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.

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

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

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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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.

Table I. Raman Spectra of the Oxotetrachloroselenate(IV) and Related Anions[a]

$bpyH_2SeOCl_4$[b]	$SeOCl_3^-$[c]	$SeCl_5^-$[c]	$[Ph_4As]_2$-$SeOCl_4$[d]	$[Et_4N]_2$-$SeOCl_4$[e]	$SeOCl_4^{2-}$ in MeCN	assign ($SeOCl_4^{2-}$, C_{4v} symmetry)
32 (3)				31 (sh, 0)		ν_9(E) and lattice modes
75 (3)			74 (10)			
			83 (9)			
94 (2)						
	129 (0)	143 (0)	118 (sh, 0)	104 (0)		$\nu_6(B_2)$, δ_{sym}($SeCl_4$, in plane)
151 (3)	169 (2)	150 (2, p)	133 (sh, 1)	135 (3)	142 (1, p?)	$\nu_3(A_1)$, δ($SeCl_4$, umbrella)
		239 (8) 260 (8)	205 (3)	190 (4)	203 (2)	$\nu_4(B_1)$, ν_{sym}($SeCl_4$, out of phase) ν_7(E), ν_{asym}($SeCl_4$)
222 (5)	231 (10)					
255 (4)	261 (7)	272 (10, p)	243 (8)	233 (10)	242 (10, p)	$\nu_2(A_1)$, ν_{sym}($SeCl_4$, in phase)
	280 (3)					
326 (10)	313 (10)					
		171 (0)	282 (1)	274 (1)	285 (2)	ν_8(E), δ_{SeO} wag
884 (1)						
941 (4)	949 (3)	333 (1, p)	945 (3)	945 (3)	944 (3, p)	$\nu_1(A_1)$, ν(SeO)

[a] Raman spectra listed up to 1000 cm^{-1}. [b] Cation peaks: 54 (8), 66 (sh, 1), 106 (2), 130 (2), 161 (1), 226 (1), 333 (0), 398 (0), 433 (0), 544 (0), 611 (1), 736 (1), 756 (1), 844 (0), 997 (2). [c] Reference 1. [d] Cation peaks: 47 (5), 84 (7), 99 (10), 176 (2), 191 (1), 222 (sh, 1), 236 (3), 256 (1), 356 (0), 467 (0), 607 (1), 665 (1), 670 (0), 850 (0), 924 (0), 997 (5). [e] Cation peaks: as listed in ref 1.

Analysis. Chloride analyses were done by the Volhard method. Carbon, hydrogen, and nitrogen analyses were done by Chemalytics, Tempe, Ariz.

Solutions. Solutions in acetonitrile were made up by weight in the drybox and were near saturation with respect to Et_4NCl.

Spectroscopy. The equipment and technique used are described in ref 1. The argon ion line at 514.5 nm was used throughout to excite the spectra.

Results and Discussion

When the preparation of R_2SeOCl_4 ($R^+ = Ph_4As^+$, Et_4N^+) compounds from 2:1 mole ratio $RCl/SeOCl_2$ solutions in MeCN by evaporation to dryness is attempted, mixtures of $RSeOCl_3$ and a second Se(IV) compound, as well as excess RCl presumably, result as shown by Raman spectroscopy. Crystallization of the product from starting solution by cooling usually leads to $RSeOCl_3$ compounds, which are apparently less soluble than the R_2SeOCl_4 products. The Raman spectra of MeCN solutions with $Et_4NCl/SeOCl_2$ mole ratios from 1:1 up to 4.7:1 show that there is an equilibrium present.

$$SeOCl_3^- + Cl^- = SeOCl_4^{2-}$$

The Raman spectra of MeCN solutions with 1:1, 1.76:1, and 4.7:1 mole ratios are shown in Figure 1. The spectrum of the 1:1 solution is that of the $SeOCl_3^-$ ion,[1] but as the chloride content of the solution increases while $SeOCl_2$ concentration is held constant, the intensity of the peak at 336 cm^{-1} decreases relative to the other anion peaks and the pair of strong peaks of the $SeOCl_3^-$ ion at 228 and 248 cm^{-1} are replaced by a trio of peaks with a sharp central feature at 242 cm^{-1}. At 4.7:1 mole ratio $Cl^-/SeOCl_2$, the bands due to the $SeOCl_3^-$ ion have disappeared and only the spectrum of the new species is observed. Cooling of such a solution yields crystals, which gave the correct analysis for $[Et_4N]_2SeOCl_4$ and which give a Raman spectrum like that of the anion in solution.

The Raman spectra of solid $bpyH_2SeOCl_4$, $[Ph_4As]_2SeOCl_4$, and $[Et_4N]_2SeOCl_4$ are listed, along with those of related species and the $SeOCl_4^{2-}$ ion in MeCN, in Table I. The spectrum of "$SeOCl_4^{2-}$" in $bpyH_2SeOCl_4$ differs markedly from those of $[Ph_4As]_2SeOCl_4$ and $[Et_4N]_2SeOCl_4$. The crystal structure of $bpyH_2SeOCl_4$[3] shows the presence of two different trigonal-bipyramidal $SeOCl_3^-$ groups each with a fourth chloride near neighbor at $d(SeCl) \approx 3.0$ Å. The selenium–oxygen distances in the two $SeOCl_3^-$ anions are 1.61 and 1.65 Å and this should result in two SeO stretching bands in the Raman spectrum. These bands are observed at 941 and 884 cm^{-1}. There is a correlation between the SeO bond distances in this compound and that in 8-hydroxyquinolinium trichloroselenate(IV) and the frequencies of the bands. The SeO distance in the latter compound[2] is 1.59 Å and ν_{SeO} is at 956 cm^{-1}.[1] Compared to the SeO bond distances, the axial and equatorial SeCl bonds differ little respectively between the two [$SeOCl_3$] trigonal-bipyramidal units in the bipyridinium(II) tetrachloroselenate(IV). As a consequence the SeCl stretching region of the spectrum is relatively simple. As expected, the Raman spectrum parallels that of the $SeOCl_3^-$ ion[1] in the position of the bands, although the SeO deformation ($\nu_4(A')$) and the symmetric $SeCl_2$ (axial) stretch ($\nu_3(A')$) are

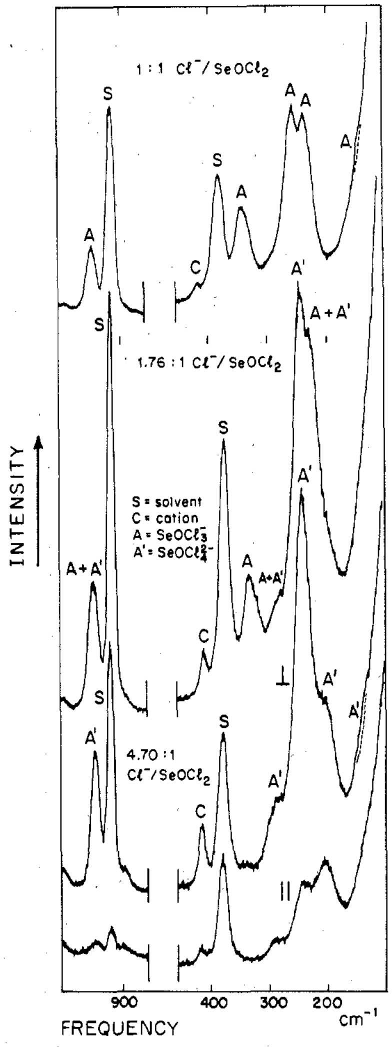
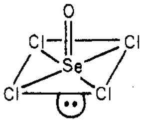


Figure 1. Raman spectra of acetonitrile solutions of Et_4NCl–$SeOCl_2$ at mole ratios 1:1, 1.76:1, and 4.7:1. Resolution = 6 cm^{-1}.

apparently coincident.

The Raman spectra of $[Et_4N]_2SeOCl_4$ and $[Ph_4As]_2SeOCl_4$ and $[Et_4N]_2SeOCl_4$ in MeCN are very similar to each other and very different from that of the $SeOCl_3^-$ ion. This, combined with the synthetic and equilibrium evidence above, indicates the presence of a new ion, the oxotetrachloroselenate(IV) anion, $SeOCl_4^{2-}$. The expected stereochemistry for this anion is that of a square pyramid with the oxygen axial and trans to the lone electron pair:



For this C_{4v} structure, nine normal modes are expected (3 A_1 + 2 B_1 + B_2 + 3 E). The spectra in Table I show six definite bands, of which two are clearly polarized, and some low-frequency bands, which represent lattice modes but could also include low-frequency internal vibrations. The spectra are more consistent with the C_{4v} structure than with other possible structures such as a square pyramid with the oxygen cis to the lone electron pair (C_s: 8 A′ + 4 A″) or models with a stereochemically inactive lone electron pair (trigonal-bipyramid models) such as that with the oxygen equatorial (C_{2v}: 5 A_1 + A_2 + 3 B_1 + 3 B_2) and that with the oxygen axial (C_{3v}: 4 A_1 + 4 E). In the first two cases, C_s and C_{2v}, more Raman-active bands would be expected and a greater number would be polarized than are actually observed. The elimination of the C_{3v} structure on the basis of the observed spectra is less certain and rests solely on the observation of too few polarized modes in the Raman spectra. However, the C_{3v} structure with a doubly bonded oxygen at 90° to three neighboring chlorines will be a higher energy structure than the C_{2v} structure where there are only two 90° repulsions between oxygen and chlorine.

A partial assignment under C_{4v} symmetry is given in Table I. On the basis of their intensity and polarization, the bands at 944 and 242 cm^{-1} are readily assigned to ν_1 and ν_2, respectively. The third A_1 mode ν_3, is assigned at 142 cm^{-1}, which is close to the frequency of this mode in the $SeCl_5^-$ ion. Furthermore, this band, in spite of its weakness, appears to be polarized in the spectrum in Figure 1. By comparison, with the frequency of the SeO wagging mode in the spectrum of the $SeOCl_3^-$ ion (280 cm^{-1}), the band at 285 cm^{-1} is probably the comparable SeO wagging mode, $\nu_8(E)$, under C_{4v} symmetry. The remaining SeCl stretching vibrations, $\nu_4(B_1)$ and $\nu_7(E)$, are assigned at 203 cm^{-1}. These two modes lie close together in the spectrum of the $SeCl_5^-$[1] and IOF_4^-[6] ions, which also have C_{4v} symmetry and it is not unexpected that they should be coincident here. The remaining peak at 104 cm^{-1} in the spectrum of solid $[Et_4N]_2SeOCl_4$ is assigned to the symmetric in-plane $[SeCl_4]$ deformation, $\nu_6(B_2)$, which normally lies below ν_3 in the Raman spectra of comparable C_{4v} species.[6] Of the remaining modes, $\nu_5(B_1)$ and $\nu_9(E)$, the former is normally not observed for related C_{4v} species[4,6] and the latter will lie at low frequencies and it is not possible to differentiate between it and the lattice modes of $[Ph_4As]_2SeOCl_4$ and $[Et_4N]_2SeOCl_4$.

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Registry No. $bpyH_2SeOCl_4$, 27380-13-8; $[Ph_4As]_2SeOCl_4$, 71213-95-1; $[Et_4N]_2SeOCl_4$, 71213-96-2; $SeOCl_4^{2-}$, 71213-94-0.

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Halo- and Carboxylato-Bridged Binuclear Iron Carbonyls

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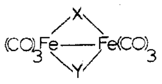
Halide and carboxylate ligands contribute three electrons and occupy two coordination sites when they are present as bridging ligands in transition-metal organometallic chemistry. We have been interested in developing synthetic routes to binuclear complexes of type **1** in which one of the groups X (X = halide or carboxylate) can be readily removed as X^- by treatment with $AgPF_6$ (X = halide) or by protonation with a strong acid such as HBF_4 (X = carboxylate) to generate binuclear cations with a vacant coordination site on each metal. To maintain the binuclear framework in such reaction sequences the Y group should be flexible but inert. In this paper we describe the synthesis of a series of binuclear iron carbonyls of type **1** in which Y is a phosphido bridge and X is a halide or carboxylate. Halo-bridged complexes of iron carbonyls are rare, the only examples known to us being the thermally unstable $Fe_2(CO)_6X_2$ (X = Br, I),[1] the methylenimino-bridged complexes $Fe_2(CO)_6(I)(N{=}CR'R'')$ (R′ = R″ = Ph, R′ = R″ = *p*-MeC_6H_4; R′ = Ph, R″ = *t*-Bu),[2] and the σ–π vinyl derivatives $Fe_2(CO)_6(X)(\mu\text{-}CH{=}CHX')$ (X = X′ = Br, I, Cl; X = Br, X′ = F; X = Br, X′ = I).[3] We describe herein the synthesis of **1** (X = Cl, Br, I, HCOO, CH_3COO, C_2H_5COO, CF_3COO; Y = PPh_2) via reaction of the organometallic zwitterions **2** (R = H; R′ = CH_3, C_2H_5) with the appropriate acid HX. The carboxylates of type **1** are the first examples of carboxylate-bridged binuclear iron carbonyls to be described.



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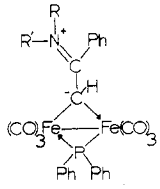

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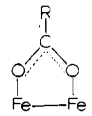

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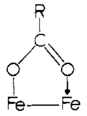

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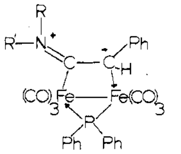

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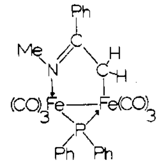

6

Experimental Section

All reactions were carried out in Schlenk tubes on a double manifold under a blanket of dry nitrogen. The starting materials of type **2** (R = H; R′ = Me, Et) were synthesized according to procedures already established for $Fe_2(CO)_6\{CHC(Ph)NHC_6H_{11}\text{-}c\}(PPh_2)$[4] and $Fe_2(CO)_6\{CHC(Ph)NEt_2\}(PPh_2)$.[5] Thus reaction of $Fe_2(CO)_6(C_2Ph)(PPh_2)$[6] (0.57 g; 1.0 mmol) with $MeNH_2$ (0.31 g; 10 mmol) or $EtNH_2$ (0.45 g; 10 mmol) in 1:1 benzene–petroleum ether between −10 and +10 °C followed by chromatography on Florisil (100–200 mesh, 18 in. × 1 in.) afforded dark red bands eluted with benzene, containing the required complexes. After recrystallization from 1:1

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