SHORT PAPER

J. Chem. Research (S),
2000, 486–487

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

A. R. Mahjoub*, S. Ghammami, A. R. Abbasi and A. Hossainian

Department of Chemistry, Faculty of Science, Tarbiat Modarres University. Tehran, Iran, PO Box 14155–4838

Reaction between tetramethylammonium fluoride $(CH_3)_4NF$ and MoO_3 in 1:1 molar ratio in the minimum amount of dry acetonitrile gives tetramethylammonium trioxyfluoromolybdate (VI), $(CH_3)_4N[MoO_3F]$ 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, $(CH_3)_4NF$, 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 $(CH_3)_4[NMoO_3F]$ 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 MoO_3 was used and anhydrous tetramethylammonium fluoride $(CH_3)_4NF$ was prepared by the method reported by Christe in 1990.[18]

In a typical preparation, molybdenum trioxide, MoO_3, 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 $(CH_3)_4NF$:MoO_3 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 $(CH_3)_4N[MoO_3F]$ 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
$(CH_3)_4NMoO_3F$	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 MHF_2(M= NH_4, K, Rb or Cs) with MoO_3 and is based on the concept of strong action of tetramethylammonium fluoride $(CH_3)_4NF$ and its power to fluorinate many compounds. Previously fluoro molybdates were synthesised by reaction of molybdic acid with NH_4HF_2, or reaction of MF (M=Na, Cs) with MoO_3 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:

$$MoO_3 + (CH_3)_4NF \rightarrow (CH_3)_4N[MoO_3F]$$

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 trioxyflouromolybdate (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 Absoprtions of compounds

Compound	IR signals
$(CH_3)_4N[MoO_3F]$	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 $(CH_3)_4N$ counter ion
MoO_3	—
$(CH_3)_4NF$	1490(s), ν_{15} N-C 2980(m), ν_{CH3}C-H 468(m), ν_{19}N-C

The authors wish to express their sincere thanks to the TMU Tehran, for financial help and Dr N. Safari of Sh.Beh. University, Tehran for his assistance.

Received 23 April 2000; accepted 16 October 2000
Paper 00/280

Reference

1 S. Ghammami, *Synthesis and characterization of some complexes with coordination number greater than six*, M.Sc thesis, Tarbiat Modarres University, 1995.
2 A.R. Farrokhi, *Reaction of tetramethyl ammonium fluoride with some complexes of molybdenum*, M.Sc Thesis, Tarbiat Modarres University, 1998.
3 B. Sadeghi, *Reaction of tetramethylammonium fluoride with some complexes of rhenium*, M.Sc Thesis, Tarbiat Modarres University, 1998.

* To receive any correspondence. Mahjouba@net1cs.modares.ac.ir
† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

4 A.R. Abbasi, *Reaction of tetramethylammonium fluoride with some tungsten complexes*, M.Sc Thesis, Tarbiat Modarres University, 2000.
5 A.R. Mahjoub, S. Ghammami, A.R. Abbasi and A. Hosseinian, *Ind. J. Chem.* 2000, **39A**, 434–435.
6 A.R. Mahjoub and K. Seppelt, *J. Chem. Soc. Chem. Commun.*, (1991) 840.
7 A.R. Majoub D. Leopold and K Seppelt, *Z. anorg. allgem. chem*, (1992) **618**, 83.
8 J.P. Chaminade, M. Cerver-Marzal and M. Pouchard *J. Cryst. Growth.* 1984, **66**, 477–479
9 I.V. Sidorova, A. V. Gusarov and L.N. Gorokhov *Int. J. Mass Spectr. Ion Phys.* 1979, **31**, 367–372
10 J.P. Doumerc, M. Elaatmani, J. Ravex, M. Pouchard and P. Hagenmuller, *Solid State Commun.* 1979, **32**, 111.
11 G. Peraudeau, J. Ravez, P. Hagenmuller and J. Arend, *Solid State Commun*. 1978, **27**, 591.
12 O. Schmitz-Dumont and I. Heckmann, *Z. Anorg. Allgem. Chem.* 1952, **267**, 277.
13 M. Cervera-Marzal, J.P. Chaminade, J. Ravez, M. Pouchard and P. Hagenmuller, *J. Cryst. Growth* 1983, **64**, 516.
14 M. Lundberg and O. Savborg, *Chem. Scripta* 1978–79, **13**, 197.
15 C.L. Rollinson, *The chemistry of chromium, molybdenum and tungsten*, Pergamon Press, Oxford, 1975, pp. 695.
16 F.A. Cotton and G. Wilkinson, *Advanced inorganic chemistry*, John Wiley, New York, 1972, pp. 850.
17 J.E. Ferguson, *Halide chemistry of chromium, molybdenum and tungsten: Halogen chemistry*, Vol.3 edited by V. Gutman, Academic Press, New York, 1967, pp. 248.
18 K.O. Christe, W.W. Wilkinson and R.D. Bau; *J. Am Chem Soc*, 1990, 112, 7619.
19 K. Nakamoto, *Infrared and Raman spectra of inorganic and coordination compounds*, 3rd ed., John Wiley, New York, 1978.
20 R. Colton and J.H. Conterford, *Halides of the transition elements: Halides of the first row transition metals* Wiley-Interscience, New York, 1969, pp. 190.