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CANOGA PARK, CALIFORNIA 91304

Vibrational Spectra and Force Constants of the Square-Pyramidal Anions SF_5^-, SeF_5^-, and TeF_5^-

BY KARL O. CHRISTE,* E. C. CURTIS, CARL J. SCHACK, AND D. PILIPOVICH

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The adducts of CsF with SeF_4 and SF_4 have been prepared and characterized by vibrational spectroscopy. The observed spectra closely resemble those of BrF_5 and ClF_5, respectively, indicating ionic structures with square-pyramidal anions of symmetry C_{4v}. Force constants have been computed for the series SF_5^-, SeF_5^-, and TeF_5^- and are compared to those of the isoelectronic ClF_5, BrF_5, and IF_5 molecules, respectively.

Introduction

The chalcogen tetrafluorides SF_4, SeF_4, and TeF_4 are known to be amphoteric and to form adducts with Lewis acids and bases. Whereas numerous papers dealing with the vibrational spectra and structure of their Lewis acid adducts have been published,[1-6] of their Lewis base adducts only the complexes of TeF_4 have been studied[7-9] in detail. These $TeF_4\cdot$(Lewis base) adducts were shown[7-9] to contain a TeF_5^- anion of symmetry C_{4v}. The existence of 1:1 adducts between SeF_4 and alkali metal fluorides was reported[10] in 1952 by Aynsley, Peacock, and Robinson. However, their adducts were only characterized by elemental analyses. Whereas Bartlett and Robinson[4] and Tunder and Siegel[11] reported that alkali metal fluorides, such as CsF, do not form adducts with SF_4, Tullock, Coffman, and Muetterties[12] successfully prepared a stable $CsF\cdot SF_4$ adduct. Furthermore, Tunder and Siegel obtained[11] evidence for a $(CH_3)_4NF\cdot SF_4$ adduct of marginal stability at ambient temperature. No further information has been published on either the SF_4 or SeF_4 adducts.[12a] In this paper, we wish to report the vibrational spectra of the SeF_5^- and SF_5^- anions and their force constants. Since the vibrational spectra of the series of square-pyramidal molecules ClF_5, BrF_5, and IF_5 are known,[13-15] it appeared particularly interesting to compare them with those of the isoelectronic series SF_5^-, SeF_5^-, and TeF_5^-.

Experimental Section

Materials and Apparatus.—Volatile materials used in this work were manipulated in a well-passivated (with ClF_3) stainless steel vacuum line equipped with Teflon FEP U traps and 316 stainless steel bellows-seal valves (Hoke, Inc., 425 1F4Y). Pressures were measured with a Heise Bourdon tube-type gauge (0–1500 mm ± 0.1%). Selenium tetrafluoride was prepared by the method[16] of Pitts and Jache from selenium powder and ClF and was purified by fractional condensation. Cesium fluoride was fused in a platinum crucible and powdered in a drybox prior to use. The purity of the volatile starting materials was determined by measurements of their vapor pressures and infared spectra. Solid products were handled in the dry nitrogen atmosphere of a glove box.

The infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer in the range 4000–250 cm^{-1}. The spectra of gases were obtained using 304 stainless steel cells of 5-cm path length fitted with AgCl windows. Screw-cap metal cells with AgCl or AgBr windows and Teflon FEP gaskets were used for obtaining the spectra of solids as dry powders at ambient temperature. The quality of the infrared spectra could be somewhat improved by pressing two small single-crystal platelets of either AgCl or AgBr to a disk in a pellet press. The powdered sample was placed between the platelets before starting the pressing operation. The low-temperature infrared spectra of dry powders were obtained by attaching the AgCl windows to a coolable copper block of a conventional, low-temperature Pyrex cell.

The Raman spectra were recorded using a Coherent Radiation Laboratories Model 52 Ar laser as a source of 1.3 W of exciting light at 5145 Å. The scattered light was analyzed with a Spex Model 1400 double monochromator, a photomultiplier cooled to ~25°, and a dc ammeter. Pyrex-glass tubes (7-mm o.d.) with a hollow inside glass cone for variable sample thicknesses or melting point capillaries were used as sample containers. For the conical tubes, the axial viewing–transverse excitation technique and, for the capillaries, the transverse viewing–transverse excitation technique were used.

Preparation of the Adducts. **$Cs^+SF_5^-$.**—A 30-ml prepassivated stainless steel cylinder was loaded with powdered CsF (36.2 mmol) and SF_4 (46.9 mmol). The adduct was formed by shaking the cylinder at room temperature for several days, followed by heating to 125° for several more days. On cooling to room temperature, the unreacted SF_4 was removed by pumping. The white solid product that remained in the cylinder was a single fused mass which was chipped from the cylinder. The weight of the solid (7.41 g) indicated that approximately half the CsF charged (5.50 g) had been converted to the adduct. This was confirmed by pyrolyzing *in vacuo* a portion of the adduct at 150° and trapping the evolved gas at −196°. From 0.82 g of the adduct, 1.88 mmol of pure SF_4 was obtained, indicating a mixture of 48 mol % $Cs^+SF_5^-$ and 52 mol % CsF.

$Cs^+SeF_5^-$.—Powdered CsF (13.1 mmol) was loaded into a prepassivated 30-ml stainless steel cylinder followed by SeF_4 (8.04 mmol). The cylinder was allowed to stand at room temperature overnight. Pumping on the cylinder revealed that all the SeF_4 had reacted since no volatile product was recovered. The weight

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[12a] NOTE ADDED IN PROOF.—After submission of this paper for publication, L. F. Drullinger and J. E. Griffiths [*Spectrochim. Acta, Part A*, **27**, 1793 (1971)] reported the vibrational spectrum of the SF_5^- anion. Their spectrum, assignment, and conclusions concerning the structure of SF_5^- agree with those of this study except for the assignment of ν_8(E). In related molecules and ions this mode is of appreciable intensity and we did not observe the weak infrared band at 388 cm^{-1} assigned by Drullinger and Griffiths to ν_8. Consequently, we prefer to assume a double coincidence between ν_4 and ν_8 as in the case of isoelectronic ClF_5.

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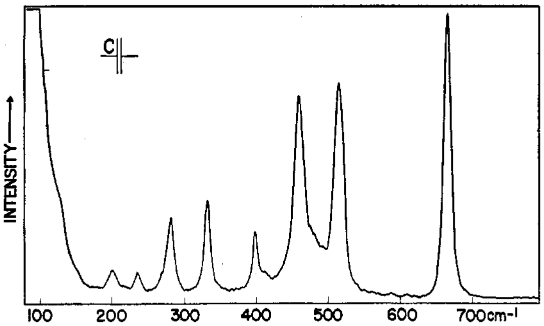


Figure 1.—Raman spectrum of solid $Cs^+SeF_5^-$. The sample container was a glass capillary. C indicates spectral slit width

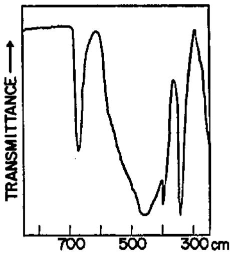


Figure 2.—Infrared spectrum of solid $Cs^+SeF_5^-$, recorded as a dry powder between AgBr plates at −196°.

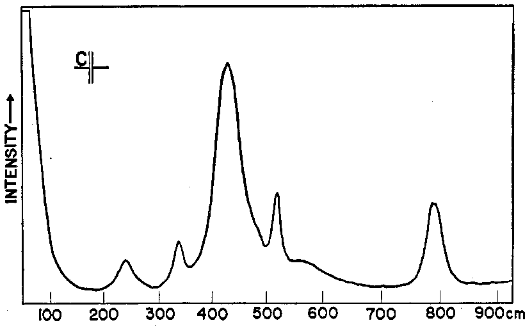


Figure 3.—Raman spectrum of solid $Cs^+SF_5^-$. The sample container was a glass capillary.

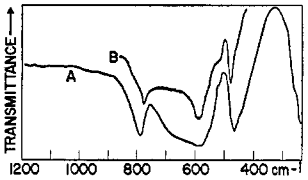


Figure 4.—Infrared spectrum of solid $Cs^+SF_5^-$, recorded as an AgBr disk at ambient temperature (trace A) and a dry powder between AgBr plates at −196° (trace B).

of the white solid adduct (3.25 g) obtained was in agreement with this observation. Therefore, the product was a mixture of 61 mol % $Cs^+SeF_5^-$ and 39 mol % CsF.

Results and Discussion

Synthesis and Properties.—The reaction conditions used for the synthesis of $Cs^+SeF_5^-$ were similar to those[10] used by Aynsley, Peacock, and Robinson. Since the presence of some unreacted CsF was not expected to interfere with the spectroscopic investigation, no attempt was made to achieve complete conversion of CsF to $CsSeF_5$. Our product appeared to be completely stable *in vacuo* at ambient temperature contrary to the claim of Aynsley, *et al.*, who reported[10] slight decomposition under similar conditions.

TABLE I

VIBRATIONAL SPECTRA OF $Cs^+SF_5^-$, $Cs^+SeF_5^-$, AND $Cs^+TeF_5^-$ AND THEIR ASSIGNMENTS COMPARED TO THOSE OF ISOELECTRONIC ClF_5, BrF_5, AND IF_5

Obsd freq, cm^{-1}, and rel intens												Assignment in point group	Approx description of vib
$Cs^+SF_5^-$		$Cs^+SeF_5^-$		$Cs^+TeF_5^-$ [a]		ClF_5 [b,c]		BrF_5 [b]		IF_5 [b]			
Ir	Raman	Ir	Raman	Ir	Raman	Ir	Raman	Ir	Raman	Ir	Raman	C_{4v}	
793 s	796 (3.7)	665 vs	666 (10)	618 ms	611 vs	708 m	709 (3)	383 s	682 (7)	710 s	710 s, p	A_1 ν_1	$\nu(XF')$
520 w, sh	522 (2.7)	520 sh	515 (7.5)	[466 vs, br]	504 s	539 w	538 (1)	587 m	570 (10)	(595)[e]	616 vs, p	ν_2	$\nu_s(XF_4)$ in phase
466 s	469 sh	335 s	332 (3.2)	283 m	282 mw	495 mw	[480 (10)]	369 s	365 (2)	318 m	318 m, p	ν_3	$\delta_s(XF_4)$ umbrella
...	[435 (10)][d]	...	460 (7.0)	...	[472 s]	...	[480 (10)]	...	535 (10)	...	604 m	B_1 ν_4	$\nu_s(XF_4)$ out of phase
...	269 sh	...	236 (0.6)	...	...	...	...	...	...	...	...	ν_5	$\delta_{as}(XF_4)$ out of plane
...	342 (1.6)	...	282 (2.6)	...	231 mw	...	375 (1)	...	312 (1)	...	276 w	B_2 ν_6	$\delta_s(XF_4)$ in plane
590 vs, br	590 sh	475 vs, br	480 sh	[466 vs, br]	[472 s]	725 vs	...	644 vs	...	640 vs	631	E ν_7	$\nu_{as}(XF_4)$
430 sh	[435 (10)[d]	398 mw	399 (1.9)	336 m	338 mw	484 m	[480 (10)]	415 m	414 (1)	372 m	372 w	ν_8	$\delta(F'XF_4)$
...	241 (1.2)	...	202 (0.7)	164 mw	...	299 mw	296 (0.4)	...	237 (0+)	...	200 vw	ν_9	$\delta_{as}(XF_4)$ in plane

[a] Data from ref 7. [b] Data from ref 13, 14. [c] Data from ref 15. [d] Frequencies in brackets indicate coincidences with other modes, thus resulting in increased relative intensities. [e] Frequency estimated from combination bands.

The $CsF \cdot SF_4$ adduct was prepared by the method[12] of Tullock, *et al.*, confirming the existence of a stable complex. Again, no attempt was made to achieve complete conversion of CsF to $Cs^+SF_5^-$.

Vibrational Spectra.—Figures 1 and 2 show the Raman and infrared spectra, respectively, of the solid $CsF \cdot SeF_4$ adduct. Figures 3 and 4 show the corresponding spectra of solid $CsF \cdot SF_4$. The observed frequencies are listed in Table I. The Raman spectra are of better quality than the infrared spectra as is generally the case for this type of compound. Consequently, assignments will be based mainly on the Raman spectra. The absorption between 300 and 240 cm^{-1} in the infrared spectra is mainly due to the AgBr window material.

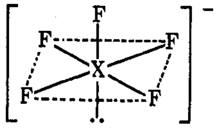
Since the chalcogen tetrafluoride–Lewis acid adducts[1-6] and $CsF \cdot TeF_4$[7-9] were shown to be ionic, the same might be expected for the CsF adducts of SF_4 and SeF_4. In the pentafluorochalcogenate(IV) anions, the central atoms possess a free electron pair which should be sterically active. Hence, these anions should have a square-pyramidal structure of symmetry C_{4v} similar to that of the isoelectronic halogen pentafluoride series.[13]

For a pentafluorochalcogenate(IV) anion, XF_5^-, of symmetry C_{4v} nine fundamental vibrations should be observed. These are classified as $3\,A_1 + 2\,B_1 + B_2 + 3\,E$. All nine modes should be Raman active whereas only the A_1 and E modes should be infrared active. Table I lists the vibrational frequencies of the two isoelectronic series SF_5^-, SeF_5^-, TeF_5^- and ClF_5, BrF_5, IF_5. As can be seen from Table I, the vibrational frequencies of the two series are very similar. In particular, the Raman spectra of SF_5^- and SeF_5^- strongly resemble those of ClF_5 and BrF_5, respectively,[13] considering the expected frequency decreases when going from the neutral molecules to the anions. Since the assignments for the halogen pentafluorides are well established,[13-15] the spectra of SF_5^- and SeF_5^- can be assigned (see Table I) by complete analogy. For TeF_5^-, the previously reported[7] assignments have been slightly revised to fit the overall intensity and frequency patterns. Greenwood, *et al.*, assigned[7] the symmetric out-of-phase stretching vibration ν_4 to a weak Raman band at 572 cm^{-1} and the antisymmetric stretching vibration ν_7 to a strong Raman band at 472 cm^{-1}. This assignment results in ν_4 having a higher frequency than ν_2 which was not observed for any other member in this series. It appears more satisfactory to assign the strong Raman line at 472 cm^{-1} to ν_4 and to assume that the low-intensity Raman counterpart of the intense infrared band at 466 cm^{-1} is hidden under the 472-cm^{-1} band.

Comparison of the vibrational spectra of the XF_5^- series with those of the isoelectronic XF_5 molecules[13-15] reveals several interesting features. The Raman spectra of the corresponding members of each series are very similar. The frequency trends within each series are consistent. Thus, the stretching modes ν_2 and ν_4, involving very little motion of the central atom, show frequency values reflecting the expected change in bond strength, whereas the stretching modes ν_1 and ν_7, involving a motion of the central atom, exhibit an additional mass effect. The deformational modes show, as expected, a pronounced frequency increase with decreasing size of the central atom.

An unexpected, but explicable, feature in the spectra of SeF_5^- and TeF_5^- is the unusual occurrence of the antisymmetric XF_4 stretching mode, $\nu_7(E)$, at a frequency lower than that of the totally symmetric XF_4 stretching mode, $\nu_2(A_1)$. In SF_5^- the frequency value of ν_7 is only 68 cm^{-1} higher than that of ν_2. Since the mass of the central atom increases from SF_5^- toward TeF_5^- and since only the frequency of ν_7 is mass dependent, for SeF_5^- and TeF_5^- this frequency becomes lower than that of ν_2. A similar unusual occurrence of the symmetric out-of-phase stretching mode, $\nu_2(E_g)$, at a frequency higher than that of the totally symmetric $\nu_2(A_{1g})$ mode was recently established for the octahedral IF_6^+ ion.[17] These two cases demonstrate the possibilities for incorrect assignments[7,18] when ignoring relative intensities of bands and frequency trends in related molecules.

In summary, the vibrational spectra of SF_5^-, SeF_5^-, and TeF_5^- show that these anions are isostructural with ClF_5, BrF_5, and IF_5. Consequently, the following square-pyramidal structure of symmetry C_{4v} can be assigned to these anions



Force Constants.—Force constants were computed for the three isoelectronic pairs SF_5^-–ClF_5, SeF_5^-–BrF_5, and TeF_5^-–IF_5. The required potential and kinetic energy metrics were computed with a machine method[19] adopting the geometries given in Table II.

TABLE II

ASSUMED MOLECULAR PARAMETERS FOR SQUARE-PYRAMIDAL PENTAFLUORIDE IONS AND MOLECULES

	SF_5^- [a]	ClF_5 [b]	SeF_5^- [a]	BrF_5 [c]	TeF_5^- [d]	IF_5 [e]
R, Å	1.62	1.62	1.68	1.68	1.86	1.83
r, Å	1.72	1.72	1.78	1.78	1.95	1.87
β, deg	90	90	84.5	84.5	79.0	82

[a] Assumed values. [b] Values assumed in ref 13. [c] R. D. Burbank and F. N. Bensey, Jr., *J. Chem. Phys.*, **27**, 982 (1957). [d] Reference 9. [e] Unpublished electron diffraction data by T. G. Hewitt, A. G. Robiette, and G. M. Sheldrick referred to by S. J. Cyvin, J. Brunvoll, and A. G. Robiette, *J. Mol. Struct.*, **3**, 259 (1969).

The force constant definitions used are those of Begun, Smith, and Fletcher,[13] except that the deformation coordinates are weighted by unit (1 Å) distance. The force constants were adjusted by trial and error, assuming the simplest possible modified valence force field, to give an exact fit between the observed and computed frequencies. Since an excellent transferability of interaction force constants was noted for the pairs SeF_5^-–BrF_5 and TeF_5^-–IF_5, the interaction constants were assumed precisely equal and all force constants were adjusted for a best fit by the reparameterization method.[19] The results are given in Table III. For the pair SF_5^-–ClF_5, the transferability was not quite so good. Hence, Table III gives different interaction constants for this pair. The similarity of the interaction constants reported for these molecules is remarkable.

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TABLE III
FORCE CONSTANTS[a] FOR SOME XF_5 MOIETIES COMPUTED FOR BrF_5–SeF_5^- AND IF_5–TeF_5^- FORCING TRANSFERABILITY OF INTERACTION TERMS AND FOR ClF_5 AND SF_5^- BY REQUIRING A PERFECT FIT

	ClF_5	SF_5^- [b]	BrF_5	SeF_5^-	IF_5	TeF_5^-
f_R	3.47	4.12	4.03	3.82	4.82	3.56
f_r	2.67	2.06	3.24	2.41	3.82	2.27
f_β	2.86	2.26	2.23	1.95	2.10	1.86
f_α	1.14	0.86	0.82	0.63	0.72	0.54
$f_{rr'}$	0.24	0.52	0.27		0.36	
$f_{\beta\beta'}$	0.75	0.55	0.32		0.43	
$f_{\alpha\alpha'}$	0.01	0.11	0.04		0.04	
f_{rr}	0.16	0.23	0.15		0.06	
$f_{R\beta}$	0.4	0.25				
$f_{r\beta}$	0.15	0.15				
$f_{r\beta''}$	−0.15	−0.15				
f_r/f_R	0.77	0.50	0.82	0.63	0.79	0.64

[a] Stretching constants in mdyn/Å, deformation constants in mdyn/Å radian², and stretch–bend interaction constants in mdyn/Å radian. [b] For SF_5^-, $f_{\beta\beta}$ was also computed and has a value of 0.20 mdyn/Å radian².

The values reported for $f_{R\beta}$, $f_{r\beta}$, and $f_{r\beta''}$ for the pair ClF_5–SF_5^- can be accounted for by orbital-following arguments. Numerical experiments indicated no need to assume other interaction constants and convincingly showed that the observed frequencies could not be fitted unless values were accepted near those shown.

Comparison of the general trends within XF_5 and XF_5^- series shows a remarkable difference. Whereas the deformation force constants in each series have comparable values and follow the same trends, the valence force constants f_R and f_r show reverse trends. Thus, for the XF_5 group, the lightest member, ClF_5, shows the lowest stretching force constant values, but for XF_5^- the heaviest member, TeF_5^-, exhibits the lowest f_R value. However, a closer inspection of the trends of the valence force constants of fluorides throughout the periodic system[20] reveals a general reversal of the direction of that trend either within or close to the sixth main group. Furthermore, increasing stretching force constant values from chlorine to the corresponding bromine fluorides were also found for the ClF_3 and BrF_3 molecules[21] and the ClF_4^- and BrF_4^- anions.[22,23]

The usefulness of stretching force constants for the distinction between mainly covalent and semiionic three-center four-electron (3c-4e) bonds has previously been demonstrated for numerous halogen fluorides.[23,24] The square-pyramidal pentafluorides of the present study contain two types (*i.e.*, axial and equatorial) of fluorine ligands and a comparison of their stretching force constants should permit some conclusions concerning the nature of their bonds. Since ionic bonds do not contribute to the stretching force constants, semiionic bonds ideally should exhibit values half as large as those of covalent bonds. As can be seen from Table III, the f_r/f_R ratios of the pentafluorochalcogenate anions range from 0.50 for SF_5^- to 0.64 for TeF_5^-. This indicates strong contributions from semiionic 3c-4e p-pσ bonds[25–28] to the bonding of the four equatorial fluorine ligands and mainly covalent character for the single axial fluorine bond. This finding agrees with a model involving an sp hybrid of the central atom for the sterically active, free-electron pair and the single, axial fluorine atom while two p electrons of the central atom form two semiionic 3c-4e bond pairs with the remaining four equatorial fluorine atoms.

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CONTRIBUTION FROM ROCKETDYNE,
A DIVISION OF NORTH AMERICAN ROCKWELL, CANOGA PARK, CALIFORNIA 91304

Iodine Tris(perchlorate) and Cesium Tetrakis(perchlorato)iodate(III)

BY KARL O. CHRISTE* AND CARL J. SCHACK

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The syntheses and some properties of the novel iodine perchlorates $I(OClO_3)_3$ and $Cs^+I(OClO_3)_4^-$ are reported. Their vibrational spectra were recorded and confirm their formulation as covalent perchlorates. A square-planar configuration is proposed for the $I(OClO_3)_4^-$ anion, whereas $I(OClO_3)_3$ appears to be polymeric.

Introduction

The preparation of iodine tris(perchlorate) from iodine, ozone, and anhydrous $HClO_4$ is described in ref 1. However, a cross-check with the original publication,[2] from which the preparation was abstracted, reveals that the original paper deals only with a compound having the empirical composition $I(ClO_4)_3 \cdot 2H_2O$. Numerous attempts have been reported to prepare iodine perchlorates in organic solvents from I_2 and $AgClO_4$. Whereas the experimental data were consistent with the formation of iodine perchlorates as unstable intermediates, all attempts to isolate and characterize these compounds were unsuccessful, owing

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