

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} MCIF_5 ^{12,13} ($M = \text{S, Se, Te}$)) 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}).

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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^- , $\text{CO}_2\text{F}_2^{2-}$, and NO_2F_2^-

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The reported synthesis of the salts of $\text{CO}_2\text{F}_2^{2-}$ 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 reported¹ but not characterized. There have been conflicting reports⁷ 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 $\text{CO}_2\text{F}_2^{2-}$ 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 ($\text{Et}_4\text{NF}\cdot 2\text{H}_2\text{O}$, Eastman Organic Chemicals) was dehydrated by the method of Miller, Freid, and Goldwhite¹¹ 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 $\text{Et}_4\text{NF}\cdot 2\text{H}_2\text{O}$. CH_3CN (43.2 mmol) was condensed into a glass vessel containing $\text{Et}_4\text{NF}\cdot 2\text{H}_2\text{O}$ (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 $\text{Et}_4\text{NF}\cdot 2\text{H}_2\text{O}$ 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.

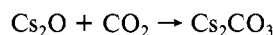
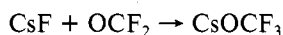
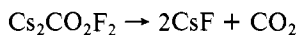
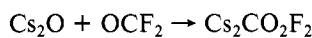
Reaction of CsNO_3 and SF_4 . CH_3CN (68.5 mmol) was condensed into a Monel can containing CsNO_3 (5.85 mmol). SF_4 (18.0 mmol) was condensed into the can which was allowed to react at room temperature for 10 days with continuous stirring. The infrared

spectrum of the gaseous products indicated the presence of SF₄ and OSF₂. 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 CsNO₃. The solid product was identified as unreacted CsNO₃ by its infrared spectrum and X-ray powder diffraction photograph. In a similar experiment in which SF₄ was reacted with solid, powdered CsNO₃, the starting materials were recovered, indicating that no reaction had occurred.

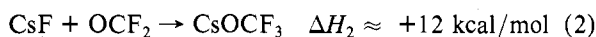
Reaction of CsF and FNO₂. FNO₂ (5.54 mmol) was condensed into a well-passivated Monel can containing CsF (2.83 mmol). The reaction vessel was held at room temperature for 7 days. The gaseous products were quickly pumped from the reaction vessel held at -78 °C. The weight of solid product was found to be the same as the weight of starting CsF. Fresh FNO₂ (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 Cs₂CO₂F₂ and CsCO₂F.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 CO₂ will react with Et₄NF·2H₂O but not Et₄NF further supports the suggestion. The products from the reaction of Cs₂O with OCF₂ could possibly be rationalized by the initial formation of an unstable CO₂F₂²⁻ anion as described in the sequence



The recently reported gas-phase fluoride ion affinities¹³ of CO₂ [*D*(CO₂-F⁻) = 33 ± 3 kcal/mol] and OCF₂ [*D*(OCF₂-F⁻) = 35 ± 3 kcal/mol] allow the heats of reactions 1 and 2 to be estimated.



The crystal-lattice energies of CsCO₂F and CsOCF₃ can be determined, with the assumption that the sizes of CO₂F⁻ and OCF₃⁻ are the same as those of CO₃²⁻ and PO₄³⁻, by the Kapustinski equation¹⁴ as 147 and 129 kcal/mol, respectively.

CsOCF₃ is readily prepared, and therefore it would not be unreasonable to expect that CsCO₂F 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 Et₄NF is estimated to be more exothermic by 20 kcal/mol, but no reaction with CO₂ was observed. The fact that NO₂F did not form a salt with CsF under conditions where OCF₂ 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 Cs₂CO₂F₂ from CsF and CO₂, as the fluoride ion affinity of CO₂F⁻ is unknown.

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Registry No. CO₂F₂²⁻, 43800-36-8; NO₂F₂⁻, 71001-79-1; CsCO₂F, 2700-82-5; CsOCF₃, 71001-81-5.

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The Oxotetrachloroselenate(IV) Ion, SeOCl₄²⁻

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Recent work on chloroselenates¹ has revealed that the trichloroselenate(IV) ion, SeOCl₃⁻, exhibits a tendency to form chloride-bridged structures depending upon the size of the counteranion. The polymeric nature of some of these compounds suggests that the SeOCl₃⁻ ion should readily accept a chloride ion to give the SeOCl₄²⁻ ion. The crystal structure of 8-hydroxyquinolinium oxochloroselenate(IV)² consists of SeOCl₂ 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 SeOCl₃⁻ anions each with a distant weakly bonded chloride anion. The oxotetrafluorotellurate(IV) anion, TeOF₄²⁻,⁴ which is isoelectronic in valence electrons with the SeOCl₄²⁻ 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 SeO₂, SeOCl₂, Ph₄AsCl, Et₄NCl, and acetonitrile (MeCN) are given in ref 1. Bipyridinium dichloride (bpyH₂Cl₂) was prepared by crystallizing bipyridyl (Fisher) from an excess of concentrated hydrochloric acid. Anal. Calcd for bpyH₂Cl₂: Cl, 30.95. Found: Cl, 30.71.

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

bpyH₂SeOCl₄. Stoichiometric amounts of bpyH₂Cl (790 mg) and SeOCl₂ (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 bpyH₂SeOCl₄: Cl, 35.90. Found: Cl, 35.68.

[Ph₄As]₂SeOCl₄ and [Et₄N]₂SeOCl₄. A 4:1 mole ratio of Ph₄AsCl(Et₄NCl) to SeOCl₂ was made up in dry MeCN (approximately 166 mg of SeOCl₂/6 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 [Ph₄As]₂SeOCl₄: Cl, 14.13; C, 57.45; H, 4.02. Found: Cl, 13.43; C, 57.34; H, 4.43. Calcd for [Et₄N]₂SeOCl₄: 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.