CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
PORTLAND STATE COLLEGE, PORTLAND, OREGON 97207

Chromyl Fluorosulfonate, $CrO_2(SO_3F)_2$[1]

BY W. V. ROCHAT AND G. L. GARD

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It has been reported[2] that $CrO_2(SO_3F)_2$, the IUPAC name for which is dioxobis(fluorosulfanato)chromium(VI), prepared by the reaction

$$CrO_2Cl_2 + S_2O_6F_2 \xrightarrow{\text{room temp}} CrO_2(SO_3F)_2 + Cl_2 \qquad (1)$$

is a dark brown, slightly volatile solid which decomposes very slowly at room temperature into a greenish compound. In our work with this reaction, we have obtained results not wholly consistent with the previous report.

It was found that when $S_2O_6F_2$ and CrO_2Cl_2 react at room temperature, a moss green solid is formed. In Table I are the results of five different preparative runs.

TABLE I

SYNTHESIS RUNS FOR GREEN $CrO_2(SO_3F)_2$

Run no.	Moles of CrO_2Cl_2 added $\times 10^3$	Moles of $S_2O_6F_2$ added $\times 10^3$	Moles of $CrO_2(SO_3F)_2$ produced $\times 10^3$	Reactant:product ratio, $CrO_2Cl_2:CrO_2(SO_3F)_2$
1[a]	5.2	7.5	5.2	1.000:0.990
2[b]	32.46	9.23	9.48	...
3	3.95	6.50	3.90	1.000:0.988
4	7.59	8.71	7.57	1.000:0.998
5[c]	7.46	9.92	7.24	1.000:0.970

[a] In run 1, the Cl_2 given off was found to have a molecular weight of 71.8 (calcd, 70.9). The amount of Cl_2 expected in run 1 was 0.3700 g (found, 0.3812 g). A very small amount of $S_2O_6F_2$ transferred. [b] Final composition ratio for this reaction for $S_2O_6F_2:CrO_2(SO_3F)_2$ was 1.000:1.027. The excess CrO_2Cl_2 was very difficult to remove. [c] In several of these synthetic runs some O_2 was produced. In run 5, 3.5 mg of oxygen was produced. However, in run 1, no oxygen was detected.

This is the first report (to our knowledge) of a green chromyl compound. The product is relatively stable and nonvolatile at room temperature, and when it was stored in glass over dry air for approximately 10 months, no change was noticed in color or composition. It reacts violently with water, going from a moss green solid to a brown solid to a bright orange-red solid and finally producing a yellow solution. The solution has an ozone-like odor that disappears upon the addition of a base. It is thought that the reaction with water for complete hydrolysis is

$$CrO_2(SO_3F)_2 + 4H_2O = H_2CrO_4 + 2H_2SO_4 + 2HF \qquad (2)$$

Chemical analysis of the green product based on eq 2 gave the results shown below.

	Calcd	Found
% Cr from iodometric titration	18.4	17.6
% Cr from acidity titration		18.4
% S from $BaSO_4$	22.7	23.4
% S from EDTA		21.0

The infrared spectrum of the neat material measured between sodium chloride plates gave the following absorption bands (values in wave numbers, cm^{-1}; w, weak; m, medium; s, strong; vs, very strong): 1438 (w), 1374 (vs), 1245 (s), 1215 (vs), 1161 (s), 1061 (s), 1020 (vs), 992 (s), 948 (m), 926 (s), 853 (ms), 825 (s). Some attack on the NaCl windows was observed as peaks attributed to $NaSO_3F$ appeared. $CrO_2(SO_3F)_2$ shows characteristic $-S(=O)_2$ stretching frequencies (1061–1374 cm^{-1}) as found in other covalent and ionic fluorosulfonates.[3] The stretching vibration at 992 cm^{-1} (b) is in the region due to Cr=O stretching vibrations as found by Hobbs for CrO_2F_2 and CrO_2Cl_2.[4]

The ^{19}F nmr spectrum at room temperature of a solution of green $CrO_2(SO_3F)_2$ in HSO_3F gave a single peak in the region for fluorine bound to sulfur at a chemical shift of -40.7 ppm from fluorine in CCl_3F (external standard). The ^{19}F resonance for HSO_3F is -40.5 ppm from CCl_3F (external).[5] As only one peak was found (solvent peak) it appears that the fluorosulfonate groups of $CrO_2(SO_3F)_2$ are exchanging with the solvent fluorosulfonate groups. No Cr–F peaks were found.

When the moss green $CrO_2(SO_3F)_2$ is heated to 75°, O_2, a stable, slightly volatile, dark-brown crystalline solid, a light green, nonvolatile solid, and very small quantities of CrO_2F_2 and $S_2O_5F_2$ are produced. The brown solid is stable in dry air and *in vacuo*.

The elemental analysis for this compound gave the following results: Cr (from iodometric titration), 17.6 and 17.9%; Cr (from acidity titration), 17.6%; S (from EDTA), 20.6%. If the brown solid was also $CrO_2(SO_3F)_2$, then the following theoretical values would be expected: Cr, 18.4%; S, 22.7%.

An infrared spectrum was taken of the brown $CrO_2(SO_3F)_2$ and was found to be substantially the same as for the green $CrO_2(SO_3F)_2$. However, the peaks in the infrared spectrum were sharper for the brown $CrO_2(SO_3F)_2$.

The X-ray powder photograph was taken (see *d* values with corresponding intensities in Table II) and was essentially the same as for the moss green $CrO_2(SO_3F)_2$, but the lines were much sharper and more clearly defined.

The brown $CrO_2(SO_3F)_2$ also reacts violently with water; the end product is a strongly oxidative yellow solution. It undergoes essentially the same color changes with water as does green $CrO_2(SO_3F)_2$. The solid is stable at room temperature and has been stored under dry air for over 1 month without any noticeable change.

The solubilities of the green $CrO_2(SO_3F)_2$ and brown $CrO_2(SO_3F)_2$ were qualitatively examined in various solvents. Both the green $CrO_2(SO_3F)_2$ and brown $CrO_2(SO_3F)_2$ were slightly soluble in CCl_4, CF_3CO_2H, and HSO_3F and insoluble in Freon 113. In water, both solids were vigorously decomposed.

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(1) Presented at the 23rd Northwest Regional Meeting of the American Chemical Society, Portland, Ore., June 1968.

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(5) Dr. F. Aubke, private communication.

TABLE II

X-RAY POWDER DATA FOR $CrO_2(SO_3F)_2$

d, Å	Intens	*d*, Å	Intens	*d*, Å	Intens	*d*, Å	Intens
7.73	w	3.22	m	2.29	vw	1.817	vw
7.02	vs	3.16	s	2.26	mw	1.809	w
6.21	w	3.12	m	2.21	w	1.796	w
5.68	w	3.06	vw	2.17	w	1.788	mw
5.16	w	2.98	w	2.14	w	1.780	w
5.01	mw	2.93	m	2.09	vw	1.720	w
4.86	w	2.86	m	2.08	w	1.710	w
4.76	w	2.74	w	2.06	vw	1.694	w
4.66	vs	2.70	w	2.02	vw	1.685	w
4.44	w	2.62	vw	1.984	w	1.672	w
4.38	vs	2.58	mw	1.958	w	1.667	mw
3.92	ms	2.57	mw	1.940	mw	1.652	w
3.86	mw	2.54	w	1.930	w	1.634	w
3.75	vw	2.51	w	1.885	w	1.526	w
3.67	w	2.48	w	1.867	vw	1.513	w
3.49	s	2.42	mw	1.850	w	1.508	vw
3.40	m	2.39	w	1.834	vw	1.444	vw
3.35	m	2.32	w	1.825	w	1.430	w

Therefore, chemical, infrared, and X-ray analyses strongly suggest that the green $CrO_2(SO_3F)_2$ and brown $CrO_2(SO_3F)_2$ are the same compound. The lack of sharpness both in the X-ray powder spectrum and, to a lesser degree, in the infrared spectrum suggests that the green form is amorphous while the brown form is crystalline. Another possibility is that the green form is slightly polymerized through Cr–O–Cr linkages while the brown form is not.

Experimental Section

(1) **Chemicals and Equipment.**—The chromyl chloride, CrO_2Cl_2, used was of technical grade (B & A chemicals). It was shaken with mercury and then pumped on at −78°. The infrared spectrum of the liquid showed no impurities. The peroxydisulfuryl difluoride, $S_2O_6F_2$, was furnished by Dr. Des Marteau (Northeastern University). An infrared spectrum and molecular weight determination showed the material to be of good quality.

The reaction vessel was a round Pyrex-glass bulb of ~125-ml capacity equipped with either a 2-mm EcK & Krebs stopcock or a Fischer and Porter Teflon stopcock and contained a Teflon stirring bar.

The infrared spectra were recorded on a Perkin-Elmer 137 Infracord spectrophotometer. The fluorine spectrum was obtained with a Varian Model HA-100 analytical nmr spectrometer operating at 94.07 Mcps.

X-Ray powder spectra were obtained for samples of brown and green $CrO_2(SO_3F)_2$. These compounds were contained in 0.7-mm Lindemann glass tubes. The tubes were filled in a drybox and flame-sealed outside the drybox. A thick layer of Kel-F grease protected the samples from moisture while they were being sealed. Exposures of 5–6 hr were made using an XRD-5 General Electric camera. Nickel-filtered copper radiation (Cu Kα radiation) was used. Our procedure was standardized using known compounds (CrO_3, Cr_2O_3, and $CrF_3 \cdot 3H_2O$) in which the calculated *d* values agreed with the published ASTM values for these compounds.

(2) **Chemical Analyses. Sulfur Determination.**—The Cr^{6+} was reduced to Cr^{3+}. After reduction, sulfur was determined as $BaSO_4$ by addition of $BaCl_2$ or by back-titration with EDTA.[6]

Chromium Determination.—The standard iodometric method was used.

Acidity Determination.—Phenolphthalein was the indicator using a standard base solution.

(3) **Preparation of Green $CrO_2(SO_3F)_2$.**—The reaction vessel was evacuated and dried. CrO_2Cl_2 was transferred by vacuum distillation and an excess of $S_2O_6F_2$ was added. The vessel was then removed from the liquid nitrogen bath and allowed to warm to room temperature. At room temperature the reaction mixture first bubbled, splattered on the walls of the vessel, slowly turned brownish, and finally turned moss green. The reaction was essentially complete in 1 hr. The volatile materials (only Cl_2 and $S_2O_6F_2$) were removed under reduced pressure and the remaining solid was maintained at reduced pressure until it achieved a constant weight.

(4) **Preparation of Brown $CrO_2(SO_3F)_2$.**—A vessel containing a weighed amount of green $CrO_2(SO_3F)_2$ was attached to a trap which was connected to a vacuum line. The evacuated vessel was placed in an oil bath and the trap in a liquid nitrogen bath. The green $CrO_2(SO_3F)_2$ was then heated, and at 75° brown crystals were seen forming in the neck of the glass vessel while a noncondensable gas was produced. This gas was oxygen (a molecular weight determination gave 35.8 g/mol; calcd, 32 g/mol). The temperature was raised to 200°, and by then, all O_2 generation had stopped. Some products had condensed out in the −195° trap. The infrared spectrum showed these materials to be $S_2O_5F_2$ and CrO_2F_2. The brown crystals were chased from the neck of the glass vessel into a trap. Left behind in the vessel was a light green solid which was analyzed for Cr in the +6 state. In Table III are the results of three different runs.

TABLE III

PREPARATION OF BROWN $CrO_2(SO_3F)_2$

Run	Green $CrO_2(SO_3F)_2$	Brown $CrO_2(SO_3F)_2$	Light green residue[a] in vessel, g	Cr^{6+} in light green residue, %	O_2 given off, g	Δt[b] from 25° to 150°, hr
1[c]	2.0706 g (7.34×10^{-3} mol)	1.0992 g (3.89×10^{-3} mol)	0.8979	5	>0.0106	3
2	2.6736 g (9.48×10^{-3} mol)	0.4222 g (1.50×10^{-3} mol)	2.1653	7	0.0873	0.5
3	1.7316 g (6.14×10^{-3} mol)	1.0938 g (3.88×10^{-3} mol)	0.6176	5	0.0202	3.5

[a] Light green residue gave no powder pattern. [b] For a small Δt (0.5 hr) a large amount of oxygen and green residue is produced and only a moderate amount of brown $CrO_2(SO_3F)_2$. However, for a larger Δt (3–3.5 hr) where the temperature is kept lower for a longer time, O_2 production is down while production of brown $CrO_2(SO_3F)_2$ is up. [c] Experimental difficulties were encountered in this run on accurately determining how much O_2 was produced. It is, however, greater than 0.0106 g.

(5) **Thermal Decompostion of Brown $CrO_2(SO_3F)_2$.**—A sample of the brown $CrO_2(SO_3F)_2$ was placed in a thick Pyrex-glass tube under an atmosphere of dry nitrogen. The tube was flame-sealed while the brown crystals were cooled in liquid nitrogen. The tube was then mounted in an oil bath (half in and half out) and the temperature was quickly raised. At approximately 85°, the formation of red-violet crystals[7] was observed in the cool end of the tube. At 165°, the brown solid turned black and fused

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[6] T. S. West and A. S. Sykes, "Analytical Applications of Diamino-Ethane-Tetra-Acetic Acid," 2nd ed, British Drug Houses, Ltd., London, p 75.

[7] These crystals behave similarly to CrO_2F_2 crystals.

into a solid cake. Raising the temperature to 200° resulted in no further change.

The black solid was moderately hygroscopic; it reacted with water and formed, first, an orange solid, and, finally, a green solution. Gas effervescence was noted during this reaction.

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CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
UNIVERSITY OF SOUTH FLORIDA, TAMPA, FLORIDA 33620

Boron-11 Nuclear Magnetic Resonance Evidence for the Structure of $Al(BH_4)_3 \cdot 6NH_3$

BY P. CALVIN MAYBURY, JEFF C. DAVIS, JR.,
AND RICHARD A. PATZ

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A number of interesting adducts of aluminum borohydride have been reported since the synthesis of this compound in 1940.[1] Extensive studies have been made of the reaction of $Al(BH_4)_3$ with trimethylamine which forms a 1:1 adduct[1–6] and which results in a cleavage of the $Al(BH_4)_3$ structure to form $(CH_3)_3NBH_3$ and various AlH_3 adducts when an excess of trimethylamine is added.[1–3,7] The reaction of $Al(BH_4)_3$ with ammonia to give a 1:1 adduct has been reported[1] as have reactions giving adducts of other stoichiometry.[1,7–11] We wish to report on our investigation of $Al(BH_4)_3 \cdot 6NH_3$, the structure of which appears to be quite different from those of the alkylamine adducts.

Results and Discussion

The ^{11}B nmr spectrum of $Al(BH_4)_3 \cdot 6NH_3$ dissolved in liquid ammonia is shown in Figure 1. This spectrum bears a striking resemblance to that reported for the diammoniate of diborane.[12] The high-field quintet, with a chemical shift of +38.4 ppm relative to $BF_3 \cdot O(C_2H_5)_2$ and $J_{BH} = 80$ cps, is unmistakably the spectrum of the BH_4^- ion. The low-field triplet, evidence for $BH_2(NH_3)_2^+$, has a chemical shift of +14.5 ppm (in the diammoniate of diborane this was reported as +14.6 ppm[12]) and $J_{BH} = 110$ cps. No ^{27}Al–^{11}B coupling is observed in any part of the ^{11}B spectrum.[6] As in the case of the diborane ammoniate, the BH_4^- quintet is easily saturated. Using sufficiently low radiofrequency power to avoid saturation, rapid-passage electronic integration of the peak areas gave the ratio of BH_4^- to $BH_2(NH_3)_2^+$ borons as 2:1. This would suggest that the structure of $Al(BH_4)_3 \cdot 6NH_3$ might be $AlH_2(NH_3)_4{}^+BH_2(NH_3)_2{}^+(BH_4{}^-)_2$ where hexacoordinated Al^{3+} has been assumed. Chemical evidence, *via* the reaction of BH_4^- with NH_4Cl,[13] also supports the presence of two BH_4^- ions per single $Al(BH_4)_3 \cdot 6NH_3$ stoichiometric unit. The ^1H nmr spectrum shows a typical BH_4^- quartet, $J_{BH} = 82$ cps, with no evidence of the ^{27}Al–^1H coupling found in the 1:1 $(CH_3)_3N$ adduct.[6] A peak arising from bound NH_3 molecules is found 3.7 ppm below the solvent ammonia peak. The line width of this peak and that of the solvent are temperature dependent because of solvent–solute exchange. A small pair of peaks appears between the triplet and quintet in the ^{11}B spectrum. The area of these peaks is only about 0.02 that of the BH_4^- quintet. Their position and separation (95 cps) suggest they may be part of a quartet arising from the presence of a small amount of H_3NBH_3. The ^{11}B shifts reported for simple alkylamines lie in the range +9.1–+13.3 (in benzene and neat) and $J_{BH} = 91$–101 cps. The ionic structure of $Al(BH_4)_3 \cdot 6NH_3$, so far unreported for any other aluminum borohydride adduct, is consistent with the similar contrast between the reaction of tertiary amines and other electron donors with boron hydrides and the corresponding reactions of ammonia. In the former case, symmetric cleavage results in the formation of amine–boranes, while ammonia results in asymmetric cleavage to form ions.[14]

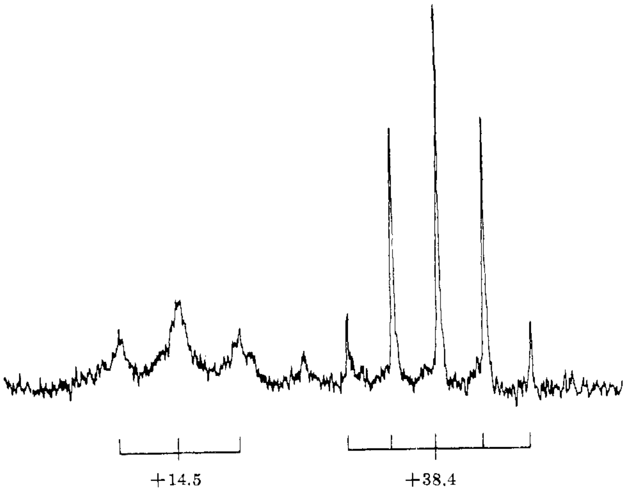

Figure 1.—Boron-11 magnetic resonance spectrum of $Al(BH_4)_3 \cdot 6NH_3$ at 19.1 MHz. Increasing magnetic field is to the right. Shifts are in ppm relative to $BF_3 \cdot O(C_2H_5)_2$.

Further study of the structure of this ammoniate as well as several other related ammoniates is in progress and will be reported shortly.

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