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## Synthesis of Pentachlorofluororhenate (V) with Tetramethylammonium Counter Ion, by New a Method

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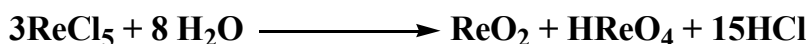
### Abstract

A new, simple and one-step method used for synthesis of new compound tetramethylammonium pentachlorofluororhenate- (V) in very high yield. This compound one of the mixed halo complexes of rhenium that have been prepared by the reaction between tetramethylammonium fluoride and ReCl<sub>5</sub> in 1:1 molar ratio in the minimum amount of dry acetonitrile. The compound has been characterized by elemental analyses and IR spectral studies.

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### Introduction

The status of the halides of rhenium has changed considerably in the last few years. Largely through the recognition of the existence of metallic clusters in the trihalides and in certain of the tetrahalides also nevertheless a number of problems, remain including the properties of the highest chloride ReCl<sub>6</sub> and so on. Rhenium pentachloride is very reactive. It is hydrolyzed immediately by water, and disproportionation to Re (IV) and Re (VII) occurs.<sup>1-3</sup>



This compound when heated with potassium chloride, Potassium hexachlororhenate-(IV) is formed,<sup>4</sup> and with oxygen it can give oxide chlorides, with phosphorus trichloride a complex of composition RePCl<sub>8</sub> is formed which has a magnetic moment of 2.37BM. This has been formulated as ReCl<sub>5</sub>.PCl<sub>3</sub>.<sup>4,5</sup>

Many efforts have been done for synthesizing mixed halo complexes of rhenium and studying their behavior but most of them gave miscellious and unknown mixed halo compounds that this condition was unwanted. As an example reaction of fluorine gas as a fluorinating agent on rhenium pentachloride at 300°C in a flow system yield the chloropenta fluoro of rhenium and other chloride fluorides are also formed but have not been identified.<sup>6</sup>

By use of our experiences on the studies of application of tetramethylammonium fluoride (CH<sub>3</sub>)<sub>4</sub>NF as a fluorinating and fluoro adding agent and after use it for fluoro addition of many main group compounds such as:

IF<sub>7</sub>,<sup>7</sup> IOF<sub>5</sub>,<sup>8</sup> TeF<sub>4</sub> and SeF<sub>4</sub>,<sup>9</sup> TeF<sub>6</sub><sup>10</sup>...

And some transition metals compounds<sup>11-13</sup> such as CrO<sub>3</sub>,<sup>14</sup> MoO<sub>3</sub>.<sup>15</sup> We were prompted to synthesize (CH<sub>3</sub>)<sub>4</sub>N[ReCl<sub>5</sub>F] with a new method. This method does not change the oxidation state and give monofluoro halo complex of rhenium simply.

Reagent grade ReCl<sub>5</sub> was used and anhydrous tetramethylammonium fluoride (CH<sub>3</sub>)<sub>4</sub>NF was prepared by the method reported by Christie in 1990.<sup>16</sup>

## Experimental

Typical procedure for the preparation like as last papers as: Rhenium pentachloride, ReCl<sub>5</sub> was dissolved in a minimum amount of dry acetonitrile in a glove box under the argon atmosphere. To this deep brown - black solution, stoichiometric amount of powdered tetramethylammonium fluoride was added with stirring, maintaining the ratio of (CH<sub>3</sub>)<sub>4</sub>NF:ReCl<sub>5</sub> 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 brown product was separated by evaporating some of solvent and filtration.

The tetramethylammonium pentachlorofluororhenat-(V) obtained is highly pure, brown compound (Table 1); yield, 95%. The compound is stable in moist air but it better stored in sealed polythene bags.(Table 1)

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Characterization data of  
Tetramethylammonium  
Pentachlorofluororhenate-(V)

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C    H    N

Found (%)	10.33	2.78	3.11
Calc(%)	10.51	2.63	3.07

The IR spectra of the newly synthesized  $(\text{CH}_3)_4\text{N}[\text{ReCl}_5\text{F}]$  recorded on a Shimadzu instrument model 420 has been compared with the corresponding reported data<sup>6,16-21</sup> (Table 2).

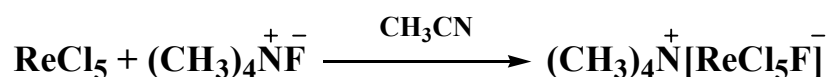
Compound	IR Signals
$(\text{CH}_3)_4\text{N}^+ [\text{ReCl}_5\text{F}]^-$	694(m), $\nu_1$ Re-F 394 (w), $\nu_2$ Re-Cl 300 (s), $\nu_3$ Re -Cl of anion 1495(s), $\nu_{15}$ N-C, 2980(m), $\nu_{\text{CH}_3\text{C-H}}$ , 444(m), $\nu_{19}$ N-C of $(\text{CH}_3)_4\text{N}$ counter ion
$\text{ReCl}_5$	467 (w), $\nu_5$ Re-Cl 300 (s), $\nu_1$ Re -Cl
$(\text{CH}_3)_4\text{N}^+\text{F}^-$	1490(s), $\nu_{15}$ N-C, 2980(m), $\nu_{\text{CH}_3\text{C-H}}$ , 468(m), $\nu_{19}$ N-C

**Table 2: IR Absorption's of Compounds**

### Results and discussions

In conclusion, we have developed a new and efficient method for the fluoride addition to rhenium complexes using TMAF that is an inexpensive, commercially available and non-toxic reagent. More over this reagent may find application in inorganic synthesis for another transition elements compounds. The method used for the synthesis does not involve direct use of  $\text{F}_2$  gas, HF or reaction of  $\text{MHF}_2$  ( $\text{M} = \text{NH}_4, \text{K}, \text{Rb}$  or  $\text{Cs}$ ) with  $\text{ReCl}_5$  and is based on the concept of strong action of tetramethylammonium fluoride  $(\text{CH}_3)_4\text{N}^+\text{F}^-$  and its power to fluorinate many compounds. Some of the pervious fluoro rhenate reported synthetic methods were contain the reaction of rhenium halides with  $\text{F}_2$ , or reaction of  $\text{MF}$  ( $\text{M} = \text{Na}, \text{Cs}$ ) with  $\text{ReCl}_5$  at very hard conditions but this 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 tetramethylammonium fluoride in acetonitrile.

The reaction can be written as:



This is a novel and efficient method for fluoride addition to various kinds of rhenium complexes by using TMAF was explored and 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 color change can be used to ascertain the completion of the reaction, (IV) The reaction done in very mild condition and the reaction conditions are not required to be strictly controlled and fluoride addition can be conducted at room temperature.

Tetramethylammonium pentachlorofluororhenate-(VI) is soluble in methanol, dimethyl sulphoxide (DMSO) and not soluble in carbon tetrachloride, dichloromethane, ethyl acetate; pyridine .It is easily hydrolyzed in water.

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