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# Easy synthesis of pyridinium fluorochromate, $C_5H_5NH[CrO_3F]$, and its crystal structure

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## Abstract

An easy synthesis of pyridinium fluorochromate (PFC), $C_5H_5NH[CrO_3F]$, was developed by reacting $CrO_3$ with $NH_4HF_2$ in the presence of pyridine. The structure of PFC was determined by X-ray diffraction. The crystals are orthorhombic, space group $Cmc2_1$, with $a = 8.360(3)$ Å, $b = 7.312(4)$ Å, $c = 12.160(5)$ Å, $V = 743.4(6)$ Å$^3$, and $Z = 4$; $R = 0.0347$ for 409 reflections with $I > 2\sigma I$. The structure consists of discrete pyridinium, $C_5H_5NH^+$, cations and fluorochromate, $[CrO_3F]^-$, anions with a crystallographic mirror plane passing through the chromium, one oxygen and a fluorine atom.

*Keywords:* Pyridinium fluorochromate; Synthesis; Crystal structure

## 1. Introduction

One of the main thrusts of research in chromium(VI) chemistry is the synthesis of halochromate(VI) compounds suitable for the effective and selective oxidation of organic substrates, particularly alcohols, under mild conditions. Two such species, i.e. pyridinium chlorochromate (PCC), $C_5H_5NH[CrO_3Cl]$, [1] and pyridinium fluorochromate (PFC), $C_5H_5NH[CrO_3F]$, [2] have emerged as very useful newer reagents for the oxidation of organic substrates. Both the reagents are very effective, with the latter having some specific advantages [2,3]. PFC, synthesized [2,4] from the reaction of $CrO_3$ with 40% hydrofluoric acid and pyridine, was first developed as an efficient oxidizing agent in this laboratory [2] in 1982 and since then it has been used extensively in preparative oxidations as well as in the kinetic and mechanistic studies of oxidation reactions [5,6]. Considering its usefulness it was decided to improvise an easier alternative synthesis of the reagent.

From our experience in the field of fluorometal chemistry [7], we thought that it should be possible to prepare this reagent without using hydrofluoric acid and to ascertain the structure of pyridinium fluorochromate (PFC) by X-ray crystallography. To our knowledge this has not been characterized crystallographically previously.

Reported herein are an easy synthesis of PFC, $C_5H_5NH[CrO_3F]$, and the crystal structure of the compound.

## 2. Experimental details

Reagent grade chemicals were used throughout. IR spectra were recorded on a Perkin-Elmer model 983 spectrophotometer. The electrical conductance of the solution was measured using a Wayne Kerr automatic precision bridge B905 conductometer.

### 2.1. *Synthesis of pyridinium fluorochromate, $C_5H_5NH[CrO_3F]$*

1 g (17.52 mmol) $NH_4HF_2$ was dissolved in 7 cm$^3$ water in a polyethylene beaker followed by the addition of 1 g (10 mmol) $CrO_3$. To the resulting orange solution 2 cm$^3$ (24.40 mmol) pyridine was added with stirring. The reaction solution was then heated on a steam-bath for ca. 15 min. On cooling to room temperature this produced a solid orange product which on recrystallization from acetone afforded crystalline orange–yellow pyridinium fluorochromate (PFC), $C_5H_5NH[CrO_3F]$: yield 0.9 g (45%), MP 106–108 °C (literature [2,4] MP 106–108 °C). Analysis calculated for $C_5H_5NH[Cr_3F]$: C, 30.16; H, 3.04; N, 7.04; F, 9.54; Cr, 26.12%. Found: C, 30.2; H, 3.06; N, 7.1; F, 9.6; Cr, 26.25%.

The chromium content of PFC, $C_5H_5NH[CrO_3F]$, was determined by iodometry; the fluoride content was estimated

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Table 1
Data collection and structure refinement parameters for PFC

| | |
|---|---|
| Molecular formula | $C_5H_6CrFNO_3$ |
| Molecular weight | 199.12 |
| Crystal size (mm) | 0.5 × 0.5 × 0.6 |
| Space group | $Cmc2_1$ |
| $Z$ | 4 |
| $a$ (Å) | 8.360(3) |
| $b$ (Å) | 7.312(4) |
| $c$ (Å) | 12.160(5) |
| $V$ (Å$^3$) | 743.4(6) |
| $d$ calculated (g cm$^{-3}$) | 1.779 |
| Temperature (°C) | 20 |
| Radiation | Mo K$\alpha$ ($\lambda$ = 0.71073 Å) |
| Scan type | $\omega$ |
| 2$\Theta$ range (deg) | 3.0–60.0 |
| Range of $h$ | $0 \leq h \leq 11$ |
| Range of $k$ | $0 \leq k \leq 7$ |
| Range of $l$ | $-16 \leq l \leq 0$ |
| Reflections collected | 507 |
| Observed reflections ($I > 2\sigma I$) | 409 |
| Number of parameters refined | 64 |
| Weighing scheme | $W^{-1} = \sigma^2(F) + 0.0001F^2$ |
| $R$ | 0.0347 |
| $R_w$ | 0.0397 |
| Goodness-of-fit | 2.13 |
| Largest difference peak (e Å$^{-3}$) | 0.34 |
| Largest difference hole (e Å$^{-3}$) | −0.21 |

by first precipitation as PbClF followed by estimation of the chloride content by Volhard's method [8]. Carbon, hydrogen and nitrogen contents were determined by the Microanalytical Laboratory, Central Drug Research Institute (CDRI), Lucknow.

### 2.2. Crystallization of PFC

A quantity of 0.5 g PFC was dissolved in ca. 8 cm$^3$ acetone and filtered. The orange–yellow solution was set aside at ca. 20 °C for 2 days by which time shiny bright orange crystals of PFC, suitable for X-ray crystallography, were formed. The crystals were isolated by filtration and dried in vacuo.

### 2.3. X-ray crystallography

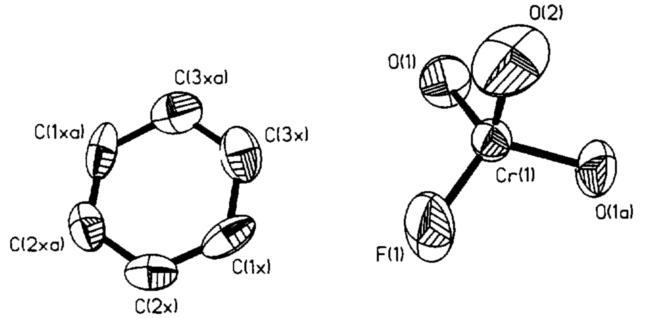

Fig. 1. ORTEP diagram of PFC showing the atom numbering scheme. The 50% probability thermal ellipsoids are shown. The crystallographic mirror plane passes through Cr(1) with O(2) and F(1) lying on it.

Data collection was performed on a Siemens $P_4$ automatic diffractometer using graphite monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å). Significant crystal data, data collection and structure refinement parameters are compiled in Table 1. Calculations for solution of the structure were done with the Siemens SHELXTL PLUS (PC version) programs. Three check reflections were measured after every 97 reflections during the period of data collection to monitor the stability of the crystal. The space group $Cmc2_1$ was identified uniquely from systematic absences observed during the collection of data. The structure was solved by the direct method (all non-hydrogen atoms were refined anisotropically). Hydrogen atoms were affixed at their idealized positions and refined isotropically with fixed thermal parameters.

## 3. Results and discussion

### 3.1. Synthesis

The reaction of $CrO_3$ with ammonium hydrogen fluoride, $NH_4HF_2$, in an aqueous medium followed by precipitation of $[CrO_3F]^-$, formed in solution, by the addition of pyridine has now provided an easy synthesis of PFC. No use of hydrofluoric acid is the main advantage of the new synthesis. The melting point, analysis and spectral features match very well with the reported data [2,4].

### 3.2. Structure of PFC

The structure of the compound (Fig. 1) consists of discrete pyridinium, $C_5H_5NH^+$, cations and fluorochromate, $[CrO_3F]^-$, anions with no significant hydrogen bonding. This results in total disorder of the $C_5H_5NH^+$ cation. Because

Table 2
Refined atomic coordinates (× 10$^4$) and equivalent isotropic displacement coefficients (Å$^2$ × 10$^3$)

| Atom | $x$ | $y$ | $z$ | $U_{eq}$ [a] |
|---|---|---|---|---|
| Cr | 0 | 1450(1) | 859 | 50(1) |
| F(1) | 0 | 57(12) | 1859(9) | 153(1) |
| O(1) | 1601(4) | 2699(5) | 802(10) | 84(1) |
| O(2) | 0 | 423(14) | −313(8) | 128(12) |
| C(1X) | 3413(5) | −29(16) | 3453(9) | 66(1) |
| C(2X) | 4189(12) | −1074(12) | 4143(7) | 59(1) |
| C(3X) | 4198(13) | 9661(13) | 2681(8) | 72(1) |

[a] $U_{eq}$ indicates one-third of the trace of the orthogonalized $U_{ij}$ tensor.

Table 3
Anisotropic displacement coefficients ($Å^2 \times 10^3$)

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| Cr | 45(1) | 50(1) | 56(1) | 0 | 0 | 10(1) |
| F(1) | 77(2) | 153(2) | 230(2) | 0 | 0 | 137(2) |
| O(1) | 63(1) | 82(2) | 106(2) | −28(1) | 1(3) | 27(3) |
| O(2) | 113(3) | 172(3) | 98(3) | 0 | 0 | −87(2) |
| C(1X) | 43(2) | 67(2) | 88(2) | −21(3) | 26(2) | −25(2) |
| C(2X) | 73(2) | 54(2) | 51(2) | −18(2) | 17(2) | −6(2) |
| C(3X) | 84(2) | 53(2) | 78(3) | 8(2) | −23(2) | −6(2) |

Table 4
Bond lengths (Å) and bond angles (deg) for PFC

| | | | |
|---|---|---|---|
| Cr–F(1) | 1.586(10) | Cr–O(1) | 1.622(3) |
| Cr–O(2) | 1.611(10) | Cr–O(1A) | 1.622(3) |
| C(1X)–C(2X) | 1.308(13) | Cr(1X)–C(3X) | 1.357(14) |
| C(2X)–C(2XA) | 1.356(20) | C(3X)–C(3XA) | 1.340(22) |
| F(1)–Cr–O(1) | 113.2(4) | F(1)–Cr–O(2) | 112.3(5) |
| O(1)–Cr–O(2) | 103.0(4) | F(1)–Cr–O(1A) | 113.2(4) |
| O(1)–Cr–O(1A) | 111.2(2) | O(2)–Cr–O(1A) | 103.0(4) |
| C(2X)–C(1X)–C(3X) | 121.1(7) | C(1X)–C(2X)–C(2XA) | 119.8(5) |
| C(1X)–C(3X)–C(3XA) | 119.0(5) | | |

nitrogen is disordered on all six positions, the non-hydrogen atoms of the cation were refined as carbon atoms (labeled as C(X)) with every ring position being 5/6th carbon and 1/6th nitrogen. The hydrogen atoms are in calculated positions and included in the refinement. The chromium atom environment in the $CrO_3F^-$ ion is nearly tetrahedral with the crystallographic mirror plane passing through the chromium atom and perpendicular to the crystallographic *a* axis. The two atoms lying on the mirror plane are an oxygen and a fluorine atom, both being disordered on the two positions. A similar disorder was observed in the case of Rb[$CrO_3F$] [9]. The three metal–oxygen bond distances (Fig. 1, Table 4), Cr–O(1), Cr–O(1A) and Cr–O(2), are 1.622(3), 1.622(3) and 1.611(10) Å respectively. As the fluorochromate unit is quite ordered, the Cr–O(1) and Cr–O(2) distances must be comparable, as observed. The Cr–F distance is 1.586(10) Å. It may be mentioned that the temperature factor for O(2) is lower compared with the lighter F(1). If one switches O(2) for F(1), the thermal parameters become unrealistic. The bond distances compare well with those [9] of $NH_4$[$CrO_3F$] and Rb[$CrO_3F$]. Final atomic coordinates and isotropic displacement coefficients are given in Table 2 while anisotropic displacement coefficients are set out in Table 3. The bond distances and bond angles are summarized in Table 4.

### 3.3. Supplementary materials

The packing diagrams (Figs. $S_1$–$S_3$), tables for fractional atomic coordinates, equivalent thermal parameters and hydrogen atom coordinates (SI–SIII) and tables of observed and calculated structure factors (two pages) are contained in supplementary material.

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