or parent–radical coupling

$$A + e^- \rightleftarrows A^{-\cdot} \quad E_i^f$$

$$A^{-\cdot} + A \rightleftarrows A_2^{-\cdot}$$

would give the net reaction in eq 6, but would be indistinguishable from one another.

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Synthesis and Structural Characterization of Fluorosulfate Derivatives of Silver(II)

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The synthesis of silver(II) fluorosulfate, $Ag(SO_3F)_2$, by a variety of routes is described. The preparations of a mixed-valency compound of the composition $Ag_3(SO_3F)_4$ and its potassium analogue $K_2Ag^{II}(SO_3F)_4$, the compounds $Ag^{II}Pt^{IV}(SO_3F)_6$ and $Ag^{II}Sn^{IV}(SO_3F)_6$, and the complex $[Ag(bpy)_2](SO_3F)_2$ are also reported. Structural studies are based on vibrational, electronic mull and diffuse reflectance, and ESR spectra as well as magnetic susceptibility measurements in the temperature range of 80 to about 300 K. Both $Ag_3(SO_3F)_4$ and $K_2Ag(SO_3F)_4$ show antiferromagnetic coupling. All other divalent silver compounds synthesized here are magnetically dilute with the Ag^{2+} ion in a square-planar or tetragonally distorted (elongated) octahedral environment.

(A) Introduction

Even though many divalent silver compounds have been reported over the years,[1-3] the fluoride AgF_2[4] has remained the only simple, binary silver(II) compound which is stable at room temperature. All other Ag(II) compounds are either derivatives of silver(II) fluoride, ternary fluorides like $K[Ag^{II}F_3]$[5] or $Ag^{II}[SnF_6]$,[6] or coordination complexes, where divalent silver is stabilized by mono- or polydentate donor ligands.

Only recently[7a] have we reported on another binary silver(II) compound, $Ag(SO_3F)_2$, in a preliminary communication. Earlier unsuccessful attempts to obtain pure $Ag(SO_3F)_2$ have been summarized.[7b] We now describe in detail the synthesis and the structural characterization of $Ag(SO_3F)_2$ and of a number of new silver(II) fluorosulfate derivatives.

(B) Experimental Section

(I) Chemicals. All chemicals obtained from commercial sources were of reagent grade or of the highest purity obtainable. All silver(I) salts were used without further purification. Metallic silver powder, 100 mesh, of 99.999% purity was obtained from the Ventron Corp.

Dichloromethane and acetonitrile were dried using standard methods, degassed in vacuo, and stored over Linde 4A molecular sieves. Trifluoromethanesulfonic acid (Minnesota Mining and Manufacturing Co.) was distilled at reduced pressure (100 mmHg) from concentrated H_2SO_4 before use. Fluorosulfuric acid (Allied Chemicals) of technical grade was doubly distilled at atmospheric pressure as described.[8] Bromine(I) fluorosulfate,[9] $BrOSO_2F$, chloryl fluorosulfate,[10] ClO_2SO_3F, bis(fluorosulfuryl) peroxide,[11] $S_2O_6F_2$, silver(II) bis(α,α'-bipyridyl) bis(trifluoromethyl sulfate),[12] and KSO_3F[8] were synthesized according to literature methods. The solvolysis of silver trifluoroacetate, AgO_2CCF_3, in HSO_3F was found to be the simplest and most convenient route to silver(I) fluorosulfate, $AgSO_3F$.

(II) Instrumentation. Infrared spectra were recorded on a Perkin-Elmer 457 or a Unicam SP1100 grating spectrophotometer. Depending on reactivity, thin films or Nujol mulls were used with BaF_2, AgCl, AgBr, KRS-5, or CsI as window materials (all obtained from Harshaw Chemicals). Spectra of gaseous materials were recorded using a Monel cell of 7-cm path length, fitted with AgCl windows and a Whitey valve.

IR spectra of liquid N_2 temperature were obtained on a Perkin-Elmer 225 grating spectrophotometer. A cell fitted with CsI windows and a "spray on" technique as described[13] previously were used. Raman spectra were obtained with a Spex Ramalog 5 spectrometer equipped with an argon ion laser using the line at 514.5 nm for excitation. The samples were contained in melting point capillaries. ESR spectra were recorded on a Varian Associates E-3 spectrometer equipped with 100-kHz field modulation at room temperature and at liquid nitrogen temperature. Powdered solids or solutions were contained in 4-mm o.d. quartz tubes.

Magnetic susceptibilities were determined using a Gouy apparatus described before.[14] Measurements were made at constant field strengths of approximately 4500 and 8000 G. All susceptibilities measured were found to be independent of field strength. Calibrations were carried out using $HgCo(CNS)_4$.[15] Diamagnetic corrections were obtained from the literature.[16] The diamagnetic correction for SO_3F^- was assumed to be identical with the value of SO_4^{2-} (40.1×10^{-6} cgsu). Electronic spectra were recorded on either a Cary 14 or a Perkin-Elmer Model 124 spectrophotometer. Diffuse reflectance spectra were recorded on a modified Bausch and Lomb Spectronic 600 spectrometer in the region of 350–740 nm.

The Mössbauer spectrometer has been described elsewhere.[17] Measurement was made at 80 K and the $Ba^{119m}SnO_3$ source at 298 K. The isomer shift is reported relative to SnO_2 absorber at 80 K. The accuracy for both isomer shift and quadrupole splitting is judged to be ±0.03 mm/s.

All moisture-sensitive solids and nonvolatile ligands were handled in a Vacuum Atmospheres Corp. "Dri-Lab", Model HE-43-2, filled with purified dry nitrogen and equipped with a "Dri-Train", Model HE-93B.

Volatile materials were distilled using vacuum-line techniques. The manifold was equipped with Kontes Teflon stem stopcocks.

Reactions involving fluorine were performed in Monel metal cans of about 150-mL contents fitted with a screw-on top and a Whitey valve. All other reactions were carried out in glass reaction vials of an approximate volume of 50 mL and fitted with Kontes Teflon stem stopcocks and equipped with Teflon-coated stirring bars. Where large amounts of highly volatile materials (O_2, CO_2) evolved, the reactions were carried out in thick-wall reaction vials. All reactions were monitored by weighing.

(III) Synthetic Reactions. (a) Silver(II) Fluorosulfate. All reactions leading to $Ag(SO_3F)_2$ together with their reaction times and tem-

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Table I. Synthetic Routes to $Ag(SO_3F)_2$

	Solid reactant[a]	Oxidizer or reagent[b]	Reacn time, h	Reacn temp, °C	Reacn products[c]
(1)	Ag	$S_2O_6F_2$	168	70	$Ag(SO_3F)_2$
(2)	Ag	$S_2O_6F_2$/ HSO_3F[d]	0.5	25	$Ag(SO_3F)_2$
(3)	Ag_2O	$S_2O_6F_2$	72	70	$Ag(SO_3F)_2$, O_2
(4)	Ag_2CO_3	$S_2O_6F_2$	72	70	$Ag(SO_3F)_2$, O_2, CO_2
(5)	$AgSO_3F$	$S_2O_6F_2$	48	25	$Ag(SO_3F)_2$
(6)	$AgSO_3CF_3$	$S_2O_6F_2$	144	25	$Ag(SO_3F)_2$, CF_3SO_3F, SO_3
(7)	AgF_2	SO_3	0.5	50	$Ag(SO_3F)_2$
(8)	Ag, Ag_2O, or $AgSO_3F$	$BrSO_3F$	48	25–70	$Ag_3(SO_3F)_4$, Br_2
	$Ag_3(SO_3F)_4$	$S_2O_6F_2$	48	70	$Ag(SO_3F)_2$

[a] Usual amount 0.5–1.2 g. [b] Always used in large excess. [c] The catalytic decomposition of $S_2O_6F_2$ at high temperatures yielded small amounts of O_2 and $S_2O_5F_2$ as by-products. [d] In 1:1 mixture (by volume).

peratures are listed in Table I. The reaction of bis(fluorosulfuryl) peroxide with argentous oxide is described below to serve as an example.

A large excess of $S_2O_6F_2$ (about 10 g) was distilled onto 606 mg (5.23 mmol) of Ag_2O in vacuo. The evacuated reactor was warmed up from liquid nitrogen temperature first to room temperature and subsequently to +70 °C with a water bath. The mixture was continuously heated and stirred for 3 days. During this time the color of the solid changed from black to dark brown. Oxygen produced during the reaction was periodically pumped off. The progress of the reaction was repeatedly checked by weighing the reaction vial after removal of all volatile materials in vacuo. After the reaction had stopped, 1600 mg (5.23 mmol) of a dark brown powder was obtained.

(b) Silver(II) Bis(α,α'-bipyridyl) Bis(fluorosulfate). A sample of 894 mg (2.92 mmol) of $Ag(SO_3F)_2$ was added under exclusion of moisture to a concentrated solution of 1109.6 mg (7.1 mmol) of α,α'-bipyridine in acetonitrile, with the reactor cooled to −40 °C. The resulting mixture was stirred and allowed to warm gradually to room temperature. A brick red solid separated from the red-brown solution. After 30 min, the solid material was filtered off. The reaction product was washed with two portions (about 5 mL each) of dichloromethane under a blanket of dry nitrogen and subsequently dried in vacuo.

(c) Trisilver Tetrakis(fluorosulfate). The mixed-valency compound $Ag^I_2Ag^{II}(SO_3F)_4$ is formed in the interaction of either silver, argentous oxide, or silver(I) fluorosulfate with bromine(I) fluorosulfate.

In a typical reaction, silver powder (796 mg or 7.38 mg-atom) dissolved under stirring at room temperature in an approximately tenfold excess of $BrSO_3F$. Removal of all volatile materials yielded 1780 mg of a black crystalline solid which analyzed as $Ag_3(SO_3F)_4$. The slightly higher weight (2.47 mmol vs. 2.46 mmol expected) may be due to a trace amount of brown material in the upper part of the reactor, presumed to be $Ag(SO_3F)_2$. Essentially the same results were obtained, when the reaction was carried out at +70 or +150 °C.

(d) Dipotassium Tetrakis(fluorosulfato)argentate(II). $K_2Ag(SO_3F)_4$ was obtained when a mixture of KSO_3F (0.768 mg or 5.56 mmol) and Ag powder (300 mg or 2.78 mg-atom) was reacted with approximately 10 mL of a mixture HSO_3F and $S_2O_6F_2$ (nearly equimolar) at 25 °C. Removal of all volatiles in vacuo yielded 1643 mg of a black solid powder of the composition $K_2Ag(SO_3F)_4$.

(e) Silver(II) Hexakis(fluorosulfato)platinate(IV). Solutions of the previously reported compound $Pt(SO_3F)_4$[18] in HSO_3F were conveniently obtained by the oxidation of platinum powder by $S_2O_6F_2$ in HSO_3F.[19] Such a solution prepared from 253 mg Pt (1.30 mg-atom) was added in the drybox to a suspension of $Ag(SO_3F)_2$ in HSO_3F, made separately from 140 mg of silver powder (1.30 mg-atom).

The mixture was magnetically stirred at room temperature for 1 day. A light green precipitate was formed and isolated by filtration. Remaining traces of volatile materials were removed in vacuo, yielding a light green powder of the composition $AgPt(SO_3F)_6$.

(f) Silver(II) Hexakis(fluorosulfato)stannate(IV). Metallic tin (257 mg or 2.16 mg-atom) was reacted with about 10 mL of a 2:1 mixture of HSO_3F and $S_2O_6F_2$ at room temperature. To the resulting milky white suspension, 233 mg or 2.16 mg-atom of silver powder was added in the drybox. The mixture was stirred at room temperature overnight. A homogeneous green precipitate was formed. Removal of all volatile materials in vacuo yielded 1770 mg of a green powdery solid which corresponded to 2.15 mmol of $AgSn(SO_3F)_6$.

(g) The Conversion of $Ag(SO_3F)_2$ into AgF_2. A metal reactor containing 0.8 g of $Ag(SO_3F)_2$ was filled with F_2 to atmospheric pressure at 25 °C. After heating for 2 h at +130 °C and removal of all excess fluorine, both $FOSO_2F$ and $S_2O_6F_2$ were identified by their vibrational spectra.[20] The residual solid had no IR bands due to the SO_3F groups. Silver analysis: calcd for AgF_2, 73.95; found, 74.09.

(IV) Analysis and Properties. The C, N, and H contents were determined by Mr. P. Borda of this department. Microanalyses for metals, sulfur, and fluorine were performed by Alfred Bernhardt Microanalytical Laboratories, Elbach, West Germany.

(a) $Ag(SO_3F)_2$ is a dark brown hygroscopic solid which is thermally stable up to +210 °C. Decomposition at this temperature yields quantitatively $AgSO_3F$ and $S_2O_6F_2$. $Ag(SO_3F)_2$ is very soluble in $BrSO_3F$ and sparingly soluble in HSO_3F or CH_3CN. Anal. Calcd for $Ag(SO_3F)_2$: Ag, 35.25; S, 20.96; F, 12.42. Found: Ag, 35.10; S, 20.69; F, 12.15.

(b) $Ag(bpy)_2(SO_3F)_2$ is a brick red solid which melts with decomposition at +218–219 °C. Anal. Calcd for $Ag(C_{10}H_8N_2)_2(SO_3F)_2$: Ag, 17.44; F, 6.14; C, 38.85; N, 9.06; H, 2.61. Found: Ag, 17.15; F, 6.29; C, 38.73; N, 9.01; H, 2.76.

The IR spectrum will not be discussed in detail, but the observed frequencies are listed here together with estimated intensities. ν is given in cm^{-1}. IR: 3100 (m), 1605 (s), 1567 (ms), 1498 (s), 1475 (ms), 1302 (vs, b), 1270 (vs, b), 1245 (mw, sh), 1205 (vw), 1178 (w), 1157 (m), 1105 (m), 1075 (vs), 1045 (vw), 1028 (ms), 1017 (m), 981 (w), 965 (vw), 915 (w, sh), 904 (mw), 818 (vw), 782 (s), 770 (s), 730 (s), 660 (m), 651 (m), 635 (vw), 580 (vs), 561 (ms), 475 (vw), 468 (vw), 440 (mw), 415 (ms).

(c) $Ag_3(SO_3F)_4$ is a black hygroscopic solid, which is thermally stable up to +170 °C. Thermal decomposition produces $S_2O_6F_2$ as volatile material. Anal. Calcd for $Ag_3(SO_3F)_4$: Ag, 44.95; S, 17.82; F, 10.56. Found: Ag, 44.85; S, 17.78; F, 10.45. IR spectrum [cm^{-1}]: 1325 (s, sh), 1278 (s), 1235 (s), 1195 (s), 1095 (w), 1082 (ms), 1055 (s), 830 (s), 810 (s).

(d) $K_2Ag(SO_3F)_4$ is a black hygroscopic solid, melting at 195 °C with gas evolution. Anal. Calcd for $K_2Ag(SO_3F)_4$: Ag, 18.52; K, 13.43; F, 13.05. Found: Ag, 18.79; K, 13.37; F, 12.90. IR spectrum [cm^{-1}]: 1370 (ms, sh), 1290 (s, b), 1240 (s), 1180 (vs), 1080 (s), 1050 (ms), 1040 (ms), 825 (s), 810 (s).

(e) $AgPt(SO_3F)_6$ is a light green powder and is very hygroscopic. On heating the material turns reversibly brownish between 110 and 180 °C and decomposes on further heating. Anal. Calcd for $AgPt(SO_3F)_6$: Ag, 12.02; Pt, 21.74; F, 12.70. Found: Ag, 12.30; Pt, 21.52; F, 12.89.

(f) $AgSn(SO_3F)_6$ is a green solid and melts above +170 °C under decomposition to a white solid. The material is very hygroscopic. Anal. Calcd for $AgSn(SO_3F)_6$: Ag, 13.14; Sn, 14.46; F, 13.89. Found: Ag, 14.27; Sn, 14.56; F, 14.03.

(C) Results and Discussion

(I) Syntheses. As listed in Table I, a number of useful synthetic routes to $Ag(SO_3F)_2$ are available, most of which involve the use of bis(fluorosulfuryl) peroxide as oxidizing agent. The most convenient preparation is the oxidation of metallic silver by $S_2O_6F_2$ in the presence of HSO_3F, requiring a very short reaction time and a low reaction temperature.

The ability of $S_2O_6F_2$ to oxidize Ag(I) to Ag(II) is not unexpected for two reasons: (a) the isoelectronic peroxydisulfate ion, $S_2O_8^{2-}$, is frequently used as oxidizing agent in the preparation of Ag(II) coordination complexes with stabilizing ligands[1-3] from suitable Ag(I) precursors, and (b) an earlier report[21] describes the synthesis of a black $Ag_2O(SO_3F)_2$ from Ag_2O or Ag_2CO_3 and $S_2O_6F_2$ according to eq 1.

$$Ag_2O\ (Ag_2CO_3) + S_2O_6F_2 \xrightarrow[3\text{-}12\ h]{+25\ ^\circ C} Ag_2O(SO_3F)_2\ (+CO_2) \qquad (1)$$

Our results (reactions 3 and 4) in Table I indicate that at higher reaction temperatures and longer reaction times silver(II) fluorosulfate is ultimately formed, presumably via the intermediate $Ag_2O(SO_3F)_2$. The conversion of metal oxides or carbonates into metal fluorosulfates has previously been reported for a number of lanthanide oxides and carbonates.[22]

The oxidation to a silver(II) compound by $S_2O_6F_2$ can be observed for a large number of silver(I) salts (e.g., Ag_2SO_4, $AgNO_3$, $AgClO_4$, $AgBF_4$, and $AgCO_2CF_3$), but only when the anion can be either replaced by or converted into a fluorosulfate group, a suitable synthetic route results, as is the case of $AgSO_3CF_3$:

$$2AgSO_3CF_3 + 3S_2O_6F_2 \rightarrow 2Ag(SO_3F)_2 + 2SO_3 + 2CF_3OSO_2F \quad (2)$$

More commonly, reaction mixtures or very impure products are obtained. The reaction of $AgNO_3$ with $S_2O_6F_2$ may serve as an example (eq 3).

$$2AgNO_3 + 3S_2O_6F_2 \rightarrow 2Ag(SO_3F)_2 + 2NO_2SO_3F + O_2 \quad (3)$$

Of some interest is the successful conversion of AgF_2 into $Ag(SO_3F)_2$ by SO_3 insertion (reaction 7, Table I). Silver(II) difluoride acts as a catalyst in the fluorination of SO_3 to $S_2O_6F_2$ or fluorine fluorosulfate, $FOSO_2F$:

$$2SO_3 + F_2 \xrightarrow[AgF_2]{+160\ ^\circ C} S_2O_6F_2{}^{23} \quad (4)$$

and

$$SO_3 + F_2 \xrightarrow[AgF_2]{+220\ ^\circ C} FOSO_2F^{24} \quad (5)$$

Even though the detailed mechanism of such a catalytic fluorination is not known, the intermediate formation of $Ag(SO_3F)_2$ or perhaps $FAgSO_3F$ is likely. The reaction of $Ag(SO_3F)_2$ with F_2 does indeed produce both $FOSO_2F$ and $S_2O_6F_2$ and the overall process observed is consistent with this

$$AgF_2 + 2SO_3 \xrightarrow{+50\ ^\circ C} Ag(SO_3F)_2 \quad (6)$$

$$Ag(SO_3F)_2 + F_2 \xrightarrow{+130\ ^\circ C} AgF_2 + S_2O_6F_2 \quad (7a)$$

$$Ag(SO_3F)_2 + 2F_2 \xrightarrow{+130\ ^\circ C} AgF_2 + 2FOSO_2F \quad (7b)$$

view. Similar divalent silver intermediates have been postulated in the catalytic fluorination of CO.[25]

The pyrolysis of $Ag(SO_3F)_2$ according to eq 8 is unusual.

$$2Ag(SO_3F)_2 \xrightarrow{+215\ ^\circ C} 2AgSO_3F + S_2O_6F_2 \quad (8)$$

The formation of $S_2O_6F_2$ in the pyrolysis of a metal fluorosulfate has only one precedent:

$$Pd^{II}Pd^{IV}(SO_3F)_6 \xrightarrow{+160\ ^\circ C} 2Pd(SO_3F)_2 + S_2O_6F_2{}^{26} \quad (9)$$

Bromine(I) fluorosulfate appears to be a weaker oxidizing agent than $S_2O_6F_2$. The resulting product $Ag_3(SO_3F)_4$ appears to be the first example of a mixed-valence state compound of silver with the valence pair Ag^I–Ag^{II}. All previously reported examples involve the valence pairs Ag^I–Ag^{III} or Ag^0–Ag^I.[27] Interestingly, a product similar in appearance is reportedly[28] formed in the electrolysis of AgF in HSO_3F, where a black, silver(II)-containing solid (with 40.4% Ag) deposits on the anode. Further oxidation of $Ag_3(SO_3F)_4$ with $S_2O_6F_2$ results in the formation of $Ag(SO_3F)_2$. When heated, the mixed-valency compound $Ag_3(SO_3F)_4$ converts into $AgSO_3F$ with evolution of $S_2O_6F_2$. Formulation of the mixed-valency compound as $Ag^I{}_2Ag^{II}(SO_3F)_4$ suggests the possibility of synthesizing similar complexes, where Ag^I is replaced by other univalent cations. The reaction of KSO_3F with Ag according to eq 10 yields indeed an example of this type. The potassium

$$2KSO_3F + Ag + S_2O_6F_2 \xrightarrow[HSO_3F]{+25\ ^\circ C} K_2Ag(SO_3F)_4 \quad (10)$$

compound has analogues in previously reported[5,29] ternary fluorides of the type $M^I{}_2AgF_4$, where M^I = K, Rb, or Cs, or $M^{II}AgF_4$, where M^{II} = Ba or Hg. Attempts to produce heterocation complexes of the type $(ClO_2)_2Ag(SO_3F)_4$ by reaction 11 produce only a thermally unstable complex, which

$$2ClO_2SO_3F + Ag(SO_3F)_2 \rightarrow (ClO_2)_2Ag(SO_3F)_4 \quad (11)$$

gradually loses ClO_2SO_3F in vacuo at +25 °C in a reversal of the formation equation. It may be concluded that $Ag(SO_3F)_2$ is not a strong SO_3F^--ion acceptor. The analogy between fluoro and fluorosulfato derivatives of divalent silver extends also to compounds of the type $Ag^{II}M^{IV}X_6$, where M^{IV} = Pt or Sn and X = F or SO_3F. Ternary fluorides of this type have been reported by Hoppe and his group.[6] The corresponding fluorosulfato complexes are obtained according to eq 12 and 13. Compounds of the type $Ba[Pt(SO_3F)_6]$[19] and

$$Ag(SO_3F)_2 + Pt(SO_3F)_4 \xrightarrow[25\ ^\circ C]{HSO_3F} AgPt(SO_3F)_6 \quad (12)$$

$$Ag + Sn + 3S_2O_6F_2 \xrightarrow[25\ ^\circ C]{HSO_3F} AgSn(SO_3F)_6 \quad (13)$$

$K_2[Sn(SO_3F)_6]$[30] have previously been synthesized. Their vibrational spectra should help in the structural characterization of the new complexes.

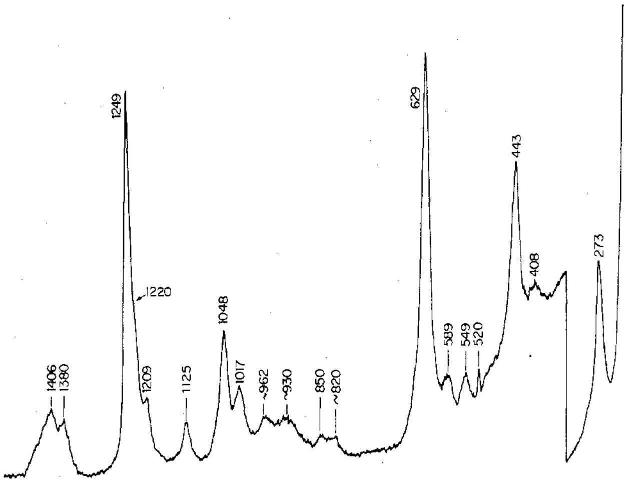

Figure 1. Raman spectrum of $AgPt(SO_3F)_6$ from 100 to 1500 cm^{-1}.

Finally, the successful conversion of $Ag(SO_3F)_2$ into an α,α'-bipyridyl complex (eq 14) completes the synthetic re-

$$Ag(SO_3F)_2 + 2bpy \xrightarrow[CH_3CN]{-40\ ^\circ C} [Ag(bpy)_2](SO_3F)_2 \quad (14)$$

actions reported here. The ligand α,α'-bipyridine (bpy) was chosen because the corresponding trifluoromethyl sulfate, $[Ag(bpy)_2](SO_3CF_3)_2$ is known.[12] In addition, the cation $[Ag(bpy)_2]^{2+}$ has been studied extensively by ESR, electronic spectra, and bulk magnetic measurements.[1-3] Two X-ray diffraction studies have also been published on $[Ag(bpy)_2](NO_3)_2$[31] and $[Ag(bpy)_2](NO_3)_2 \cdot H_2O$.[32]

(II) Vibrational Spectra. All silver(II) fluorosulfate derivatives except $[Ag(bpy)_2](SO_3F)_2$ are highly reactive toward commonly used IR window materials and mulling agents. In addition, the dark colors of most derivatives prevent the recording of meaningful Raman spectra. Only $AgPt(SO_3F)_6$ and $AgSn(SO_3F)_6$ were found suitable for Raman studies. The spectrum of $AgPt(SO_3F)_6$ is shown in Figure 1. Of the infrared window materials, only BaF_2 (transmission range extends to 800 cm^{-1}) and in some instances KRS-5 (thallium bromide–thallium iodide, transmission down to 250 cm^{-1}) were found suitable at room temperature. In addition, for $Ag(SO_3F)_2$, an IR spectrum at 80 K was obtained using a low-temperature cell fitted with CsI windows.

Table II. Infrared Spectra (cm^{-1}) of Ag(SO$_3$F)$_2$ and Related Compounds[a]

Ag(SO$_3$F)$_2$[b]	Ag(SO$_3$F)$_2$[c]	Cu(SO$_3$F)$_2$[d]	(CH$_3$)$_2$Sn(SO$_3$F)$_2$[e]	Ag(bpy)$_2$(SO$_3$F)$_2$[f]	AgSO$_3$F	Approx descrip
1320 s, b	1325 ms, sh 1310 s 1295 m, sh	1306 vs	1350 s	1302 vs 1270 vs	1310 s, b, sh 1250 s, b	SO$_3$ str region
1185 vs, b	1205 s, sh 1185 vs	1223 vs	1180 s			
1070 s, b	1068 s	1115 s	1088 m, sh 1072 s, b	1075 vs	1075 s, sh 1062 s	
820 ms	837 m 824 m 817 m	861 s	827 m	782 s	795 s 748 s	SF str
	610 mw	630 m	620 m			
	592 m	604 m	590 m	580 vs	595 s, sh 587 s	SO$_3$F def modes
	557 ms	564 m	554 ms	561 ms	577 s 561 s, sh	
	430 m	426 m 416 m	417 s	415 ms	410 vs 395 vw	SO$_3$F rock modes
	275 m	300 m	304 m			
	268 ms					M-O str

[a] Abbreviations: v, very; s, strong; m, medium; w, weak; b, broad; sh, shoulder. [b] BaF$_2$ windows. [c] At 80 K; CsI windows. [d] Reference 37. [e] Reference 35; vibrations due to the Sn(CH$_3$)$_2$ moiety are omitted. [f] SO$_3$F vibrations only.

Table III. Vibrational Spectra (cm^{-1}) of AgPt(SO$_3$F)$_6$, AgSn(SO$_3$F)$_6$, and Related Compounds

AgPt(SO$_3$F)$_6$		Ba[Pt(SO$_3$F)$_6$]	AgSn(SO$_3$F)$_6$		K$_2$[Sn(SO$_3$F)$_6$]
Raman	IR KRS-5 plates	Raman[a]	Raman	IR[b]	IR[c]
1406 m	1420 vs	1410 vw	1421 ms	1425 s, sh	1380 sb
1380 m	1380 s, sh	1397 msh	1404 s	1395 vs, b	1220 s, b
1249 vs	1215 vs, b	1386 s	1398 s, sh	1227 s	1190 s, b
~1220 m, sh	1148 vs, b	1258 vs	1263 mw	1170 vs, b	990 sb
1209 mw	1080 vw	1218 ms	1192 m	1040 s	820 s, sh
1125 m	1030 m, sh	1033 s	1120 vs	1010 s, sh	810 s, b
1048 ms	968 vs, b	1012 ms	1013 ms	984 s, b	620 s
1017 mw	925 s	~950 vw	980 vw, sh	865 s, sh	571 m
962 w	850 m, sh	857 ms	850 ms	835 s, b	550 s
~930 vw	830 s	838 w	820 msh	640 s, b	430 m
850 w	760 vw	629 vs	633 ms	625 s, sh	
~828 w	738 vw	583 w	620 ms	590 s	
629 vs	660 s	549 m	590 s	555 s	
589 mw	625 mw	460 s	560 m	452 m, sh	
549 mw	590 s	422 w, sh	523 mw	448 s	
520 m	550 s	411 ms	434 s		
443 s	520 vw, sh	283 vw	413 ms		
408 w	468 m, sh	210 ms	408 mw, sh		
273 s	452 s	178 m	278 ms		
	305 s		212 s		
	295 m, sh		158 m		
			146 mw		
			135 mw		

[a] Reference 19. [b] Composite spectrum obtained on solids between BaF$_2$ and KRS-5 windows. [c] Reference 30.

Band positions of the infrared spectra of Ag(SO$_3$F)$_2$ and some related compounds are listed in Table II. Also listed are the bands due to the SO$_3$F$^-$ group in [Ag(bpy)$_2$](SO$_3$F)$_2$. These bands are identified by comparison with the IR spectra of [Ag(bpy)$_2$](SO$_3$CF$_3$)$_2$, synthesized by us for this purpose, and of [Ag(bpy)$_2$]ClO$_4$ previously published.[33]

The vibrational spectra of the compounds Ag^{II}Pt(SO$_3$F)$_6$ and Ag^{II}Sn(SO$_3$F)$_6$ are listed in Table III together with spectra of Ba[Pt(SO$_3$F)$_6$][29] and K$_2$[Sn(SO$_3$F)$_6$.[30] For Ag$_3$(SO$_3$F)$_4$ and K$_2$Ag(SO$_3$F)$_4$ only poorly resolved IR spectra could be obtained (see Experimental Section).

The vibrational bands observed for Ag(SO$_3$F)$_2$ indicate the loss of C_{3v} symmetry for the fluorosulfate group. The band positions, in particular in the sulfur–oxygen and sulfur–fluorine stretching range, are most consistent with the presence of bidentate fluorosulfate in Ag(SO$_3$F)$_2$. Agreement is particularly good with the corresponding bands for (CH$_3$)$_2$Sn(SO$_3$F)$_2$ and related tin(IV) fluorosulfates.[34] For (CH$_3$)$_2$Sn(SO$_3$F)$_2$, the presence of bidentate bridging SO$_3$F groups is confirmed by X-ray diffraction study.[35] Cu(SO$_3$F)$_2$ is reported to have a tetragonally elongated octahedral environment for Cu^{2+}.[36-38] The IR spectrum listed in Table II shows some resemblance to the one for Ag(SO$_3$F)$_2$. In contrast, the bands due to the fluorosulfate group in [Ag(bpy)$_2$](SO$_3$F)$_2$ indicate noncoordinated SO$_3$F$^-$ ions, even though one of the degenerate modes, the asymmetric SO$_3$ stretch, is split by ~30 cm^{-1}, presumably due to site-symmetry effects. The band positions agree well with reports on ionic SO$_3$F$^-$ compounds.[34,37-39]

Retention of C_{3v} symmetry, and hence a SO$_3$F$^-$ ion, is also found for AgSO$_3$F; however, all six fundamentals are doubled. This is best explained by assuming the existence of two independent sites for the anion in the solid state. A precedent is found in the reported IR spectrum of Sr(SO$_3$F)$_2$.[37] The

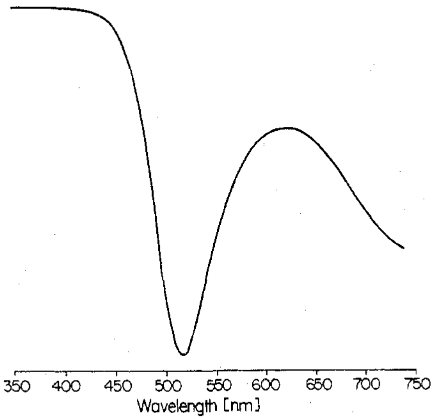

Figure 2. Diffuse reflectance spectrum of $AgSn(SO_3F)_6$ between 350 and 750 nm.

spectrum of $AgSO_3F$ agrees well with an earlier report on bands down to 650 cm^{-1}.[39]

Whereas assignments are possible for both bridging[34] and ionic SO_3F groups,[36,37,39,40] this task becomes more difficult for the complexes of the type $Ag^{II}M^{IV}(SO_3F)_6$, where M = Pt or Sn. Here, only an approximate description of the SO_3F group vibration is possible, because proliferation of bands due to slight nonequivalence or vibrational coupling is expected. While, as in $Ba[Pt(SO_3F)_6]$ or $K_2[Sn(SO_3F)_6]$, bands at ~1400, ~1250, and ~1000 cm^{-1} can be interpreted as being due to monodentate OSO_2F groups[29,30] linked to Pt or Sn, respectively, additional SO stretching vibrations at ~1150 and ~1040 cm^{-1} are observed for the silver(II) complexes. Bands in this region are generally associated with bidentate fluorosulfate groups (see Table II), and the reason for their appearance must be seen in the strong polarizing effect of the Ag^{2+} ion.

The occurrence of both mono- and bidentate SO_3F groups in the silver(II) complexes indicates that not all fluorosulfate groups seem coordinated to both M and Ag; some appear bonded to M only.

In any event, the silver(II) compounds are best regarded as ternary fluorosulfates with both metals coordinated in some way to SO_3F rather than ionic complexes allowing a formulation such as $K_2[Sn(SO_3F)_6]$.

(III) Electronic Spectra. Diffuse reflectance and mull spectra ((perfluorooctyl)sulfuryl fluoride, $C_8F_{17}SO_2F$, was used as mulling agent) are obtained on the fluorosulfate derivatives discussed here, except for the black or nearly black $Ag_3(SO_3F)_4$ and $K_2Ag(SO_3F)_4$. The remaining compounds give rather broad, asymmetrical bands. The spectrum of $AgSn(SO_3F)_6$ is shown in Figure 2 as an example.

The results are listed in Table IV and compared to published data on $[Ag(bpy)_2]X_2$ with X = NO_3^-,[41,42] $S_2O_8^{2-}$,[43] or $SO_3CF_3^-$,[12] on $Cu(SO_3F)_2$,[38] and on complexes of the type $AgMF_6$,[44] where M = Sn, Pb, Hf, or Zr.

Even though a square-planar configuration should result in at least three bands in the range of d–d transitions, assignable to ${}^2B_{1g} \rightarrow {}^2A_{1g}$, ${}^2B_{1g} \rightarrow {}^2B_{2g}$, and ${}^2B_{1g} \rightarrow {}^2E_g$ with the third band possibly split due to spin–orbit coupling, resolution is frequently poor, in particular when dealing with mull or diffuse reflectance spectra. Curve-resolving procedures have been used in the past[41,44] to extract ligand field parameters; however, where only a broad asymmetrical band is encountered, as for $[Ag(bpy)_2](SO_3F)_2$, rather than shoulders, data so obtained may not be very reliable.

In general the occurrence of a broad band at ~22 × 10^3 cm^{-1} is regarded as evidence for a square-planar environment in coordination complexes of silver(II).[3,45] Interestingly enough, $Ag(SO_3F)_2$ has, in addition to an intense UV band at 28 × 10^3 cm^{-1} or higher, a broad band at 22.0 × 10^3 cm^{-1} with a shoulder at 16.6 × 10^3 cm^{-1} and a broad band of lower intensity at 14.1 × 10^3 cm^{-1} which may be tentatively assigned as ${}^2B_{1g} \rightarrow {}^2A_{1g}$ at 14.1 × 10^3 cm^{-1}, ${}^2B_{1g} \rightarrow {}^2B_{2g}$ at 16.6 × 10^3 cm^{-1}, and ${}^2B_{1g} \rightarrow {}^2E_g$ at 22.0 × 10^3 cm^{-1} with the expected splitting unresolved. The approximate 10*Dq* value would be 16 600 cm^{-1}.

Table IV. Electronic Spectra of Silver(II) Fluorosulfate Derivatives and Related Compounds

Compd	Type of spectrum	λ_{max}, cm^{-1} × 10^3 (ϵ_{max}, M^{-1} cm^{-1})	Ref
$[Ag(bpy)_2](SO_3F)_2$	Dif refl	>28, 22.2	This work
$[Ag(bpy)_2]S_2O_8$	Dif refl	~22	41, 43
$[Ag(bpy)_2](NO_3)_2$	In H_2O	22 (2160)	42, 3
$[Ag(bpy)_2](SO_3F)_2$	In H_2O	22 (1630), 35.7 (22 000)	This work
$[Ag(bpy)_2](SO_3CF_3)_2$	In H_2O	22 (1020), 35.7 (23 000)	This work
$[Ag(bpy)_2](SO_3CF_3)_2$	Dif refl	22	This work
$Ag(SO_3F)_2$	Dif refl	>28, 22.0, 16.6 sh, 14.1 sh	This work
$Ag(SO_3F)_2$	In HSO_3F	~25	This work
AgF_2	Dif refl	22.0, 18.0 sh, 13.7	This work
$Cu(SO_3F)_2$	Mull	10.4	38
$AgPt(SO_3F)_6$	Dif refl	~25.6, 16.0	This work
$AgPt(SO_3F)_6$	Mull	~25	This work
$AgSn(SO_3F)_6$	Dif refl	>25.6, 16.1	This work
$AgSn(SO_3F)_6$	Mull	29.8, 22.3 sh, 16, 12.5	This work
$AgSnF_6$	Dif refl	15.3, 13.7, 11.7, 8.05	44

A broad band at approximately 10.4 × 10^3 cm^{-1} for $Cu(SO_3F)_2$ had been attributed to various unresolved d–d bands in an elongated octahedral complex.[38] Shifts to lower energy are expected for ligand field bands where a $4d^n$ ion is replaced by an isovalent $3d^n$ ion in an identical or similar chemical and geometrical environment.

AgF_2, which is reported to have an orthorhombic structure, space group *Pbca*-D_{2h}[15],[46,5] with a square-planar environment for Ag^{2+}, is found to give a similar diffuse reflectance spectrum to the one given by $Ag(SO_3F)_2$. Both F^- and SO_3F^- have been found to produce similar ligand field splittings,[47] and a close structural analogy is found for PdF_2 and $Pd(SO_3F)_2$.[26]

Some similarity is also found for the electronic spectra of $AgPt(SO_3F)_6$, $AgSn(SO_3F)_6$, and $AgSnF_6$.[44] The diffuse reflectance spectra of the ternary fluorosulfates are poorly resolved, but in comparison to the spectrum of $Ag(SO_3F)_2$, the d–d transitions seem to occur at lower wavelengths, with the band center shifted from 22 to ~16 × 10^3 cm^{-1}.

(IV) Magnetic Susceptibility Measurements. The silver(II) compounds studied here display two types of magnetic behavior. $Ag(SO_3F)_2$, its complex with α,α′-bipyridine, and $AgPt(SO_3F)_6$ as well as $AgSn(SO_3F)_6$ are magnetically dilute in the temperature range of 80 to ~350 K. The magnetic susceptibilities, corrected for diamagnetism, follow the Curie–Weiss law with relatively small Weiss constants. The magnetic moments, calculated from the relationship

$$\mu_{eff} = 2.828[\chi_M^{cor}(T - \Theta)]^{1/2}$$

are constant in the temperature range of the measurement. The results for these four compounds are listed in Table V.

On the other hand, both $Ag_3(SO_3F)_4$ and $K_2Ag(SO_3F)_4$ are magnetically concentrated. Antiferromagnetism is observed in the temperature range of 80 to ~330 K with Néel temperatures of 240 and 300 K, respectively. The magnetic moments, μ_{eff}, are temperature dependent and below the

Table V. Magnetic Susceptibilities and Magnetic Moments of $Ag(SO_3F)_2$, $[Ag(bpy)_2](SO_3F)_2$, $AgPt(SO_3F)_6$, and $AgSn(SO_3F)_6$

$Ag(SO_3F)_2$			$Ag(bpy)_2(SO_3F)_2$			$AgPt(SO_3F)_6$			$AgSn(SO_3F)_6$		
T, K	χ_M^{cor}, 10^6 cgsu	μ_{eff},[a] μ_B	T, K	χ_M^{cor}, 10^6 cgsu	μ_{eff},[a] μ_B	T, K	χ_M^{cor}, 10^6 cgsu	μ_{eff},[a] μ_B	T, K	χ_M^{cor}, 10^6 cgsu	μ_{eff},[a] μ_B
301	1631	1.91	305	1393	1.83	301	1994	2.19	301	1539	1.94
276	1792	1.92	280	1507	1.82	275	2168	2.19	275	1676	1.94
249	2013	1.92	255	1665	1.82	249	2381	2.18	250	1827	1.93
224	2248	1.92	232	1850	1.83	225	2633	2.18	225	2026	1.94
200	2566	1.92	203	2122	1.83	200	2980	2.18	203	2256	1.94
175	2959	1.91	187	2317	1.83	176	3347	2.18	175	2573	1.93
149	3540	1.91	154	2796	1.82	151	3895	2.17	153	2939	1.93
128	4217	1.91	129	3319	1.81	128	4570	2.17	152	2943	1.93
105	5440	1.92	109	4087	1.83	107	5633	2.20	128	3441	1.92
80	7574	1.90	80	5606	1.82	80	7602	2.21	109	4187	1.96
									79	5704	1.96

[a] Magnetic moments are calculated by using the Curie-Weiss law: $\mu_{eff} = 2.828[\chi_M^{cor}(T - \Theta)]^{1/2}$. The Weiss constants are listed in Table VII.

Table VI. Magnetic Susceptibilities and Magnetic Moments for $Ag_3(SO_3F)_4$ and $K_2Ag(SO_3F)_4$

$K_2Ag(SO_3F)_4$			$Ag_3(SO_3F)_4$		
T, K	χ_M^{cor}, 10^6 cgsu	μ_{eff}, μ_B	T, K	χ_M^{cor}, 10^6 cgsu	μ_{eff}, μ_B
336	683	1.35			
307	692	1.30	309	1130	1.67
280	689	1.24	284	1151	1.62
256	683	1.18	256	1168	1.55
231	676	1.12	232	1168	1.47
205	660	1.04	206	1160	1.38
181	632	0.96	181	1136	1.28
156	592	0.86	156	1092	1.17
131	534	0.75	131	1022	1.04
108	445	0.62	114	966	0.94
77	471	0.54	80	939	0.77

spin-only value of 1.73 μ_B for one unpaired electron. The results of our measurements for $Ag_3(SO_3F)_4$ and $K_2Ag(SO_3F)_4$ are shown in Table VI and a χ_M^{cor} vs. T plot for $Ag_3(SO_3F)_4$ is seen in Figure 3. The results of our magnetic measurements are summarized in Table VII and compared to relevant literature values.

Antiferromagnetic coupling, as observed for $Ag_3(SO_3F)_4$ and $K_2Ag(SO_3F)_4$, is very common for Cu(II) compounds, in particular for carboxylates,[48] but for silver(II) only one example seems to have been reported, the silver(II) nicotinate.[45] Judging by the magnitude of μ_{eff} in the temperature range of our measurements, the antiferromagnetic exchange interaction appears to be stronger for $K_2Ag(SO_3F)_4$ than for $Ag_3(SO_3F)_4$. Contrasting behavior is displayed by K_2AgF_4 which is reported to follow the Curie–Weiss law.[5,28]

In view of the magnetic behavior of the remaining silver(II) fluorosulfate derivatives, it seems unlikely that intermolecular antiferromagnetism, possibly via the superexchange process,[48] is involved here, since the SO_3F group is rather bulky. Intramolecular antiferromagnetism is certainly more likely. However, in the absence of any structural information of $Ag_3(SO_3F)_4$ and $K_2Ag(SO_3F)_4$, a complete insight into the exchange process is not possible. The magnetic measurements indicate that we are dealing with true compounds rather than mere mixtures of $Ag(SO_3F)_2$ and either $AgSO_3F$ or KSO_3F, because such mixtures should be magnetically dilute.

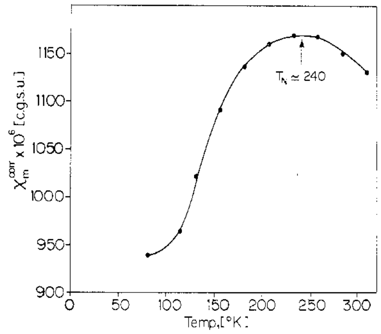

Figure 3. Magnetic susceptibility of $Ag_3(SO_3F)_4$ from 80 to 310 K.

The magnetic behavior of $Ag(SO_3F)_2$ is in strong contrast to the magnetic properties of AgF_2, which has been the subject of several studies.[49-51] Argentic fluoride is magnetically concentrated and shows ferromagnetism below 163 K.[50] The temperature dependence of χ_M^{cor} between 163 and 500 K is rather complicated with μ_{eff} at 298 K 2.0 ± 0.12 μ_B. Silver(II) fluorosulfate has a comparable magnetic moment of 1.91 ± 0.01 μ_B, but χ_M^{cor} follows the Curie–Weiss law between 80 and 300 K with a relatively small Weiss constant of 20 K. As previously noted for $Cu(SO_3F)_2$[38] and $Pd(SO_3F)_2$,[26] the SO_3F

Table VII. Magnetic Properties of Silver(II) Fluorosulfate Derivatives and Some Related Compounds

Compd	Temp range, K	χ_M^{cor},[c] 10^6 cgsu	μ_{eff},[c] μ_B	Weiss const Θ, K	Comment	Ref
$Ag(SO_3F)_2$	80–301	1653	1.92[b]	+20		This work
$Cu(SO_3F)_2$[a]	100–312		2.08		Curie–Weiss behavior	38
$[Ag(bpy)_2](SO_3F)_2$	80–305	1424	1.82[b]	+6		This work
$[Ag(bpy)_2](NO_3)_2$	298	1858	2.12			12
$[Cu(bpy)_2](ClO_4)_2$	80–300		1.96	+5		56
AgF_2	8–500		2.0 ± 0.1		Ferromagnetic <163 K	51
$AgSn(SO_3F)_6$	80–301	1545	1.94[b]	−6		This work
$AgPt(SO_3F)_6$	80–301	1998	2.18[b]	−1		This work
$AgSnF_6$	69–298	1642	1.99	−6	Curie-Weiss behavior	6
$AgTiF_6$	100–296	1654	2.21	−70	Curie-Weiss behavior	6
$Ag_3(SO_3F)_4$	80–309	1139	1.65		Antiferromagnetic, $T_N \approx 240$ K	This work
$K_2Ag(SO_3F)_4$	77–336	692	1.28		Antiferromagnetic, $T_N \approx 300$ K	This work
K_2AgF_4	82–293	1560	1.87		Curie-Weiss behavior	5

[a] The listed μ_{eff} value is corrected for temperature-independent paramagnetism (TIP = 100 × 10^{-6} cgsu). [b] Values for μ_{eff} are obtained by using the Curie-Weiss law. [c] At 298 K.

Table VIII. ESR Data of Various Silver(II) Compounds

Compd	T, K	g_0	$g_\parallel$	$g_\perp$	μ_{eff},[b] μ_B	Ref
$Ag(SO_3F)_2(s)$	295	2.220			1.92	This work
$Ag(SO_3F)_2(s)$	80	2.187			1.89	This work
$Ag(SO_3F)_2$ in $BrSO_3F$	80	2.198	2.407	2.086[c]	1.90	This work
$[Ag(bpy)_2](SO_3F)_2(s)$	295	2.099	2.178	2.058	1.82	This work
$[Ag(bpy)_2](SO_3F)_2(s)$	80	2.091	2.170	2.051	1.81	This work
$[Ag(bpy)_2](SO_3F)_2$ in CH_3CN	80	2.092	2.166	2.054	1.81	This work
$[Ag(bpy)_2](SO_3F_3)_2(s)$	80	2.087	2.164	2.047	1.81	This work
$[Ag(bpy)_2](SO_3CF_3)_2$ in CH_3CN	80	2.092	2.160	2.057	1.81	This work
$[Ag(bpy)_2]S_2O_8(s)$	80	2.077	2.164	2.032	1.80	58
$Ag_3(SO_3F)_4(s)$[a]	80	2.140				This work
$K_2Ag(SO_3F)_4(s)$[a]	80	2.173				This work
$AgPt(SO_3F)_6(s)$	295	2.266	2.494	2.143	1.96	This work
$AgPt(SO_3F)_6(s)$	80	2.258	2.486	2.134	1.96	This work
$AgSn(SO_3F)_6(s)$	295	2.255	2.481	2.134	1.95	This work
$AgSn(SO_3F)_6(s)$	80	2.245	2.480	2.117	1.94	This work
$AgSnF_6(s)$	80	2.315	2.610	2.153	2.00	44
$AgHfF_6(s)$	80	2.275	2.519	2.143	1.97	44

[a] A very broad, poorly resolved single line is observed at room temperature. [b] Calculated from the expression $\mu_{eff} = g_0[S(S+1)]^{1/2}$. [c] Average of g_x and g_y.

groups prevent magnetic exchange far more efficiently than monoatomic halide ligands.[16]

Magnetically dilute systems are also found in the ternary fluorosulfates $AgPt(SO_3F)_6$ and $AgSn(SO_3F)_6$ and, of course, $[Ag(bpy)_2](SO_3F)_2$. Agreement with older work on $[Ag(bpy)_2]X_2$ complexes[52-54] is generally rather poor. No detailed temperature-dependence measurements of χ_M^{cor} are reported in these studies and μ_{eff} values are found between 2.08 and 2.29 μ_B. Room-temperature measurements on $[Ag(bpy)_2](SO_3CF_3)_2$[12] report a χ_M value of 2551 cgsu ($\times 10^6$) which would yield a μ_{eff} value of ~ 2.5 μ_B. Our ESR measurements on $[Ag(bpy)_2](SO_3CF_3)_2$, to be discussed later, give no indication of an unusually high μ_{eff} value for this compound.

On the other hand, the observed temperature dependence, the Weiss constant, and the μ_{eff} value found for $[Ag(bpy)_2](SO_3F)_2$ agree well with the results of magnetic measurements on a series of silver(II) salts of pyridinecarboxylic acids,[45] with the exception of the previously mentioned silver(II) nicotinate. The μ_{eff} values of these complexes range from 1.78–1.82 μ_B and are only slightly higher than the spin-only value of 1.73 μ_B.

Substantially higher μ_{eff} values are found for $AgSn(SO_3F)_6$ and $AgPt(SO_3F)_6$. Even though $BaPt(SO_3F)_6$ is diagmagnetic, small contributions from Pt^{IV} to the paramagnetism of $AgPt(SO_3F)_6$ ($\mu_{eff} = 2.18$ μ_B) cannot be ruled out entirely. The ternary fluorides of the type $AgM^{IV}F_6$, with M = Sn, Pd, and Pb, show room-temperature moments in the range of 1.92–1.99 μ_B,[6] but for $AgTiF_6$ a rather high value of 2.21 μ_B is found.

The observed magnetic properties, Curie–Weiss law behavior, small Weiss constants, and magnetic moments in excess of the spin-only value for $Ag(SO_3F)_2$, $[Ag(bpy)_2](SO_3F)_2$, $AgSn(SO_3F)_6$, and $AgPt(SO_3F)_6$ suggest either a singly or doubly degenerate ground state and the involvement of spin–orbit coupling.

The magnetic moments for square-planar or octahedral (regular or distorted) complexes of Ag(II) are given by the expression

$$\mu_{eff} = \mu_{so}(1 - 2\lambda/10Dq)$$

with μ_{so}, the spin-only magnetic moment, λ, the spin–orbit coupling constant, and $10Dq$, the ligand field splitting.

Unfortunately, $10Dq$ is not accurately known, and only for $Ag(SO_3F)_2$ has a value of 16 600 cm^{-1} been suggested from its electronic spectrum. In this case the calculation of an approximate spin–orbit coupling constant is possible using the above equation. The resulting value of -910 cm^{-1} indicates a substantial reduction of λ below the free-ion value for Ag^{2+} of -1840 cm^{-1}.[47]

A reduction of λ well below the free-ion value is also evident, when structurally similar silver(II) and copper(II) complexes are compared. Since the free-ion λ value for Cu^{2+} is -830 cm^{-1},[47] magnetic moments for silver(II) complexes should be higher than the values for comparable copper(II) compounds, taking into account a difference in $10Dq$ values of about 30–50%. However, both $Cu(SO_3F)_2$[38] and $[Cu(bpy)_2](ClO_4)_2$[56] have μ_{eff} values larger by approximately 0.15 μ_B than the silver(II) compounds $Ag(SO_3F)_2$ and $[Ag(bpy)_2](SO_3F)_2$.

Both electron delocalization and a decrease in $10Dq$, indicated by shifts in d–d bands, seem to cause an increase in μ_{eff} in the series $[Ag(bpy)_2](SO_3F)_2$, $Ag(SO_3F)_2$, and $AgM^{IV}(SO_3F)_6$, with M = Sn or Pt. It is expected that α,α'-bipyridine will interact with Ag^{2+} more strongly than SO_3F^-, which is comparable to F^-[47] in this respect, and produce magnetic moments slightly above the spin-only value. Interesting is the difference displayed by the SO_3F group depending on its coordination to Ag^{2+} only or to both Ag^{2+} and Sn or Pt.

(V) ESR Spectra. Electron spin resonance spectra on polycrystalline powders or frozen solutions are obtained at 80 or 295 K. The **g** tensor values are listed in Table VIII together with relevant literature values. The magnetically concentrated compounds $Ag_3(SO_3F)_4$ and $K_2Ag(SO_3F)_4$ gave very poorly resolved spectra at 80 K.

A broad isotropic spectrum is found for $Ag(SO_3F)_2$. As discussed for similar situations in complexes of Cu(II),[56] a grossly misaligned set of tetragonal axes seems to be a more plausible explanation than regular octahedral or tetrahedral coordination around Ag^{2+}.

For all remaining silver(II) compounds anisotropic spectra were recorded. Agreement with previous work on complexes containing the $[Ag(bpy)_2]^{2+}$ ion[57,58] is good. Both $[Ag(bpy)_2](SO_3F)_2$ and the corresponding trifluoromethyl sulfate give virtually identical g values in the solid state and in frozen solutions in CH_3CN. Hyperfine splitting due to ^{107}Ag and ^{109}Ag isotopes were not observed in any case.

Like the corresponding fluorides, the ternary fluorosulfates $AgPt(SO_3F)_6$ and $AgSn(SO_3F)_6$ give vastly different $g_\parallel$ and $g_\perp$ values. Again good agreement between calculated magnetic moments and the experimental values is found except for $AgPt(SO_3F)_6$ where bulk magnetic susceptibilities indicated a rather high magnetic moment. The discrepancy is consistent with small paramagnetic contributions from the platinum-containing moiety, possibly caused by spin–orbit coupling.

(VI) ^{119}Tin Mössbauer Spectrum of $AgSn(SO_3F)_6$. The ^{119}Sn Mössbauer spectrum of $AgSn(SO_3F)_6$ at 80 K shows a quadrupole splitting of 0.53 mm/s. Previously studied compounds containing the $Sn(SO_3F)_6$ group[30,59] had produced single-line Mössbauer spectra. The observed quadrupole splitting is less than for the polymeric $Sn(SO_3F)_4$[17] where a value of 1.34 mm/s is found.

The isomer shift for $AgSn(SO_3F)_6$ is −0.211 mm/s relative to SnO_2, slightly higher than previously[30,59] reported values between −0.23 and −0.30 mm/s, but the difference is probably not significant in view of the accuracy limit of ±0.03 mm/s.

(D) Conclusions

The work discussed here establishes $Ag(SO_3F)_2$ as a novel binary compound of divalent silver, which is capable of forming a number of derivatives. All these derivatives are true divalent silver compounds as well. In particular, the results of our magnetic measurements and the ESR data speak against alternative formulations as mixed-valency Ag(I)–Ag(III) compounds. This formulation is found for AgO,[1-3] resulting in diamagnetism.

In all magnetically dilute silver(II) fluorosulfate derivatives a square-planar or a tetragonally elongated octahedral environment of the Ag^{2+} ion is most consistent with evidence from vibrational and electronic spectra, the observed magnetic behavior, and the precedents cited in the preceding discussion.

A clear distinction between these two geometries and an elucidation of the structures of $Ag_3(SO_3F)_4$ and $K_2Ag(SO_3F)_4$ will have to await X-ray diffraction studies on these compounds.

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Registry No. Ag, 7440-22-4; Ag_2O, 20667-12-3; Ag_2CO_3, 534-16-7; $AgSO_3F$, 33983-99-2; $AgSO_3CF_3$, 2923-28-6; AgF_2, 7783-95-1; $Ag_3(SO_3F)_4$, 66323-04-4; $S_2O_6F_2$, 13709-32-5; HSO_3F, 7789-21-1; SO_3, 7446-11-9; $BrSO_3F$, 13997-93-8; $Ag(SO_3F)_2$, 63397-31-9; $Ag(bpy)_2(SO_3F)_2$, 63374-87-8; $AgPt(SO_3F)_6$, 66323-05-5; $AgSn(SO_3F)_6$, 66323-06-6; $Ag(bpy)_2(SO_3CF_3)_2$, 34964-02-8; $K_2Ag(SO_3F)_4$, 66323-07-7.

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