THE REACTION OF CsAgF$_4$ WITH SO$_3$ AND THE SYNTHESIS OF CESIUM TRIS(FLUOROSULFATO)ARGENTATE (II)

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Although no simple binary compound of trivalent silver has been reported [1], ternary fluorides of the type $M^IAg^{III}F_4$, with M = K or Cs, have been synthesized and characterised [2].

We became interested in investigating the reaction of CsAgF$_4$ with SO$_3$ for two primary reasons: a) the successful insertion of SO$_3$ into AgF$_2$ at 50°C to yield Ag(SO$_3$F)$_2$ has been reported by us recently [3] and an extension of this method might yield CsAg(SO$_3$F)$_4$. Direct oxidation of metallic silver or silver compounds by bis(fluorosulfuryl)peroxide, $S_2O_6F_2$, even at elevated temperature has yielded only divalent silver fluorosulfate derivatives [3]. b) AgF$_2$ at temperatures of 160 to 220°C is found to be an effective catalyst in fluorination reactions of SO$_3$ to yield, depending on the ratio of reactants and the reaction temperature, $S_2O_6F_2$ [4] or FOSO$_2$F [5]. CsAgF$_4$ should be an even more effective fluorinating agent.

In a typical reaction, approximately 1.8 g or 5.7 mmol of CsAgF$_4$, prepared from a stoichiometric mixture of CsNO$_3$ and AgNO$_3$ at ∿300°C as described by Hoppe [2], are reacted with an excess (about 3.1 gm) of SO$_3$. Sulfur trioxide is distilled from oleum into the reactor, a 150 ml two part monel metal can equipped with a Hoke valve. The reaction mixture is magnetically stirred at 25°C for one day. The gas phase infrared spectrum of the volatile products shows besides traces of SiF$_4$ and SO$_3$, solely bis(fluorosulfuryl) peroxide, $S_2O_6F_2$ [6] as the fluorinated reaction product.

Complete removal of all excess SO$_3$ is accomplished by heating the reactor to 60°C in vacuo. Approximately 3.1 gm or ∿5.7 mmoles of a dark greenish-brown powder of the composition CsAg(SO$_3$F)$_3$ are obtained. The material is extremely moisture sensitive and shows thermal stability up to 130°C.

Elemental analysis, performed by Analytische Laboratorien (formerly A. Bernhardt), Gummersbach, West Germany, establishes the composition as $CsAg(SO_3F)_3$. Calculated: Cs, 24.71; Ag, 20.05; S, 17.88; and F, 10.59. Found: Cs, 24.84; Ag, 19.97; S, 17.68; and F, 10.47.

The overall reaction may be formulated as:

$$2CsAg^{III}F_4 + 8SO_3 \xrightarrow[25°C]{24h} 2CsAg^{II}(SO_3F)_3 + S_2O_6F_2$$
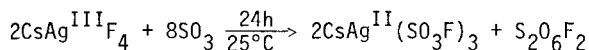
It seems that both SO_3 insertion and fluorination take place even at room temperature. A precedent for such a reaction is reported by Brown and Gard [7]:

$$CrF_5 + 5SO_3 \xrightarrow{\hspace{1.5cm}} Cr(SO_3F)_3 + S_2O_6F_2$$
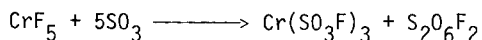
Both reactions together with others, like the photolysis of $ClOSO_2F$ [8] and the thermal decomposition of xenon fluorosulfates [9], [10] may be regarded as alternate routes to bis(fluorosulfuryl)peroxide, methods which do not involve elemental fluorine, a point frequently stressed [7] - [10]. However this is somewhat misleading, since in all cases the synthesis of the starting materials will involve eventually elemental fluorine. Only the anodic oxidation of SO_3F^- in HSO_3F reported by Dudley [11] avoids entirely the use of elemental fluorine in the overall synthesis. But none of the alternate routes to $S_2O_6F_2$ allows the convenient, large scale synthesis of this versatile reagent as does the catalytic fluorination reaction [4] [12].

The reaction of $CsAgF_4$ with SO_3 described here affords clearly a new silver (II) fluorosulfato derivative, $CsAg^{II}(SO_3F)_3$. We had previously [3] reported ternary compounds of the type $M_2^I Ag^{II}(SO_3F)_4$ where M^I = Ag or K. While both examples of this type are magnetically concentrated, $CsAg^{II}(SO_3F)_3$ is magnetically dilute. Curie-Weiss law is followed over the temperature range of 77 to 299 K with a small Weiss constant of $\theta=3.7$ K. The magnetic moments, corrected for Curie-Weiss behavior are 1.92 ± 0.02 BM over the temperature range. A similar magnetic behavior was found for $Ag^{II}(SO_3F)_2$ where the Curie-Weiss law was also followed [3]. The e.s.r. spectrum obtained on solid powder $CsAg^{II}(SO_3F)_3$ shows an isotropic spectrum, most likely due to misaligned tetragonal axes rather than octahedral or tetrahedral symmetry. Spectra recorded at 295 and 80 K give g_o-tensors of 2.182 and 2.184 respectively. The magnetic moment of 1.89 BM, calculated from the expression: $\mu_{eff} = g_o [S(S+1)]^{\frac{1}{2}}$, is in good agreement with the moments obtained from the bulk magnetic susceptibility measurements.

The electronic spectrum of $CsAg(SO_3F)_3$, obtained as mull spectrum and, in the region of 350-740 nm as diffuse reflectance spectrum, shows a very intense UV band at 245 nm, a broad band at 460 nm, a shoulder at 560 nm and a weaker band at 720 nm. Assignment of the three weak bands as due to d-d transitions in either a square planar or tetragonally distorted (elongated) octahedral environment, consistent with the magnetic data and in analogy to an assignment proposed for $Ag(SO_3F)_2$ [3], would suggest a 10 Dq value of 17,900 cm^{-1}. For $Ag(SO_3F)_2$ a 10 Dq value of 16,600 cm^{-1} is reported.

The high reactivity of $CsAg(SO_3F)_3$ allows the recording of infrared spectra only on thin, solid films in the BaF_2 transmission range. The observed bands: 1365 (sharp, s), 1330 (vs), 1200 (vs,b), 1080 (s,sh), 1060 (sh), 1045 (vs) and 810 (m) differ from the ones observed for $Ag(SO_3F)_2$ [3] and $CsSO_3F$ [13], and suggest the presence of bidentate, presumably bridging SO_3F-groups.

In summary the results of magnetic and spectroscopic measurements suggest $CsAg(SO_3F)_3$ to be a true divalent silver (II) compound with Ag^{2+} in either a square planar or a tetragonally elongated octahedral environment. Experimental details on all techniques used here are identical to those described by us previously [3].

REFERENCES
[1] J.A. McMillan, Chem. Rev. 62 (1962) 65.
[2] R. Hoppe, Z. Anorg. Allg. Chem. 292 (1957) 28.
[3] P.C. Leung and F. Aubke, Inorg. Chem. 17 (1978) 1765.
[4] F.B. Dudley and G.H. Cady, J. Amer. Chem. Soc. 79 (1957) 513.
[5] F.B. Dudley, G.H. Cady and D.F. Eggers, ibid. 78 (1956) 290.
[6] A.M. Qureshi, L.E. Levchuk and F. Aubke, Canad. J. Chem. 49 (1971) 2544.
[7] S.D. Brown and G.L. Gard, Inorg. Nucl. Chem. Letters 11, (1975) 19.
[8] C.J. Schack and K.O. Christe, ibid. 14 (1978) 293.
[9] M. Einsenberg and D.D. Des Marteau, Inorg. Chem. 11 (1972) 2641.
[10] M. Wechsberg, P.A. Bulliner, F.O. Sladky, R. Mews and N. Bartlett, Inorg. Chem. 11 (1972) 3063.
[11] F.B. Dudley, J. Chem. Soc. (1963) 3407.
[12] G.H. Cady and J.M. Shreeve, Inorg. Synthesis 7 (1963) 124.
[13] R. Ruoff, J.B. Milne, G. Kaufmann and M. Leroy, Z. Anorg. Allg. Chem. 372 (1970) 119.