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Short Communication

Structural similarity between tetramethyl ammonium fluorochromate(VI), $N(CH_3)_4CrO_3F$ and tetramethyl ammonium perchlorate, $N(CH_3)_4ClO_4$

WILLIAM A. FREY, VINCENT KUBILUS AND G. MITRA
Department of Chemistry, King's College, Wilkes-Barre, Pennsylvania 18711 (U.S.A.)
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The common salts of the tetrahedral ions such as SO_4^{2-}, PO_3F^{2-} and CrO_4^{2-} are isostructural[1]. Generally, substitution of oxygen by fluorine does not alter the parent structure to any appreciable extent. The structure of a few salts of SO_3F^- and $PO_2F_2^-$ ions have been studied, and they have been found to be isostructural. Fluorosulphonates and difluorophosphates, as expected, are also isostructural with the corresponding perchlorate salts[2].

The alkali metal salts of fluorochromate CrO_3F^- ion have been known for some time, but their crystalline forms were reported to be different from the corresponding perchlorates, though the fluorochromate ion, with C_{3v} symmetry, has approximately tetrahedral bond angles[3]. The structure of $KCrO_3F$ has been studied in detail. This compound has the "X-ray" scheelite, $CaWO_4$, structure because of random orientation of the negative ions[4].

In this laboratory, tetramethyl ammonium fluorochromate $N(CH_3)_4CrO_3F$ and tetraethyl ammonium fluorochromate $N(C_2H_5)_4CrO_3F$ were isolated for the first time and their structures were compared with those of the corresponding perchlorate salts. A typical preparative procedure is described below:

In a 500 ml Nalgene beaker were placed 12.5 g of zinc carbonate, 10.0 g of chromic acid and 40 ml of 6 *M* hydrofluoric acid. The stirred solution was heated to 60–70° for 30 min and allowed to cool. To this was added 10.9 g of tetramethyl ammonium chloride and a yellow precipitate was formed. The precipitate was filtered, washed with cold acetic acid and vacuum dried to give approximately 15.2 g of tetramethyl ammonium fluorochromate. The yield was approximately 75%.

Analysis of these compounds gave the following results*. For tetramethyl ammonium fluorochromate: Found: N, 7.55; C, 24.67; H, 6.24; Cr, 26.90; F, 9.82%. Calculated for $N(CH_3)_4CrO_3F$: N, 7.77; C, 24.86; H, 6.22; Cr, 26.94; F, 9.84%. For tetraethyl ammonium fluorochromate: Found: N, 5.45; C, 38.29;

* Carbon, nitrogen and hydrogen analyses were performed by Galbraith Laboratories Inc., Knoxville, Tenn. (U.S.A.).

H, 7.80; Cr, 20.86; F, 7.59%. Calculated for $N(C_2H_5)_4CrO_3F$: N, 5.52; C, 38.45; H, 7.93; Cr, 20.88; F, 7.63%.

The X-ray powder diffraction data for $N(CH_3)_4CrO_3F$ are given in Table 1.

TABLE 1

X-RAY POWDER DIFFRACTION DATA FOR $N(CH_3)_4CrO_3F$

hkl	*d* (Å)	Estimated intensity
021	3.410	vw
121	3.149	m
300	2.762	w
022	2.428	vw
122	2.342	vw
230	2.304	vw
222	2.095	vs
003	1.998	w
113	1.892	vw
123	1.756	w
050	1.667	w
223	1.652	w
150	1.623	vw
250	1.543	m
440	1.465	m
204	1.410	m
224	1.440	m
450	1.292	m

Unit Cell: Tetragonal: $a = b = 8.30$ Å, $c = 6.01$ Å.

The crystalline form as well as the dimensions of the unit cell are similar to those reported for $N(CH_3)_4ClO_4$[5]. The powder diffraction data of $N(CH_3)_4ClO_4$ as obtained in this laboratory were found to be identical with that of $N(CH_3)_4CrO_3F$. Thus, for the first time, a salt of the CrO_3F^- ion has been shown to be isostructural with the corresponding perchlorate.

The structure of tetraethyl ammonium fluorochromate, however, is different from that of tetraethyl ammonium perchlorate. Structures of these compounds are given in Table 2.

TABLE 2

STRUCTURES OF TETRAETHYL AMMONIUM FLUOROCHROMATE AND TETRAETHYL AMMONIUM PERCHLORATE AT 25°

	K	$N(CH_3)_4$	$N(C_2H_5)_4$
CrO_3F^-	tetragonal	tetragonal	tetragonal
ClO_4^-	orthorhombic	tetragonal	orthorhombic (?)

Sulphates and perchlorates of alkali metals are known to have more than one crystalline form. Potassium perchlorate, for instance, changes to a cubic form at approximately 300°[6]. Further work on the structural aspects of fluorochromates at different temperatures is under way and the results will be reported in future publications.

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