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The Infrared Spectra of the Tetrachlorides and Tetrabromides of Selenium and Tellurium

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The far-infrared spectra of selenium tetrachloride, selenium tetrabromide, tellurium tetrachloride, and tellurium tetrabromide are reported and the structural implications of these data considered. The infrared findings for $SeCl_4$ and $TeCl_4$ are consistent with the earlier Raman conclusions that pyramidal MCl_3^+ cations are present. Similarities among the spectra for all four substances examined suggest that MBr_3^+ is an essential component of the tetrabromides, also.

Introduction

The tetrahalides of sulfur, selenium, and tellurium display an interesting range of phase dependent structural formulations. Thus, sulfur tetrafluoride in the gaseous state consists of trigonal bipyramidal molecules of C_{2v} symmetry,[1] but association is indicated in the liquid[2] and solid states.[3] The Raman spectrum of liquid selenium tetrafluoride[4] has been interpreted in terms of molecules of C_{2v} symmetry, although a preliminary report of electrical conductivity of the liquid prompted speculation that limited ionization to $SeF_3^+SeF_5^-$ species may occur.[5] Tellurium tetrachloride also displays the trigonal bipyramidal configuration in the gas phase,[6] but in a condensed state the results of Raman spectroscopy[7] suggest an ionic formulation, $TeCl_3^+Cl^-$. Similar conclusions have been reached concerning solid selenium tetrachloride. More recently, however, a nuclear quadrupole resonance study of $TeCl_4$[8] has given results favoring a trigonal bipyramidal molecular structure for the crystalline material. In a short communication[9] we have reported infrared data supporting the $TeCl_3^+Cl^-$ constitution for $TeCl_4$, and very recently Greenwood and coworkers[10] have published infrared findings and interpretations for $TeCl_4$, $TeBr_4$, and TeI_4 in accord with ionic formulations for each of these species. In the present paper the results and structural implications of our far-infrared investigations of the tetrachlorides and tetrabromides of tellurium and selenium are presented.

Experimental Section

Commercial $TeCl_4$ (City Chemical Co.) and $TeBr_4$, $SeCl_4$, and $SeBr_4$ prepared by standard methods using elementary Se and Te of high purity were employed. Handling of the tetrahalides was carried out in polyethylene bags to minimize atmospheric hydrolysis or other contaminating effects. All spectra were obtained as Nujol mulls on KBr plates or polyethylene disks using Beckman IR-11, IR-10, and Perkin-Elmer 21 spectrometers.[11]

Results and Discussion

Tellurium Tetrachloride.—The infrared spectrum of the crystalline material is shown in Figure 1, and the observed frequencies, together with the earlier Raman data for both solid and liquid $TeCl_4$, are summarized in Table I. It is clear that the Raman results and the infrared data correspond quite closely. In this investigation the very weak absorptions at 130 and 242 cm^{-1} reported by Greenwood, *et al.*,[10] were not observed but several absorptions below 130 cm^{-1} not listed in their study were noted. The breadth and intensity of the absorption centered at 57 cm^{-1} suggest, by analogy with the low-frequency absorption of thallium(I) chloride,[12] that this is associated with lattice modes. The weak, sharp frequencies at 73 and 101 cm^{-1} are probably due to impurities.

The vibrational data may be considered in connection with several structural models for crystalline $TeCl_4$. If the material were present primarily in molecular units a distorted tetrahedral configuration of C_{2v} symmetry should require a much more complicated spectrum with nine fundamental frequencies, only one of which is infrared inactive. While the relative weakness of some of these eight infrared-active fundamentals could result in their being unobservable, it is to be noted that study[3] of solid SF_4, known to be trigonal bipyramidal in the vapor phase, has led to the identification of five, and probably seven, of the expected fundamentals. Accordingly, it is believed that the presence of molecules of C_{2v} symmetry in solid $TeCl_4$ is improbable. Similar considerations lead to a rejection of the inherently less likely tetrahedral, T_d, or square-planar, D_{4h}, molecular species. Of the ionic

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[1] R. E. Dodd, L. A. Woodward, and H. L. Roberts, *Trans. Faraday Soc.*, **52**, 1052 (1956).

[2] E. L. Muetterties and W. D. Phillips, *J. Am. Chem. Soc.*, **81**, 1084 (1959).

[3] (a) E. E. Aynsley, R. E. Dodd, and R. Little, *Spectrochim. Acta*, **18**, 1005 (1962); (b) R. L. Redington and C. V. Berney, *J. Chem. Phys.*, **43**, 2027 (1965).

[4] J. A. Rolfe, L. A. Woodward, and D. A. Long, *Trans. Faraday Soc.*, **49**, 1388 (1953).

[5] M. A. Hepworth, P. L. Robinson, and G. Westland, *Chem. Ind.* (London), 1516 (1955).

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[7] H. Gerding and H. Houtgraaf, *Rec. Trav. Chim.*, **73**, 737 (1954).

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[9] N. Katsaros and J. W. George, *Chem. Commun.*, 613 (1965).

[10] N. N. Greenwood, B. P. Straughn, and A. E. Wilson, *J. Chem. Soc.*, 1479 (1966).

[11] We are grateful to Professor H. L. Strauss of the University of California, Berkeley, and to Dr. R. E. Weston, Jr., of the Brookhaven National Laboratory for permission to use far-infrared instrumentation in their laboratories, and to Mrs. Helene Gabelnich, University of California, and Mr. S. Mylonakis, Brookhaven, for technical assistance.

[12] A. Mitsuishi, Y. Yamada, and H. Yoshinga, *J. Opt. Soc. Am.*, **52**, 14 (1962).

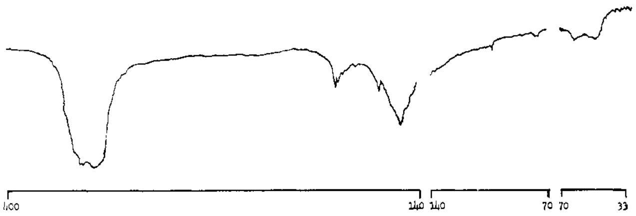

Figure 1.—Infrared spectrum of $TeCl_4$, 400–33 cm^{-1}.

Table I

Vibrational Data (cm^{-1}) and Fundamental Assignments for $TeCl_4$

Raman[a]			
Liquid	Solid	Infrared[b]	Assignment[c]
[499] (1−)	[492] (0)		
[458] (1-2)			
	415 (0+)		
377 (20), p	374 (18)	358, vs	ν_1 (a_1)
342 (16), dp	342 (20)	347, vs	ν_3 (e)
330 (0-1)			
	[290] (0 − 1)		
	[246] (0+)		
231 (1-2)			
195 (0+)	191 (2−)	191, m	ν_2 (a_1)
[176] (0-1)			
148 ± 5 (1-2), dp?	143 (3)	150, s	ν_4 (e)
	87 (6)	101, vw	
		73, vw	
		57, m, br	Lattice

[a] Data from ref 7. Figures given in brackets are uncertain. Relative intensity estimates are given in parentheses; p = polarized; dp = depolarized. [b] This work. [c] For C_{3v} symmetry these modes are described as follows: ν_1, symmetric Te–Cl stretch; ν_2, symmetric Cl–Te–Cl bend; ν_3 antisymmetric Te–Cl stretch; ν_4, degenerate Cl–Te–Cl bend.

models similar considerations rule out a $TeCl_3^+TeCl_5^-$[13] composition since the probable C_{4v} symmetry of the $TeCl_5^-$ ion again requires a greater number of fundamentals than may reasonably be found in the observed vibrational spectrum. A report of the infrared spectra of crystalline hexachlorotellurates[14] indicates a strong absorption at approximately 230 cm^{-1}, a finding confirmed by independent examination of potassium hexachlorotellurate. It appears probable, therefore, that $TeCl_6^{2-}$ ions are not present as a major species in crystalline $TeCl_4$.

Thus, the most reasonable formulation is the ionic one, $TeCl_3^+Cl^-$, with the cation of C_{3v} symmetry, as proposed by Gerding and Houtgraaf[7] and in agreement with Greenwood, *et al.*[10] Exposure of our $TeCl_4$ sample to the atmosphere resulted in the appearance of weak absorptions at 415 and 492 cm^{-1}, perhaps accounting for two of the weaker Raman lines observed.

If the $TeCl_3^+Cl^-$ formulation is accepted it is necessary to provide an alternative interpretation of nuclear quadrupole resonance results.[8] The conclusion that the six ^{35}Cl resonances observed be treated as two groups of three lines each and require a molecular $TeCl_4$ species of C_{2v} symmetry is questionable in view of the frequent occurrence of multiple nqr frequencies due to packing effects. Thus, for the ICl_2^- anion a multiplicity of resonances over a wide frequency range is found despite the equivalence of chlorine positions in the ion;[15] it is suggested that such effects may be responsible for the multiple resonances observed in crystalline $TeCl_4$.

Tellurium Tetrabromide.—The infrared spectrum, Figure 2, and the absorption frequencies summarized in Table II parallel the findings for $TeCl_4$. Symmetry considerations such as those noted above for the tetrachloride suggest $TeBr_3^+Br^-$ as the most satisfactory formulation for the crystalline material. Interestingly the presence of $TeBr_3^+$ in the Te(IV)–Br^-–H_2O equilibrium system has been suggested on the basis of spectrophotometric investigation.[16] While only very limited Te–Br bond vibrational data are available in the literature it is apparent by comparison with the $TeCl_4$ spectrum, and through consideration of the infrared spectrum of pyramidal $SbBr_3$,[17] that the strong absorptions at 240 and 223 cm^{-1} are probably the symmetric and antisymmetric stretching frequencies of a pyramidal $TeBr_3^+$ species. Greenwood, *et al.*,[10] have assigned the a_1 and e deformation modes to their 110 and 87 cm^{-1} absorptions, respectively. Our spectrum suggests the possibility of three peaks in this region. While the a_1 absorption is expected to lie at a higher frequency than that of the degenerate mode it is not certain whether the 125 cm^{-1} or the 110 cm^{-1} absorption in our spectrum should be assigned to the a_1 mode. Polarization data would be of assistance in making this determination. It is interesting that the deformation modes for both $TeCl_3^+$ and $TeBr_3^+$ occur at higher frequencies than those reported for the isoelectronic $SbCl_3$ and $SbBr_3$ species[18] although the reverse is true for the stretching modes.

Figure 2.—Infrared spectrum of $TeBr_4$, 350–33 cm^{-1}.

Table II

Infrared Data for Crystalline $TeBr_4$ (cm^{-1})

Frequency	Assignment
240 vs	ν_1 (a_1)
223 vs	ν_3 (e)
125 w	ν_2 (a_1), ν_4 (e)
110 s	
92 w	
46 m, br	Lattice

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(13) K. W. Bagnall, "The Chemistry of Selenium, Tellurium and Polonium," Elsevier Publishing Co., New York, N. Y., 1966, p 108.

(14) N. N. Greenwood and B. P. Straughn, *J. Chem. Soc.*, 962 (1966).

(15) C. D. Cornwall and R. S. Yamasaki, *J. Chem. Phys.*, **27**, 1060 (1957).

(16) B. D. Stepin and G. M. Serebrennikova, *Zh. Neorgan. Khim.*, **11**, 1807 (1966); *Chem. Abstr.*, **65**, 16480*b* (1966).

(17) J. C. Evans, *J. Mol. Spectry.*, **4**, 435 (1960).

(18) See tabulation of data in K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 86.

Preliminary X-ray reports[19,20] have noted the crystallographic similarities of monoclinic $TeBr_4$ and $TeCl_4$. Patterson projections have shown that tellurium atoms occupy one-quarter of the octahedral interstices in the halogen array and that the Te atoms are slightly displaced so that either a distorted tetrahedral or a pyramidal TeX_3^+ could result. It was not possible, however, to make a distinction between these formulations on the basis of the X-ray data. Although not conclusive, the vibrational data are strongly suggestive of the $TeBr_3^+$ species in $TeBr_4$. In view of the absorption[14] by the $TeBr_6^{2-}$ ion at 195 cm^{-1} the presence of this ion in solid $TeBr_4$ is considered improbable.

Selenium Tetrabromide.—Table III and Figure 3 present the data for this substance. In the absence of Raman information, and considering a broad, strong absorption centered at 222 cm^{-1} for K_2SeBr_6,[14] it is difficult to present with confidence a structural interpretation. However, the intense absorptions in the 265–230 cm^{-1} region and the two well-defined frequencies observed at 127 and 107 cm^{-1} suggest a pattern similar to those observed for $TeCl_4$ and $TeBr_4$. It is noteworthy that the shapes and relative intensities of the 127 and 107 cm^{-1} absorptions are very similar to those of the ν_2 (a_1) and ν_4 (e) frequencies observed for crystalline $AsBr_3$ dispersed in a polyethylene matrix.[21] There is a report[22] that solid $SeBr_4$ has a specific electrical conductivity of 1.3×10^{-8} ohm^{-1} cm^{-1} at 20° and 2000 atm and that this increases with temperature to 45°, at which point some decomposition is observed. This is substantially greater than the conductivity value reported for NaCl and most ionic substances at room temperature.[23] The tentative assignments presented in Table III thus assume the presence of a pyramidal cation, $SeBr_3^+$. Note that the occurrence of several peaks in the 265–230 cm^{-1} range is not unlike the complex infrared absorption pattern reported for $SbBr_3$ in the 250–220 cm^{-1} region.[24] It is suggested that the several peaks between 265 and 230 cm^{-1}, and the broadening of ν_4 (e), in the $SeBr_4$ spectrum are the result of a removal of degeneracy in ν_3 (e) and ν_4 (e) due to crystal effects, as has been proposed for $SbBr_3$.[17] It is believed that the appearance of the absorption at 298 cm^{-1} may be the result of thermal decomposition of the sample in the spectrometer beam with attendant formation of Se_2Br_2. This frequency is close to the antisymmetric Se–Br stretching assignment based upon Raman study of Se_2Br_2.[25] Further, our infrared examination of $SeBr_4$ dissolved in CCl_4 solution also shows this absorption. Spectrophotometric studies[26] have suggested the complete decomposition of $SeBr_4$ and the establishment of an equilibrium involving $SeBr_2$, Se_2Br_2, and Br_2 in CCl_4 solution.

TABLE III

INFRARED DATA FOR CRYSTALLINE $SeBr_4$ (CM^{-1})

Frequency	Assignment[a]
298, m	Se_2Br_2 impurity?
265, vs	ν_1 (a_1)
247 227 } vs	ν_3 (e)
127 s	ν_2 (a_1)
107 s, br	ν_4 (e)
85 vw	
72, w, br	See text
57 w, sp	See text

[a] Assuming $SeBr_3^+Br^-$; see text.

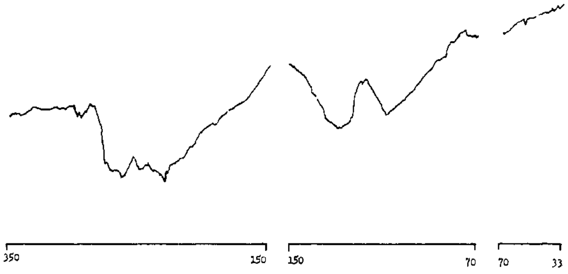

Figure 3.—Infrared spectrum of $SeBr_4$, 350–33 cm^{-1}.

Lattice vibrations of $SeBr_4$ might be expected to lie in a range between those absorptions assigned above for $SeCl_4$ and $TeBr_4$. The 57 cm^{-1} peak for $SeBr_4$ is rather sharp, however, and may instead be a fundamental of Se_2Br_2; Raman study[25] has found such an absorption at 50 cm^{-1}. Thus, the 72 cm^{-1} band may be due to lattice motions.

Selenium Tetrachloride.—In their discussion of the Raman data for $SeCl_4$ Gerding and Houtgraaf[7,27] made a persuasive argument for the occurrence of pyramidal $SeCl_3^+$ ions in solid $SeCl_4$. The similarity of these Raman data to those of $AsCl_3$ and $TeCl_4$, the appearance of the strong Raman lines, although shifted, of solid $SeCl_4$ in the Raman spectrum of the addition compound $SeCl_4 \cdot AlCl_3$ ($SeCl_3^+AlCl_4^-$), and a comparison of calculated force constants for $AsCl_3$, $SeCl_4$, $TeCl_4$, and $SbCl_3$ were offered in support of this conclusion. The infrared spectrum, Figure 4, and data, Table IV, are compatible with the assumption of $SeCl_3^+$ in solid $SeCl_4$, but are by no means conclusive in excluding other selenium-containing species. Gerding and Houtgraaf rejected the C_{2v} model for solid $SeCl_4$, as well as the

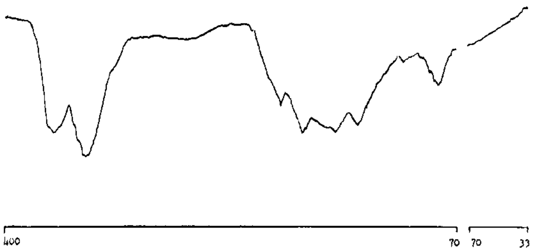

Figure 4.—Infrared spectrum of $SeCl_4$, 400–33 cm^{-1}.

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(19) C. B. Shoemaker and S. C. Abrahams, *Acta Cryst.*, **18**, 296 (1965).

(20) P. Khodadad, P. Laruelle, and J. Flahaut, *Compt. Rend.*, **259**, 794 (1964).

(21) T. R. Manley and D. A. Williams, private communication.

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(27) H. Gerding, *Rec. Trav. Chim.*, **75**, 589 (1956).

TABLE IV

VIBRATIONAL DATA (CM^{-1}) FOR $SeCl_4$ AND RELATED SPECIES

$SeCl_4$ (solid)[a] Raman	$SeCl_6{}^{2-}$ (aqueous)[b] Raman	$SeCl_4$ (solid)[c] Infrared	
[560] (0–1)			
[515] (0)			
474 (1−)			
ca. 441 (1−)			
388 (15)		371, vs; ν_1 (a_1)	
346 (15)	346, ν_1 (a_1)	348, vs; ν_2 (e)	
ca. 258 (1−)	273, ν_2 (e)	275, m, br	
206 (3–4)		205, w	br ν_2 (a_1), ν_4 (e)
164 (1–2)	166, ν_5 (f_{2g})	190, s	
127 (2)		165, m	
96 (4)		145, m	
69 (1)		80, m, br, lattice	

[a] Reference 7. [b] Reference 28. [c] This work.

possible presence of $SeCl_5{}^-$ ions, because of the small number of Raman lines of sufficient intensity to be considered fundamentals. The infrared spectrum is ambiguous in this regard. In their discussion Gerding and Houtgraaf did not consider the possibility of $SeCl_6{}^{2-}$ ions, a much more likely species than $SeCl_5{}^-$. The observed Raman fundamentals[28] for octahedral $SeCl_6{}^{2-}$ at 346 and 166 cm^{-1} are readily accommodated by the Raman results for $SeCl_4$, but the other allowed $SeCl_6{}^{2-}$ fundamental at 273 cm^{-1} would have to experience a shift to about 258 cm^{-1} in $SeCl_4$ if $SeCl_6{}^{2-}$ were to be considered present in the solid tetrachloride. Infrared examination[14] of $[(CH_3)_4N]_2SeCl_6$ yields absorption at 294 and 182 cm^{-1}, the former of which could be shifted to 275 cm^{-1} in the infrared spectrum of solid $SeCl_4$. Thus, the available vibrational data are in accord with the presence of $SeCl_3{}^+$ species in solid $SeCl_4$ but are inconclusive regarding the nature of the anionic species.

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(28) O. Redlich, T. Kurz, and W. Stricks, *Monatsh. Chem.*, **71**, 1 (1937)

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A Kinetic Study of the Reactions of Chromium(II) and the Isomeric Dichlorotetraaquochromium(III) Ions[1a]

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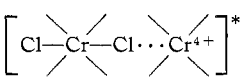
Measurements using the stopped-flow technique were carried out on the rate of the chromium(II)-catalyzed aquation reactions of *trans*- and *cis*-dichlorotetraaquochromium(III) ions which produce monochlorochromium(III) ion. Each reaction is first-order with respect to the chromium(III) complex and with respect to chromium(II). Both reactions proceed by a chloride-bridged Cr(II)–Cr(III) exchange process that leads to chromium exchange and accompanying aquation of the nonbridging chloride ion. The reaction rates were studied as a function of temperature to determine the activation parameters. For *trans*, $k = 401 \pm 33\ M^{-1}\ sec^{-1}$ at 25.0°, with $\Delta H^* = 4.9 \pm 0.5$ kcal $mole^{-1}$ and $\Delta S^* = -30.2 \pm 1.8$ cal $mole^{-1}$ deg^{-1}; for *cis*, $k = 288 \pm 11\ M^{-1}\ sec^{-1}$ at 25.0°, with $\Delta H^* = 5.7 \pm 0.3$ and $\Delta S^* = -28.2 \pm 1.0$. The mechanism is discussed and compared to some related Cr(II)–Cr(III) electron-transfer processes.

Introduction

The reaction of dichlorochromium(III) and chromium(II) ions was one of the first electron-transfer reactions shown by Taube and Myers[2] to proceed by an "inner-sphere" or "bridged" transition state



on the basis of formation of the monochlorochromium(III) ion in a reaction (eq 1) in which chromium(II) acts

$$trans\text{-}CrCl_2{}^+ = CrCl^{2+} + Cl^- \qquad (1)$$

as a rather efficient catalyst for the partial aquation of *trans*-$CrCl_2{}^+$. The feature of net aquation allows the reaction rate to be followed by virtue of the chemical change without resort to isotopic labeling.

Replacement of chloride ion by water in the dichloro complexes is quite favorable thermodynamically,[3] with <0.1% of the dichloro species remaining at equilibrium in a solution initially 0.01 *M*. Spontaneous aquation proceeds slowly,[4] however, and metastable dichloro species have been isolated and their geometrical isomers separated.[5] In a single rate measurement on the very rapid chromium(II) catalysis, Taube and Myers[2] found that the rate constant (presuming a rate law first order in each component) was $1.7 \times 10^2\ M^{-1}\ sec^{-1}$ at 0.2° in 1 *F* perchloric acid.

Again in a single rate experiment, Johnson and Rey-

(1) (a) This work was performed at the Ames Laboratory under the auspices of the U. S. Atomic Energy Commission; Contribution No. 2001. (b) Undergraduate research participant, summer 1966.

(2) H. Taube and H. Myers, *J. Am. Chem. Soc.*, **76**, 2103 (1954).

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