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Synthesis and Characterization of Two New Fluorocomplexes, [(C4H9)4N][VCl3F] and [(C4H9)4N][ScCl3F]

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Abstract:
The reaction between tetrabutylammonium fluoride and $ScCl_3$ and VCl_3 produced two new ionic fluorocomplexes with tetrabutylammonium cation. One of them is tetrabutylammonium fluorotrichloroscandate (Ⅲ), $(C_4H_9)_4N[ScCl_3F]$, TBAFS, that is easily synthesized in a nearly quantitative yield using a direct reaction of $ScCl_3$ and tetrabutylammonium fluoride. Another is tetrabutylammonium flurotrichlorovanadate (Ⅲ), $[(C_4H_9)_4N][VCl_3F]$, TBAFV, that has been synthesized by reaction of tetrabutylammonium fluoride with VCl_3 salt. These compounds were characterized by IR, UV/Visible, 19^F-NMR, 13^C-NMR and 1^H-NMR techniques. The electronic and vibrational spectra of TBAFS and TBAFV have been measured and studied.

Keywords: Synthesis, Characterization, Tetrabutylammonium flurotrichlorovanadate (III), Tetrabutylammonium fluorotrichloroscandate (III).

Introduction

Nobel gas compounds have always been of great interest to both theoretically and experimentally oriented chemists [1], particularly the fluorides have been subject of an intense scientific discussion since the first synthesis of such a compound [2,3]. This is because of the important prerequisites for a fluorinating agents to be useful are its mildness, versatility, selectivity and operational simplicity. The subject of this investigation is prepared inorganic fluorides and complexes[4]. Another reason that encouraged researchers for synthesizing this rang of fluorinated compounds is the fewer and rare amounts of the spectroscopic data of this compounds especially 19^F-NMR data. Some of the reported data [5-8] about tungsten complexes collected and shown in Table 1. For the above reasons and in the course of our investigations on fluorocompounds of transition metals [9-13] and in continuation of our studies on the use of tetrabutylammonium fluoride $(C_4H_9)_4NF$ as a fluorinating agent [14] and after the synthesis of the $(C_4H_9)_4N[ScCl_3F]$, $(C_4H_9)_4N[VCl_3F]$, we were prompted to react $ScCl_3$ and VCl_3 with $(C_4H_9)_4NF$. We had prepared and reported synthesis of a number of $[ScCl_3F]$- and $[VCl_3F]$- anions with tetraalkylammonium counter ion previously [15,16]. We have managed to prepare two new fluorocompounds of vanadium and

scandium that are the analog of the above transition metal compounds. Fluorotrichloroscandate (Ⅲ) and flurotrichlorovanadate (Ⅲ) have not been synthesized and reported so far. In this paper a direct, simple and one-step method has been used to synthesize these compounds. There were two primary incentives for selection of $(C_4H_9)_4N^+$ as the counter ion. Firstly, quaternary ions such as tetrabutylammonium are often used as phase transfer catalysts. Secondly, quaternary ions such as tetrabutylammonium are used as crystal growing agents.

Results and discussion

We had reported the synthesis of a number of halometales, with the belief that those reagents could be used for the fluorination of organic substrates. It has been shown that halometales were useful as new fluorination agents for organic chemists [9,10]. Those compounds showed fluorination properties like as other previous reported halometales [11-13 We now report the synthesis of the TBAFV that is analog of the above mentioned vanadium compounds. The advantages of the new method are:
a) there is no side product,
b) the reaction is quite fast,
c) mild conditions and
d) the accompanied color change that providing visual means for ascertaining the progress of the reaction.

Tetrabutylammonium flurotrichlorovanadate (III) $(C_4H_9)_4N][VCl_3F]$ (TBAFV)

$(C_4H_9)_4N[VCl_3F]$ was prepared by the reaction of $(C_4H_9)_4NF$ and VCl_3 in a 1:1 ratio in MeCN solvent as follows:

$$(C_4H_9)_4NF + VCl_3 \longrightarrow (C_4H_9)_4N[VCl_3F]$$

In the vibrational spectrum of this compound the known bands of cation and anion were seen such as $\nu_{V\text{-}F}$ (A1) that was found at 994.53 cm^{-1} that confirmed with literature data (Table 1). There are two absorptions in the compound electronic spectrum. Electronic spectrum of TBAFV shows two shifts for acetonitrile at 212 nm (ε= 281 $mol.^{-1}lit.cm^{-1}$) that belongs to $^1E\rightarrow{}^1A$ ($e\rightarrow a_1$) transition and for vanadium at 342 (ε= 549 $mol.^{-1}lit.cm^{-1}$) that belongs to $^1E\rightarrow{}^1E$ (e→e) (Table 3). These transitions are expected as in mono substituted vanadate ions, because of the position of vanadium in the first series of transition metal elements and making of strong crystalline field complexes.

The expected signals were found in the ^{1}H-NMR and ^{13}C-NMR.

Tetrabutylammonium fluorotrichloroscandate (III), [$(C_4H_9)_4N$][ScCl3F]

$(C_4H_9)_4N[ScCl_3F]$ was prepared by the reaction of $(C_4H_9)_4NBr$ and $ScCl_3$ in a 1:1,1 ratio in MeCN solvent as follows:

$$(C_4H_9)_4NF + ScCl_3 \longrightarrow (C_4H_9)_4N[ScCl_3F]$$

In the vibrational spectrum of TBAFS the cationic and anionic bands were seen such as $\nu_{Sc\text{-}F}$ that was found at 884.29 cm^{-1} that along the literature data (Table 2). There are three absorption bands in this compound electronic spectrum (Table 4). The expected signals were found in the^{19}F-NMR, ^{1}H-NMR and ^{13}C-NMR.

Experimental

Material and instruments

Acetonitrile (Fluka, P.A.) was distilled several times from phosphorus pentaoxide before use, thereby reducing its water content to <4 ppm. Tetrabutylammonium fluoride was bought from Merck. $ScCl_3$ and VCl_3 (Merck, p.a.) were used without further purification. Solvents were purified by standard methods. Infrared spectra were recorded as KBr disks on a Shimadzu model 420 spectrophotometer. The UV/Visible measurements were made on an Uvicon model 922 spectrometer. ^{1}H and ^{13}C-NMR were recorded on a Bruker AVANCE DRX 500 spectrometer at 500 and 125 MHz, respectively. All the chemical shifts are quoted in ppm using the high-frequency positive convention; ^{1}H and ^{13}C-NMR spectra were referenced to external $SiMe_4$. Vanadium and scandium were estimated iodometrically. The percent compositions of elements were obtained from the Microanalytical Laboratories, Department of Chemistry, OIRC, Tehran.

Synthesis of Tetrabutylammonium fluorotrichloroscandate (III),[$(C_4H_9)_4N$][$ScCl_3F$]

Tetrabutylammonium fluorotrichloroscandate (Ⅲ), $[(C_4H_9)_4N][ScCl_3F]$ was prepared by dissolving $ScCl_3$ (0.162 g, 1.07 mmol) in MeCN and addition of this solution to a solution of tetrabutylammonium fluoride (0.338 g, 1.07 mmol) in MeCN under stirring at room temperature until a white precipitate was formed. After 2 hours stirring, the mixture was filtered, washed with ether and dried at room temperature. The tetrabutylammonium salts are some what hygroscopic, and it better stored under a layer of hexane, whereas all of the salts aren't photosensitive and moisture-sensitive, both in solution and solids. $C_{16}H_{36}Cl_3FNSc$:
Cacl. %C, 46.55; %H, 8.72.
Found: %C, 48.40; %H, 8.91.
UV/Visible, IR, ^{1}H-NMR and ^{13}C-NMR were all consistent with the TBAFS structure. Mp: 130°C.

Synthesis of Tetrabutylammonium fluorotrichlorovanadate (III),[$(C_4H_9)_4N$][VCl_3F]

Tetrabutylammonium flurotrichlorovanadate (Ⅲ), $[(C_4H_9)_4N][VCl_3F]$ was prepared as follow: To a solution of a vanadium trichloride VCl_3 (0.166 g, 1.05 mmol) in MeCN the solid powder tetrabutylammonium fluoride (0.33 g, 1.05 mmol) was added under stirring at room temperature until a green solid precipitate was formed. After 2 hours stirring, the mixture was filtered, washed by ether, and dried at room temperature. $C_{16}H_{36}Cl_3FNV$:
Cacl. %C, 45.88; %H, 8.6.
Found: %C, 47.62; %H, 9.01.
UV/Visible, IR, 1H-NMR and 13C-NMR were all consistent with the TBAFV structure.

Conclusion

Two tetrabutylammonium fluoride salts of $ScCl_3$ and VCl_3 were synthesized simply. $(C_4H_9)_4N[VCl_3F]$ was prepared by the reaction of $(C_4H_9)_4NF$ and VCl_3 in a 1:1 ratio in MeCN solvent and $(C_4H_9)_4N[ScCl_3F]$ was prepared by the reaction of $(C_4H_9)_4NF$ and $ScCl_3$ in a 1:1,1 ratio in MeCN solvent. Electronic and vibrational spectra of these two new Fluorocomplexes studied. These compounds were characterized by IR, UV/Visible, and ^{13}C-NMR and ^{1}H-NMR techniques. Production of these compounds shows the ability of tetrabutylammonium fluoride in fluoride addition to transition metal and main group elements compounds.

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Table 1. *The frequencies (cm^{-1}) and assignment of cation and anion of TBAFV*

ν (cm^{-1})	Assignment	Intensity	ν (cm^{-1})	Assignment	Intensity
$(C_4H_9)_4N^+$			1476	ν_{16}	(s)
3425	$\nu_{CH3} + \nu_{19}$	(w, br.)	1383	ν_{16}	(m)
3315	$\nu_{CH3} + \nu_8$	(w, br.)	1921	ν_{rock}	(w)
3105	$\nu_{CH3,}$ asym.str	(sh.)	940	ν_{18}	(vs)
3010	$\nu_{13,}\nu_{CH3,}$asym.str	(w, br.)	475	ν_{19}	(ms)
2960	$\nu_{14,}\nu_{CH3,}$asym.str	(w, br.)	438	ν_{19}	(ms)
2785	$\nu_{14,}\nu_{CH3,}$asym.str	(w, br.)	VCl_3F^-		
2625	$\nu_7 + \nu_{16}$	(w)	994	ν V-F (E)	(s)
2568	$\nu_3 + \nu_8 + \nu_{16}$	(w)	537	ν V-Cl (A)	(m)
			434	ν V-Cl (B)	(w)

Table 2. *The frequencies (cm-1) and assignment of cation and anion of TBAFS*

ν (cm^{-1})	Assignment	Intensity	ν (cm^{-1})	Assignment	Intensity
$(C_4H_9)_4N^+$			1476	ν_{16}	(s)
3425	$\nu_{CH3} + \nu_{19}$	(w, br.)	1383	ν_{16}	(m)
3315	$\nu_{CH3} + \nu_8$	(w, br.)	1921	ν_{rock}	(w)
3105	$\nu_{CH3,}$ asym.str	(sh.)	940	ν_{18}	(vs)
3010	$\nu_{13,}\nu_{CH3,}$asym.str	(w, br.)	475	ν_{19}	(ms)
2960	$\nu_{14,}\nu_{CH3,}$asym.str	(w, br.)	438	ν_{19}	(ms)
2785	$\nu_{14,}\nu_{CH3,}$asym.str	(w, br.)	$ScCl_3F^-$		
2625	$\nu_7 + \nu_{16}$	(w)	884	ν Sc-F (E)	(s)
2568	$\nu_3 + \nu_8 + \nu_{16}$	(w)	569	ν Sc-Cl (A)	(m)

Table 3. *Transitions specifications of TBAFV*

λ (nm) (ε, $M^{-1}cm^{-1}$)	λ (nm) (ε, $M^{-1}cm^{-1}$)
212 (281)	342 (549)

Table 4. *Transitions specifications of TBAFS*

λ (nm) (ε, $M^{-1}cm^{-1}$)	λ (nm) (ε, $M^{-1}cm^{-1}$)	λ (nm) (ε, $M^{-1}cm^{-1}$)
214 (347)	308 (144)	358 (131)