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Vibrational Spectra of Trihaloselenate(IV) Ions, $SeOX_3^-$

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Several trifluoro- and tribromoselenate(IV) compounds, $MSeOF_3$ and $MSeOBr_3$, have been made and characterized by IR and Raman spectroscopy. Comparison of the spectra with those of the trichloroselenate(IV) compounds previously reported has been made. In all cases the spectra are consistent with trigonal-bipyramidal stereochemistry predicted by valence-shell-electron-pair repulsions with the oxygen and lone electron pair equatorial. Anion polymerization via oxygen or halogen bridging is very weak for $MSeOF_3$ (M = K, Cs) but becomes significant for $MSeOCl_3$ where M = K and for $MSeOBr_3$ where M = Me_4N. Compounds with larger cations contain isolated $SeOX_3^-$ anions. Normal-coordinate analysis has been used to assist in assigning the spectra. The force constants calculated show the equatorial halogen is more strongly bound to selenium than is the axial halogen.

The halo complexes of selenium(IV) exhibit great variety in their stereochemistry. While some complexes may exist as isolated anions that obey the simple valence-shell electron-pair repulsion rules, others are polymerized by bridging through oxygen or halogen.[1] The stereochemistry adopted is often determined by the nature of the cation in these complexes.[2,3] Another interesting feature involves the stereochemical activity of the lone electron pair in selenium(IV) species, which is active in complexes of low coordination number but inactive in $SeCl_6^{2-}$ and $SeBr_6^{2-}$, where ligand crowding quenches its effect. Interligand repulsions are not strong enough, however, to overcome the effect of the lone pair and cause isolated $SeOCl_3^-$[2] and $SeOCl_4^{2-}$[3] ions to adopt tetrahedral and trigonal-bipyramidal structures, respectively. The tribromoselenate(IV) ion has not been studied before and is of interest with respect to the question of interligand repulsions and lone-pair activity as well as the question of the halide bridging. A related species, the $SeOF_3^-$ ion, is known, but there is only limited information concerning its vibrational spectrum.[4] The question of whether this ion is polymerized in $KSeOF_3$ like the corresponding chloro anion in $KSeOCl_3$[2] is unanswered. In addition, normal-coordinate analysis of these $SeOX_3^-$ (X = F, Cl, Br) anions has not been attempted before. For these reasons, it was considered of interest to prepare the F and Br members of the $SeOX_3^-$ series, measure their vibrational spectra, and establish their stereochemistry. In addition, through normal-coordinate analysis of the F, Cl, and Br species, it was hoped to confirm the assignment of the bands and explore any consequences for the bond model stemming from the calculated force constants.

Experimental Section

The preparation and purification of the seleninyl halides was the same as that described earlier.[5] Acetonitrile was purified by refluxing over phosphorus pentoxide followed by distillation. Potassium trifluoroselenate(IV) was prepared by the method of Paetzold and Aurich.[4] The preparation was also carried out in acetonitrile. A mixture of equimolar amounts of $SeOF_2$ and KF (Alfa) or CsF (Alfa), previously dried under vacuum at 125 °C, in a small volume of dry acetonitrile, was allowed to react for 24 h, and then the insoluble solid was filtered out. Anal. Calcd for $KSeOF_3$: F, 29.83. Found: 29.93. The analogous preparation of the cesium compound gave only 90% conversion to $CsSeOF_3$. The tribromoselenate(IV) compounds were prepared by crystallization from 1:1 molar mixtures of seleninyl bromide and anhydrous tetramethylammonium (Aldrich), tetraethylammonium (Aldrich), and tetraphenylstibonium (Alfa) bromides in dry acetonitrile. Anal. Calcd for $Me_4NSeOBr_3$: C, 11.75; H, 2.96; N, 3.42; Br, 58.63. Found: C, 11.60; H, 2.60; N, 3.46; Br, 59.06. Calcd for $Et_4NSeOBr_3$: C, 20.66; H, 4.33; N, 3.01; Se, 16.98; Br, 51.56. Found: C, 20.42; H, 4.01; N, 2.90; Se, 16.77; Br 51.47. Calcd for $Ph_4SbSeOBr_3$: C, 37.71; H, 2.64; Br, 31.36. Found: C, 35.87; H, 2.25; Br, 30.95; Tetra-*n*-butylammonium oxotribromoselenate(IV) was very soluble in MeCN. The compound was made by pumping a 1:1 mixture of *n*-butylammonium bromide and seleninyl bromide in MeCN to dryness. $Et_4NSeOBr_3$ was also prepared from aqueous hydrobromic acid solution. A mixture with $Et_4NBr/SeO_2/HBr$ (as 8.39 M HBr) in mole ratio 1:1:4 was prepared. Sufficient water was added to just dissolve the orange precipitate that formed, and the mixture was then cooled on an ice bath. The yellow precipitate that formed was washed with cold alcohol and ether. The product had a Raman spectrum identical with that of $Et_4NSeOBr_3$ prepared from MeCN, but the bands were better resolved.

All nonaqueous preparations were carried out in a drybox.

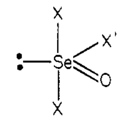
Analysis. Bromide analyses were done by the Volhard method. Selenium was determined by iodometry. Fluoride was determined by titration with standard thorium nitrate, using a fluoride-sensitive electrode. Carbon, hydrogen, and nitrogen analyses were done by Canadian Microanalytical Services Ltd., Vancouver, B.C.

Spectroscopy. Raman spectra were taken with a Jobin–Yvon grating monochromator in conjunction with PAR photon counting. The spectra of the tribromoselenate(IV) compounds were taken by using the 632.8-nm line of a Spectra Physics 125-A He/Ne laser. Raman lines due to R_4N^+ cations were, in general, weak and not observed. Spectra of the fluorides were taken by using the 514.5-nm line of a Control Laser argon ion laser. Calibration was carried out by using plasma lines present when the interference filters were not used.

Infrared spectra were taken on Perkin-Elmer 180 and 283 spectrometers using Nujol mulls and CsBr plates. Normal-coordinate analysis and force constant calculations were carried out by using CART, GMAT, and FPERT programs developed by H. Fuhrer et al. at the National Research Council of Canada and described in Bulletin 15 from the NRCC. The programs are based upon the original approach of Schachtschenider[6].

Results and Discussion

On the basis of valence-electron-pair repulsions, all of the $SeOX_3^-$ anions are expected to adopt a trigonal-bipyramidal shape with oxygen and lone electron pair equatorial.



This structure has C_s symmetry, and nine normal modes are expected [$\Gamma_{C_s} = 6\,A' + 3\,A''$], all active in the Raman and IR spectra. The structure may be modified, however, in two ways; polymerization via halide or oxide bridging may occur, which would give a more complex spectrum, or the stereochemical effect of the lone electron pair may be quenched,

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Table I. Vibrational Spectra of $KSeOF_3$ and $CsSeOF_3$

$KSeOF_3$					
	IR[b]				
Raman[a]	this work	Paetzold and Aurich[c]	$CsSeOF_3$ Raman[d]	mode no.	approx descripn of mode
79 (5)			53 (10)		lattice modes
103 (6)			72 (5)		
200 (0)			197 (1)	6 (A′)	$\delta_{FSeF'}(s)$[g]
225 (0) sh[e]			230 (0)		
310 (1)	312 w		303 (2)	5 (A′)	$\delta_{OSeF}(s)$[f]
358 (0)	351 s		350 (2)	9 (A″)	$\delta_{FSeF'}(a)$
377 (2) sh			375 (1)	4 (A′)	$\delta_{OSeF'}$
393 (5)	397 vs	413 vs	420 (8) br	8 (A″)	$\delta_{OSeF}(a)$
446 (3)	435 s, sh	430 vs		3 (A′)	$\nu_{SeF_2}(s)$
		450 w			
		484 s			
		513 w			
564 (7)			560 (10)	2 (A′)	$\nu_{SeF'}$
589 (1)	590 vs	585 vs		7 (A″)	$\nu_{SeF_2}(a)$
975 (10)	976 vs	982 vs	958 (10)	1 (A′)	ν_{SeO}

[a] Excited at 514.5 nm. [b] Scan to 200 cm^{-1} with Nujol mull in CsBr plates. [c] Reference 4; down to 400 cm^{-1}. [d] Excited at 632.8 nm. [e] Elemental selenium. [f] 36.1% of the potential energy is associated with f_β while 32.2% is associated with f_γ and 16% with $f_{\beta\gamma}$. [g] 58.3% of the potential energy is associated with f_γ while 51.2% is associated with f_β and −25.6% with $f_{\beta\gamma}$.

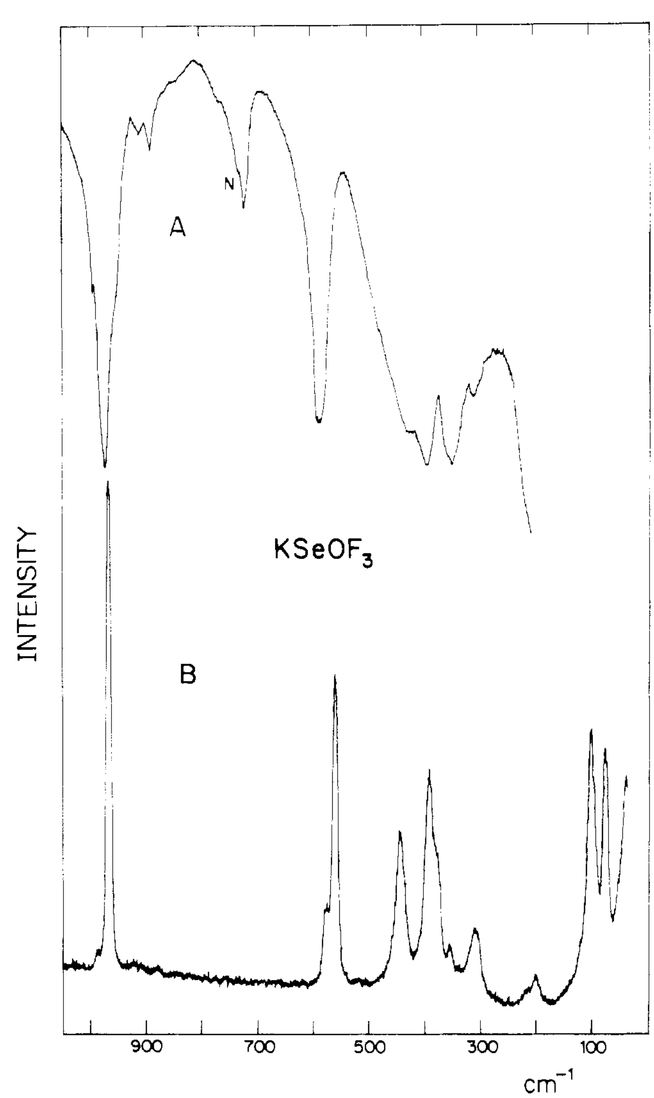

Figure 1. Raman and IR spectra of $KSeOF_3$: (A) IR; (B) Raman. N = Nujol peak.

leading to a tetrahedral structure and a simpler vibrational spectrum ($\Gamma_{T_d} = 3\ A_1 + 3\ E$).

Trifluoroselenate(IV) Ion. The vibrational spectra of $KSeOF_3$ and $CsSeOF_3$ are listed in Table I. The Raman and IR spectra of $KSeOF_3$ are shown in Figure 1. The IR spectrum of $KSeOF_3$ is in agreement with that reported by Paetzold and Aurich[4] insofar as the strongest bands are concerned. Bands at 450, 484, and 513 cm^{-1} reported earlier[4] are not observed in this work and may well be due to impurities as mentiond by the authors[4] or to hydrolysis products. Some very weak bands near 900 cm^{-1} due to $KSeO_2F$[7] are observed in the IR spectrum in Figure 1. Judging from the spectra of SeO_2F^-[7] and $SeOF_2$[5] none of the normal modes of the $SeOF_3^-$ ion are expected to lie below 200 cm^{-1}. Of the ten bands above 200 cm^{-1}, which are observed, the weak band near 230 cm^{-1} in the spectrum of both $KSeOF_3$ and $CsSeOF_3$ is due to elemental selenium. This peak is often observed in the Raman spectra of Se(IV) compounds, and upon long exposure of the sample to laser light, the pink coloration of elemental selenium is often observed.[2,7] Only six bands are observed in the IR spectrum above 200 cm^{-1}. The spectra are consistent with the presence of an isolated $SeOF_3^-$ anion in these compounds. The possibility of strong fluorine bridging to give a polymeric structure is unlikely in view of the simplicity of the SeF stretching region in the spectra. In the case of the related $KSeOCl_3$ compound, the Raman spectrum shows considerably more bands than expected for the isolated ion.[2] Moreover, the very weak bridging in solid $SeOF_2$[8] and the evidence against any bridging in monofluoroselenate(IV) compounds[7,9] suggest that any bridging will be weak for trifluoroselenate(IV)

Table II. Vibrational Spectra of $Et_4NSeOCl_3$

Raman[a]	IR[b]	mode no.	approx descripn of mode
	116 m	6 (A′)	$\delta_{ClSeCl'}(s)$
139 (1, p)	130 m	5 (A′)	$\delta_{OSeCl}(s)$
	168 w	9 (A″)	$\delta_{ClSeCl'}(a)$
228 (7, p?)	230 m	3 (A′)	$\nu_{SeCl_2}(s)$
248 (7, p)	258 sh	4 (A′)	$\delta_{OSeCl'}$
287 (1, dp)	295 vs	7 (A″)	$\nu_{SeCl_2}(a)$
	326 sh	8 (A″)	$\delta_{OSeCl}(a)$
336 (3, p)		2 (A′)	$\nu_{SeCl'}$
951 (2, p)	954 vs	1 (A′)	ν_{SeO}

[a] $Et_4NSeOCl_3$ in MeCN.[2] [b] $Et_4NSeOCl_3$ in Nujol mull with CsBr plates.

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Table III. Raman Spectra of Oxotribromoselenate(IV) Compounds

$Me_4NSeOBr_3$	$Et_4NSeOBr_3$	n-$Bu_4NSeOBr_3$	$Ph_4SbSeOBr_3$	$SeOBr_3^-$ in MeCN[a]	assignt: mode no.	assignt: approx descripn
	47 (10)					lattice mode
	65 (1) sh		74 (1) sh		6 (A′)	$\delta_{\mathrm{BrSeBr'}}(s)$
93 (0)	85 (0)		85 (2)		5 (A′) 9 (A″)	$\delta_{\mathrm{OSeBr}}(s)$ $\delta_{\mathrm{BrSeBr'}}(a)$
134 (1) sh						
150 (10)	117 (1)	154 (9)		135 (10, p)	3 (A′)	$\nu_{\mathrm{SeBr_2}}(s)$
165 (5)	164 (10)	173 (10)		163 (8)	7 (A″)	$\nu_{\mathrm{SeBr_2}}(a)$
186 (5)		183 (0) sh				
198 (1)						
215 (4)	194 (7)	198 (10)	195 (2)	194 (8, p)	4 (A′)	$\delta_{\mathrm{OSeBr'}}$
230 (1)						
247 (2)	251 (3)	252 (4)	162 (2)	260 (2)	8 (A″)	$\delta_{\mathrm{OSeBr}}(a)$
256 (2)	270 (1)	267 (5)	185 (0)	261 (3, p)	2 (A′)	$\nu_{\mathrm{SeBr'}}$
265 (1)						
296 (1)						
907 (0)	936 (2)	939 (1)	928 (1)	936 (1, p)	1 (A′)	ν_{SeO}

[a] n-$Bu_4NSeOBr_3$.

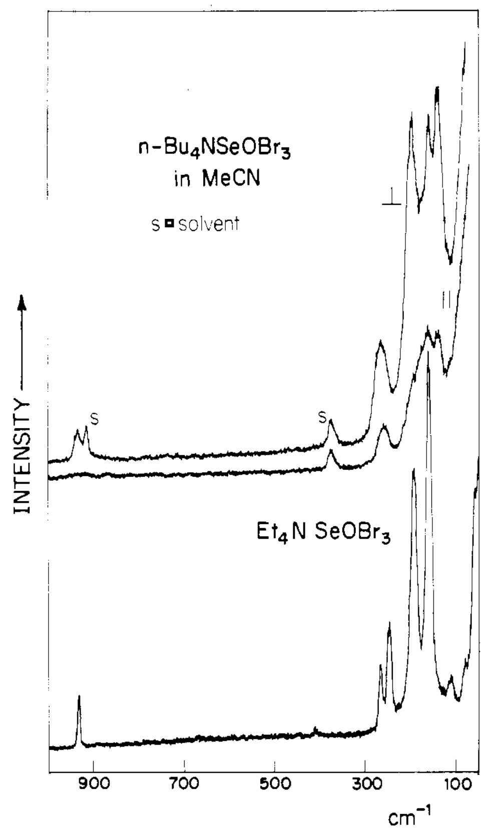

Figure 2. Raman spectra of $Et_4NSeOBr_3$ (solid) and n-$Bu_4NSeOBr_3$ (in solution in MeCN).

ions. The presence of a very weak Raman peak at 990 cm^{-1}, slightly higher than the strong SeO stretching mode at 975 cm^{-1}, and the dissymmetric shape of the SeO stretching mode at 982 cm^{-1} in the IR spectrum indicate that there are some interionic effects. It is not possible to establish the exact form of the isolated trigonal-bipyramidal $SeOF_3^-$ ion from these spectra, but in view of the known structures of related species $ClOF_3$[10] and $SeOCl_3^-$,[2] the structure with oxygen and lone electron pair equatorial is likely.

Trichloroselenate(IV) Ion. The Raman spectrum of the $SeOCl_3^-$ ion in solids and in solution has been reported previously[2] and is listed along with the IR spectrum of $Et_4NSeOCl_3$ in Table II.

Table IV. Structural Parameters[a]

parameter	$SeOF_3^-$	$SeOCl_3^-$	$SeOBr_3^-$
D(SeO)	1.60	1.63	1.63
R(SeX′)	1.73	2.25	2.45
r(SeX)	1.90	2.48	2.71
α(X′SeO)	102	102	102
β(XSeO)	96	96	96
γ(X′SeX)	89	89	89

[a] Bond distances in Å; angles in deg.

Tribromoselenate(IV) Ion. The Raman spectra of the $SeOBr_3^-$ ion in solid and solution are shown in Figure 2 and listed along with the spectra of $Me_4NSeOBr_3$, $Et_4NSeOBr_3$, and $Ph_4SbSeOBr_3$ in Table III. The Raman spectra of n-$Bu_4NSeOBr_3$ in MeCN and solid $Et_4NSeOBr_3$, n-$Bu_4NSeOBr_3$, and $Ph_4SbSeOBr_3$ are quite similar and are consistent with an isolated trigonal-bipyramidal $SeOBr_3^-$ ion with oxygen and lone electron pair equatorial. A tetrahedral structure is ruled out by the observation of four polarized bands and three Se–Br stretching bands.

While the 936-cm^{-1} peak is readily assigned to the SeO stretching mode, $\nu_1(A')$, the assignment of the remaining bands is more difficult because of the close proximity of the SeBr stretching and SeOBr deformation modes. In seleninyl bromide, however, the SeBr stretching modes lie more than 50 cm^{-1} above the deformations,[5] and it is almost certain that the polarized band at 261 cm^{-1} in the $SeOBr_3^-$ spectrum is due to the SeBr′ (equatorial) stretching mode. The Br′SeBr deformation modes are expected to lie below 100 cm^{-1} by analogy with this mode in $SeOBr_2$.[5] A definitive assignment was made on the basis of normal-coordinate analysis.

The Raman spectrum of $Me_4NSeOBr_3$ consists of 13 anion lines in the spectral region studied (50–1000 cm^{-1}), and the structure is apparently more complex than that of the isolated $SeOBr_3^-$ ion. Bridging over oxygen appears likely, judging from the shift to lower frequency of the SeO stretching vibration and the increase in the number of bands in the SeO deformation region. Both halogen and oxygen bridgings are observed in oxochloroselenate(IV) ions[2,11] and the smaller cation size favors polymerization of this anion.[2] Attempts to prepare $CsSeOBr_3$ from CsBr and $SeOBr_2$ in acetonitrile lead to the formation of SeO_2 and Cs_2SeBr_6.

Normal-Coordinate Analysis. The structural parameters chosen for the isolated $SeOX_3^-$ anion are given in Table IV.

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Table V. Force Constants for Trihaloselenate(IV) Ions

force const[a]	$SeOF_3^-$ [b]	$SeOCl_3^-$ [c]	$SeOBr_3^-$ [d]
f_D	7.38	7.06	6.85
f_R	2.78	1.49	1.46
f_r	2.17	1.01	0.63
f_α	1.63	1.05	0.75
f_β	1.79	1.26	0.86
f_γ	1.64	1.12	0.78
f_{rr}	0.04	0.07	0.22
$f_{\beta\beta}$	0.25	0.18	0.15
$f_{\gamma\gamma}$	0.21	0.11	0.08
$f_{r\beta} = -f_{r\beta'}$	−0.11	0.16	0.07
$f_{\beta\gamma} = f_{\beta\gamma'}$	−0.20	0.08	0.05

[a] Stretching force constants are in mdyn/Å, deformation constants, in mdyn Å/rad², and stretch–bend interaction constants, in mdyn/rad. [b] Frequencies fit to those of $KSeOF_3$ Raman spectrum. [c] Frequencies fit to the Raman spectrum of $Et_4NSeOCl_3$ in MeCN solution except for bands observed only in the IR spectrum (116, 169, and 326 cm⁻¹). [d] Frequencies fit to the Raman spectrum of *n*-$Bu_4NSeOBr_3$ in MeCN solution except for bands observed only in the spectrum of solid $Et_4NSeOBr_3$ (65 and 85 cm⁻¹).

They are based upon the structure of the $SeOCl_3^-$ anion[11] with extrapolation to give SeO and SeX bond lengths for $SeOF_3^-$ and $SeOBr_3^-$ based upon ratios determined from $SeOX_2$ structural parameters.[5] The force field was that established for $ClOF_3$,[10] which is isoelectronic in valence electrons with $SeOX_3^-$ species, and the symmetry coordinates for this C_s structure are also given in this reference. The force field requires 11 force constants, 6 main and 5 interaction constants, but only 9 frequencies are available for the analysis. One of the interaction constants, $f_{\beta\beta}$, was borrowed from the $SeOX_2$ set.[5] The $\beta\beta$ interaction in an $SeOX_3^-$ ion is expected to be closely related to the $\alpha\alpha$ ($\angle$(OSeX)–($\angle$(OSeX)) interaction in the related $SeOX_2$ molecule. It was found in initial calculations that f_D, the SeO stretching force constant, was highly independent of the other force constants. At worst, 99.7% of the potential energy for the SeO stretching mode was due to the f_D force constant. For this reason, it was considered acceptable to hold the f_D, as determined from initial calculations where it reproduced ν_{SeO} exactly, constant.

A starting set of the stretching force constants was generated by using Badger's rule as adapted by Herschbach and Laurie.[12] Initial deformation constants were those for $SeOX_2$ molecules.[5] The final force constants, which give an exact fit to the observed frequencies, are given in Table V.

The approximate descriptions of the normal modes listed in Tables I–III are based upon the potential energy matrices from the normal-coordinate calculations. In some instances the mode is not well described in terms of one of the potential force constants, and this is indicated in the tables. For all of the $SeOX_3^-$ ions the antisymmetric mode (modes 7–9) lies at higher frequency than the corresponding symmetric mode (modes 3, 5, and 6, respectively).

As expected, the force constants decrease in general with the increasing atomic number, which reflects the decreasing electronegativity of the halogen as well as a general weakening of the bonding by the heavier halogen. Furthermore, the force constant for the SeX′ bond, f_R, is greater than that for the SeX bond, f_r, which is generally true in trigonal-bipyramidal molecules.[13] The stretching force constants are lower than those in seleninyl halides.[5] The ratios of the axial to equatorial force constants decrease markedly as one passes through the series from $SeOF_3^-$ to $SeOBr_3^-$, which may be a result of greater crowding of the halogen ligands in the anion with the larger halogen and consequent repulsion of the axial ligands. A further result of such crowding is a general weakening of the bonding and resultant decrease in the deformation constants, which is considerably more pronounced in the more crowded $SeOX_3^-$ species than it is in the analogous $SeOX_2$ compounds.[5]

Conclusion

The tendency of trihaloselenate(IV) compounds to form polymeric structures increases with the atomic number of the halogen. This is apparently a function of halogen size and electronegativity. In the case of $MSeOF_3$ compounds, both the potassium and cesium salts contain isolated $SeOF_3^-$ anions. On the other hand, potassium trichloroselenate(IV) shows evidence of bridging while the compounds with larger cations have isolated $SeOCl_3^-$ anions. The tribromoselenate(IV) compounds have isolated anions when the cation size is that of Et_4N^+ or is larger but polymeric in the case of the tetramethylammonium cation, and in the case of the cesium salt, disproportionation to SeO_2 and Cs_2SeBr_6 takes place. The tendency toward halogen bridging suggests a greater degree of ionic character in the SeX bonding for the heavier halogen. This correlates with the relative ease of deformation of the $SeOX_3^-$ ions with greater halogen atomic number.

Acknowledgment. The Natural Sciences and Engineering Research Council of Canada is thanked for financial support.

Registry No. $KSeOF_3$, 86238-37-1; $CsSeOF_3$, 86238-38-2; $Et_4NSeOCl_3$, 68757-90-4; $Me_4NSeOBr_3$, 86238-40-6; $Et_4NSeOBr_3$, 86238-41-7; *n*-$Bu_4NSeOBr_3$, 86238-42-8; $Ph_4SbSeOBr_3$, 86271-99-0; $SeOBr_3^-$, 86238-39-3; $SeOF_3^-$, 86238-43-9; $SeOCl_3^-$, 58782-34-6.

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