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AROYLOXYMETHYL)TETRAFLUORO- AND PENTAFLUOROSILICATES. THE POSSIBILITY OF THE EXISTENCE OF HEPTACOORDINATE SILICON COMPOUNDS

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SUMMARY

Some representatives of a new class of fluorosilicon organic compounds containing a silicon atom with a high coordination number, potassium and ammonium (aroyloxymethyl)tetrafluoro- and pentafluorosilicates with a general formula $M_{n-3}[ArCOOH_2SiF_n]$, where $M = K^+$, NH_4^+; n = 4,5 have been prepared for the first time. IR and UV spectroscopic data show that these compounds may have a $C{=}O \rightarrow Si$ intramolecular coordination. It is suggested that the silicon atom in $M_2[ArCOOCH_2SiF_5]$ is heptacoordinate.

INTRODUCTION

Organylpentafluorosilicates of alkali metals and ammonium which contain a hexacoordinate silicon atom have been already described [1,2]. Similar compounds such as $M_2[R_{6-n}SiF_n]$ with n = 2-5 [3] and tetraalkylammonium organotetrafluorosilicates with a pentacoordinate silicon atom $M[RSiF_4]$ have been studied. Recently some new compounds of pentacoordinate silicon, (aroyloxymethyl)trifluorosilanes(I) containing an intramolecular coordinate bond $C{=}O \rightarrow Si$ have been synthesized [4-6].

The purpose of this research was to transform (aroyloxymethyl)trifluorosilanes(I) into silicon derivatives such as $M[ArCOOCH_2SiF_4]$(II) and $M_2[ArCOOCH_2SiF_5]$(III,IV) with high coordination. We hoped that the preservation of the intramolecular coordinate bond in compounds of the type $M_2[ArCOOCH_2SiF_5]$ would enable us to obtain hitherto unknown compounds of heptacoordinate silicon*. Organotin compounds containing a heptacoordinate tin atom (sterically more available than the silicon atom) have been described in the literature [8]. The yields and the data of analyses of the compounds studied are given in Table 1.

RESULTS AND DISCUSSION

Synthesis of (aroyloxymethyl)tetrafluoro- and pentafluorosilicates

(Aroyloxymethyl)pentafluorosilicates of potassium(III) and ammonium(IV) containing $4\text{-}CH_3C_6H_4$ groups as aryl residues were synthesized by the reaction of (aroyloxymethyl) trifluorosilane(I) with KF and NH_4HF_2, respectively :

$$ArCOOCH_2SiF_3 + 2MF\ (MHF_2) \longrightarrow M_2[ArCOOCH_2SiF_5]$$

$$M = K^+ (III),\ NH_4^+ (IV);\ Ar = 4\text{-}CH_3C_6H_4$$

We were not able to prepare ammonium (aroyloxymethyl)tetrafluorosilicates(II, $M = NH_4^+$) using this reaction. In excess of compound I ammonium (aroyloxymethyl)pentafluorosilicates(IV) are formed only. The corresponding potassium tetrafluorosilicate(III) was obtained in a minor amount under similar conditions.

Nevertheless, we have managed to prepare potassium (aroyloxymethyl)-tetrafluorosilicate(II, $M = K^+$) from products of alkaline hydrolysis according to a general scheme :

$$\underset{I}{3ArCOOCH_2SiF_3} + 3MOH \longrightarrow \underset{V}{ArCOOCH_2Si(OH)_3} + \underset{II}{M[ArCOOCH_2SiF_4]} +$$

$$+ \underset{III}{M_2[ArCOOCH_2SiF_5]}$$

$$Ar = 4\text{-}CH_3C_6H_4;\ M = K^+.$$

Intermediate (aroyloxymethyl)silantriols(V) transform into (aroyloxymethyl)silsesquioxane $(ArCOOCH_2SiO_{1.5})_m$(VI) during isolation.

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* X-ray diffraction data have shown that silicon in $(NH_4)_3SiF_7$ is six-coordinate [7].

TABLE 1

$M_{n-3}\left[4\text{-}CH_3C_6H_4COOCH_2SiF_n\right]$ (4-methylbenzoyloxymethyl)tetrafluoro- and pentafluorosilicates

Compound	M	n	Found (%)				Empirical formula	Calculated (%)				Yield,%
			C	H	Si	F		C	H	Si	F	
II	K^+	4	37.00	3.25	10.10	24.89	$C_9H_9O_2SiF_4K$	36.99	3.11	9.59	26.03	16
III	K^+	5	31.59	2.67	6.98	26.46	$C_9H_9O_2SiF_5K_2$	30.86	2.57	8.00	27.10	42
IV*	NH_4^+	5	35.08	5.41	8.87	29.46	$C_9H_{17}N_2O_2SiF_5$	35.06	5.52	9.09	30.84	12

* Nitrogen content: found 9.03%, calculated 9.09%

Potassium and ammonium (aroyloxymethyl)tetrafluorosilicates and pentafluorosilicates are colourless non-melting powdery substances. They are scarcely soluble in the majority of organic solvents, almost insoluble in water, but readily soluble in dimethylsulphoxide.

Infrared spectra

The spectral characteristics of the compounds studied with general formula $M_{n-3}[4\text{-}CH_3C_6H_4COOCH_2SiF_n]$ ($M = K^+$, NH_4^+; $n = 3\text{-}5$) are represented in Table 2. The aromatic ring vibrations in the spectra of these compounds are similar to and coincident with those for the compounds such as $4\text{-}CH_3\text{-}C_6H_4COOCH_2R$ with R = $SiO_{1.5}$(VI), $Si(OC_2H_5)_3$(VII) and CH_3(VIII), and do not depend on M or n. The OCH_2Si group is characterized by a strong band in the 750 cm^{-1} region and a weak maximum near 1250 cm^{-1}.

The carbonyl group frequencies in the spectrum of compound I containing the $C{=}O\rightarrow Si$ intramolecular coordinate bond (n = 3) are shifted as compared with those of $4\text{-}CH_3C_6H_4COOCH_2R$ compounds (VI-VIII). For the latter, ν(CO) is observed at 1720 cm^{-1} and ν_{as}(COC) in the 1270-1310 cm^{-1} region. The ν(C=O) position does not depend on the nature of the substituent R whereas the ν_{as}(COC) is shifted to high frequency region for compounds VI and VII possibly due to geminal interaction in the OCH_2Si system [9]. The SiF stretch is known to be in the 800-1000 cm^{-1} region in the spectra of organic fluorosilanes containing an sp^3 hybridized silicon atom. An SiF absorption in the 400-800 cm^{-1} region is observed in organic derivatives of pentacoordinate and hexacoordinate silicon [3, 10].

Si-F vibrations in the spectra of (aroyloxymethyl)trifluorosilanes are also observed in the 800-1000 cm^{-1} range and there is also a strong peak in the 780 cm^{-1} region (Fig. 1). The above data on SiF vibrations and the absence of the band at 780 cm^{-1} in the spectrum of (γ-benzoyloxypropyl)trifluorosilane, $C_6H_5COO(CH_2)_3SiF_3$ which shows no $C{=}O\rightarrow Si$ interaction [6], support the assumption that the 780 cm^{-1} band arises from SiF stretching vibrations, since the effective positive charge at the silicon atom is increased in (aroyloxymethyl)trifluorosilanes*. Thus in (aroyloxy-

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* The absorption at 780 cm^{-1} is absent in the spectra of compounds VII and VIII which contain no SiF bonds.

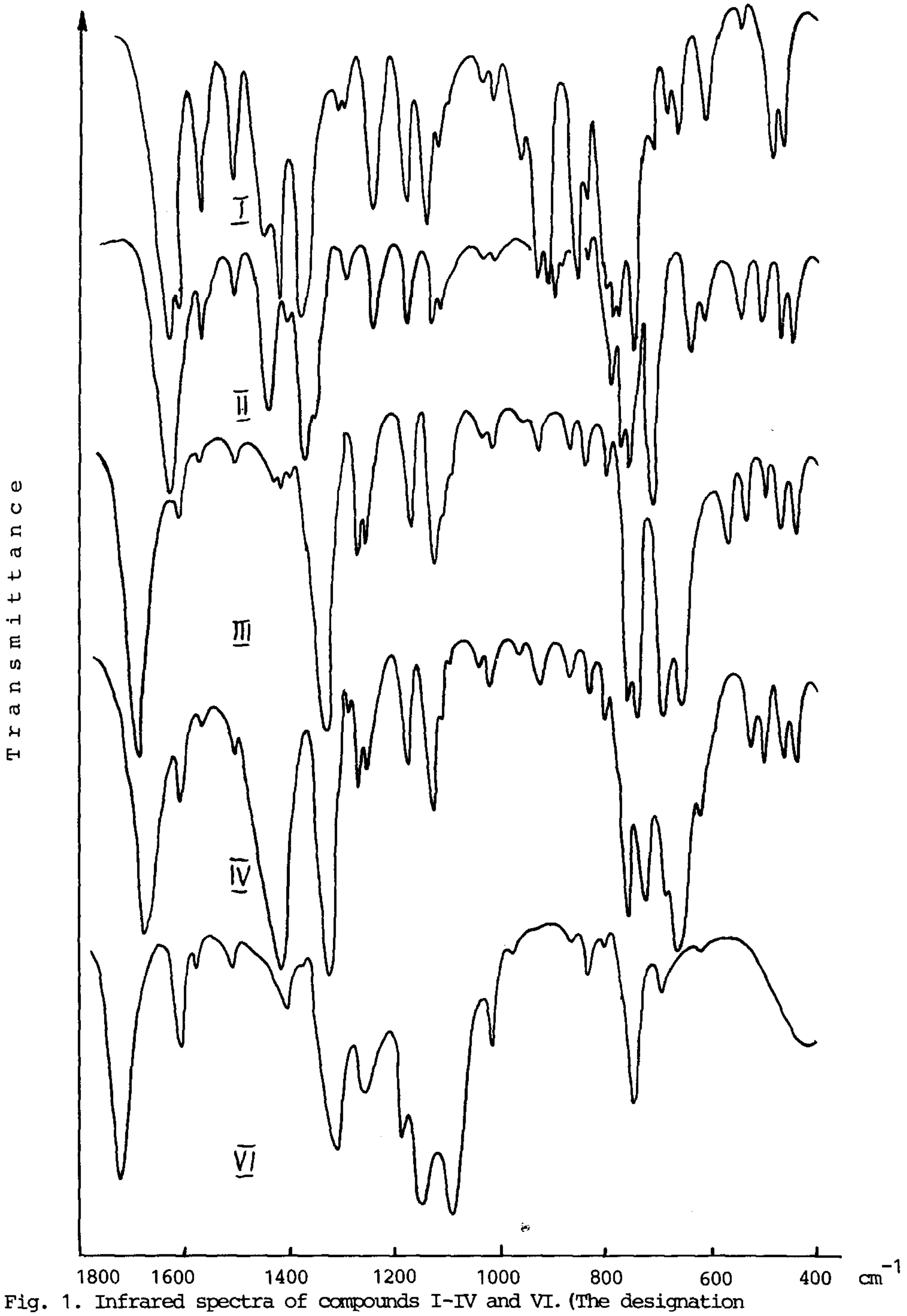

Fig. 1. Infrared spectra of compounds I-IV and VI. (The designation is the same as that in Table 2).

methyl)trifluorosilanes(I) the silicon atom hybridization character is intermediate between $RSiF_3$ and $[RSiF_4]^-$.

To establish the presence and the character of intramolecular C=O⟶Si coordination in compounds I-IV we have analyzed the dependence of their IR spectra on the number of fluorine atoms, n, attached to silicon. The COO symmetrical and antisymmetrical stretching vibrations in the spectra of I are observed at 1379 and 1625 cm^{-1}, respectively. These frequencies are characteristic of the carboxylate ion [11]. The ν(COO) values for I and II are similar. At the same time, ν(SiF) turned out to be characteristic for the $[R_{6-n}SiF_n]^{2-}$ and $[R_{5-n}SiF_n]^-$ anions, i.e. they have absorption maxima lower than 800 cm^{-1} [3].

The absorption bands in the 400-750 cm^{-1} region common to the $[RSiF_5]^{2-}$ group [10] are present in the spectra of compounds $K_2[4\text{-}CH_3C_6H_4COOCH_2SiF_5]$-(III) and $(NH_4)_2[4\text{-}CH_3C_6H_4COOCH_2SiF_5]$(IV) (Fig. 1). Upon the introduction of an electron-withdrawing substituent, or when the fluorine atom and the carbonyl oxygen atom are coming together [12] a considerable increase in ν(C=O) and a decrease in ν_{as}(COC) might be expected in the absence of coordinate interaction [6]. Thus the ν_{as}(COC) values observed for compounds III and IV give evidence for intramolecular C=O⟶Si coordination (Table 2). In chloroform solution this interaction is still present (ν(C=O) in the spectrum of II solution in $CHCl_3$ being at 1680 cm^{-1}). The degree of this interaction is weaker than in I and II molecules because of steric factors and higher co-ordination of the central silicon atom. The structure of the $[4\text{-}CH_3C_6H_4COOCH_2SiF_5]^{2-}$ ion of compounds III and IV is most likely to be pentagonal bipyramidal similar to that of 7-co-ordinate tin [8].

Ultraviolet absorption spectra

The absorption in the 230-255 nm region with log ε = 4.18-4.30 is due to the π-π* transition corresponding to ^1L_a in the UV spectra of the compounds listed in Table 3 (in chloroform and methanol). The C=O⟶Si interaction in compound I causes a bathochromic shift of this maximum when compared with VI-VIII. The red shift of this band is also observed in the spectra of compounds II-IV. The presence of the bathochromic shift in the spectra of II-IV solutions in $CHCl_3$ and CH_3OH shows that the cyclic group formed because of C=O⟶Si coordination is preserved in methanol.
This indicates that the silicon atom is hexacoordinate in (aroyloxymethyl)-

TABLE 2

Infrared group frequencies (cm^{-1}) in spectra of $M_{n-3}\left[4\text{-}CH_3C_6H_4COOCH_2SiF_n\right]$ and $4\text{-}CH_3C_6H_4COOCH_2R$

Compound	M	n	R	$4\text{-}CH_3C_6H_4$	$O\text{-}CH_2\text{-}Si$	COO	SiF_n
I			SiF_3	838 1015 1182 1250 1120 1140 1510 1570 1613	751 1250 1423	1379 1625	470 490 547 778 783 857 917
II	K^+	4		837 1016 1123 1133 1183 1245 1513 1570	763 1245 1410	1380 1630	453 470 510 551 710 773 793
III	K^+	5		837 1020 1115 1125 1173 1260 1507 1577 1613	757 1275 1406 1423	1330 1693	443 470 503 537 657 680 747
IV	NH_4^+	5		830 1017 1113 1123 1173 1257 1505 1573 1610	753 1270	1327 1677	440 467 500 527 660 727
VI			$SiO_{1.5}$	837 1017 1177 1260 1503 1577 1610	747 1267 1407	1307 1718	
VII			$Si(OC_2H_5)_3$	849 1030 1170 1515 1587 1622	755 1257 1413	1304 1720	
VIII			CH_3	848 1020 1180 1515 1580 1620	760 1410	1270 1720	

TABLE 3

^1L_a transition bands (λ_{max}, nm) in UV spectra of $M_{n-3}\left[4\text{-}CH_3C_6H_4COOCH_2SiF_n\right]$ and $4\text{-}CH_3C_6H_4COOCH_2R$

Compound	M	n	R	Solvent $CHCl_3$	CH_3OH	80% CH_3OH	0.1 N KOH in 80% CH_3OH	0.1 N KOH in 50% CH_3OH	
I			SiF_3	253.5	243.7	240.1	239.1	239.7	233.9*
II	K^+	4		251.4	242.5	-	238.9	-	234.0*
III	K^+	5		-	242.0	-	239.0**	-	233.9*
IV	NH_4^+	5		252.6	243.8	241.8	239.0	240.3	233.6*
VI			$SiO_{1.5}$	239.3	-	-	238.9	241.0	234.7*
VII			$Si(OC_2H_5)_3$	241.0	239.0	240.6	239.7	-	-
VIII			CH_3	239.3	239.2	239.7	237.2	235.3	233.3*
IX	$4\text{-}CH_3C_6H_4COOH$			245.1	236.0	238.2	232.6	233.7	233.7*

* 15 hours after preparing of the solution. **. In 90% CH_3OH (0.1 N NH_4OH).

tetrafluorosilicates and heptacoordinate in (aroyloxymethyl)pentafluorosilicates. The absorption bands in the spectra of I,IV,VII and VIII solutions in 80% water-methanol are similar. This indicates that there is no C=O$\rightarrow$Si interaction in the presence of water in compounds I and IV.

In excess alkali, the absorption maxima of compounds I-IV and VI-VII are located in the same region as those of VIII but about 6 nm from the band of 4-toluic acid (IX). As the SiF bonds are hydrolyzed to Si-OH in an alkaline medium (from amperometric titration data, Fig. 2) it follows that the ester group undergoes no hydrolysis immediately after preparing the alkaline solutions of I-IV and VI-VIII compounds. The absorption bands of alkaline solutions of these compounds become identical with the band of 4-toluic acid after 10-15 hours.

The spectroscopic data support the possible existence of the heptacoordinate silicon atom in species of the $M_2[ArCOOCH_2SiF_5]$ type. Evidently pentafluorosilicates III and IV do not exist in the form of double salt, $M[ArCOOCH_2SiF_4].MF$. This is shown by the absence of the ^1L_a transition shift in the absorption spectra of compound VIII in saturated KF solution in $CHCl_3$ and $CHCl_3$+C_2H_5OH (1:1) containing a 4-fold excess of KF relative to compound VIII.

We hope to confirm our conclusions on the co-ordinate numbers by X-ray diffraction studies.

EXPERIMENTAL

IR spectra of the compounds studied (I-VIII) were recorded on a Specord 75 IR spectrometer in the 400-3600 cm^{-1} region (in KBr pellets and Nujols mulls). Liquid compounds VII and VIII were studied as thin layers.

UV absorption spectra as 5.10^{-4}-5.10^{-3} $mol.l^{-1}$ solutions were recorded on a Specord UV VIS spectrophotometer. The cell thickness was 0.1-0.01 cm.

Amperometric measurements were performed in 50% water ethanol on the background of 0.1 N $LiClO_4$ with cathode potential -1.8 volt relative to saturated calomel comparative electrode using an LP-7 polarograph and a mercury drop electrode.

(4-methylbenzoyloxymethyl)trifluorosilane(I)

was obtained by the previously described method [4].

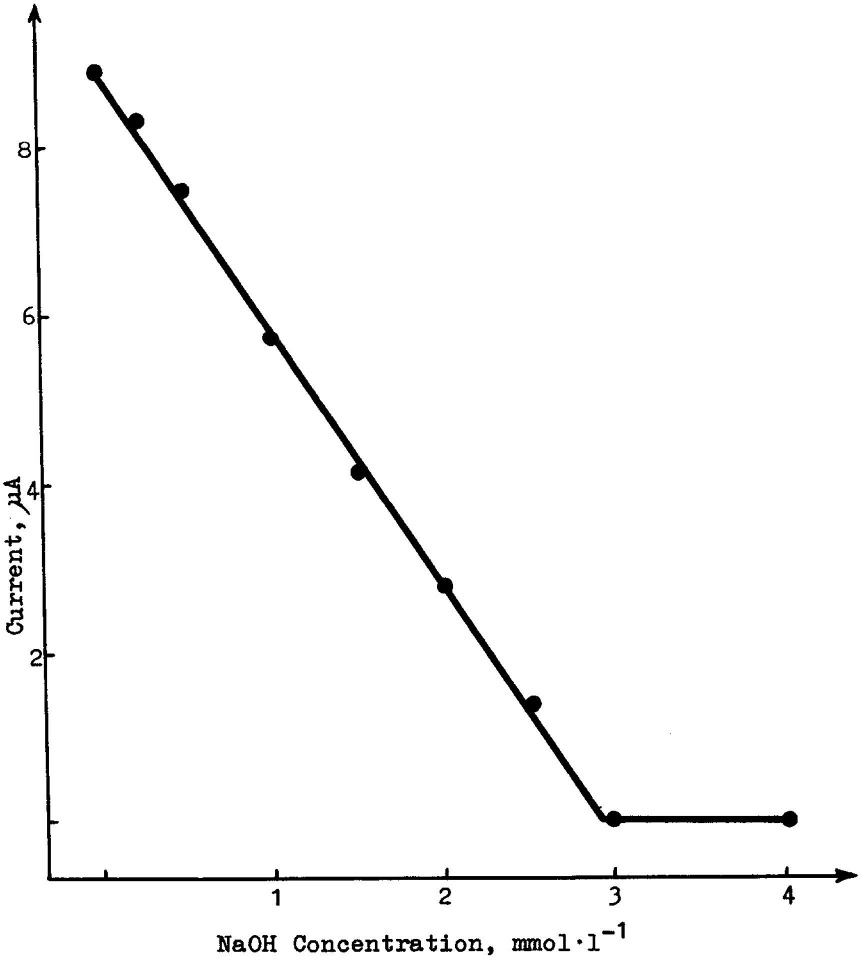

Fig. 2. The dependence of the 4-$CH_3C_6H_4COOCH_2SiF_3$ reduction limiting current on the NaOH concentration. The concentration of compound I is 1 mmol. l^{-1}.

Potassium (4-methylbenzoyloxymethyl)pentafluorosilicate(III) (reaction 1)

25 ml of 0.1 N solution of potassium fluoride in 80% water methanol was added to 0.188 g (0.8 mM) solution of substance I in 25 ml of 80% water methanol. The precipitate was washed with methanol and dried. The yield was 61% (0.172 g).

Ammonium (4-methylbenzoyloxymethyl)pentafluorosilicate(IV)

20 ml of 0.3 mol.l^{-1} solution $NH_4F.HF$ in methanol was added to 0.188 g (0.8 mM) of solution of substance I in 20 ml of methanol. The precipitate was filtered, washed with methanol and dried. The yield of compound IV was 86% (0.212 g).

Ammonium (4-methylbenzoyloxymethyl)pentafluorosilicate(IV) (reaction 2)

0.2 ml of 30% water solution of ammonium hydroxide was added to 0.188 g (0.8 mM) of solution of substance I in 20 ml of chloroform. The precipitate of substance IV as white flakes was filtered, washed with a minimum amount of methanol and dried. The yield was 12% (0.023 g).

Potassium (4-methylbenzoyloxymethyl)tetrafluorosilicate(II)

0.018 g (0.32 mM) potassium hydroxide solution in 2 ml of methanol was added to 0.188 g (0.8 mM) solution of substance I in 20 ml of methanol. The precipitate of compound II was filtered, washed with a small quantity of methanol and dried. The yield was 16% (0.29 g).

(4-methylbenzoyloxymethyl)silsesquioxane(VI)

0.180 g (3.2mM) of potassium hydroxide in 20 ml of methanol was added to 0.188 g (0.8 mM) of substance I in 20 ml of methanol and then to 0.024 g (0.64 mM) of hydrogen chloride in 1 ml of water. The white precipitate of (4-methylbenzoyloxymethyl)silsesquioxane(VI) was filtered, washed with methanol and dried. The yield was 51% (0.096 g).Found, %: C 53.91, H 4.79, Si 14.19. $C_9H_9SiO_{3.5}$. Calculated, %: C 53.73, H 4.51, Si 13.93.

Potassium (4-methylbenzoyloxymethyl)pentafluorosilicate(III)

0.036 g (0.96 mM) of hydrogen chloride in 1.5 ml of water was added to a filtrate previously obtained after removal of silsesquioxane(VI). The white powdery precipitate of substance III was filtered, washed with a small quantity of methanol and dried. The yield was 42% (0.079 g).

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