Spectrochimica Acta, Vol. 38A, No. 5, pp. 569–574, 1982
Printed in Great Britain.

0584-8539/82/050569–06$03.00/0

Raman spectra of seleninyl halides

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(*Received* 8 *June* 1981)

Abstract—The Raman spectra of selenium oxide difluoride, dichloride, dibromide, chloride fluoride and bromide chloride have been measured in solid and liquid phases and in solution in acetonitrile (MeCN). In all cases, as the state of molecular aggregation increases, the SeO stretching frequency falls, indicating the formation of oxygen bridges. Vibrational assignments are given for selenium oxide dibromide, bromide chloride and chloride fluoride and force constants have been calculated for all of the selenium oxide halides. The degree of formation of selenium oxide fluoride from selenium oxide dichloride and difluoride is shown to be less than that of selenium oxide bromide chloride from the dibromide and dichloride and this attributed to the importance of the back bonding mechanism in SeF bonds, which favours increased SeF bond strength when the second halogen is fluorine instead of chlorine, a mechanism which is not as significant for SeCl and SeBr bonds.

INTRODUCTION

Selenium oxide halides with one type of halogen, $SeOX_2$, are known for all of the halides except the iodide. Selium oxide iodide is apparently unstable due to autooxidation of iodide be Se(IV). Among the mixed halides, SeOXY, the chloride and bromide chloride are known. The vibrational spectra of selenium oxide difluoride[1–3] and selenium oxide dichloride[2, 4] have been thoroughly studied by several groups. The spectra are consistent with a pyramidal shape in both cases, and this is confirmed for the fluoride by a recent X-ray[5] and microwave studies[6] and for the chloride by electron diffraction[7]. Raman spectral studies of selenium oxide chloride, pure and in solution[8,9] indicate significant association, which may take place by oxygen[4, 9] or by chlorine[8] bridging. Such bridging is not as apparent in the spectra of the fluoride[3]. The Raman spectrum of selenium oxide bromide has been reported for the pure compound[10] and in solution[10, 11].

Little work has been done on the characterization of mixed halides. The selenium-77 NMR spectra of selenium oxide chloride fluoride and of a mixture of selenium oxide chloride and bromide have been reported[12] and the preparation of pure selenium oxide bromide chloride has been described[13]. No vibrational spectroscopic characterization of these mixed compounds has been reported and the assignment of the Raman spectrum of selenium oxide bromide is incomplete. For these reasons and as part of a continuing experimental study on halogen compounds of Se(IV), I have carried out a complete Raman spectral characterization of the selenium oxide halides.

EXPERIMENTAL

Selenium oxide was prepared from the oxide chloride (Baker) and potassium fluoride (BDH) by the method of PAETZOLD and AURICH[14]. The purity was monitored by Raman spectroscopy after each vacuum distillation step. The product was shown to be chloride free by testing an aqueous solution with silver nitrate. Particularly sensitive as criteria of purity were the peak at 201 cm^{-1} due to the chloride fluoride and the ratio of the peak height at *ca.* 375 cm^{-1}, due to the fluoride, the chloride and the chloride fluoride, to that at 309 cm^{-1}, due to the fluoride, which for the pure fluoride is 0.80, using the 514.5 nm exciting line. Final vacuum distillation from dry potassium fluoride was done in a break seal apparatus and this yielded a colourless clear liquid.

Selenium oxide chloride (Baker) was vacuum distilled before use (83°C at 15 torr).

Selenium oxide bromide was prepared from stoichiometric quantities of selenium (Baker), selenium dioxide (Alfa) and bromine (BDH) by the method of LENHER[15]. The product was further purified by vacuum sublimation, which yielded bright yellow crystals. Anal. calcd: Br, 62.73; found: Br, 62.42.

Selenium oxide bromide chloride was made by mixing equimolar quantities of the chloride and the bromide. The product was a red-orange liquid with a sharp melting point at 17°C. The preparation of the bromide chloride by chlorination of a mixture of diselenium dibromide and selenium dioxide has been reported earlier[13] but yields were low(13%).

Acetonitrile was purified by refluxing over phosphorus pentoxide followed by distillation.

Raman spectra were recorded as described earlier[16]. The 514.5 nm argon ion line was used to excite the spectra while the slits were fixed to give a resolution of 8 cm^{-1} at 300 cm^{-1}. The spectra were recorded at ambient temperature (23°C) unless otherwise specified.

Normal coordinate analysis and force constant calculations were carried out 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 N.R.C.C. The programs are based upon the original approach of SCHACHTSCHNIEDER[17].

RESULTS AND DISCUSSION

The Raman spectra of the selenium oxide halides, $SeOX_2$ (X = F, Cl, Br), and the mixed halides, SeOXY (X = Cl, Y = F, Br), are given in Tables 1 and 2. The spectra of the fluoride, the chloride and a mixture of the two are shown in Fig. 1 while that of the bromide in acetonitrile and the bromide chloride are shown in Fig. 2.

Selenium oxide halides

The spectra of liquid and solid selenium oxide fluoride recorded in this work agree well with those reported earlier[3]. Similarly, the spectra of liquid chloride and solid bromide are in good agreement with previous work[4, 10]. The Raman spectrum of solid chloride differs from that reported previously[4] and this is no doubt the result of a phase change. The spectrum listed in Table 1 was recorded at −12°C while that reported in the literature was taken at −196°C. In general the frequencies of the stretching modes of the fluoride and chloride decrease when passing from the isolated molecular state (vapour or matrix isolated states) to the liquid and solid states, indicating that both halogen and oxygen bridges are formed in the condensed phases. There is abundant evidence of this in the structures of solid fluoride[5] and $Me_4NCl\cdot 5SeOCl_2$[18]. The tendency of Se(IV) in these oxide halides, to increase its coordination number by forming bridges is indicative of their electron acceptor properties, which are also reflected in the formation of many adducts by these compounds [16, 19, 20]. This Lewis acid behaviour is also evident in the spectra of solutions of selenium oxide fluoride and chloride in acetonitrile where the solvent is acting as the electron donor. This interaction results in a decrease in all of the stretching frequencies of the halides relative to those in the isolated molecule as seen in Table 1. A similar situation arises for iodine pentafluoride in acetonitrile[21].

The Raman spectrum of selenium oxide bromide has been reported by two groups[10,11] but no complete assignment has been made. My results, which are given in Table 1 and Fig. 2 (trace A), show good agreement with those of BROCKER and DEMİRAY[10] although there are significant differences in the solid spectra. The spectrum

Table 1. Raman spectra of selenium oxide halides, $SeOX_2$

$SeOF_2$			$SeOCl_2$					$SeOBr_2$	
vapour[a]	MeCN soln	liquid	vapour[b]	matrix isol[c]	MeCN soln	liquid	solid	MeCN soln	solid
1049	1003(10,p)	1007(10,p)	969	982	972(3,p)	943(3,p)	994(2) 911(5)	961(2,p)	908(4) 889(3)
667	648(8,p)	664(7,p)	379	378	367(10,p)	379(10,p)	404(10) 394(4,sh)	284(9,p)	297(7) 287(5,sh)
637	604(3)	599(3)	-	352	339(3)	341(3)	349(1) 341(1,sh)	-	270(5)
362	372(2,p)	375(2,p)	-	281	268(3,p)	264(3,p)	276(3)	223(10,p)	227(10)
282	305(2)	309(2)	259	264	242(2)	237(2)	257(3) 243(1)	199(2)	205(7)
253	278(1,p)	284(1,p)	154	155	151(3,p)	148(3,p)	155(4) 104(1)	96(7,p)	102(10)

[a] L. E. ALEXANDER and I. R. BEATTIE, *J. Chem. Soc.* 1745 (1972).
[b] W. BUES, W. BROCKNER and F. DEMIRAY, *Z. Anorg. Allg. Chem.* **434**, 249 (1977).
[c] G. H. WESTPHAL and F. ROSENBERGER, *J. Molec Spectrosc.* **83**, 355 (1980).

Table 2. Raman spectra of mixed selenium oxide halides SeOXY

SeOClF in $SeOF_2/SeOCl_2$ liquid	SeOClF in MeCN/ $SeOF_2/SeOCl_2$	SeOBrCl liquid	SeOBrCl solid (-50°C)	SeOBrCl in MeCN
975(3)	992	930(3,p)	909(6)	957(4)
			895(5)	
			385(8)	
620(3)	596	356(6,p)	357(4,sh)	350(4)
			298(8)	
365(10)	-	267(10,p)	280(8)	277(9)
			265(5,sh)	254(2)
-	-		234(8,sh)	
			226(9,sh)	
250(2)	255	205(9,p)	215(10)	205(10)
			159(1)	
			135(5)	
201(1)	204	119(2,p)	105(7)	-

reported by BROCKNER and DEMIRAY was taken at −196°C while mine was recorded at 25°C. The differences are due, no doubt, to some phase change occurring between these two temperatures. The spectrum of FUTEKOV and SPECKER[11] has two bands at 172 and 310 cm^{-1} which do not appear in my spectrum or that of BROCKER and DEMIRAY.

A complete assignment of the spectrum of the bromide presents some difficulty particularly with regard to the symmetric SeBr stretch, ν_2, and the symmetric SeOBr deformation, ν_3. The highest and lowest bands in the solution spectrum (961 and 96 cm^{-1}), both of which are polarized, are readily assigned to ν_1, the SeO stretch and ν_4, the $SeBr_2$ deformation. The two remaining polarized modes belong to ν_2 and ν_3. On the basis of intensity, the band at 227 cm^{-1} would appear to be due to ν_2, the SeBr symmetric stretching mode but this would mean that the symmetric SeO deformation, ν_3, would be at higher frequency than the comparable mode in selenium oxide chloride. An unequivocal assignment can however, be made with the aid of normal coordinate analysis.

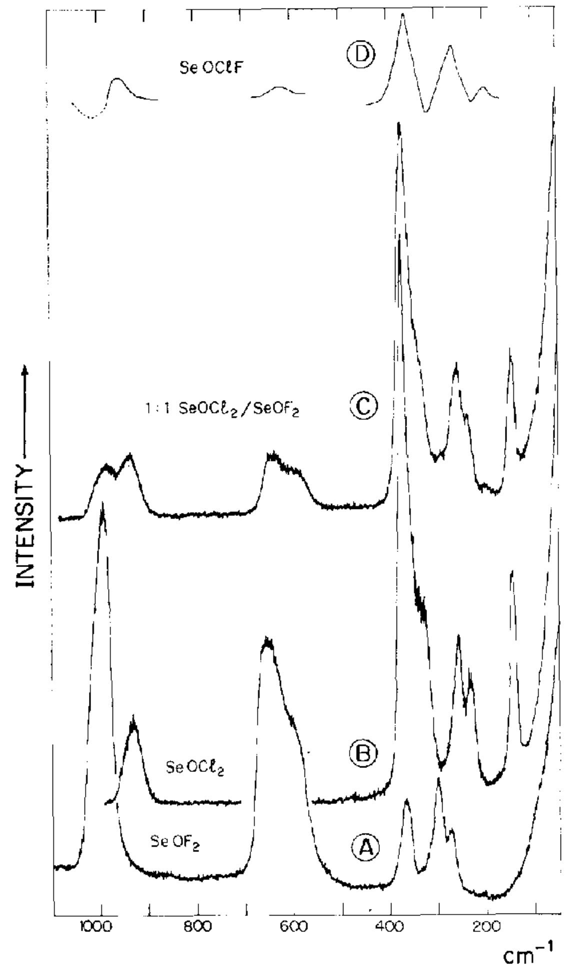

Fig. 1. Raman spectra of liquid $SeOF_2$ (trace A), $SeOCl_2$ (trace B) and an equimolar mixture of $SeOCl_2$ and $SeOF_2$ (trace C). Trace D is the spectrum of SeOClF made up from traces A, B and C.

Force constants have been calculated for selenium oxide fluoride and chloride, assuming tetrahedral angles and using estimated bond distances[3]. Structure determinations have now been reported for both of these compounds in the vapour phase[6, 7] and a more accurate normal coordinate analysis is warranted. The structural parameters for the halides are given in Table 3. The values for the bromide have been estimated from parameters for the thionyl halides[22]. Normal coordinate analysis was carried out for the spectra of the halides in acetonitrile as well as for the spectra of fluoride vapour[3] and matrix isolated chloride[23]. The force constants are listed in Table 4. The force constants for the isolated and unsolvated fluoride and chloride are no doubt more meaningful in terms of the nature of the bonding in these molecules but, in as much as selenium oxide bromide is thermally of low stability and not readily studied in the vapour phase, the results for the halides dissolved in acetonitrile are useful for comparison purposes. Comparison of force constants for the thionyl halides[22] permitted an estimate to be made from the force constants for selenium oxide fluoride and chloride, for the force constants of selenium oxide bromide. These force constants were used as a starting point to calculate the constants listed in Table 4 and confirmed the assignment of the band at 284 cm^{-1} to the symmetric SeBr stretching mode, ν_2, and that at 223 cm^{-1} to the symmetric SeO

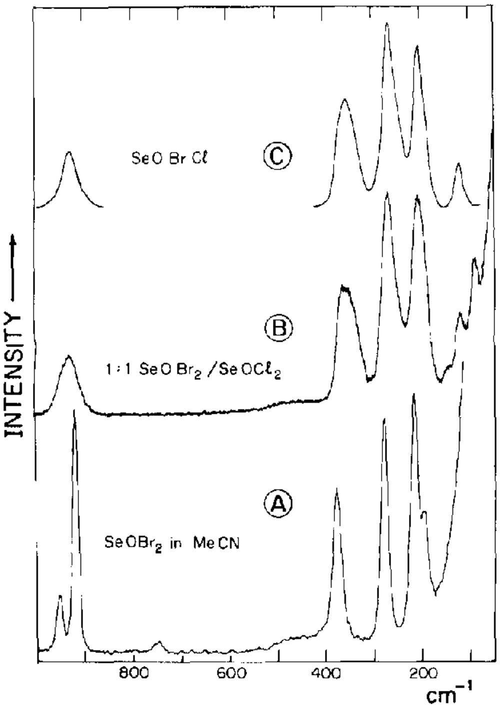

Fig. 2. Raman spectra of $SeOBr_2$ in MeCN (trace A) (solvent peaks at 376, 752 and 917 cm^{-1}) and an equimolar mixture of $SeOBr_2$ and $SeOCl_2$ (trace B). Trace C represents the corrected spectrum of SeOBrCl.

deformation, ν_3. The potential energy distribution shows that the d(SeBr) internal coordinate is 70.1% involved in the 284 cm^{-1} mode and the $\angle$(OSeBr) internal coordinate is 70.7% involved in the 223 cm^{-1} mode.

The remaining depolarized band in the spectrum of selenium oxide bromide in acetonitrile at 199 cm^{-1} is assigned as the antisymmetric SeOBr deformation, ν_6. This mode lies below the symmetric SeOBr deformation, ν_3, in the other halides also. The antisymmetric SeBr stretching mode, ν_5, is expected to lie close to the symmetric SeBr stretch, ν_2, as it does in the other halides and, for the bromide, it is hidden by the strong band of ν_2 at 284 cm^{-1}. Two strong bands appear in this region in the spectrum of solid bromide. The complete assignment for selenium oxide bromide, as well as the chloride and fluoride, appears in Table 5.

Force constants for the halides are listed in Table 4. These constants reproduce the observed frequencies exactly. All of the force constants decrease with decreasing halogen electronegativity as expected. On passing from the isolated to the solvated fluoride and chloride, the stretching force constants decrease reflecting a decrease in bond strength. This results from a reduction in positive charge on selenium as a result of electron donation from the solvent. The effect is more pronounced for the fluoride than for the chloride due to the greater Lewis acidity of the former. The deformation constants, on the other hand, show an increase upon solvation in the case of the fluoride which indicates greater steric restrictions in the coordination sphere of the selenium atom due to the presence of the solvent molecules. This effect is not observed for the chloride, where solvent coordination is less strong.

Table 3. Structural parameters for selenium oxide halides, $SeOX_2$

$SeOX_2$	$SeOF_2$[a]	$SeOCl_2$[b]	$SeOBr_2$[c]
d_1(SeO) (Å)	1.580	1.612	1.61
$d_2 = d_3$(SeX) (Å)	1.727	2.204	2.40
$\alpha_1 = \alpha_2$((OSeX))	104.8	105.8	105
β($\angle$(XSeX))	92.4	96.8	97.0

[a] I. C. Bowater, R. D. Brown and F. R. Burden, *J. Molec. Spectrosc.* **23**, 272 (1967).

[b] D. Gregory, I. Hargittai and M. Kolonits, *J. Mol. Struct.* **31**, 261 (1976).

[c] Estimated.

MIXED SELENIUM OXIDE HALIDES

Selenium oxide chloride fluoride

Selenium-77 NMR measurements on mixtures of the chloride and fluoride show evidence for the formation of the chloride fluoride in the

Table 4. Force constants for selenium oxide halides, $SeOX_2$

Force constant (mdyn/Å)	$SeOF_2$	$SeOCl_2$	$SeOBr_2$	$SeOF_2$	$SeOCl_2$
		(in MeCN)		(vapour)	(matrix isol.)
k_1(SeO stretch)	7.82	7.37	7.20	8.56	7.52
k_2(SeX stretch)	3.51	1.70	1.62	3.81	1.78
k_α/d_1d_2(XSeO bend)	0.48	0.31	0.24	0.43	0.36
k_β/d_2^2(XSeX bend)	0.37	0.18	0.13	0.30	0.19
k_{22}(stretch interaction)	0.28	0.25	0.16	0.22	0.28
$k_{\alpha\alpha}/d_1d_2$(bend interaction)	0.09	0.05	0.04	0.10	0.03

Table 5. Assignment of the normal modes of selenium oxide halides, $SeOX_2$

$SeOF_2$	$SeOCl_2$	$SeOBr_2$	Mode	Approximate Description
1003	972	961	$\nu_1(A')$	ν(SeO)
648	367	284	$\nu_2(A')$	$\nu(SeX_2)_{sym}$
372	268	223	$\nu_3(A')$	$\delta(SeOX)_{sym}$
278	151	96	$\nu_4(A')$	$\delta(SeX_2)$
604	339	[284][b]	$\nu_5(A'')$	$\nu(SeX_2)_{antisym}$
305	242	199	$\nu_6(A'')$	$\delta(SeOX)_{antisym}$

[a] Spectra of MeCN solutions.

[b] Not observed due to coincidence with ν_2.

mixture[12]. The Raman spectrum of the liquid formed by a 1 : 1 mole ratio mixture of the fluoride and chloride is given in Fig. 1 and careful comparison of this spectrum with that of liquid fluoride and chloride (given in the same figure) shows that it is not simply the sum of the spectra of the pure compounds. Because these compounds have a tendency to be bridged, the differences may be due to $SeOF_2$–$SeOCl_2$ bridging but the overall consistency of the interpretation in terms of the formation of SeOClF both in the pure liquid mixture and in acetonitrile solutions and the known presence of this compound in the mixture[12] favours this latter interpretation with other effects secondary. Visual comparison of the spectra of the fluoride and chloride with that of the mixture shows peaks due to chloride fluoride at 201 cm^{-1} and *ca.* 250, 370 and 975 cm^{-1}. The peaks due to the chloride fluoride are weak, indicating that it is present in relatively low concentration. Quantitative subtraction of the normalized spectra of the fluoride and chloride from that of the mixture gives trace D in Fig. 1. These bands as well as those arrived at by the same procedure for acetonitrile solution are listed in Table 2. Force constants for the chloride fluoride may be estimated from those for the chloride and fluoride (acetonitrile solutions) listed in Table 4 and structural parameters may be calculated to a good approximation from the data in Table 3. For instance, the mean values for d(SeO) and f(SeO) for the fluoride and chloride may be used while f(SeCl) and f(SeF) as well as the corresponding distances may be taken from their respective molecules directly. These parameters may be used to calculate an approximate spectrum for the chloride fluoride, which is listed in Table 6. The agreement with the observed frequencies is reasonable and the location by this calculation of the sixth normal mode at 337 cm^{-1} indicates that this mode is obscured by the stronger band due to the chloride fluoride at 365 cm^{-1}. Assignment of the observed bands of the chloride fluoride (C_1 symmetry; $\Gamma = 6A$) is also given in Table 6. A complete normal coordinate analysis is not warranted in this case due to the uncertainty in the value of the interaction constants and the observation of only five normal modes. The spectrum of a frozen equimolar mixture of the fluoride and chloride (−12°C) showed only bands for solid fluoride and chloride.

Selenium oxide bromide chloride

The selenium-77 NMR spectrum of an equimolar mixture of selenium oxide bromide and chloride shows a single resonance, indicating rapid exchange between the reactants and any product formed, or complete formation of the bromide chloride[12]. It is reported that the bromide chloride can be distilled and the liquid is regarded as a pure compound[13]. An equimolar mixture of chloride and bromide has a sharp melting point at 17°C indicating that the solid is a pure compound. The Raman spectra of solid (−50°C) and liquid bromide chloride and the bromide chloride in acetonitrile are listed in Table 2 and the spectrum of the liquid is shown in Fig. 2. The spectrum of the solid equimolar mixture of bromide and chloride differs substantially from that of the solid bromide and chloride alone. For instance, the strongest band in the spectrum of solid chloride at 404 cm^{-1} is missing. The solid consists apparently of only bromide chloride as indicated by the melting point. The spectrum of the liquid mixture of the chloride and bromide, however, consists of seven bands instead of the expected six. Moreover, weak bands are found at 92 and 149 cm^{-1} closely coincident with bands of the bromide and chloride respectively. However, the strongest band in the spectrum of liquid chloride at 379 cm^{-1} is not evident, apparently masked by a new band at 357 cm^{-1}. It is obvious that the liquid mixture consists principally of bromide chloride with small amounts of chloride and bromide. Quantitative subtraction of the normalized spectra

Table 6. Assignments of the normal modes of SeOXY molecules

SeOClF		SeOBrCl		Mode	Approximate Description
obs'd	predicted	obs'd	predicted		
992	981	957	960	ν_1	ν(SeO)
596	621	350	353	ν_2	ν(SeY)
365^b	353	277	280	ν_3	ν(SeX)
-	337	254	258	ν_4	δ(OSeY)
255	246	205	195	ν_5	δ(OSeX)
204	205	119^b	112	ν_6	δ(XSeY)

[a] MeCN solution spectra.

[b] Taken from spectra of liquid SeOXY.

[c] Calculated assuming force constant and structural parameters taken or calculated from $SeOX_2$ values (Table 4).

of the chloride and bromide from the spectrum of the mixture results in trace C in Fig. 2.

The spectrum of a solution of an equimolar mixture of chloride and bromide in acetonitrile shows no evidence of bands due to the pure reactants.

A normal coordinates calculation, using force constants and molecular parameters worked out as for the chloride fluoride, was carried out. The calculated frequencies are listed in Table 6 and the agreement with the observed values for the bromide chloride in acetonitrile is reasonable. The potential energy matrix from this calculation indicates that for ν_3 (280 cm^{-1}) 44.5% of the energy is involved in SeBr stretching (32.7% in SeOBr angle bending) while for ν_4 (258 cm^{-1}), 64.6% of the energy is involved in SeOCl angle bending (29.7% in SeBr stretching). Obviously assignment of these modes as SeBr stretching and SeOBr deformation modes respectively is questionable. More complete treatment of the normal coordinate analysis is not warranted in view of the uncertainty in the interaction constants and in the frequency of the lowest energy mode.

Selenium oxide bromide fluoride

Selenium oxide bromide is not soluble in selenium oxide fluoride over the entire composition range. The highest bromide/fluoride mole ratio, which produced an homogeneous mixture, was 1 : 3. This solution as well as an equimolar bromide/fluoride mixture in acetonitrile showed only peaks due to the bromide and fluoride. If any selenium oxide bromide fluoride was formed, it was not detectable by Raman spectroscopy.

CONCLUSION

It is of interest that the chloride fluoride is the minor constituent in an equimolar mixture of the chloride and fluoride while the mixed halide, selenium oxide bromide chloride, is the major component in the equimolar mixtures of bromide and chloride. This is true for the liquid mixtures, the acetonitrile solutions and the solids. Statistically the mole ratio of $SeOX_2/SeOY_2/SeOXY$ should be 1 : 1 : 2. Entropy considerations favour formation of SeOXY and, provided that bond energies are transferable from the $SeOX_2$ species to the mixed halides, one would expect a mixture. The degree of formation of chloride fluoride and bromide chloride indicates that the bond energies are not transferable and enthalpy plays a role in the disproportionation equilibria. Apparently, the SeF bonding in the fluoride is strengthened by the presence of the second fluorine relative to the SeF bond in the chloride fluoride and this increase in SeF bond strength is larger than any gain in SeCl bond strength as a result of replacement of Cl by F on going from the chloride to the chloride fluoride. Perhaps, the tendency for fluorine to form π back bonds provides a mechanism for strengthening of bonds to fluorine when the atom to which it is bonded becomes effectively more electronegative by binding to another fluorine, while such a mechanism does not arise for bonds to Cl. Such a bonding mechanism would not be important for the mixtures of bromide and chloride, entropy effects would dominate and disproportionation to bromide chloride would be more extesnive.

Acknowledgements—PIERRE LAHAIE is thanked for technical assistance and the National Research Council of Canada is thanked for financial support.

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