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Chloro and Oxochloro Anions of Selenium(IV)

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The Raman spectra of four chloroselenate anions, SeO_2Cl^-, $SeOCl_3^-$, $SeCl_5^-$, and $SeCl_6^{2-}$, two of which have not been reported before (SeO_2Cl^- and $SeCl_5^-$), are discussed. Both solid and MeCN solution spectra with polarization measurements are considered. The spectra are consistent with a pyramidal SeO_2Cl^- ion (C_s), a trigonal-bipyramidal $SeOCl_3^-$ ion with two Cl's axial (C_s), a square-pyramidal $SeCl_5^-$ ion (C_{4v}), and an octahedral $SeCl_6^{2-}$ ion (O_h). Spectral evidence for chloride bridging is found for the compounds $KSeOCl_3$, 8-hydroxyquinolinium oxotrichloroselenate(IV), Et_4NSeCl_5, and $Ph_4AsSeCl_5$.

Introduction

The complex chloro anions of selenium(IV) exhibit a varied and interesting stereochemistry. The stereochemical inactivity of the lone valence electron pair in the hexahalo complexes, SeX_6^{2-} (X = Cl, Br, I), has been a puzzle of longstanding interest.[1,2] Interligand repulsions are sufficiently strong to overcome the stereochemical effect of the lone electron pair in these cases. It would be of interest to determine whether such repulsions are dominant for any of the SeX_5^- series of anions.

The chloro anions derived from $SeOCl_2$ show an intriguing range of stereochemistries. The 1:1 complex of KCl and $SeOCl_2$, which was first prepared by Wise[3] and later formulated as $K[SeOCl_3]$ by Jackson and Smith,[4] has been studied by Raman spectroscopy.[5] The spectrum was assigned assuming monomeric $SeOCl_3^-$ units. However, Cordes[6] has shown that there are essentially infinite chains of $SeOCl_2$ molecules linked by Cl^- bridges in 8-hydroxyquinolinium oxotrichloroselenate(IV). The one known example of an oxotetrachloroselenate(IV) compound, dipyridinium oxotetrachloroselenate(IV), has been shown to consist of cation, chloride, and oxotrichloroselenate(IV) units.[7] Wasif and Salama[8] have shown that only a 1:1 complex is formed between $SeOCl_2$ and Cl^- in Me_2SO.

Complex formation between SeO_2 and X^- (X = Cl, Br, I) in Me_2SO has been studied by UV and visible spectroscopy.[8] Evidence was found only for 1:1 complexes.

Because many of the chloroselenate(IV) anions have not been studied in detail by vibrational spectroscopy and in some cases not at all and since the nature of their stereochemistry is varied and interesting, a program of synthesis and investigation of vibrational spectra of chloro- and oxochloroselenate(IV) anions was begun and is reported here.

Experimental Section

Materials. Selenium dioxide (Alfa) and tetraphenylarsonium (Baker), tetraethylammonium (Baker), and tetramethylammonium (Aldrich) chlorides were all dried overnight on the vacuum line before use. In the case of Et_4NCl, the dehydration was carried out at 0 °C to prevent decomposition. Potassium chloride (BDH, AnalaR) was dried in an oven at 110 °C. Ammonium chloride (BDH, AnalaR) and 8-hydroxyquinoline (Anachemia) were used directly. Hydrogen chloride was from Matheson. Selenium oxychloride (Baker) was vacuum distilled before use. Selenium tetrachloride was prepared according to Novak and Suttle.[9] Anal. Calcd: Cl, 64.24. Found: Cl, 64.20. 8-Hydroxyquinolinium chloride was prepared by crystallizing 8-hydroxyquinoline from an excess of 6 M hydrochloric acid required for neutralization. Anal. Calcd: Cl, 19.52. Found: Cl, 19.01. Acetonitrile was dried by refluxing over P_2O_5 for 1 h and then distilled.

Preparation of Chloroselenate(IV). $MSeO_2Cl$. Tetramethylammonium monochloroselenate(IV) was prepared by dissolving stoichiometric amounts of Me_4NCl and SeO_2 in a minimum amount of MeCN and cooling on ice. White crystals of Me_4NSeO_2Cl were filtered out and dried over P_2O_5 in a vacuum desiccator. Anal. Calcd: Cl, 16.07. Found: Cl, 15.93. The tetraphenylarsonium monochloroselenate(IV) is considerably more soluble in MeCN and was prepared by pumping a stoichiometric mixture in MeCN to dryness.

$MSeOCl_3$. $KSeOCl_3$ was prepared by dissolving KCl in an excess of $SeOCl_2$ by warming. Upon cooling, pale yellow crystals were formed. These were collected by filtration and washed with cold CCl_4. Anal. Calcd: Cl, 44.23. Found: Cl, 43.83. This product could also be prepared from a 1:1 mole ratio of reactants in dry MeCN or as

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Table I. Raman Spectra of the Monochloroselenate(IV) Ion[a]

Me_4N-SeO_2Cl[b]	Ph_4As-SeO_2Cl[c]	SeO_2Cl^- in MeCN[d]	assignment
69 (5)			lattice modes
81 (1)	119 (1)		
193 (10)	209 (10)	201 (10, p)	$\nu_2(A')$, $\nu(SeCl)$
267 (2)	279 (4)	280 (2, p)	$\nu_4(A')$, $\delta(SeO_2Cl)$
396 (1)	379 (1)		$\nu_3(A')$, $\delta(SeO_2)$
841 (1)	845 (0)	852 (0, dp?)	$\nu_5(A'')$, $\nu_a(SeO_2)$
903 (3)	895 (8)	897 (10, p)	$\nu_1(A')$, $\nu_s(SeO_2)$

[a] Measured up to 1000 cm^{-1}. [b] Cation bands. [c] Cation bands: 189 (0), 240 (1), 350 (0), 460 (0), 570 (0), 605 (1), 665 (2), 745 (0), 995 (10) cm^{-1}. [d] This solution was prepared from Et_4NCl and SeO_2 in MeCN. Cation bands: 390 (0), 465 (0), 590 (0), 662 (1, p). Solvent bands: 376 (10, dp), 752 (1, p), 917 (20, p) cm^{-1}.

a melt. The tetraethylammonium and tetraphenylarsonium compounds were both prepared by mixing 1:1 mole ratios of the chloride and $SeOCl_2$ in a minimum amount of MeCN and cooling on ice. The product was filtered and dried in a vacuum desiccator. Anal. Calcd. for $Ph_4AsSeOCl_3$: Cl, 18.19. Found: Cl, 17.18. Calcd for $Et_4NSeOCl_3$: Cl, 32.07. Found: Cl, 32.22. The 8-hydroxyquinolinium compound was prepared by mixing 8-hydroxyquinolinium chloride and $SeOCl_2$ in 1:1 stoichiometric amounts in MeCN. Because the product and starting 8-hydroxyquinolinium chloride were of low solubility in MeCN the reaction was slow. The mixture was allowed to react for 24 h with periodic mixing, and then the product was filtered out and washed with MeCN. The product was a slightly brighter yellow than 8-hydroxyquinolinium chloride itself. Anal. Calcd: Cl, 30.61. Found: 29.91.

$MSeCl_5$. Both the tetraethylammonium and tetraphenylarsonium pentachloroselenate(IV) were prepared by mixing 1:1 mole ratios of the chloride and $SeCl_4$ in MeCN, evaporating the solvent to the point of crystallization, cooling and filtering the mixture, and drying the bright yellow crystals under vacuum. Anal. Calcd for $Ph_4AsSeCl_5$: Cl, 27.72. Found: Cl, 27.76. Calcd for Et_4NSeCl_5: Cl, 42.66. Found: Cl, 42.09.

M_2SeCl_6. Ammonium hexachloroselenate(IV) was prepared from a saturated aqueous solution of 2:1 molar ratio NH_4Cl/SeO_2 by bubbling HCl gas through at ice temperature to saturation. Fine crystals of bright yellow $(NH_4)_2SeCl_6$ are deposited from the yellow solution on standing at 0 °C. Anal. Calcd: Cl, 64.90. Found: Cl, 65.14. $(Et_4N)_2SeCl_6$ and $(Ph_4As)_2SeCl_6$ were prepared by mixing in a 2:1 mole ratio the ionic chloride and $SeCl_4$ in dry acetonitrile and evaporating to dryness.

Methods. Analysis. Chloride analyses were done by the Volhard method.

Spectroscopy. Raman spectra were taken using a Jobin-Yvon grating monochromator in conjunction with PAR photon counting. The spectra were excited with a Control Laser argon ion laser. The 4880-Å line was used for solutions and the 5145-Å line for the solids. Spectra were calibrated by means of the argon lines present when the spike filter was not used. Low wattages were used, especially for the solids (100–500 mW), to avoid decomposition of the sample. The slits were fixed at 1000 μm for the solids and 1500 μm for the solutions. All samples were contained in melting point tubes. In the case of the solution spectra saturated solutions in MeCN were used.

Results and Discussion

$MSeO_2Cl$ Compounds. The Raman spectra of Me_4NSeO_2Cl, Ph_4AsSeO_2Cl, and the SeO_2Cl^- ion in MeCN solution are listed in Table I. The spectra of Me_4NSeO_2Cl and SeO_2Cl^- ion in MeCN solution are given in Figure 1. The spectra show no peak corresponding to an SeO single bond stretching vibration and the spectra of the SeO_2Cl^- ion in solids and solution are essentially the same. These two observations indicate that in these cases the anion like the SeO_2F^- ion[10] is monomeric and not bridged. The SeO_2Cl^- ion is expected to have C_s symmetry, giving six normal modes (4 A′ + 2 A″) of which four will vary in intensity according to the direction of the polarization vector of the exciting laser beam. The two highest frequency bands in the spectra, 890 and 840 cm^{-1}, are readily assigned to the symmetric and antisymmetric SeO stretching vibrations, ν_1 (A′) and ν_5 (A″). Both the intensity and polarization of the band at 890 cm^{-1} support its assignment as ν_1. The most intense band in the spectrum is that near 200 cm^{-1} and this is assigned to the SeCl stretching mode, ν_2 (A′). The SeCl stretching vibration is generally found at higher frequencies than this (see the assignments for $SeOCl_3^-$, $SeCl_5^-$, and $SeCl_6^{2-}$ below) but a similar shift (ca. 100 cm^{-1}) to lower frequencies is found for the SeF stretch in the spectrum of the SeO_2F^- ion,[13] compared to the mean of the SeF stretching frequencies in the SeF_5^- ion.[11] The SCl stretching frequency observed for the SO_2Cl^- ion[12] (215 cm^{-1}) also lies substantially below the expected value. The weakness of the selenium to halogen bonds in dioxohaloselenate(IV) anions indicates that SeO_2 is a weak Lewis acid and parallels the behavior of SO_2 in this regard. Of the deformations, the symmetric SeO_2 deformation, ν_3 (A′), is expected to have the highest frequency[13] and the band at ca. 380 cm^{-1} is assigned to this. The remaining band at 273 cm^{-1} is polarized and therefore must be due to the A′ deformation mode, ν_4. The antisymmetric deformation, ν_6 (A″), is not observed. The low-frequency bands in the spectra of the solids (≤ 110 cm^{-1}) are due to lattice vibrations.

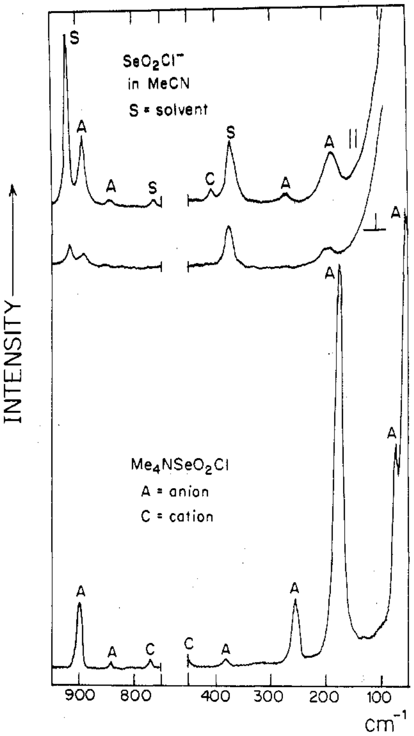


Figure 1. Raman spectra of solid Me_4NSeO_2Cl and the SeO_2Cl^- ion in MeCN solution.

Wasif and Salama[8] have shown that SeO_2 forms a 1:1 complex with halide ion in Me_2SO. According to their equilibrium constants, a 1 M SeO_2Cl^- solution in Me_2SO is over 15% dissociated. No evidence of dissociation of the SeO_2Cl^- ion in MeCN has been found. Apparently, the superior anion solvating properties of Me_2SO relative to MeCN and the favorable solvation of SeO_2 by Me_2SO,[8] which results in the solubility of SeO_2 in Me_2SO (SeO_2 is insoluble in MeCN), favor some dissociation of SeO_2Cl^- in Me_2SO. Further addition of Cl^- to a solution of SeO_2Cl^- ion in MeCN up to 2:1 Cl^-/SeO_2 gives no change in the Raman spectrum and shows that no complex ion other than SeO_2Cl^- is formed in MeCN solution.

M^ISeOCl_3 Compounds. The Raman spectra of solid $KSeOCl_3$ and $C_9H_8NOSeOCl_3$ are given in Figure 2 and those of $Et_4NSeOCl_3$, $Ph_4AsSeOCl_3$, and $Et_4NSeOCl_3$ in MeCN solution are given in Figure 3. All spectra are listed in Table II.

Table II. Raman Spectra of Some Trichloroselenate(IV) Complexes[a]

$KSeOCl_3$	$KSeOCl_3$[b]	C_9H_8NO-$SeOCl_3$[c]	$SeOCl_2$[d]	$Et_4NSeOCl_3$[e]	$Ph_4AsSeOCl_3$[f]	$SeOCl_3^-$ in MeCN[g]	assignment (isolated $SeOCl_3^-$, C_s symmetry)
84 (2)		91 (5)		129 (0)			
101 (1)							
118 (2)							
151 (1)		153 (2)	138 (3, p)	169 (2)	179 (1)	139 (1, p)	$\nu_5(A')$, $\delta(SeCl_{eq})$
194 (0)							
	234[h]						
262 (0)	250 (0)	244 (3)	228 (3, dp)	231 (10)	236 (10)	228 (7, dp?)	$\nu_7(A'')$, $\nu_{asym}(SeCl_{ax})$
277 (2)	281 (2)						
291 (2)	294 (2)	270 (2)	254 (3, p)	261 (7)	267 (8)	248 (7, p)	$\nu_3(A')$, $\nu_{sym}(SeCl_{ax})$
319 (8)	323 (5)	295 (10)	337 (3, dp)	280 (3)	277 (sh, 6)	287 (1, p?)	$\nu_4(A')$, $\delta(SeO)$
337 (1)	341 (1)						
351 (3)	353 (3)						
375 (10)	272 (7)	343 (8)	374 (10, p)	313 (10)	321 (7)	336 (3, p)	$\nu_2(A')$, $\nu(SeCl_{eq})$
923 (3)	924 (10)	956 (3)	937 (3)	949 (3)	954 (3)	951 (2, p)	$\nu_1(A')$, $\nu(SeO)$

[a] Measured up to 1000 cm^{-1}. [b] R. Paetzold and K. Aurich, *Z. Anorg. Allg. Chem.*, 348, 94 (1966). [c] Cation bands: 35 (1), 51 (2), 57 (10), 65 (2), 76 (5), 107 (4), 141 (1), 158 (0), 196 (1), 275 (0), 311 (0), 411 (1), 466 (1), 477 (2), 540 (1), 576 (1), 620 (0), 714 (3), 759 (0), 783 (0), 801 (0), 830 (0), 887 (0), 914 (0) cm^{-1}. [d] Liquid. [e] Cation bands: 390 (1), 662 (1), 791 (0), 896 (0), 998 (0) cm^{-1}. [f] Cation bands: 465 (0), 610 (0), 670 (1), 750 (0), 1000 (4) cm^{-1} (other bands are completely obscured by anion bands, e.g., 189 and 244 cm^{-1}). [g] Cation bands (Et_4N^+): 390 (0), 465 (0), 590 (0), 662 (1, p) cm^{-1}. Solvent bands: 376 (5, dp), 752 (1, p), 917 (10, p) cm^{-1}. [h] Peak due to elemental Se.

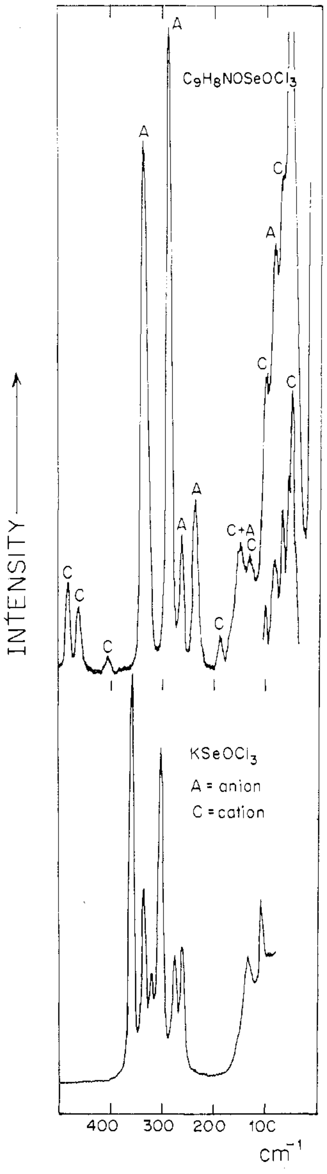


Figure 2. Raman spectra of solid $KSeOCl_3$ and $C_9H_8NOSeOCl_3$.

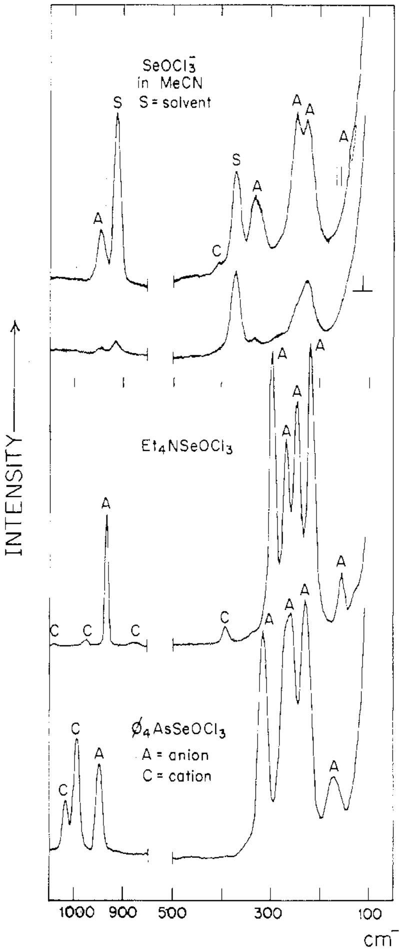


Figure 3. Raman spectra of solid $Et_4NSeOCl_3$ and $Ph_4AsSeOCl_3$ and $Et_4NSeOCl_3$ in MeCN solution. Slits for $Ph_4AsSeOCl_3$ spectrum were 1400 μm. All others were 1000 μm.

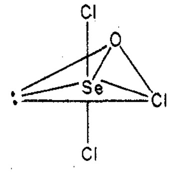
$KSeOCl_3$. The spectrum of $KSeOCl_3$ recorded in this work is similar to that reported by Paetzold and Aurich.[5] The main difference is in the relative intensities of the peaks. Paetzold and Aurich found the highest frequency peak (SeO stretch) to be the strongest, while in this work it is 30% of the intensity of the strongest peak which is the SeCl stretch. These differences are probably the result of preresonance Raman effects.[14]

In addition, the peak at 234 cm^{-1}, reported previously, was not observed in this work. This peak is probably due to the presence of elemental selenium. The same peak is observed in the Raman spectrum of M^ISeO_2F compounds where it has been shown to be due to amorphous selenium.[13]

Moreover, five additional bands below 200 cm^{-1}, not observed in the previous work, have been recorded in this work. Paetzold and Aurich[5] assumed that the $SeOCl_3^-$ ion in $KSeOCl_3$ was not polymeric and assigned the Raman spectrum on the basis of an isolated $SeOCl_3^-$ ion. In this work 11 bands are observed in the Raman spectrum of $KSeOCl_3$ above 100 cm^{-1} while for $Et_4NSeOCl_3$, $Ph_4AsSeOCl_3$, and C_9H_8NO-$SeOCl_3$ only 7, 6, and 6 anion bands respectively are observed in the same region. The isolated $SeOCl_3^-$ ion with C_s symmetry (see below) is expected to exhibit 9 vibrational modes. The greater complexity of the $KSeOCl_3$ spectrum and the large shifts in some of the bands, especially the SeCl stretching modes, from those for $Et_4NSeOCl_3$ and $Ph_4AsSeOCl_3$, which have isolated $SeOCl_3^-$ ions (see below), indicate that strong anion bridging, probably over chloride but also possibly over oxygen, occurs in this compound. The K^+ ion is smaller than the Et_4N^+ and Ph_4As^+ ions and, therefore, favors anion bridging. The X-ray crystal structure of 8-hydroxyquinolinium trichlorooxyselenate[6] shows weak chloride bridging resulting in anion chains which run normal to the flat plane of the cation.

$C_9H_8NOSeOCl_3$. Cordes[6] has shown that this compound may be approximated by the formula $C_9H_8NO^+[SeOCl_2]Cl^-$ where the anion consists of $SeOCl_2$ units with Se–Cl distances of 2.234 and 2.271 Å linked into chains by Cl^- ions 2.963 and 2.992 Å distant from the selenium atom. These latter distances lie between the sum of the nonbonded radii (3.8 Å) and a normal Se–Cl bond distance. Except for the peak at 91 cm^{-1}, the Raman spectrum of the $[SeOCl_3^-]_n$ ion in $C_9H_8NOSeOCl_3$ approximates to that for $SeOCl_2$ itself (Table II), although the frequencies of most of the bands lie between those of $SeOCl_2$ and those of the isolated $SeOCl_3^-$ ion in $Et_4NSeOCl_3$ and $Ph_4AsSeOCl_3$. Chloride bridging in $C_9H_8NOSeOCl_3$ is also reflected in the large differences in spectral band intensities compared to those of $SeOCl_2$, although this could in part be due to the difference in physical state of the two substances. The medium-intensity peak at 91 cm^{-1} may be tentatively assigned to the stretching vibration of a selenium to bridging Cl^- bond.

$Et_4NSeOCl_3$, $Ph_4AsSeOCl_3$, and $SeOCl_3^-$ in MeCN. The Raman spectra of $Et_4NSeOCl_3$ and $Ph_4AsSeOCl_3$ are very similar to each other and to the spectrum of the $SeOCl_3^-$ ion in MeCN solution. The very small differences between the spectra of solid $Et_4NSeOCl_3$ and the $SeOCl_3^-$ ion in solution and between the anion spectra of solids with different size pseudospherical cations (Et_4N^+ and Ph_4As^+) indicate that in these cases an isolated $SeOCl_3^-$ anion is present. Paetzold and Aurich[5] have pointed out that the most probable structure for the $SeOCl_3^-$ ion is based on a trigonal bipyramid with two axial chlorines and the lone electron pair, oxygen, and a chlorine equatorial.



This ion has C_s symmetry and nine bands are expected in the Raman spectrum ($\Gamma = 6\,A' + 3\,A''$) of which six will be polarized. Because of the greater bond strength of equatorial ligands compared to axial ligands in a trigonal-bipyramidal structure, two sets of SeCl stretching vibrations are expected, a single mode at higher frequency for the equatorial chlorine and two bands (antisymmetric and symmetric) for the axial chlorines. This expectation has been fulfilled in related $SeOX_3^-$ species.[5] Judging from the Raman spectra of the SeO_2Cl^- ion and $SeOCl_2$, the SeCl stretching vibrations are expected to be the most intense in the spectrum of the $SeOCl_3^-$ ion. The spectrum of $Et_4NSeOCl_3$ in MeCN has three strong bands in the SeCl stretching region (228, 248, and 336 cm^{-1}), two at lower frequencies corresponding to the axial Cl ligands and one at higher frequency due to the equatorial Cl atom, as expected for the stereochemistry proposed. The polarization measurements (Figure 3) show the higher frequency vibration of the Se–Cl_{ax} stretching modes (241 cm^{-1}) to be an A′ mode. The relative order and frequencies of these modes are comparable to what is observed in the Raman spectra of the linear $BrCl_2^-$[15] (ν_s 267 cm^{-1}, ν_a 223 cm^{-1}) and ICl_2^-[16] (ν_s 272 cm^{-1}, ν_a 218 cm^{-1}) ions, which are reasonable uninegative models for the linear $SeCl_2$ group in the $SeOCl_3^-$ ion. A partial assignment of the spectrum of the isolated $SeOCl_3^-$ ion is given in Table II. The normal modes ν_6, ν_8, and ν_9 (all A′′) are not observed.

Table III. Raman Spectra of Some Pentachloroselenate(IV) Complexes[a]

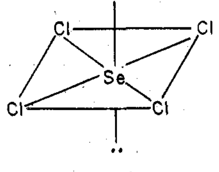
Et_4N-$SeCl_5$[b]	Ph_4As-$SeCl_5$[c]	Et_4N-Te-Cl_5[d]	$SeCl_5^-$ in MeCN[e]	assignment ($Cl'XCl_4$)
	42 (3)			$\nu_9(E)$ and lattice modes
65 (8)	62 (4)			
	94 (3)			
129 (0)	115 (0)			
	143 (0)	143		$\nu_6(B_2)$, $\delta_{sym}(XCl_4)$ in plane
146 (2)	154 (1)		150 (2, br, p)	$\nu_3(A_1)$, $\delta_{sym}(XCl_4)$ umbrella
	171 (0)	115		$\nu_8(E)$, $\delta(Cl'XCl_4)$ wag
213 (1)	213 (1)	208	239 (8, dp)	$\nu_7(E)$, $\nu_{asym}(XCl_4)$
237 (1)	230 (2)	244		
260 (5)	262 (10)	295	260 (8, sh, dp?)	$\nu_4(B_1)$, $\nu_{sym}(XCl_4)$ out of phase
288 (10)	282 (9)	266	272 (10, p)	$\nu_2(A_1)$, $\nu_{sym}(XCl_4)$ in phase
333 (6)	356 (6)	336	333 (1, p)	$\nu_1(A_1)$, $\nu(XCl')$

[a] Measured up to 1000 cm^{-1}. [b] Cation bands: see Table II. [c] Cation bands: 90 (1), 183 (0), 244 (1), 465 (0), 610 (0), 670 (0), 1000 (1) cm^{-1}. [d] Reference 17. [e] Cation (Et_4N^+) bands and solvent bands: see Table II.

Thus, the Raman spectra of M^ISeOCl_3 compounds show a variety of anion stereochemistries. $KSeOCl_3$ has a polymeric structure with strong Cl^- bridges. 8-Hydroxyquinolinium oxotrichloroselenate(IV) exhibits weak chloride bridging and the spectrum is that of $SeOCl_2$ units moderately perturbed by the chloride bridges. Finally, the $Et_4NSeOCl_3$ and $Ph_4AsSeOCl_3$ compounds have isolated or very weakly bridged $SeOCl_3^-$ units.

M^ISeCl_5 Compounds. The Raman spectra of solid Et_4NSeCl_5 and $Ph_4AsSeCl_5$ and a saturated solution of Et_4NSeCl_5 in MeCN are shown in Figure 4 and the spectra are listed in Table III. Included in Table III are the spectra of the $TeCl_5^-$ ion,[17] for comparison, and an assignment under C_{4v} symmetry.

All three $SeCl_5^-$ spectra are closely parallel, which indicates that the $SeCl_5^-$ ion has a similar stereochemistry in solution as well as in the two solids. The isolated $SeCl_5^-$ ion is expected to have C_{4v} symmetry ($\Gamma_{vib} = 3\,A_1 + 2\,B_1 + B_2 + 3\,E$).



All nine vibrational modes will be active in the Raman spectrum and of these, three will be polarized. Four of the normal modes involve SeCl stretching motions and are ex-

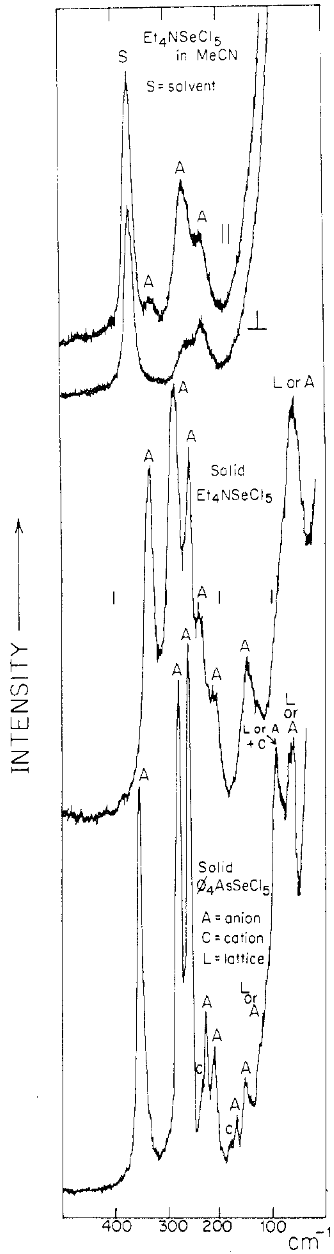


Figure 4. Raman spectra of solid Et_4NSeCl_5 and $Ph_4AsSeCl_5$ and Et_4NSeCl_5 in MeCN solution.

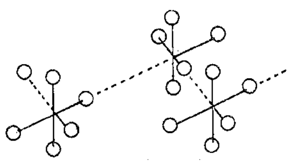
Table IV. Raman Spectra of Some Hexachloroselenate(IV) Complexes[a]

$(NH_4)_2$-$SeCl_6$	$(Et_4N)_2$-$SeCl_6$[b]	$[Ph_4As]_2$-$SeCl_6$[c]	$SeCl_6^{2-}$[d] in MeCN	assignment
128 (0)	53 (2)	64 (1)		ν_L[e]
171 (7)	147 (6)	148 (3)	171 (1, p?)	ν_5 (T_{2g})
248 (10)	241 (10)	232 (10)	235 (10, dp)	ν_2 (E_g)
292 (10)	284 (8)	274 (7)	284 (9, p)	ν_1 (A_{1g})

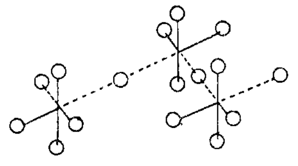
[a] Measured to 1000 cm⁻¹. [b] Cation modes: see Table II. [c] Cation modes: 90 (3), 183 (1), 465 (0), 610 (0), 670 (0), 1000 (2) cm⁻¹. [d] Cation modes (Ph_4As^+): 245 (0), 670 (0), 1000 (4) cm⁻¹. Solvent modes: 376 (20, dp), 752 (0, p), 917 (30, p) cm⁻¹. [e] Lattice mode.

pected to occur at frequencies greater than 200 cm⁻¹. Two of these stretching modes will be polarized. The solution spectrum has four stretching bands, 239, 260, 272 (p), and 333 (p) cm⁻¹, of which two are polarized and a single broad deformation mode, 150 (p) cm⁻¹, which is also polarized and this is consistent with C_{4v} symmetry. The observations are not consistent with a trigonal-bipyramidal geometry (D_{3h}; $\Gamma = 2A_1 + 2A''_2 + 3E' + E''$) for which three stretching modes, two of which are polarized, are active in the Raman effect and for which all of the deformations are depolarized. In the spectra of square-pyramidal species (ZX_5), the axial ligand stretching vibration, ν_1 (A_1), has the highest frequency, followed by the in-phase ZX_4 stretching vibration of the equatorial ligands, ν_2 (A_1).[11,18] Both of these modes are polarized and are readily assigned in the $SeCl_5^-$ solution spectrum (ν_1 333 cm⁻¹; ν_2 272 cm⁻¹). The third A_1 mode, ν_3, the umbrella deformation, is also observed in the solution spectrum at 150 cm⁻¹. The remaining two bands in the spectrum are assigned by analogy with the assignment of other C_{4v} species. The two bands are stretching modes and, of the two, the B_1 mode, ν_4, is more intense than the E mode, ν_7, in the Raman spectra of other C_{4v} species.[11,17] Upon consideration of the intensities of the analogous bands in the solids listed in Table III, the higher frequency peak near 260 cm⁻¹, which is more intense than that near 235 cm⁻¹, is assigned as ν_4 and the other band is assigned as ν_7. The ν_4 mode (B_1) appears at higher frequency than the ν_7 mode (E) in the spectrum of the $TeCl_5^-$ ion[17] in agreement with the assignment given here.

The Raman spectra of solid Et_4NSeCl_5 and $Ph_4AsSeCl_5$ both show five stretching mode bands which suggest that there is weak chloride bridging or anion site symmetry lower than C_{4v} in these compounds. The lowest frequency stretching mode, which is assigned to ν_7 and is doubly degenerate, is split into two peaks. A similar observation has been made for the spectrum of the analogous Et_4NTeCl_5 compound.[17] The crystal structure of $PCl_4^+TeCl_5^-$ shows $[TeCl_5^-]_n$ chains with cis bridging and pseudooctahedral coordination of Te.[19] The chloride bridges in the structure are symmetric and have relatively long Te–Cl bonds (2.8 Å) while the Te–Cl bonds trans to the bridging Cl's and the Te–Cl bonds above and below the bridging plane are short (2.4 and 2.5 Å, respectively). The vibrational spectra for the compound[20] show four stretching bands above 300 cm⁻¹, which correspond to the symmetric and antisymmetric stretching modes of the two pairs of closely bound Cl ligands. This spectrum differs greatly from that of Ozin and Vander Voet[17] which shows only one band above 300 cm⁻¹. The observation of strong chloride bridging for $PCl_4^+TeCl_5^-$ is probably due to cation size. The radius of the PCl_4^+ cation is 3.6–3.8 Å (the sum of the P–Cl distance in PCl_4^+ [19] and the Cl van der Waals radius) while that of the Et_4N^+ cation is 4.0–4.2 Å.[21] Thus the $TeCl_5^-$ anions can approach each other more closely in $PCl_4^+TeCl_5^-$ than in $Et_4N^+TeCl_5^-$ and symmetric bridges are formed while in the latter compound asymmetric bridges may be favored, since the anions cannot approach as closely.



asymmetric bridging



symmetric bridging

In the asymmetric bridged structure, each anion approaches square-pyramidal symmetry. The Raman spectra of the M^ISeCl_5 compounds parallel that of Et_4NTeCl_5[17] with respect to stretching frequencies and the $SeCl_5^-$ anion is probably weakly bridged in these solids. On this basis (C_{4v} symmetry), the bands observed in the solid spectra, additional to those in the solution spectra, may be tentatively assigned. The ν_5 mode is rarely observed in the Raman spectra of C_{4v} (ZX_5) species and is, therefore, not considered here. In other related C_{4v} species[11,18] the remaining unassigned modes decrease in order of frequency $\nu_8(E) > \nu_6(B_2) > \nu_9(E)$ and the next highest bands

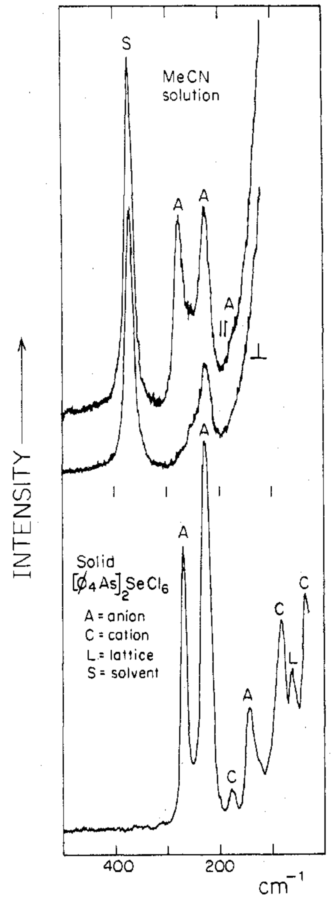


Figure 5. Raman spectra of $[Ph_4As]_2SeCl_6$ as solid and in MeCN solution.

at 171 and 143 cm^{-1} in the $Ph_4AsSeCl_5$ spectrum are assigned accordingly to ν_8 and ν_6, respectively. The ν_9 mode, which has the lowest frequency of all of the vibrations, cannot be assigned definitely among the four remaining unassigned bands, which are due, in part, to lattice modes of similar frequency. The assignment proposed is given in Table III. The relative order of the bands differs from that given for the $TeCl_5^-$ ion[17] but this is not unexpected, since, first of all, the central atom differs in the two anions, second, the Et_4NTeCl_5 work did not include polarization measurements, and finally, the assignment for $TeCl_5^-$ depends upon a force constant calculation based upon models of doubtful validity.[22,23]

$M^I{}_2SeCl_6$ Compounds. The spectra of solid $[Ph_4As]_2SeCl_6$, $[Et_4N]_2SeCl_6$, and $[NH_4]_2SeCl_6$ and the $SeCl_6^{2-}$ ion in solution are listed in Table IV. The spectra of $[Ph_4As]_2SeCl_6$ in the solid state and in solution are given in Figure 5. The spectra of solid compounds exhibit four modes: a lattice mode (ν_L) and three internal vibrational modes (ν_1, ν_2, and ν_5). Of the vibrational modes the highest and lowest are polarized in the solution spectrum and the former has a polarization ratio of 0. All of these observations are consistent with exact octahedral symmetry as concluded from spectroscopy, by other authors.[1]

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Registry No. Me_4NSeO_2Cl, 68796-72-5; Ph_4AsSeO_2Cl, 68757-88-0; $KSeOCl_3$, 68757-89-1; $Et_4NSeOCl_3$, 68757-90-4; $Ph_4AsSeOCl_3$, 68757-91-5; $C_9H_8NOSeOCl_3$, 68757-93-7; Et_4NSeCl_5, 68832-74-6; $Ph_4AsSeCl_5$, 68832-75-7; $(NH_4)_2SeCl_6$, 59250-59-8; $(Et_4N)_2SeCl_6$, 68782-43-4; $(Ph_4As)_2SeCl_6$, 68782-44-5; SeO_2, 7446-08-4; $SeOCl_2$, 7791-23-3; $SeCl_4$, 10026-03-6.

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