams, and F. Aubke, *Inorg. Chem.*, **15**, 1452 (1976).

Table I. Vibrational Frequencies (80 K), cm^{-1}, and Intensities[a]

$[I(SO_3F)_2][Au(SO_3F)_4]$		$[Br(SO_3F)_2][Au(SO_3F)_4]$	$[Br(SO_3F)_2][Sn(SO_3F)_6]^{b,d}$	$Br_3[Au(SO_3F)_4]$		$Br_5[Au(SO_3F)_4]$	$[Cs(Au(SO_4F)_4]^{c,d}$
Raman	IR[d]	Raman	Raman	Raman	IR	Raman	Raman
1476 w	1458 w, sh	1505 ms	1500 ms				
		1491 w, sh	1487 mw, sh				
1460 w	1440 w, sh	1476 w					
1413 ms	1410 s, sh	1425 ms	1420 mw	1408 ms	1410 vs, sh	1409 m	1404 ms
1400 m		1416 m					
1388 vw	1388 s	1400 mw					
1380 w	1382 vs	1389 mw	1387 ms	1386 m	1392 vs	1392 m	1380 vw
		1252 m, sh					
1237 m, sh		1235 s	1248 s				
1227 ms	1225 s, sh	1220 ms		1218 s	1220 s	1224 s	1239 vs
1217 vs	1198 vs	1195 ms	1197 s	1192 m	1190 s, sh	1201 mw	1205 w
1174 ms	1175 s, sh	1174 m	1145 s				
1135 m	1130 m, sh						
			1092 s				
1039 ms							
1022 ms	1025 w	1022 s	1020 ms	1016 s	1020 w	1020 m	1011 s
990 vw		1008 m, sh	985 m			1014 m	
964 ms	960 s, b	963 mw, b		960 vw	955 vs, sh		960 vw, b
930 vw	925 vs	921 vw			930 vs		
865 w	860 m	887 vw					
855 w	840 m, sh	864 m	865 vs				
842 w		852 m	850 ms				
830 vw		817 w, b	830 w	829 mw	830 s, b	820 vw	830 mw
813 ms	815 vs			814 w			814 w
773 vw		745 ms	745 s		678 s		
651 vs	670 m, sh	648 vs	640 s	645 v		650 s	649 vs
646 vs						645 s, sh	
631 s, sh	635 s						
589 w	579 s	581 w	596 mw	590 vw	585 s		580 w
569 w		571 w					
553 mw	555 m, sh	549 w	558 m	545 w	548 s		550 w
548 w, sh	542 s	530 vw	530 m	520 w	520 vw		
453 s	452 s	452 s	464 s	454 s	462 m	452 ms	452 s
			430 vw				
399 vw		410 vw	414 ms		405 w	400 vw	405 w
390 vw		390 vw	386 m				391 w
						304 m	
298 s, sh		308 vs	309 s		300 ms	294 m	
290 s, sh		296 vw					
278 vs		281 vs	264 ms	286 vs	285 w	282 m	282 vs
~210 vw		213 w		275 s, sh	267 m	279 vs	
				220 s			
205 w						205 ms, b	
181 w				188, 178 w, sh			
159 w		151 m		167, 150 w		150 m	150 m
135 w		108 w					127 m
109 m		100 w, sh					
		168 w, sh					

[a] Abbreviations: s = strong, m = medium, w = weak, b = broad, v = very, sh = shoulder. [b] Reference 13. [c] Reference 1. [d] Room temperature.

In most cases good correspondence between the band positions in the IR and Raman spectra are found and we have primarily listed the Raman bands, because resolution is so much better.

As can be seen in Table I, both $[Br(SO_3F)_2][Au(SO_3F)_4]$ and the iodine analogue give rather complex Raman spectra, extending over the range of 1500–100 cm^{-1}. A detailed band assignment is certainly not possible, since obviously, coincidences, in particular in the region of the deformation modes (below 600 cm^{-1}), seem to occur. A few rather general comments in favor of a heteropolar structure consisting of $[X(SO_3F)_2]^+$ and $[Au(SO_3F)_4]^-$ can however be made.

It can be easily seen that strong characteristic Raman bands for the $[Au(SO_3F)_4]^-$ ion[1] at 1410, 1230 (with an additional weaker band at 1200), 650, 455, and 280 cm^{-1} are all found in the Raman spectra of all four new compounds with very similar intensities. We had previously[1] noted that for the $[Au(SO_3F)_4]^-$ ion all observed Raman bands show little cation dependence, except perhaps for additional band splittings. While it is true that the anion $[X(SO_3F)_4]^-$, with X = Br or I, gives rather similar Raman spectra,[14] the strong and sharp low-frequency bands occur here at about 620, 440, and 240 cm^{-1}.

In addition, characteristic bands due to the cation $[X(SO_3F)_2]^+$ are also readily recognized by comparison to the reported spectra[13] for the hexakis(fluorosulfato)stannates(IV). In particular for the bromine compound, a medium-strong Raman band at ~1500 cm^{-1} is found for $[Br(SO_3F)_2]^+[Au(SO_3F)_4]^-$ as well. This band, assigned to an asymmetric SO stretch, is very rarely found at such a high frequency and may be termed diagnostic for the $[Br(SO_3F)_2]^+$ cation.

The rationale apparent in the spectra suggests a frequency shift of the SO_3F stretching modes of a monodentate fluorosulfate to higher frequencies when the moiety carries a positive net charge and to lower frequencies when a negative net charge is found. This is quite evident from the positions of $\nu(SF)$ at 800–900 cm^{-1}.

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(14) H. A. Carter, S. P. L. Jones, and F. Aubke, *Inorg. Chem.*, **9**, 2485 (1970).

The postulated formulation as $[X(SO_3F)_2]^+$ and $[Au(SO_3F)_4]^-$ may however be an oversimplification. Bands in the region of ~1150 cm^{-1} are normally rather characteristic for bidentate bridging fluorosulfate groups,[15] and occurrence of these bands in both the $[Au(SO_3F)_4]^-$ and $[Sn(SO_3F)_6]^{2-}$ derivatives does indicate covalent anion–cation interaction. Such interaction is not really surprising as evidenced by the molecular structures of related interhalogen cation complexes[16] such as BrF_2SbF_6[17] and ICl_2SbCl_6.[18] In these two cases, the short interionic distances suggest the presence of interactions, but not to the extent that the compounds could be classified as being polymeric.

Our preference for an ionic formulation for $[X(SO_3F)_2][Au(SO_3F)_4]$, consistent with the observed vibrational spectra and their similarity to those for the $[Sn(SO_3F)_6]^{2-}$ complexes[13] (here the ^{119}Sn Mössbauer spectrum shows a single line with an isomer shift characteristic for the hexakis(fluorosulfato)stannate(IV) ion), is also based on the solution behavior of the binary fluorosulfates of Au, Br, and I in fluorosulfuric acid. The former is a strong SO_3F^- ion acceptor while the halogen fluorosulfates $I(SO_3F)_3$[19] and $Br(SO_3F)_3$[20] are very weak electrolytes.

The presence of the tetrakis(fluorosulfato)aurate(III) ion in both $Br_5[Au(SO_3F)_4]$ and $Br_3[Au(SO_3F)_4]$ is evident from their vibrational spectra. Differences between the band positions observed for the two compounds are small. Unfortunately a clear identification and subsequent assignment of bands due to the two polybromine cations are rather difficult. A very intense Raman band at ~280 cm^{-1} observed for the $[Au(SO_3F)_4]^-$ ion[1] falls into the same region where the stretching fundamentals for Br_3^+ are expected.[7,10] The 280-cm^{-1} band has only low intensity in the IR spectrum at 80 K, but this region is found on the very end of the working range of our spectrophotometer (Perkin-Elmer 225) and identification is not entirely unambiguous.

The following additional bands, not found for the anion, are observed and may in part be due to the Br_n^+ ion, but the occurrence of lattice modes and of bands due to some covalent anion–cation interaction is possible in this region. For $Br_3[Au(SO_3F)_4]$ these bands are found in the Raman spectrum at 275, 220, 188, and 178 cm^{-1} with a band at 300 cm^{-1} found in the IR spectrum. $Br_5[Au(SO_3F)_4]$ has additional bands at 304, 295, 267, and 205 in the Raman spectrum and at 305, 295, and 260 cm^{-1} in the IR spectrum. It is noteworthy that the Raman spectrum of $Br_5[Au(SO_3F)_4]$ provides no evidence for the presence of free bromine, with ν(Br–Br) expected at 320 cm^{-1}.[10]

Conclusions. The four examples discussed here indicate that unusual cations may be stabilized by the $[Au(SO_3F)_4]^-$ ion, provided suitable synthetic routes can be found. An extension of our synthetic work in this direction is planned.

Acknowledgment. Financial support by the Natural Sciences and Engineering Research Council of Canada through an operating grant and a postgraduate scholarship to K.C.L. is gratefully acknowledged.

Registry No. $Br_3[Au(SO_3F)_4]$, 72030-07-0; $Br_5[Au(SO_3F)_4]$, 72016-94-5; $[Br(SO_3F)_2][Au(SO_3F)_4]$, 72030-08-1; $[I(SO_3F)_2][Au(SO_3F)_4]$, 72016-95-6; $BrSO_3F$, 13997-93-8; $S_2O_6F_2$, 13709-32-5.

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(15) P. A. Yeats, J. R. Sams, and F. Aubke, *Inorg. Chem.*, **11**, 2634 (1972).
(16) R. J. Gillespie and M. J. Morton, *Q. Rev., Chem. Soc.*, **25**, 553 (1971).
(17) A. J. Edwards and G. R. Jones, *J. Chem. Soc.*, 1467 (1969).
(18) C. G. Vonk and E. H. Wiebenga, *Acta Crystallogr.*, **12**, 859 (1959).
(19) R. J. Gillespie and J. B. Milne, *Inorg. Chem.*, **5**, 1236 (1966).
(20) F. Aubke, unpublished results.

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Crystal and Molecular Structure of 2,3-Dimethyl-4,7-dihydroxy-10-bromo-2,3-dicarba-*closo*-undecaborane

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Received February 5, 1979

2,3-Dimethyl-4,7-dihydroxy-10-bromo-2,3-dicarba-*closo*-undecaborane, $(CH_3)_2C_2B_9H_6(OH)_2Br$, crystallizes in the space group *Fddd* [D_{2h}^{24}; No. 70, second setting] with $a = 21.484$ (2) Å, $b = 26.252$ (5) Å, $c = 17.169$ (3) Å, $V = 9683$ Å^3, and $Z = 32$. Diffraction data were collected with a Picker FACS-I four-circle diffractometer using Zr-filtered Mo Kα radiation. The structure has been refined by full-matrix least-squares methods to residuals $R = 0.082$ and weighted $R = 0.094$, for 145 variables and 1459 significant observations. The OH groups are located on adjacent vertex positions B(4, 7) and the bromine at the B(10) position. The configuration of the polyhedral cage is intermediate between the closo C_{2v} structure and nido C_{5v} icosahedral fragment. The distortion from the closo structure toward an approximate nido fragment is attributed to donation of electron density from the lone-pair electrons on the oxygens to the molecular-orbital framework of the polyhedron. This, in effect, increases the skeletal electron count from the closo $n + 1$ pairs of electrons toward the nido $n + 2$, where n = number of vertex positions.

Introduction

In previous papers[2,3] the preparation and chemistry of the bis(*B,B'*-dihydroxy) derivative of 2,3-dimethyl-2,3-dicarba-*closo*-undecaborane have been described. On the basis of chemical and spectroscopic evidence, the two hydroxy groups were assigned to the B(4, 7) positions. The X-ray structure determination of the bis(*B,B'*-dihydroxy)-*B*-bromo derivative[2] reported herein confirms the location of the *B*-hydroxy groups and also details the distortions of polyhedral geometry in the cage structure. The distortion is attributed to the interaction between the exopolyhedral *B*-hydroxy groups and polyhedral framework.

Experimental Section

A clear irregular octahedron of $(CH_3)C_2B_9H_6(OH)_2Br$, with approximate maximum dimensions 0.54 × 0.70 × 0.40 mm, was sealed within a thin-walled capillary under inert atmosphere. X-ray diffraction photographs revealed a face-centered orthorhombic lattice ($h + k = 2n + 1$, $k + l = 2n + 1$, $h + l = 2n + 1$ for hkl) with additional systematic extincitions ($h + k = 4n + 1, 2, 3$ for $hk0$, $k + l = 4n + 1, 2, 3$ for $0kl$, $h + l = 4n + 1, 2, 3$ for $h0l$) that uniquely

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(2) G. D. Mercer and F. R. Scholer, *Inorg. Chem.*, **12**, 2102 (1973).
(3) G. D. Mercer, J. Lang, R. Reed, and F. R. Scholer, *Inorg. Chem.*, **14**, 761 (1975).

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