

A direct, simple and one-step synthesis of tetramethylammonium trioxyfluoromolybdate (VI)[†]

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Reaction between tetramethylammonium fluoride (CH₃)₄NF and MoO₃ in 1:1 molar ratio in the minimum amount of dry acetonitrile gives tetramethylammonium trioxyfluoromolybdate (VI), (CH₃)₄N[MoO₃F] in very high yields. The compound has been characterized by elemental analyses and IR spectral studies. The advantages of the new method are discussed.

In the course of our investigation on the fluoro compounds of transition metals^{1–4} and in continuation of our studies on the use of tetramethylammonium fluoride, (CH₃)₄NF, as a fluorinating agent^{5–7} and because the trioxyfluoromolybdate compounds with different counter ions are used as fluorescence, luminescence and electrical materials, we were prompted to synthesize (CH₃)₄N[MoO₃F] by a new method.

Trioxyfluoromolybdates (VI) have been known for many years and many methods have been used to synthesize them,^{8–17} but trioxyfluoromolybdate (VI) with the counter ion tetramethylammonium has not been synthesized so far. We used a direct and novel method for this synthesis.

Reagent grade MoO₃ was used and anhydrous tetramethylammonium fluoride (CH₃)₄NF was prepared by the method reported by Christie in 1990.¹⁸

In a typical preparation, molybdenum trioxide, MoO₃, was dissolved in a minimum amount of dry acetonitrile in a glove box under an argon atmosphere. To this pale yellow solution, a stoichiometric amount of powdered tetramethylammonium fluoride was added with stirring, maintaining the ratio of (CH₃)₄NF:MoO₃ as 1:1. The reaction was very fast, but for the sake of ensuring completion of reaction stirring was continued for 1 hour, and the white product was separated with the addition of dry dichloromethane followed by filtration.

The tetramethylammonium trioxyfluoromolybdate- (VI) obtained is a highly pure, white compound (Table 1); yield, 99%. The compound is stable in moist air but it better stored in sealed polythene bags.

The IR spectra of the newly synthesized (CH₃)₄N[MoO₃F] recorded on a Shimadzu instrument model 420 has been compared with the corresponding reported data^{18–20} (Table 2).

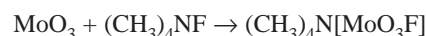
Table 1 Characterization data of tetramethylammonium trioxyfluoromolybdate (VI)

	Found (%)				
	(Calc)				
	C	H	N	Mo	F
(CH ₃) ₄ NMoO ₃ F	20.4 (20.25)	5.12 (5.06)	6.01 (5.90)	40.2 (40.50)	8.36 (8.01)

The method used for the synthesis does not involve direct use of HF or reaction of MHF₂ (M= NH₄, K, Rb or Cs) with MoO₃ and is based on the concept of strong action of tetramethylammonium fluoride (CH₃)₄NF and its power to fluorinate many compounds. Previously fluoro molybdates were synthesised by reaction of molybdic acid with NH₄HF₂, or reaction of MF

(M=Na, Cs) with MoO₃ at very hard conditions, but our new method is very simple and is based on the concept of the reaction of the naked fluoride ion of tetramethylammonium fluoride that is produced by the dissociation of tetramethyl ammonium fluoride in acetonitrile.

The reaction can be written as:



The advantages of the new method are as follows: (i) there is no side product, (ii) the reaction is quite fast and (iii) the accompanied colour change can be used to ascertain the completion of the reaction, (iv) the reaction done in very mild conditions.

Tetramethylammonium trioxyfluoromolybdate (VI) is soluble in acetonitrile, acetone, methanol and dimethyl sulphoxide (DMSO) but not soluble in dichloromethane, ethyl acetate, and pyridine. It is easily hydrolysed in water.

Table 2 IR Absorptions of compounds

Compound	IR signals
(CH ₃) ₄ N[MoO ₃ F]	915 (vs), ν _s Mo-O 698 (s), ν Mo-F 949 (vs) ν _{as} Mo-O of anion 1495(s), ν ₁₅ N-C 2980(m), ν _{CH₃} C-H, 444(m), ν ₁₉ N-C of (CH ₃) ₄ N counter ion
MoO ₃	—
(CH ₃) ₄ NF	1490(s), ν ₁₅ N-C 2980(m), ν _{CH₃} C-H 468(m), ν ₁₉ N-C

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