repulsion would be greater between I_3^+ cations than I_5^+ cations.

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Registry No. $[I_5^+][AsF_6^-]$, 99618-36-7; AsF_5, 7784-36-3; I_2, 7553-56-2; Cl_5^+, 99618-37-8.

Supplementary Material Available: A stereoview of the unit cell of $[I_5^+][AsF_6^-]$ (Figure I) and tables of anisotropic thermal parameters and calculated and observed structure factors (9 pages). Ordering information is given on any current masthead page.

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Chromium Oxide Trifluoride ($CrOF_3$). Preparation and Crystal Structure

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A new high-yield preparative route to chromium oxide trifluoride, $CrOF_3$, has been accomplished via the reaction of xenon difluoride with chromyl fluoride. The deep purple product was obtained for the first time in crystalline form via this route. Its crystal structure was determined by a single-crystal X-ray study. The crystals are tetragonal, space group $P4_1$ or $P4_3$, and have the following cell parameters: $a = 5.174$ (2) Å, $c = 8.921$ (6) Å, $V = 238.8$ Å^3, $Z = 4$, $\rho = 3.50$ g/cm^3. The crystal structure consists of an infinite three-dimensional array of corner-shared $CrOF_5$ octahedra. The structure is unrelated to other MOX_3 structures and appears to be a new structure type.

Introduction

The first successful preparation of pure $CrOF_3$ has been previously reported.[2] The synthesis route involved the brick red interhalogen compound, with a variable composition of $CrOF_3{\cdot}0.10ClF$ to $CrOF_3{\cdot}0.21ClF$, formed from the reaction of ClF with CrO_3 or CrO_2F_2. When subjected to multiple treatments with fluorine at 120 °C, this product was converted to the bright purple solid $CrOF_3$. Also, $CrOF_3$ can be prepared from CrO_3 and BrF_3, followed by cautious fluorination.[3] More recently, it was found that hydrolysis of CrF_5 in liquid HF produces $CrOF_3$.[4] We have found a new method for not only preparing $CrOF_3$ of the highest purity but also preparing it in a crystalline form. Heating chromyl fluoride (CrO_2F_2) with XeF_2 at temperatures up to 278 °C produces crystalline $CrOF_3$ in high yields:

$$XeF_2 + 2CrO_2F_2 \rightarrow 2CrOF_3 + Xe + O_2 \quad (1)$$

It is possible that chromium oxide tetrafluoride, $CrOF_4$, was formed as an intermediate in eq 1; this behavior was noted for MoO_2F_2 or WO_2F_2 when treated with xenon difluoride in anhydrous fluoride.[5] Decomposition of $CrOF_4$ would give $CrOF_3$ and fluorine. The fluorine would react with xenon to re-form XeF_2 (this cycle would operate until all the fluorine from XeF_2 was consumed).

The $CrOF_3$ produced by this route was essentially the same material as originally reported; close agreement was found for both the infrared spectrum and X-ray powder spectrum. However, it was noted that the $CrOF_3$ produced from XeF_2 was less hygroscopic and could be exposed to moist air for several minutes without change. The $CrOF_3$ produced from XeF_2 resulted in crystals suitable for an X-ray structure determination.

The XeF_2 route is superior to other known routes, particularly in light of possible interhalogen contamination[2,3] with ClF/BrF_3 and with the difficulties associated in the preparation of CrF_5 and the handling of liquid hydrogen fluoride.[4]

Table I. Experimental Data for the X-ray Diffraction Study of $CrOF_3$

temp	25 °C
crystal habit; dimens	prismatic needle; 0.28 × 0.38 × 0.38 mm
crystal system	tetragonal
space group	$P4_1$ or $P4_3$
cell params	$a = 5.174$ (2) Å $c = 8.921$ (6) Å $V = 238.8$ Å $Z = 4$ $\rho = 3.50$ g/cm^3
Data Collection Parameters	
diffractometer	Picker four-circle
radiation	Mo Kα (0.71069 Å)
reflcns collcd	$hkl \geq 0$
2θ range	2°–78.0°
scan type	θ–2θ
scan speeds	2 s/0.05° step
std reflcns	3 every 41 reflcns
no. of reflcns collcd	846
no. of reflections obsd	724 unique, 644 with $F > 2\delta$
abs. coeff	$\mu/\rho = 13.736$
transmission factors	0.63–0.67
$R_w = \sum w\|F_o^2 - F_c^2\|/\sum wF_o^2$	0.056
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.053 ($F > 2\sigma$)

Table II. Positional Parameters for Chromium(V) Oxide Trifluoride

atom	x	y	z
Cr	−0.1096 (1)	−0.4171 (1)	0.00000
F(1)	0.1563 (7)	−0.4272 (7)	0.1201 (4)
F(2)	0.0617 (7)	−0.1960 (6)	−0.1274 (4)
F(3)	−0.4333 (7)	−0.3136 (6)	−0.0934 (4)
O	−0.0745 (9)	−0.6686 (9)	−0.0905 (5)

Experimental Section

Chemicals. Chromyl fluoride (CrO_2F_2) was prepared[6] via the reaction of WF_6 with dry CrO_3 at 125 °C. The CrO_2F_2 was stored over dry KF in a stainless-steel vessel.[2] The other compounds used in this work were obtained from commercial sources: CrO_3 (Mallinckrodt, reagent grade),

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Table III. Interatomic Distances (Å) and Angles (deg) for Chromium(V) Oxide Trifluoride

Cr–O	1.542 (5)	Cr–F(3)[a]	1.914 (3)
Cr–F(1)	1.744 (4)	Cr–F(3)	1.946 (3)
Cr–F(2)	1.840 (3)	Cr–F(2)[b]	2.185 (3)
O–Cr–F(1)	101.7 (2)	F(2)–Cr–F(3)[a]	165.4 (2)
O–Cr–F(2)	98.3 (2)	F(2)–Cr–F(3)	88.8 (2)
O–Cr–F(3)[a]	96.1 (2)	F(2)–Cr–F(2)[b]	83.4 (2)
O–Cr–F(3)	96.3 (2)	F(3)–Cr–F(3)[a]	87.1 (2)
O–Cr–F(2)[b]	174.8 (2)	F(3)–Cr–F(2)[a,b]	82.1 (1)
F(1)–Cr–F(2)	91.0 (2)	F(3)–Cr–F(2)[b]	78.9 (1)
F(1)–Cr–F(3)[a]	88.5 (2)	Cr–F(2)–Cr[c]	147.3 (2)
F(1)–Cr–F(3)	161.8 (2)	Cr–F(3)–Cr[d]	144.3 (2)
F(1)–Cr–F(2)[b]	83.1 (2)		

[a] $y, -1 - x, {}^1/_4 + z$. [b] $y, -x, {}^1/_4 + z$. [c] $-y, x, -{}^1/_4 + z$. [d] $-1 - y, x, -{}^1/_4 + z$.

WF_6 (Ozark-Mahoning), XeF_2 (PCR).

Preparation of $CrOF_3$ from CrO_2F_2. To 4.25 mmol of XeF_2 in a passivated 75-mL stainless-steel vessel equipped with a Whitey valve was added 11.3 mmol of CrO_2F_2. The reaction mixture was heated from 230 to 270 °C (4.4 h). Analysis of the volatile product at −196 °C found oxygen to be present (mol wt calcd 32.0, found 32.9); since only 2.19 mmol of oxygen was produced, the reaction mixture was reheated from 240 to 278 °C for 8.3 h. The total product loss at −196 °C corresponded to 3.75 mmol of O_2. Analysis of the volatile material at −98 °C found 4.05 mmol of xenon to be present (mol wt calcd 131.3, found 130.9). Removal of the volatile material present at room temperature (identified as CrO_2F_2 via its characteristic infrared spectrum) left behind 7.52 mmol of $CrOF_3$ in 88% yield. The reaction vessel was opened under nitrogen in a drybox; small shiny deep purple crystals were formed in the neck of the vessel with the powdered form coating the innner walls. An infrared spectrum and X-ray powder pattern of the $CrOF_3$ agreed closely with that originally reported[2] and more recently found by others.[3,4] Anal. Calcd: Cr, 41.6; F, 45.6. Found: Cr, 42.3; F, 44.6.

X-ray Crystallographic Measurements. Following a brief exposure to air, crystals were immersed in oil for microscopic examination. An appropriate crystal was chosen and subsequently mounted in a Lindemann glass capillary. Intensity data for $CrOF_3$ were collected on an automated Picker four-circle diffractometer using Mo Kα radiation (λ = 0.71069 Å). Most parameters pertaining to data collection, structure solution, and refinement are reported in Table I. A decay of approximately 28% was observed and taken into account. The structure was solved by direct methods and subsequent difference Fourier synthesis. Refinement by minimization of the weighted residual, R_w, with full-matrix least-squares techniques progressed to the reported R values in Table I. The two structural enantiomorphs presented no statistically significant differences in the final molecular parameters, and the one reported ($P4_3$) is that associated with a very slightly lower value of R_w.

All calculations were performed on an Amdahl V-8 computer using programs from a local library[7] (including MITHRIL for direct methods and ORTEP for drawings) and the physicl constants tabulated therein. The final positional parameters are listed in Table II, and interatomic distances and angles can be found in Table III.

Discussion

The crystal structure consists of an infinite three-dimensional array of corner-shared $CrOF_5$ octahedra. The basic coordination geometry for the Cr(V) ion can be described as square pyramidal, with the apical position occupied by the oxygen atom and the four basal positions by fluorine atoms (Figure 1). The Cr atom sits 0.260 (1) Å above the basal plane. The sixth octahedral site is occupied by a fluorine from an adjacent molecule. Two basal fluorines form bridges to adjacent octahedra related by the 4-fold screw axes, forming a helical structure around each axis in the structure (Figure 1). Adjacent helices are also bridged by fluorine atoms, but each of the bridges involves one basal bond and the long Cr–F bond trans to the Cr–O bond. Thus, in the $CrOF_5$ octahedra, one terminal Cr–F bond and four bridging Cr–F bonds exist in addition to the terminal Cr–O bond. These results are consistent with the conclusions drawn previously[3] concerning the nature of the Cr–X bonds, although the structure is different from that proposed in that paper.

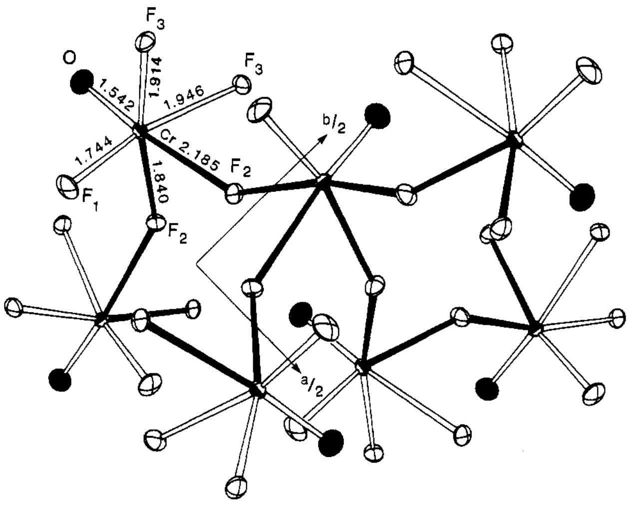

Figure 1. View of the crystal structure of $CrOF_3$ parallel to the c axis.

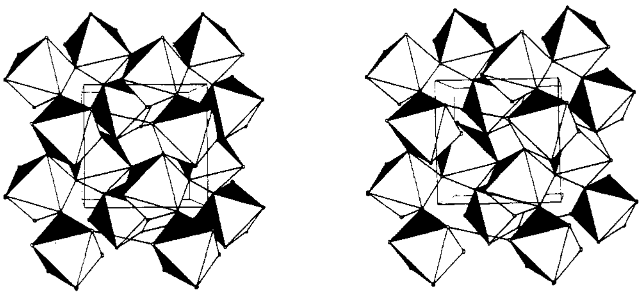

Figure 2. Stereographic view of the stacking of octahedra in $CrOF_3$.

A stacking diagram, based on the corner-sharing octahedra, is shown in Figure 2. This reveals that the structure is closely related to the α-crystallite SiO_2 structure[8] (space group $P4_12_12$) by replacing the silica tetrahedra with octahedra. The presence of the oxygen in the octahedra destroys the 2 and 2_1 axes. The structure is unrelated to other MOX_3 structures[9,10] and appears to be a new structural type.

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Registry No. $CrOF_3$, 43997-25-7; CrO_2F_2, 7788-96-7; XeF_2, 13709-36-9.

Supplementary Material Available: Tables of observed and calculated structure factors and anisotropic thermal parameters (5 pages). Ordering information is given on any current masthead page.

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