

withdrawing groups enhance the donation of electron density from the chlorine atoms to the zinc atom, so that the σ bonding between the chlorine and zinc atoms becomes stronger. Therefore the results of the present work indicate that the zinc to chlorine π bonding in the complexes $[\text{Zn}(4\text{-Rpy})_2\text{Cl}_2]$ is more sensitive to pressure than the σ bonding in the Zn-Cl bonds.

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Registry No. $[\text{Zn}(\text{py})_2\text{Cl}_2]$, 6843-20-5; $[\text{Zn}(4\text{-CH}_3\text{py})_2\text{Cl}_2]$, 13869-84-6; $[\text{Zn}(4\text{-CNpy})_2\text{Cl}_2]$, 19234-43-6.

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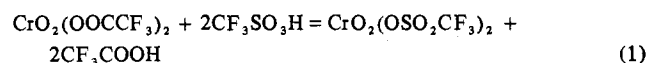
New Chromyl Compounds. II.¹ Reaction of Chromyl Trifluoroacetate with Strong Acids

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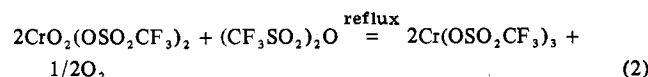
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Two new chromyl compounds, $\text{CrO}_2(\text{OSO}_2\text{CF}_3)_2$ and $\text{CrO}_2\text{NO}_3(\text{OCCF}_3)$, have been prepared and characterized. When chromyl trifluoroacetate reacts with trifluoromethanesulfonic acid, chromyl trifluoromethanesulfonate is formed in $\sim 100\%$ yield according to the equation



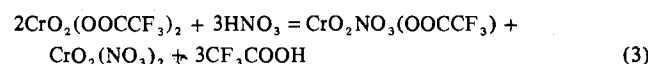
Chromyl trifluoromethanesulfonate is a mustard yellow crystalline solid which is extremely hygroscopic, fumes in the atmosphere, and reacts with a large excess of water to form a yellow chromate solution. The compound is soluble in CCl_4 and $\text{CF}_3\text{SO}_3\text{H}$.

In excess trifluoromethylsulfonyl anhydride, $(\text{CF}_3\text{SO}_2)_2\text{O}$, $\text{CrO}_2(\text{OSO}_2\text{CF}_3)_2$ is reduced



$\text{Cr}(\text{SO}_3\text{CF}_3)_3$ is soluble in water, $\text{CH}_3\text{CH}_2\text{OH}$, CH_3OH , and $(\text{CH}_3\text{CH}_2)_2\text{O}$ and is insoluble in CCl_4 .

With anhydrous nitric acid, chromyl trifluoroacetate yields a new mixed-chromyl compound



Chromyl nitrate trifluoroacetate is an amorphous deep red-brown solid which is easily hydrolyzed. It is the second

example of a mixed-ligand chromyl compound, the first being CrO_2ClF_2 .

Chromyl trifluoroacetate also reacts with fluorosulfuric acid (HSO_3F) according to the equation



Chromyl fluorosulfate has been reported previously.³

The infrared spectra for $\text{CrO}_2(\text{OSO}_2\text{CF}_3)_2$ and $\text{Cr}(\text{OSO}_2\text{CF}_3)_3$ are more complex than one would expect if the SO_3CF_3 group were a monodentate ligand. The observed complexity is presumed to be caused by SO_3CF_3 groups of different functionality. For $\text{CrO}_2(\text{SO}_3\text{CF}_3)_2$ the bands at 1380 and 1220 cm^{-1} are interpreted as sulfur-oxygen stretching modes of a monodentate trifluoromethanesulfonate group primarily on the basis of their similarity to the corresponding bands for this group in $[\text{I}(\text{OSO}_2\text{CF}_3)_4]^-$ and $\text{I}(\text{OSO}_2\text{CF}_3)_3$.⁴

The bands at 1340, 1105, and 975 cm^{-1} for $\text{CrO}_2(\text{OSO}_2\text{CF}_3)_2$ and the bands at 1352, 1100, and 995 cm^{-1} for $\text{Cr}(\text{OSO}_2\text{CF}_3)_3$ are similar in position to those found for the sulfur-oxygen stretching modes for a bidentate SO_3CF_3 group.⁴ The remaining bands for $\text{CrO}_2(\text{OSO}_2\text{CF}_3)_2$, in this region, at 1220, 1155, and 1000 cm^{-1} may be attributed to CF_3 stretching modes. The bands at 937 and 912 cm^{-1} are attributable to the asymmetric and symmetric CrO stretching modes, respectively. In $\text{CrO}_2(\text{OSO}_2\text{CF}_3)_2$ the band at 385 cm^{-1} is assigned to the Cr-O deformation mode. Additional bands in the 400- cm^{-1} region are tentatively assigned to Cr-O deformation modes. The Cr-O deformation mode in CrO_2Cl_2 is located at 357 cm^{-1} and at 304 cm^{-1} in CrO_2F_2 .⁵

The infrared spectrum of $\text{CrO}_2\text{NO}_3(\text{OCCF}_3)$ is more complex due to the overlapping of similar vibration bands for the NO_3 and CF_3COO groups. However, bands arising from both unidentate and bidentate nitrate groups appear to be present. We tentatively assign the bands at 1570 and 1365 cm^{-1} , respectively, to $\nu_{\text{asym}}(\text{NO}_2)$ and $\nu_{\text{sym}}(\text{NO}_2)$ of the unidentate nitrate group and the band at 1660 cm^{-1} to the $\nu(\text{NO})$ of the bidentate group. The band at 670 cm^{-1} in the nitrate-bending region is likely, by comparison with $\text{VO}(\text{NO}_3)_3$, to be associated with the symmetric deformation of the bidentate nitrate group and the band at 765 cm^{-1} is assigned to the symmetric deformation mode of the unidentate group. The bands at 450 and 370 cm^{-1} are probably due to vibrations of the metal-bidentate nitrate linkage. These assignments are also based on previous work with $\text{VO}(\text{NO}_3)_3$ ⁶ and $\text{VO}(\text{N-O}_3)_3 \cdot \text{CH}_3\text{CN}$.⁷ Additional bands attributable to the nitrate group occur at 1150 cm^{-1} ($\nu_{\text{sym}}(\text{NO}_2)$), 795 cm^{-1} ($\rho(\text{NO}_3)$), and 720 cm^{-1} ($\delta(\text{ONO})$).

The tentative assignments for the CF_3COO groups are 1772 cm^{-1} ($\nu_{\text{asym}}(\text{COO})$), 1660 cm^{-1} ($\nu_{\text{asym}}(\text{COO})$), 1470 cm^{-1} ($\nu_{\text{sym}}(\text{COO})$), 1430 cm^{-1} ($\nu_{\text{sym}}(\text{COO})$), 855 cm^{-1} (C-C), 720 cm^{-1} ($\delta(\text{COO})$), 645 cm^{-1} ($\delta(\text{CCO}_2)$), and 325 cm^{-1} ($\rho(\text{C-CF}_3)$). Of particular importance are the CF_3 deformation modes (620 + 530 cm^{-1}) which are located essentially at the same frequencies as found for $\text{Cu}(\text{CF}_3\text{COO})_2$ and $\text{Cu}(\text{py})_2(\text{CF}_3\text{COO})_2$.⁸ Since both of these copper compounds have bidentate attachment of the trifluoroacetate group, it is reasonably safe to assume that the CF_3COO groups in our compound show bidentate behavior as well.

The absorption band at 945 cm^{-1} is assigned to the asymmetric and symmetric stretching frequencies of the CrO_2 group. The presence of bridging nitrate and trifluoroacetate groups would explain the amorphous characteristics of $\text{CrO}_2\text{NO}_3(\text{OCCF}_3)$.

The vibrational frequencies for the green form of $\text{CrO}_2(\text{SO}_3\text{F})_2$ which are due to the fluorosulfate group are located at 1350 cm^{-1} ($\nu(\text{SO})$), 1195 cm^{-1} ($\nu_{\text{asym}}(\text{SO}_2)$), 1050 cm^{-1} ($\nu_{\text{sym}}(\text{SO}_2)$), 810 cm^{-1} ($\nu(\text{SF})$), 618 cm^{-1} ($\rho(\text{SO})$), 575 cm^{-1} ($\delta(\text{SO}_2)$), 550 cm^{-1} ($\rho(\text{SO}_2)$), 450 cm^{-1} ($\rho(\text{SF})$), and 330 cm^{-1} (SO_2F torsion) and agree very closely with frequencies found

for corresponding modes in $(\text{CH}_3)_2\text{Sn}(\text{SO}_3\text{F})_2$ and $\text{IO}_2\text{SO}_3\text{F}$.⁹ On the basis of the similarity between these compounds and $\text{CrO}_2(\text{SO}_3\text{F})_2$ we assign the fluorosulfate vibrations to a bidentate fluorosulfate group. The observed physical properties, e.g., the lack of volatility and the slow and sparing solubility of $\text{CrO}_2(\text{SO}_3\text{F})_2$ in HSO_3F favor a bidentate bridging group over a bidentate chelating arrangement, resulting in a polymeric structure. Similar physical properties were found for $\text{IO}_2\text{SO}_3\text{F}$.⁹ The bands at 955 and 910 cm^{-1} are attributable to the asymmetric and symmetric CrO stretching modes, respectively.

It is interesting to point out the X-ray data for CrO_2F_2 ¹⁰ and the positive and negative ion mass spectra of CrO_2Cl_2 and CrO_2F_2 ¹¹ demonstrate the presence of dimers. Therefore, it is reasonable to suggest, from our infrared data, bridging CF_3SO_3 , NO_3 , CF_3COO , and SO_3F groups by analogy to the bridging groups in the CrO_2F_2 dimer.

The ultraviolet spectra for $\text{CrO}_2(\text{OSO}_2\text{CF}_3)_2$ and $\text{CrO}_2(\text{SO}_3\text{F})_2$ in CCl_4 are similar to those reported for other chromyl compounds.¹ In diethyl ether, the uv spectrum of $\text{Cr}(\text{OSO}_2\text{CF}_3)_3$ corresponded to that reported for $\text{Cr}(\text{Et}_2\text{O})_6^{3+}$.¹² $\text{CrO}_2\text{NO}_3(\text{OOCFF}_3)$ is unstable in CCl_4 .

Experimental Section

1. Chemicals and Equipment. $\text{CrO}_2(\text{OOCFF}_3)_2$ was prepared by the method of Gerlach and Gard.¹ $\text{CF}_3\text{SO}_3\text{H}$ and $(\text{CF}_3\text{SO}_2)_2\text{O}$ were purchased from PCR, Inc., and were vacuum distilled prior to use. HSO_3F was obtained from B & A and was doubly distilled prior to use. Anhydrous nitric acid was prepared according to the method of Brauer.¹³

The infrared spectra were recorded on a Perkin-Elmer 467 infrared spectrophotometer. Infrared spectra of gaseous samples were obtained with a Monel cell (AgCl windows) equipped with a Whitney brass valve. The path length of the cell was 8.25 cm. The spectra of solid samples were obtained neat between KRS-5 windows and were calibrated with polystyrene film. Attempts made to obtain Raman spectra of $\text{CrO}_2(\text{OSO}_2\text{CF}_3)_2$ and $\text{Cr}(\text{OSO}_2\text{CF}_3)_3$ were unsuccessful.

The ultraviolet spectra were recorded using a Cary Model 14 recording ultraviolet spectrophotometer. The samples were dissolved in either spectroquality CCl_4 (Mallinckrodt) or diethyl ether (Mallinckrodt). The path length of the cell was 1.00 cm.

Standard analyses were performed by Beller Laboratories, Göttingen, West Germany.

The X-ray powder spectra were obtained using an XRD-5 General Electric Camera. Nickel-filtered $\text{Cu K}\alpha$ radiation was used. The procedure was standardized using known compounds (CrO_3 , Cr_2O_3 , $\text{CrF}_3 \cdot \text{H}_2\text{O}$) in which the calculated d values agreed with the published ASTM values. Only the very strong (vs), strong (s), and medium (m) intensity lines are reported in this paper.

2. Preparation of $\text{CrO}_2(\text{OSO}_2\text{CF}_3)_2$. To 8.9 mmol of $\text{CrO}_2(\text{OOCFF}_3)_2$ in a 100-ml Pyrex glass vessel, equipped with a Kontes Teflon stopcock and a Teflon-covered stirring bar, 17.85 mmol of $\text{CF}_3\text{SO}_3\text{H}$ was added in a drybox. After 2 days at room temperature in the dark, the materials volatile at room temperature were pumped away through a trap cooled to -195° . The volatile material was identified as CF_3COOH (17.8 mmol) from its infrared spectrum. A mustard yellow solid product [8.9 mmol of $\text{CrO}_2(\text{OSO}_2\text{CF}_3)_2$] was obtained in $\sim 100\%$ yield based on eq 1; mp $90\text{--}92^\circ$ dec. The uv spectrum (CCl_4) showed peaks at 407 nm (s, br) with shoulders at 525 nm (s), 284 nm (s, br), and 228 nm (w). Its infrared spectrum showed the following bands (cm^{-1}): 1380 (s), 1340 (s), 1220 (s, br), 1155 (m), 1105 (s), 1000 (s, sh), 975 (s), 937 (m), 912 (m, br), 770 (m), 630 (m, sh), 610 (s), 570 (m), 530 (m), 510 (m), 450 (mw), 420 (w), 385 (w), 345 (w), 320 (w), 300 (w). The powder spectrum gave the following d values (in Å) with their respective intensities: 10.22 (s), 7.41 (s), 7.08 (s), 5.49 (vs), 5.06 (m), 4.66 (vs), 4.48 (m), 4.34 (m), 4.09 (s), 3.95 (m), 3.72 (vs), 3.51 (m), 3.11 (m), 3.06 (m), 2.82 (s), 2.69 (m), 2.66 (m), 2.56 (m), 2.41 (s), 2.35 (m), 2.23 (m), 1.99 (m), 1.94 (m), 1.90 (s), 1.71 (m), 1.41 (m), 1.25 (m), 1.22 (m), 1.09 (m).

Anal. Calcd for $\text{CrO}_2(\text{OSO}_2\text{CF}_3)_2$: Cr, 13.61; C, 6.28; S, 16.75; F, 29.84. Found: Cr, 13.55; C, 6.35; S, 16.83; F, 29.30.

3. Preparation of $\text{Cr}(\text{OSO}_2\text{CF}_3)_3$. To 1.5 mmol of $\text{CrO}_2(\text{OSO}_2\text{CF}_3)_2$ in a 25-ml round-bottom flask 26.7 mmol of $(\text{CF}_3\text{SO}_2)_2\text{O}$

was added in a drybox. The mixture was refluxed under dry air for 8 days. The resultant material was placed in a Schlenk tube and washed with 50 ml of Spectrograde CCl_4 and then with 20 ml of cold anhydrous ether. A light green solid [1.3 mmol of $\text{Cr}(\text{OSO}_2\text{CF}_3)_3$] was obtained in 89% yield based on eq 2; mp $136\text{--}138^\circ$ with decomposition to a green-black solid at 150° . The uv spectrum (Et_2O) showed peaks at 610 nm (m), 434 nm (m), 250 nm (m, br). Its infrared spectrum showed the following bands (cm^{-1}): 1352 (s, br), 1250 (s, sh), 1205 (s, vbr), 1160 (m, sh), 1100 (s, br), 995 (s, br), 770 (m), 620 (s), 602 (s, sh), 570 (m, sh), 530 (m, sh), 500 (m), 465 (mw), 350 (w). The powder spectrum gave the following d values (in Å) with their respective intensities: 9.60 (m), 8.70 (vs), 4.31 (s), 3.25 (m), 3.05 (m).

Anal. Calcd for $\text{Cr}(\text{OSO}_2\text{CF}_3)_3$: Cr, 10.43; C, 7.22; S, 19.25; F, 34.3. Found: Cr, 10.66; C, 7.18; S, 19.05; F, 33.2.

4. Preparation of $\text{CrO}_2(\text{NO}_3)(\text{OOCFF}_3)$. To 6.77 mmol of $\text{CrO}_2(\text{OOCFF}_3)_2$ in a 100-ml Pyrex glass vessel, equipped with a Kontes Teflon stopcock and a Teflon-covered stirring bar, 11.80 mmol of anhydrous HNO_3 was added in a drybox. After 4 hr at 0° in the dark, the materials volatile at -10° were pumped away through a trap cooled to -195° . The volatile material was determined to be CF_3COOH (10.7 mmol) from its infrared spectrum. The materials volatile at 30° were then pumped away through a trap cooled to -195° . A liquid infrared spectrum showed this material to be $\text{CrO}_2(\text{NO}_3)_2$ (3.68 mmol). Small quantities of HNO_3 were found along with CF_3COOH and $\text{CrO}_2(\text{NO}_3)_2$. A deep red-brown solid [2.74 mmol of $\text{CrO}_2(\text{NO}_3)(\text{OOCFF}_3)$] was obtained in 81% yield based on eq 3; mp $45\text{--}48^\circ$ with decomposition to a green solid at 110° . Its infrared spectrum showed the following bands (cm^{-1}): 1772 (m, sh), 1660 (s, sh), 1570 (s, vbr), 1470 (s), 1430 (s, sh), 1365 (s), 1150 (s, br), 945 (s, br), 855 (m), 795 (s, sh), 765 (s), 720 (m, sh), 670 (s, sh), 645 (s), 620 (s), 530 (s), 450 (s), 370 (s), 325 (w). A powder spectrum showed this material to be amorphous. Anal. Calcd for $\text{CrO}_2(\text{NO}_3)(\text{OOCFF}_3)$: Cr, 20.1; C, 9.27; N, 5.40; F, 22.0. Found: Cr, 19.53; C, 10.5; N, 5.25; F, 21.4.

5. Preparation of $\text{CrO}_2(\text{SO}_3\text{F})_2$. To 2.75 mmol of $\text{CrO}_2(\text{OOCFF}_3)_2$ in a 100-ml Pyrex glass vessel, equipped with a Kontes Teflon stopcock and a Teflon-covered stirring bar, 6.38 mmol of anhydrous HSO_3F was added under N_2 . After 3 hr at 25° in the dark the materials volatile at room temperature were pumped away through a trap cooled to -195° . The volatile material was found to be CF_3COOH (5.41 mmol) from its infrared spectrum. A moss green solid product [2.72 mmol of $\text{CrO}_2(\text{SO}_3\text{F})_2$] was obtained in 99% yield based on eq 4; dec pt 113° . The uv spectrum (CCl_4) showed peaks at 360 nm (s, br), 285 nm (s), 300–550 (w, br). Its infrared spectrum showed the following bands (cm^{-1}): 1420 (w), 1350 (s), 1195 (s, br), 1050 (s, br), 955 (s, br), 910 (s, sh), 810 (s), 618 (m), 575 (m), 550 (s), 450 (m, sh), 330 (m).

Anal. Calcd for $\text{CrO}_2(\text{SO}_3\text{F})_2$: Cr, 18.5; S, 22.7; F, 13.5. Found: Cr, 18.2; S, 21.5; F, 12.7.

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Registry No. $\text{CrO}_2(\text{OSO}_2\text{CF}_3)_2$, 55660-42-9; $\text{Cr}(\text{OSO}_2\text{CF}_3)_3$, 55660-44-1; $\text{CrO}_2(\text{NO}_3)(\text{OOCFF}_3)$, 55660-46-3; $\text{CrO}_2(\text{SO}_3\text{F})_2$, 55660-47-4; $\text{CrO}_2(\text{OOCFF}_3)_2$, 55660-48-5; $\text{CF}_3\text{SO}_3\text{H}$, 1493-13-6; $(\text{CF}_3\text{SO}_2)_2\text{O}$, 358-23-6; HNO_3 , 7697-37-2; HSO_3F , 7789-21-1.

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