Four Raman-polarized bands appeared at 707, 646, 326, and 257 cm^{-1} and are therefore a_1 modes and are assigned by comparison with related molecules ($SBrF_5$,[10,11] $MClF_5$[12,13] (M = S, Se, Te)) as $\nu_1(a_1)$, $\nu_2(a_1)$, $\nu_3(a_1)$, and $\nu_4(a_1)$. Three corresponding infrared bands occur at 648, 330, and 248 cm^{-1} with the 707-cm^{-1} band presumably hidden under the intense 715-cm^{-1} band. The depolarized band at 720 cm^{-1} in the Raman with a strong counterpart in the infrared at 715 cm^{-1} is readily assigned as $\nu_8(e)$. The low-frequency depolarized bands at 244 and 144 cm^{-1} are assigned as $\nu_{10}(e)$ and $\nu_{11}(e)$, respectively, by comparison with related molecules. The Raman band at 306 cm^{-1} appears to have a counterpart in the infrared at 302 cm^{-1} (sh) and can be assigned as $\nu_9(e)$. One of the b_1 modes, ν_6, is too low in intensity to be observed in similar molecules,[12,13] and $\nu_5(b_2)$ is probably hidden under the strong 646-cm^{-1} band.

Those vibrations involving motions of the TeF_5 part of the molecule are rather similar in frequency to those reported for $TeClF_5$.[12] The TeBr stretching frequency of the 257-cm^{-1} (ν_4) band is similar to the highest TeBr stretch in $TeBr_4$[14] (250 cm^{-1}).

Acknowledgment. We thank the National Research Council (Canada) for financial assistance and a postgraduate scholarship to L.L. We are indebted to E. K. Richardson and R. Kaiser for the ^{19}F NMR spectra.

Registry No. $TeBrF_5$, 21975-45-1; bromine, 7726-95-6; fluorine, 7782-41-4.

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Existence of Cesium Salts of CO_2F^-, $CO_2F_2^{2-}$, and $NO_2F_2^-$

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Received March 27, 1979

The reported synthesis of the salts of $CO_2F_2^{2-}$ [1] and NO_4^{3-} [2] anions extends the series of known isoelectronic, 32-valence-electron species BF_4^-, CF_4, NF_4^+,[3] ONF_3,[4,5] and OCF_3^-.[6] The formation of salts of CO_2F^-, a member of the series BF_3, CO_3^{2-}, NO_3^-, FNO_2, OCF_2, and ONF_2^+, has been reported[1] but not characterized. There have been conflicting reports[7] of the synthesis of $CsNO_2F_2$. While attempting to prepare derivatives of $NO_2F_2^-$ (a 32-valence-electron species), we repeated the syntheses of $CO_2F_2^{2-}$- and CO_2F^--containing species without success. We wish to report the results of a careful reexamination of the reported reactions of carbon dioxide and nitrosyl fluoride with cesium fluoride and the reaction of dicesium oxide with carbonyl fluoride.

Experimental Section

Techniques and apparatus are described in ref 8. Purity of starting materials was routinely established by X-ray powder photography or infrared spectroscopy. Cesium fluoride (Ozark Mahoning) was dried by heating at 150 °C in vacuo for 12 h and then finely ground before use. Molecular sieve, 3 Å (Davidson Chemical), was heated at 350–400 °C in vacuo for 24 h before use.

Acetonitrile (Matheson Coleman and Bell) was purified by method B of Walter and Ramaley.[9] In addition, the acetonitrile was vacuum distilled through a 60-cm column containing dehydrated molecular sieve and collected in a glass vessel also containing molecular sieve. The acetonitrile was then distilled twice into similarly prepared vessels. For a further check on the purity of starting materials, cesium fluoride pretreated as above was reacted with OCF_2 in acetonitrile according to ref 6 and was shown to readily give $CsOCF_3$.[6,10]

FNO_2 was prepared by the reaction of excess F_2 (Matheson) with NO_2 (Matheson) in a Monel can. Excess F_2 was removed by pumping on the reaction vessel held at −196 °C. FNO_2 (bp −72.5 °C) was distilled as needed from the reaction vessel held at −78 °C. Tetraethylammonium fluoride dihydrate ($Et_4NF\cdot 2H_2O$, Eastman Organic Chemicals) was dehydrated by the method of Miller, Freid, and Goldwhite[11] and finely ground before use. CO_2 (Matheson, Bone Dry), Cs_2O (Alfa-Ventron), OCF_2 (Pierce Chemical Co.), SF_4 (Columbia Organic Chemicals), and $CsNO_3$ (PCR Research Chemicals) were used without further purification.

Reaction of CsF and CO_2. In a typical experiment, acetonitrile (12.2 mmol) was condensed into a 50-cm^3 Parr bomb containing CsF (13.5 mmol). CO_2 (71.6 mmol) was condensed into the bomb which was allowed to stand at room temperature, with continuous stirring, for 7 days. The excess CO_2 was removed by pumping on the reaction vessel held at −78 °C. The acetonitrile was distilled from the reaction vessel held at −22 °C. The weight of solid product was identical with the weight of starting CsF. The product was identified as unreacted CsF by its X-ray powder diffraction photograph. Various experiments were done with pressures of CO_2 up to 110 atm.

Reaction of CO_2 and $Et_4NF\cdot 2H_2O$. CH_3CN (43.2 mmol) was condensed into a glass vessel containing $Et_4NF\cdot 2H_2O$ (2.32 mmol) with partial dissolution. The reaction vessel was opened to the vacuum line, and CO_2 was expanded into the line to a pressure of 1000 torr. Some CO_2 was taken up immediately, and the insoluble $Et_4NF\cdot 2H_2O$ was taken into solution. The CO_2 pressure was increased to 1500 torr, and the reaction vessel was closed and held at room temperature for 1 day with occasional shaking. The volatiles were condensed from the reaction vessel held at room temperature, leaving behind a pasty white solid (0.48 g).

Reaction of CO_2 and Et_4NF. Acetonitrile (56.1 mmol) was condensed into a glass vessel containing Et_4NF (1.76 mmol). The reaction vessel was opened to the vacuum line, and CO_2 was expanded into the line to a pressure of 760 torr. The pressure remained constant over several hours, indicating no uptake of CO_2. The vessel was closed and held at room temperature overnight. The volatiles were quickly condensed out from the reaction vessel held at room temperature. The weight of product was identical with the weight of starting Et_4NF.

Reaction of Cs_2O and OCF_2 in CH_3CN. CH_3CN (40.7 mmol) was condensed into a Monel can containing Cs_2O (4.40 mmol). COF_2 (7.12 mmol) was also condensed into the can which was held at room temperature for 6 days with continuous stirring. The infrared spectrum of the volatiles showed CO_2 and a trace of CF_4 (an impurity in COF_2) to be present. The presence of a noncondensable gas was also observed. The CO_2 was pumped from the reaction vessel held at −78 °C, and the CH_3CN (1.74 g) was condensed out at room temperature. The infrared spectrum of the volatiles above the CH_3CN showed CO_2 to be present. The product remaining in the reaction vessel was a tan-brown solid (1.43 g). The infrared spectrum of the solid showed $CsOCF_3$, possibly Cs_2CO_3, and traces of $CsHF_2$. Cs_2CO_3 is difficult to identify in the presence of the other two anions since their spectra overlap. The solid product was heated to 100 °C for 1 h, and the volatiles given off were shown to be CO_2 and OCF_2 by infrared spectroscopy.

Reaction of $CsNO_3$ and SF_4. CH_3CN (68.5 mmol) was condensed into a Monel can containing $CsNO_3$ (5.85 mmol). SF_4 (18.0 mmol) was condensed into the can which was allowed to react at room temperature for 10 days with continuous stirring. The infrared

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spectrum of the gaseous products indicated the presence of SF_4 and OSF_2. The volatiles were condensed from the reaction vessel held at room temperature. The weight of solid product recovered was the same as the weight of starting $CsNO_3$. The solid product was identified as unreacted $CsNO_3$ by its infrared spectrum and X-ray powder diffraction photograph. In a similar experiment in which SF_4 was reacted with solid, powdered $CsNO_3$, the starting materials were recovered, indicating that no reaction had occurred.

Reaction of CsF and FNO_2. FNO_2 (5.54 mmol) was condensed into a well-passivated Monel can containing CsF (2.83 mmol). The reaction vessel was held at room temperature for 7 days. The gaseous products were quickly pumped from the reaction vessel held at −78 °C. The weight of solid product was found to be the same as the weight of starting CsF. Fresh FNO_2 (6.77 mmol) was condensed into the can which was heated at 130 °C for 4 days. The volatiles were removed as above, and the weight of solid product was again found to equal the weight of starting CsF. The product was identified as unreacted CsF by its X-ray powder diffraction photograph.

Discussion

The above experiments cast doubt on the reported synthesis of $Cs_2CO_2F_2$ and $CsCO_2F$.[1] The products formed may have been caused by the presence of water especially in acetonitrile which is a difficult solvent to purify.[12] That CO_2 will react with $Et_4NF{\cdot}2H_2O$ but not Et_4NF further supports the suggestion. The products from the reaction of Cs_2O with OCF_2 could possibly be rationalized by the initial formation of an unstable $CO_2F_2^{2-}$ anion as described in the sequence

$$Cs_2O + OCF_2 \rightarrow Cs_2CO_2F_2$$

$$Cs_2CO_2F_2 \rightarrow 2CsF + CO_2$$

$$CsF + OCF_2 \rightarrow CsOCF_3$$

$$Cs_2O + CO_2 \rightarrow Cs_2CO_3$$

The recently reported gas-phase fluoride ion affinities[13] of CO_2 [$D(CO_2{-}F^-) = 33 \pm 3$ kcal/mol] and OCF_2 [$D(OCF_2{-}F^-) = 35 \pm 3$ kcal/mol] allow the heats of reactions 1 and 2 to be estimated.

$$CsF + CO_2 \rightarrow CsCO_2F \quad \Delta H_1 \approx -4 \text{ kcal/mol} \qquad (1)$$

$$CsF + OCF_2 \rightarrow CsOCF_3 \quad \Delta H_2 \approx +12 \text{ kcal/mol} \qquad (2)$$

The crystal-lattice energies of $CsCO_2F$ and $CsOCF_3$ can be determined, with the assumption that the sizes of CO_2F^- and OCF_3^- are the same as those of CO_3^{2-} and PO_4^{3-}, by the Kapustinski equation[14] as 147 and 129 kcal/mol, respectively.

$CsOCF_3$ is readily prepared, and therefore it would not be unreasonable to expect that $CsCO_2F$ should be made under similar conditions; however, errors in such simple calculations are large (>15 kcal/mol) and kinetic factors may also be involved. The corresponding reaction with Et_4NF is estimated to be mare exothermic by 20 kcal/mol, but no reaction with CO_2 was observed. The fact that NO_2F did not form a salt with CsF under conditions where OCF_2 does is perhaps due in part to the difference in C–F and N–F bond strengths (ca. 50 kcal/mol). It is not possible to estimate the heat of formation of $Cs_2CO_2F_2$ from CsF and CO_2, as the fluoride ion affinity of CO_2F^- is unknown.

Acknowledgment. We thank the National Science and Engineering Research Council (Canada) for financial support and a fellowship (L.L.), Dr. T. B. McMahon for useful discussions, and Dr. J. B. Milne for providing a more detailed account of experiments reported in ref 1 and for helpful comments.

Registry No. $CO_2F_2^{2-}$, 43800-36-8; $NO_2F_2^-$, 71001-79-1; $CsCO_2F$, 2700-82-5; $CsOCF_3$, 71001-81-5.

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The Oxotetrachloroselenate(IV) Ion, $SeOCl_4^{2-}$

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Received January 11, 1979

Recent work on chloroselenates[1] has revealed that the trichloroselenate(IV) ion, $SeOCl_3^-$, exhibits a tendency to form chloride-bridged structures depending upon the size of the countercation. The polymeric nature of some of these compounds suggests that the $SeOCl_3^-$ ion should readily accept a chloride ion to give the $SeOCl_4^{2-}$ ion. The crystal structure of 8-hydroxyquinolinium oxochloroselenate(IV)[2] consists of $SeOCl_2$ units linked by chloride bridges where the selenium has a distorted square-pyramidal coordination with oxygen trans to the lone electron pair. The structure of bipyridinium(II) oxotetrachloroselenate(IV)[3] also contains five-coordinate selenium and is best approximated as $SeOCl_3^-$ anions each with a distant weakly bonded chloride anion. The oxotetrafluorotellurate(IV) anion, $TeOF_4^{2-}$,[4] which is isoelectronic in valence electrons with the $SeOCl_4^{2-}$ ion, has a discrete square-pyramidal structure with the oxygen occupying the axial position. A related five-coordinate tellurium(IV) anion has been reported,[5] but it is uncertain whether the structure consists of oxo- or hydroxotetrachlorotellurate(IV) anions.

Since no compounds with discrete oxotetrachloroselenate(IV) ions had been prepared, an investigation of their possible existence and their stereochemistry was begun.

Experimental Section

Materials. Sources and purification procedures for SeO_2, $SeOCl_2$, Ph_4AsCl, Et_4NCl, and acetonitrile (MeCN) are given in ref 1. Bipyridinium dichloride ($bpyH_2Cl_2$) was prepared by crystallizing bipyridyl (Fisher) from an excess of concentrated hydrochloric acid. Anal. Calcd for $bpyH_2Cl_2$: Cl, 30.95. Found: Cl, 30.71.

Preparation of Oxotetrachloroselenate(IV). All preparations were carried out in a drybox.

$bpyH_2SeOCl_4$. Stoichiometric amounts of $bpyH_2Cl$ (790 mg) and $SeOCl_2$ (332 mg) were mixed in MeCN (4 g) and left overnight to react. The white product was insoluble in MeCN and could be simply filtered out. Anal. Calcd for $bpyH_2SeOCl_4$: Cl, 35.90. Found: Cl, 35.68.

$[Ph_4As]_2SeOCl_4$ and $[Et_4N]_2SeOCl_4$. A 4:1 mole ratio of $Ph_4AsCl(Et_4NCl)$ to $SeOCl_2$ was made up in dry MeCN (approximately 166 mg of $SeOCl_2$/6 mL of MeCN). This was cooled with mixing in dry ice until a large amount of pale yellow product had crystallized out and then quickly filtered and dried in the drybox. Anal. Calcd for $[Ph_4As]_2SeOCl_4$: Cl, 14.13; C, 57.45; H, 4.02. Found: Cl, 13.43; C, 57.34; H, 4.43. Calcd for $[Et_4N]_2SeOCl_4$: Cl, 28.51; C, 38.65; H, 8.11; N, 5.63. Found: Cl, 28.04; C, 38.07; H, 8.23; N, 6.05.

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