

Powder Diffraction Analysis of a Number of New Salts of 6 Group Elements with Tetramethylammonium Counter Ion

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ABSTRACT

X-ray diffraction pattern showed that in unit cell of fluorotrioxochromate the ions arranged in a hexagonal closest packing with $Z = 4$. The cation and anion moieties are separated from each other and arranged in an alternative AB layering pattern. In the molybdenum and tungsten derivatives the powder diffractions data show the new prepared compounds. The crystalline forms are similar to those reported for NaMoO_3F and CuNbO_3F . NaMoO_3F and CuNbO_3F have been described as infinite zig-zag strings of edge-sharing $M(\text{O}, \text{F})_6$ (where $M = \text{Mo}$ and Nb in NaMoO_3F and CuNbO_3F respectively) octahedral along the c -axis direction.

Keywords: powder diffraction, analysis, salts, tetramethylammonium counter ion.

INTRODUCTION

In recent years there has been a great deal of interest in the transition metal oxyfluoro compounds especially of group VIB elements. These because of the important prerequisites for an oxidant to be useful are its mildness, versatility, selectivity and operational simplicity [1-3]. Considering these, the development of oxidizing agents based upon higher-valent transition metal oxo derivatives has been the objective of many research laboratories and a host of such reagents derived from ruthenium, osmium, iron, manganese, molybdenum, tungsten, vanadium and chromium have all proven to be capable of alcohol oxidation [4-6].

MATERIALS AND METHODS

Acetonitrile (Fluka, P.A.) was distilled several times from phosphorus pentoxide before use, thereby reducing its water content to <4 ppm. Tetramethylammonium fluoride was prepared by previously reported method [7]. CrO_3 , MoO_3 and WO_3 (Merck, P.A.) were used without further purification. Other solvents dried and purified by standard methods. Infrared spectra were recorded as KBr disks on a Shimadzu model 420 spectrophotometer. The UV/Visible measure-

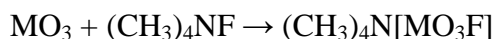
ments were made on a Shimadzu model 2100 spectrometer. Proton, ^{13}C , ^{19}F NMR were carried out on a Bruker AVANCE DRX 500 spectrometer at 500, 125, 470.66 MHz. All the chemical shifts are quoted in ppm using the high-frequency positive convention; ^1H and ^{13}C NMR spectra were referenced to external SiMe_4 and ^{19}F NMR spectra to external CFCl_3 . The percent composition of carbon, hydrogen and nitrogen were obtained from the microanalytical laboratories, Department of Chemistry, OIRC, and Tehran. X-ray diffraction patterns of powdered samples in sealed 0.5-mm quartz capillaries were obtained by using a general Electric Model XRD-6 diffractometer, Ni-filtered Cu K_α radiation, and a 114.6 mm diameter Philips camera.

Synthesis of tetramethylammonium fluoro compound (VI), $(\text{CH}_3)_4\text{N}[\text{MO}_3\text{F}]$

Metal trioxide, MO_3 was suspended in 20 ml of dry acetonitrile in a glove box under the argon atmosphere. To this mixture stoichiometric amount of powdered tetramethylammonium fluoride was added with stirring, maintaining the ratio of $(\text{CH}_3)_4\text{NF}:\text{MO}_3$ as 1:1. The reaction was fast, but for the sake of ensuring completion of reaction stirring was continued for 24 hours, and the white product was filtered, washed two times by dry isopropyl alcohol and diethyl ether then dried under vacuum. The tetramethylammonium trioxofluoro compound (VI), obtained is a highly pure, white compound. The compound is stable in air, but react by water and it better stored in sealed polythene bags.

RESULTS AND DISCUSSION

$(\text{CH}_3)_4\text{N}[\text{MO}_3\text{F}]$ were prepared by the reaction of $(\text{CH}_3)_4\text{NF}$ and MO_3 in a 1:1 ratio in acetonitrile solvent as follows:



Chemically, the free fluoride anion in $(\text{CH}_3)_4\text{NF}$ acts, as a very strong Lewis base and readily complexes with suitable Lewis acids, such as BF_3 , PF_5 , SbF_5 ,..., forming the corresponding complex fluoro anions. In the absence of good fluoride acceptor molecules, it can abstract even relatively firmly bound protons from compounds such as CH_3CN . The $(\text{CH}_3)_4\text{N}^+$ cation is coordinatively saturated and due to the relatively high strength of the carbon-nitrogen bond, possesses high activation energy toward chemical reactions [7]. In the above reaction $(\text{CH}_3)_4\text{NF}$ was used for fluoride addition to CrO_3 Lewis acid.

Our work provided tetramethylammonium fluorochromate (TMAFC) that is a useful new oxidant for organic chemists. The chemistry of TMAFC has been explored as an oxidizing agent [8]. This compound shows oxidative properties like as other halochromates [9, 10]. Tetramethylammonium fluoromolybdate (VI), $(\text{CH}_3)_4\text{N}[\text{MoO}_3\text{F}]$, showed oxidative properties in the presence of acids such as acetic acid. Tetramethylammonium fluorotungstate (VI), $(\text{CH}_3)_4\text{N}[\text{WO}_3\text{F}]$, did not show any oxidative properties with and without of acids. This reactivity could be explained by the point to the size of these group elements.

Crystal growing from tetramethylammonium salts are difficult. These compounds commonly give very fine crystals (micro crystals) that are not suitable for X-ray single crystal diffraction. With many efforts the compound $(\text{CH}_3)_4\text{N}[\text{CrO}_3\text{F}]$ crystallizes in the non-centrosymmetric tetragonal space group $\text{P-42}_1\text{m}$. The tetramethylammonium cations are located in two different symmetry environments. This is indeed a rather complex crystal from the point of view of symmetry. Single crystal X-ray diffractions showed that in the unit cell of this compound the ions were arranged in a hexagonal closest packing with $Z = 4$. The cation and anion moieties are separated from each other and arranged in an alternative AB layering pattern. It seems that each Cr atom is surrounded by two F and five O atoms. But obviously, with the Cr atom sitting on a crys-

tallographic mirror plane, what we have is a disordered situation in which Cr is actually four-coordinated, with the Cr and one O atom situated on the mirror plane and two oxygens and one fluorine off the plane, which result in the appearance of a seven-coordinate species [11]. Tetramethylammonium fluoromolybdate (VI), $(\text{CH}_3)_4\text{N}[\text{MoO}_3\text{F}]$ and Tetramethylammonium fluorotungstate (VI), $(\text{CH}_3)_4\text{N}[\text{WO}_3\text{F}]$, give very fine crystals that are not suitable for X-ray single crystal diffraction. These compounds studied with powder X-ray diffraction technique. Table 1 shows the indexed X-ray diffraction pattern of $(\text{CH}_3)_4\text{N}[\text{WO}_3\text{F}]$. These data show the new prepared compound.

Table 1. X-ray diffraction data for the $(\text{CH}_3)_4\text{N}[\text{WO}_3\text{F}]$

Angle [2θ]	d-value a_1 [Å]	d-value a_2 [Å]	T.width [2θ]	Height [counts]	Backgr. [counts]	Rel.int. [%]	Signific
10.590	8.34709	8.36762	0.060	8	0	5.6	0.83
13.350	6.62696	6.64326	0.100	37	1	26.7	0.97
13.525	6.54160	6.55769	0.100	90	1	64.8	3.22
14.480	6.11224	6.12728	0.120	15	2	10.9	1.44
14.725	6.01109	6.02588	0.100	11	3	7.8	1.02
15.540	5.69762	5.71164	0.120	27	3	19.4	2.84
15.930	5.55900	5.57267	0.160	12	4	8.3	0.84
16.740	5.29179	5.30481	0.160	55	4	39.3	4.78
18.115	4.89311	4.90514	0.320	7	6	4.9	1.72
18.730	4.73380	4.74545	0.140	25	7	18.0	1.48
20.115	4.41088	4.42173	0.200	42	8	30.3	1.33
20.460	4.33727	4.34794	0.240	38	8	27.6	1.99
21.020	4.22297	4.23336	0.160	66	9	47.1	1.61
21.740	4.08471	4.09476	0.120	90	10	64.8	1.26
21.905	4.05431	4.06429	0.060	139	10	100.0	1.64
22.105	4.01808	4.02797	0.100	137	10	98.3	1.65
22.595	3.93204	3.94171	0.160	34	11	24.2	0.90
23.105	3.84639	3.85585	0.160	29	12	20.9	1.37
23.750	3.74337	3.75258	0.080	88	12	63.5	0.91
24.365	3.65026	3.65924	0.160	31	13	22.5	1.17
25.305	3.51675	3.52540	0.280	114	14	82.2	6.33
25.890	3.43860	3.44706	0.060	132	14	95.0	0.81
26.610	3.34717	3.35541	0.200	21	15	15.2	1.30
27.055	3.29312	3.30122	0.120	14	16	9.8	1.14
28.350	3.14557	3.15330	0.200	18	18	13.3	0.98
29.115	3.06463	3.07217	0.160	88	18	63.5	1.06
30.045	2.97186	2.97917	0.060	108	19	77.7	0.77
30.410	2.93701	2.94424	0.160	114	20	82.2	1.71
30.905	2.89109	2.89820	0.120	64	20	46.0	0.94
31.610	2.82820	2.83516	0.160	69	21	49.5	1.07
32.010	2.79376	2.80064	0.200	59	22	42.6	1.65
32.810	2.72745	2.73416	0.320	36	22	25.9	2.21
33.835	2.64713	2.65364	0.240	72	24	51.9	3.76
34.955	2.56483	2.57114	0.160	56	25	40.4	1.45
35.280	2.54195	2.54820	0.120	44	25	31.3	1.25
36.230	2.47744	2.48354	0.200	56	26	40.4	1.07
38.260	2.35053	2.35632	0.200	50	29	36.2	1.42
41.080	2.19545	2.20086	0.160	61	34	43.7	0.87
42.685	2.11654	2.12175	0.320	21	36	15.2	0.88
44.610	2.02958	2.03457	0.160	31	38	22.5	0.98
46.660	1.94507	1.94986	0.120	37	42	26.7	0.80
46.875	1.93665	1.94142	0.060	74	42	53.1	0.89
47.230	1.92292	1.92765	0.160	62	44	44.8	0.94
47.700	1.90506	1.90975	0.120	44	44	31.3	1.04
49.500	1.83992	1.84445	0.480	21	46	15.2	2.09
50.260	1.81386	1.81833	0.200	56	48	40.4	1.33
51.655	1.76811	1.77246	0.200	28	50	20.2	0.90
52.250	1.74937	1.75367	0.960	15	50	10.9	5.29
53.200	1.72034	1.72458	0.240	21	52	15.2	1.70
54.595	1.67964	1.68377	0.640	5	55	3.8	1.10
56.805	1.61943	1.62341	0.320	45	59	32.2	0.95
57.525	1.60086	1.60479	0.100	41	59	29.4	1.19
60.935	1.51918	1.52292	0.280	50	62	36.2	1.27

The crystalline form is similar to those reported for NaMoO_3F and CuNbO_3F . NaMoO_3F and CuNbO_3F have been described as infinite zig-zag strings of edge-sharing $\text{M}(\text{O}, \text{F})_6$ (where $\text{M} = \text{Mo}$ and Nb in NaMoO_3F and CuNbO_3F respectively) octahedral along the c -axis direction, with cation atoms (Na in NaMoO_3F and Cu in CuNbO_3F) inserted between the strings [12, 13].

CONCLUSION

By examination of the powder X-ray diffraction pattern of tetramethylammonium ion salts it is possible to predict the lattice, the approximate size of the anion, the closeness of approach of the cation to each other, the presence or absence of cation to anion hydrogen bonding and whether or not the cation is distorted from tetrahedral.

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