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Chloro Complexes in Molten Salts. III. Raman Study of the Chloro Complexes Formed in the Molten $KCl-AlCl_3-TeCl_4$ System

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Raman spectra have been recorded for a series of $KAlCl_4$ melts containing 0.4, 0.8, and 1.6 *F* Te(IV) and for the molten mixtures of $TeCl_4$–KCl and $TeCl_4$–$AlCl_3$ as well as for molten $TeCl_4$. The spectra are rationalized with the prior knowledge from a potentiometric study of the coordination chemistry of Te(IV) in $KAlCl_4$. Bands are assigned for the following complexes in these systems: $AlCl_4^-$, $TeCl_6^{2-}$, $TeCl_5^-$, $TeCl_4$, and $TeCl_3^+$. The spectra of $TeCl_4$ change little in going from 0.4 *F* $TeCl_4$ solutions in $KAlCl_4$ to pure molten $TeCl_4$, which is *ca.* 9.1 *F* in $TeCl_4$. This fact indicates that polymeric units such as Te_4Cl_{16} found in solid $TeCl_4$ are not present in these melts. The structure of $TeCl_4$ in the molten state is suggested to be $Cl_3Te–Cl$ of C_{3v} symmetry with three strongly and one weakly bound chlorides in contrast to the C_{2v} molecule observed in gaseous $TeCl_4$.

Introduction

Recently[2] it has been shown by potentiometric and spectrophotometric measurements that stepwise chloro complex formation of $TeCl_3^+$, $TeCl_4$, $TeCl_5^-$, and $TeCl_6^{2-}$ can be obtained in dilute solutions of Te(IV) in $KAlCl_4$ by a systematic variation of the chloride activity. In the present work an attempt is made to investigate these complexes by an analysis of the Raman spectra of the melts.

The interesting general question in the chemistry of the chloro complexes of Te(IV) is whether monomeric or polymeric units are present. It has been shown that solid $TeCl_4$ consists of Te_4Cl_{16} units.[3] Furthermore it has been shown that it is possible to obtain crystals containing the $Te_3Cl_{13}^-$ and $Te_2Cl_{10}^{2-}$ units.[4] The crystal structure shows the $Te_3Cl_{13}^-$ unit, which can be regarded as the fraction, which is left of Te_4Cl_{16}, when the $TeCl_3^+$ ion is removed.[4] The preliminary suggestion for the structure of the $Te_2Cl_{10}^{2-}$ complex involves the suppositions that Te(IV) obtains hexacoordination and two $TeCl_6$ octahedra are linked together along an edge.[4] Determinations of molecular weights of $TeCl_4$ in benzene solutions show that in the concentrated solutions tetrameric and trimeric species[5] are present, whereas in dilute solution tellurium is present in a monomeric unit.[6] Also, chainlike structures are reported for Te(IV) complexes.[7,8] The compound $TeCl_4PCl_5$ contains $TeCl_5^-$ units bound together in such a way that a distorted octahedral coordination is obtained around the tellurium atom. An example of a monomeric Te(IV) unit is found in solid $TeCl_4AlCl_3$, which contains the $TeCl_3^+$ cation together with the $AlCl_4^-$ anion.[9,10] Also, compounds like $(TeCl_3)AsF_6$ are known to be monomeric.[11] From phase diagrams of the $MCl-TeCl_4$ systems (M = Li, Na, K, Rb, Cs), the solid compounds with overall composition M_2TeCl_6 (M = K, Rb, Cs) and $MTeCl_5$ (M = Rb, Cs) are known to exist.[12] M_2TeCl_6 solids contain the $TeCl_6^{2-}$ anion, whereas it is not clear whether the $MTeCl_5$ solids contain the $TeCl_5^-$ ion. However, it seems clear that the $TeCl_5^-$ ion is found in solid $(C_2H_5)_4NTeCl_5$.[13]

Experimental Section

Materials and Measurements. $AlCl_3$ was made from the pure metal (99.999%) and HCl gas (electronic grade from Matheson). KCl (analytical reagent from Riedel-de Haen) was purified by first passing HCl gas over the solid and then through the melt, flushing with pure N_2, and finally filtering the melt. The $TeCl_4$ was made by reaction between tellurium (99.999%) and chlorine (Fluka >99.9%). The optical cells (of Ultrasil from Helma) had outside dimensions of 12.5 × 12.5 × 45 mm and an inside cross section of 10 × 5 mm. The amounts of KCl, $AlCl_3$, and $TeCl_4$ that made up a melt were weighed in a nitrogen-filled glove box and added to the cells. The cells were generally sealed under $^1/_3$ atm nitrogen pressure. Due to impurities the melts were slightly reducing. The formation of small amounts of tellurium in lower oxidation states[14] were in such cases prevented by sealing the cells under $^1/_3$ atm of Cl_2 gas. The density of the solutions of Te(IV) was calculated assuming ideal mixtures of $TeCl_4$ and KCl–$AlCl_3$. The densities of $TeCl_4$ and of KCl–$AlCl_3$ systems were obtained from the work of Simons[15] and of Morrey and Carter,[16] respectively.

The Raman spectra were recorded using a Coderg PH 1 laser spectrometer with 632.8-nm (~60–80-mW) excitation and cooled photomultiplier (EMI 9558). A 90° scattering was used and the polarization of the laser beam was kept fixed. The depolarization measurements were made by the conventional method of two different analyzer orientations in the scattered beam ($\rho = 0.75$ for depolarized lines). The uncertainty due to the instrument in the measured Raman shifts was ± 2 cm^{-1}.

The furnace for the Raman spectroscopic studies is shown schematically in Figure 1. It consisted of a inner cylindrical core of aluminum (diameter 50 mm and length 140 mm) (B), orientated in an upright position. In this core provision was made for a stainless steel cell holder (C) with a hole of square cross section (12.7 × 12.7 mm) and outside diameter 20 mm. Two holes perpendicular to each other and to the axis of the core were drilled through the core and cell holder. The hole for the laser beam (H) had a diameter of 3 mm. The other hole, which had a conical shape on each side of the core, allowed the scattered light to reach the spectrometer. The diameters of each conical hole were 13 mm at the outer surface and 10.5 mm at the inner surface of the core. The furnace was heated by four cylindrical heating elements (diameter 10 mm and length 130 mm)

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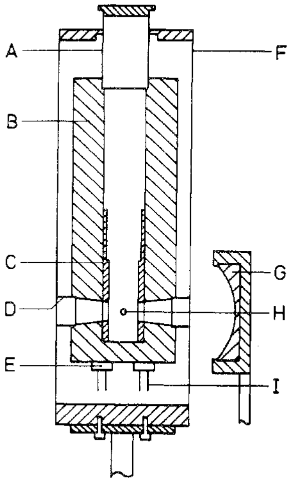

Figure 1. Furnace for laser-Raman spectroscopy: A, horizontal stainless steel tube; B, core of aluminum; C, stainless steel cell holder; D, vertical stainless steel tube; E, end of heating elements; F, water-cooled housing; G, mirror; H, hole for laser beam; I, electric lead.

(E) placed in holes drilled in the core. The aluminum core was suspended inside a water-cooled cylindrical housing (diameter 64 mm and length 195 mm) (F), by means of five thin-walled stainless steel tubes: two horizontal tubes for the laser beam (with inside diameters 3 mm), two horizontal tubes (with inside diameters 13 mm) (D) permitting the scattered light to leave the furnace, and one vertical tube (with inside diameter 23.5 mm) (A) providing access to the cell holder. No insulation (except air) was used between the core and the housing. The temperature of the core could be kept constant within ±0.1° in the range 100–500° by a Eurotherm regulator, Type DHS/PID/SCR. However, since no windows were used to seal the horizontal tubes, the temperature variation through the melt was rather large. At 400° the temperature was found to be about 7° lower at the position of the laser beam than in the rest of the melt.

General Considerations

It was not found practical to perform the Raman measurements under exactly the same conditions as used in the potentiometric and spectrophotometric work, where 0.1, 0.2, and 0.3 *F* solutions of Te(IV) were examined. In order to obtain good Raman spectra, higher concentrations were used. However, it is still reasonable to consider the melts as dilute solutions since there were in most cases about eight $AlCl_4^-$ ions for each Te(IV) unit. Due to the higher concentrations a temperature of 400° instead of 300° was needed in order to keep the Te(IV) units in solution. It has been shown[2] that at 300° a precipitate assumed to be K_2TeCl_6 separates out at Te(IV) concentrations higher than *ca.* 0.17 *M*, if the melt is saturated with KCl.

The potentiometric measurements[2] show that it is not possible to get a pure solution of any single Te(IV) complex. It is clear therefore that it is not easy to get detailed information about the structure of each complex, especially since the vibrations give rise to Raman shifts smaller than 400 cm^{-1}. Furthermore bands from the solvent interfere. In order to solve this problem it was necessary to examine the concentrated solutions.

A survey of the predicted and observed modes of Raman-active vibrations for the various Te(IV) complexes found in the potentiometric study[2] is given in Table I.

Results and Discussion

Raman Spectra of Diluted Te(IV) Solutions in Molten $KAlCl_4$. In Figure 2 the Raman spectra of a series of melts in which $TeCl_6^{2-}$, $TeCl_5^-$, $TeCl_4$, and $TeCl_3^+$ are the predominant tellurium species are compared with the spectrum of the solvent, molten $KAlCl_4$. An inspection of the spectra shows that gradual but significant changes take place on going from the basic solutions, Figure 2(A), where $TeCl_6^{2-}$ should be the predominant species according to the potentiometric measurements,[2] to the acid solution, Figure 2(D), where $TeCl_3^+$ is predicted to obtain its relative maximum concentration. The spectrum of the pure $KAlCl_4$ (Figure 2(E)) has been described by numerous authors[17-21] and is in agreement with the $AlCl_4^-$ complex having T_d symmetry.

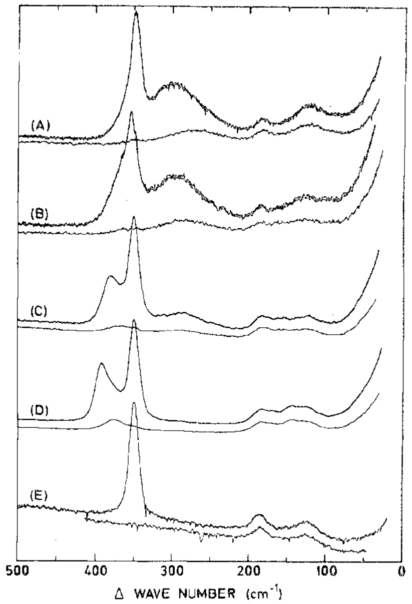

Figure 2. Series of Raman spectra (parallel and perpendicular polarizations) of 0.8 *F* Te(IV) in molten $KAlCl_4$. The concentrations and temperatures were respectively as follows: A, 1.6 *F* KCl, 0.8 *F* $TeCl_4$, 400°; B, 0.8 *F* KCl, 0.8 *F* $TeCl_4$, 400°; C, 0.8 *F* $TeCl_4$, 275°; D, 0.8 *F* $AlCl_3$, 0.8 *F* $TeCl_4$, 275°; E, pure solvent, 400°.

Table I. Predicted and Observed Raman-Active Modes for Chloro Complexes of Te(IV)[a]

$TeCl_3^+$ (C_{3v})		$TeCl_4$ ($TeCl_3$–Cl (C_{3v})		$TeCl_5^-$ (C_{4v})		$TeCl_6^{2-}$ (O_h)	
Pred	Obsd	Pred	Obsd	Pred	Obsd	Pred	Obsd
2 A_1	1 p, 1 p?	3 A_1	1 p	3 A_1	1 p	1 A_{1g}	1 p
2 E	2 dp	3 E	2 dp	2 B_1	1 dp	1 E_{1g}	
				1 B_2		1 F_{2g}	
				3 E	1 dp		

[a] Key: dp, depolarized; p, polarized.

The spectra are tabulated in Table II, and where possible an assignment is given for each band based on spectra given in the literature[13,18,22] or from the work on the more concentrated melts to be discussed later. It should be noted here that the errors in the band positions given in Table II (and in the other tables) are larger than the instrumental uncertainty. This is due to difficulties in resolving the measured bands. However, some of the variations in the band positions for the same bands given in Table II might be due to interactions between the ions in the system.

In Figure 2(A) is shown the spectrum of a melt in which tellurium should be present predominantly as $TeCl_6^{2-}$. It

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Table II. Raman Frequencies of Te(IV) Solutions in Molten $KAlCl_4$ (cm^{-1})[a]

0.8 *F* Te(IV) $KCl:TeCl_4 = 2:1$ 400°, A	0.8 *F* Te(IV) $KCl:TeCl_4 = 1:1$ 400°, B	0.8 *F* Te(IV) $KCl:TeCl_4 = 0:1$ 275°, C	0.8 *F* Te(IV) $AlCl_3:TeCl_4 = 1:1$ 275°, D	$KAlCl_4$ 400°, E	Assignment
			388 m, p		ν_1 (A_1) $TeCl_3^+$
	375 sh?	381 m, p			(A_1) $TeCl_4$
			376 w, dp		ν_3 (E) $TeCl_3^+$
		366 w, dp			(E) $TeCl_4$
349 vs, p	354 vs, p	350 vs, p	351 vs, p	349 vs, p	ν_1 (A_1) $AlCl_4^-$
300 s, p	295 s, p				ν_1 (A_{1g}) $TeCl_6^{2-}$
270 m, dp?	281 m, dp?	286 w, dp?			(A_1) $TeCl_5^-$
185 m, dp	185 m, dp	184 m, dp	183 m, dp	182 m, dp	ν_4 (F_2) $AlCl_4^-$
	170 w, p?		169 m, p?		ν_2 (A_1) $TeCl_3^+$
			144 m, dp		ν_4 (E) $TeCl_3^+$
124 m, dp	129 m, dp	122 m, dp	125 m, dp	123 m, dp	ν_2 (E) $AlCl_4^-$
	100 m, dp				(E) $TeCl_5^-$

[a] Key: m, medium; s, strong; sh, shoulder; v, very; w, weak; dp, depolarized; p, polarized.

Table III. Raman Frequencies of $TeCl_4$ Dissolved in Molten $KAlCl_4$ at 275° and at Different Concentrations (cm^{-1})[a]

0.4 *F* $TeCl_4$ A	0.8 *F* $TeCl_4$ B	1.6 *F* $TeCl_4$ C	Assignment
380 m, p	381 s, p	380 s, p	(A_1) $TeCl_4$
363 w, dp	366 m, dp	366 m, dp	(E) $TeCl_4$
350 vs, p	350 vs, p	350 vs, p	ν_1 (A_1) $AlCl_4^-$
287 w, p?	286 m, p?	287 m, p?	(A_1) $TeCl_5^-$
184 m, dp	184 m, dp	181 m, dp	ν_4 (F_2) $AlCl_4^-$
		~153 m, dp	(E) $TeCl_4$
124 m, dp	122 m, dp	123 m, dp	ν_2 (E) $AlCl_4^-$

[a] Key: m, medium; s, strong; v, very; w, weak; dp, depolarized; p, polarized.

was only possible to obtain this spectrum in dilute solution due to the strong absorption in the visible range. Figure 2(B) shows the spectrum of a dilute solution of predominantly $TeCl_5^-$ in $KAlCl_4$. As one can see the relative intensities of the bands have changed, as the $KCl:TeCl_4$ ratio has changed from 2 to 1. Also a new band has appeared around 100 cm^{-1} and this band is assigned to $TeCl_5^-$. It should be noted here that the lowest lying observed band in solid Et_4NTeCl_5 is at 115 cm^{-1}, but according to the normal-coordinate analysis of Ozin, *et al.*,[13] a degenerate E mode should be located at 96 cm^{-1}.

A fairly large difference is observed between Figure 2(B) and Figure 2(C), and again a small change is observed comparing Figure 2(C) and Figure 2(D). This means that Figure 2(C), which should mainly show the spectrum of $TeCl_4$, has a remarkable resemblance to the spectrum of $TeCl_3^+$ dissolved in $KAlCl_4$ seen in Figure 2(D). A simple explanation of this would be that neutral $TeCl_4$ species do not exist in the former system. However, in the potentiometric study[2] of 0.3 *F* Te(IV) solutions in molten $KAlCl_4$ we found that the stability constants for $TeCl_6^{2-}$, $TeCl_5^-$, and $TeCl_4$ were of quite normal magnitude and that models, omitting $TeCl_4$, could not possibly be fitted to the pCl^- measurements. Realizing that $TeCl_4$ in these melts has a Raman spectrum very similar to that of $TeCl_3^+$ one encounters a situation exactly parallel to the findings of Mamantov and coworkers[23] that the Raman spectra of molten $SbCl_3$ and KCl-$SbCl_3$ (1:1) are almost indistinguishable, even if $SbCl_3$ is a Lewis acid and a good Cl^- acceptor. Their final conclusion, however, is that no appreciable quantities of $SbCl_4^-$ (which is isoelectronic with $TeCl_4$) exist in the molten mixture. In the present case we propose a structure, which can be represented as $TeCl_3$-Cl with three equivalent Te-Cl bonds and one longer and weaker Te-Cl bond. A similar explanation is that $TeCl_4$ in $KAlCl_4$ is forming neutral ion pairs $[TeCl_3^+,Cl^-]$, which can explain the spectral similarity between $TeCl_4$ and $TeCl_3^+$. The observed frequency shifts of the $TeCl_3^+$ complex are discussed in the last section of this paper.

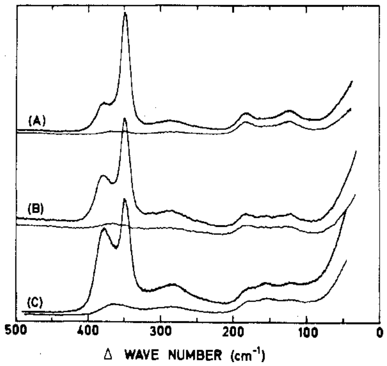

Figure 3. Series of Raman spectra (parallel and perpendicular polarizations) of $TeCl_4$ dissolved in molten $KAlCl_4$ at 275°: A, 0.4 *F* $TeCl_4$; B, 0.8 *F* $TeCl_4$; C, 1.6 *F* $TeCl_4$.

Solid $TeCl_4$ has been shown to contain polymeric Te_4Cl_{16} units,[3] which are essentially ionic consisting of $TeCl_3^+$ and Cl^- ions. It therefore seemed appropriate to investigate whether the polymerization equilibrium $4TeCl_4 \rightleftharpoons Te_4Cl_{16}$ was present in molten $KAlCl_4$. This equilibrium should be very sensitive to concentration variations. In Figure 3 are shown spectra of 0.4, 0.8, and 1.6 *F* $TeCl_4$ solutions in molten $KAlCl_4$ at 275°. The relative intensities of all bands assigned to the tellurium species grow in proportion to the concentration of $TeCl_4$, which excludes the presence of any polymerization reactions. The close similarity between the spectra of 1.6 *F* $TeCl_4$ in $KAlCl_4$ and the spectrum of pure molten $TeCl_4$ shown in Figure 4(C) further indicates that pure molten $TeCl_4$ consists of monomeric $TeCl_3$-Cl units. This is in contrast to the molecular weight determinations of $TeCl_4$ in benzene,[6] where polymerization was proved to exist in 0.1 *F* solution and stronger solutions. A Raman spectrum of 0.08 *F* $TeCl_4$ in benzene[6] was rather similar to the spectrum of monomeric gaseous $TeCl_4$. Taking into account the higher temperature and the profound differences of $KAlCl_4$ and benzene as solvents, these results are not incompatible. In Table III the frequencies for the observed bands in Figure 3 are given together with the tentative assignments.

Raman Spectra of Molten KCl-$TeCl_4$ Mixtures. This system represents an extreme of the basic solutions, where indeed the solvent has been omitted. Spectra of mixtures containing KCl and $TeCl_4$ in the molar ratios 1:1, 1:2, and 0:1 are shown in Figure 4. Due to the strong coloration of the melts it was not possible to exceed the ratio 1:1 shown in

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[23] K. W. Fung, G. M. Begun, and G. Mamantov, *Inorg. Chem.*, 12, 53 (1973).

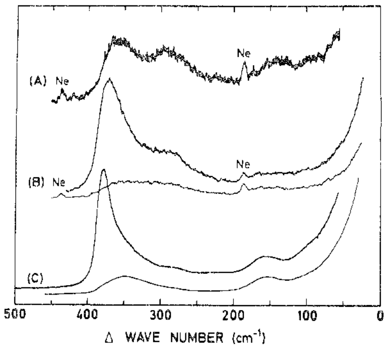

Figure 4. Series of Raman spectra (parallel and perpendicular polarizations except for spectrum (A)) of KCl-$TeCl_4$ mixtures. Formality ratio KCl:$TeCl_4$ and temperature: A, 1:1, 300°; B, 1:2, 400°; C, 0:1, 410°.

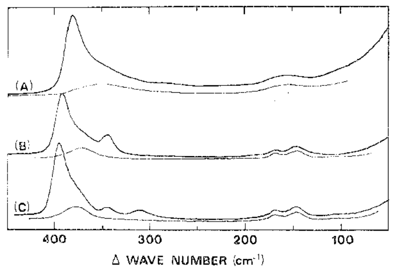

Figure 5. Series of Raman spectra (parallel and perpendicular polarizations) of molten $AlCl_3$-$TeCl_4$ mixtures. Formality ratio $AlCl_3$:$TeCl_4$ and temperature: A, 0:1, 250°; B, 1:1, 200°; C, 2:1, 150°.

Table IV. Raman Frequencies of Molten KCl-$TeCl_4$ Mixtures (cm^{-1})[a]

KCl: $TeCl_4$ = 1:1 410°, A	KCl: $TeCl_4$ = 1:2 400°, B	KCl: $TeCl_4$ = 0:1 300°, C	Assignment
		381 s, p	(A_1) $TeCl_4$
	374 s, p		?
358 m	354 m, dp?	350 m, dp	(E) $TeCl_4$
295 m	290 m, p?	283 vw, p?	ν_1 (A_{1g}) $TeCl_6^{2-}$, (A_1) $TeCl_5^-$
	150 w, dp	153 m, dp	(E) $TeCl_4$
~140 m			(B_2) $TeCl_5^-$
~100 w	100 vw		(E) $TeCl_5^-$

[a] Key: m, medium; s, strong; v, very; w, weak; dp, depolarized; p, polarized.

Figure 4(A). Even here the spectral quality is not satisfactory. The phase diagram of the KCl-$TeCl_4$ system[12] shows only one stable intermediate compound in the phase, *i.e.*, K_2TeCl_6, melting at 570°. The complexity of molten systems is nevertheless often more intricate than indicated by the phase diagram. In this case it means that besides the hexachlorotellurate complex other species can be present in the molten mixture.

The spectrum of solid Et_4NTeCl_5[13] has bands at 336, 295, 266, 244, 208, 143, and 115 cm^{-1}; however, the bands at 244 and 208 cm^{-1} are weak. When the spectrum of the 1:1 molten mixture, Figure 4(A), is compared with the spectrum of Et_4NTeCl_5, it is clear that the bands at 295, ~140, and 100 cm^{-1} can be assigned to a $TeCl_5^-$ complex of C_{4v} symmetry. Although the melt composition corresponds to an average coordination number of 5 for Te(IV), it must be realized that the available number of chloride ligands are distributed between hexa- and pentacoordinated and lower coordinated species. In this way the band at 295 cm^{-1} probably gains intensity from the ν_1 vibration of the octahedral $TeCl_6^{2-}$ complex found to be 296 cm^{-1} in solid K_2TeCl_6[24] and the band at 336 cm^{-1} cannot be observed due to overlap with the band located at 354 cm^{-1}. The latter band must be associated with tellurium species with average coordination numbers lower than 5. The gradual shift to higher frequencies of the highest lying band for a 1:1 mixture of KCl-$TeCl_4$ to pure molten $TeCl_4$ is in agreement with the general observation that the ligands are more strongly bound, the lower the coordination number. The spectrum in Figure 4(B), where the KCl:$TeCl_4$ ratio is 1:2, is intermediate between the spectrum of the 1:1 composition and that of pure molten $TeCl_4$ shown in Figure 4(C). It must be concluded that the melt at 1:2 composition contains smaller amounts of six- and five-coordinate Te(IV) and a major proportion of $TeCl_4$.

The traditional formulation of molten $TeCl_4$ as an ionized melt consisting of $TeCl_3^+$ and Cl^- was first given by Gerding and Houtgraaf,[9] partly from spectral evidence, since the Raman spectrum of molten $TeCl_4$ has no resemblance to that of gaseous $TeCl_4$,[6] which is known to consist of monomeric units of C_{2v} symmetry and partly to account for the fairly high electrical conductivity of the melt.[25] However, potentiometric determination of the chloride concentration in molten $TeCl_4$ at 300° by a previously described method[2,26] shows that it contains less than 10^{-2} *M* free Cl^- ions.[27] The ionized model is likewise contradicted by the short liquidus range of molten $TeCl_4$ (225-390°).[15] The high conductivity can probably be explained in terms of a chloride-transfer mechanism.[28]

It can be concluded that molten $TeCl_4$ contains a monomeric four-coordinate tellurium species, which has a structure different from the gas-phase molecule. This species is furthermore only slightly dissociated. In Table IV the frequencies for the observed bands in Figure 4 are given together with the tentative assignments.

Raman Spectra of the Molten $TeCl_4$-$AlCl_3$ System. In Figure 5 is shown a comparison between the spectra of molten $TeCl_4$ (A) and of $TeCl_4$-$AlCl_3$ in the molar ratio 1:1 (B) and in the ratio 1:2 (C). Addition of $AlCl_3$ to molten $TeCl_4$ up to the ratio 1:1 will give rise to a strong (and polarized) band at 344 cm^{-1}, due to the formation of $AlCl_4^-$ (T_d). This band can be assigned as ν_1 (A_1).[20] The bands due to Te(IV) are then the four bands located at 392, 371, 169, and 147 cm^{-1}. The band at 392 cm^{-1} is strongly polarized. If we take the strong chloride affinity of $AlCl_3$ into consideration, then the reactions must be in accordance with findings of Gerding and Houtgraaf:[9] $TeCl_4 + AlCl_3 \rightarrow TeCl_3^+ + AlCl_4^-$, with more or less complete reaction. $TeCl_3^+$ is isoelectronic with the pyramidal $SbCl_3$ molecule, which has C_{3v} symmetry. An assignment of the $TeCl_3^+$ spectrum under assumption of a C_{3v} symmetry based on comparison with the spectrum of $SbCl_3$[23] is given in Table V. If the ratio of $AlCl_3$ to $TeCl_4$ is increased to more than 1:1, the band at 344 cm^{-1} decreases in intensity, and a new polarized band at 311 cm^{-1} appears. This behavior is quite analogous to the behavior in the MCl-$AlCl_3$ systems[19-21] (M = Li, Na, K, Cs), and this band has been shown to be due to $Al_2Cl_7^-$. The ratio 2:1 corresponds stoichiometrically to the formation of $TeCl_3^+$ and $Al_2Cl_7^-$. However, since at this composition there is a considerable

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Table V. Raman Frequencies of Molten $AlCl_3$-$TeCl_4$ Mixtures (cm^{-1})[a]

$AlCl_3$: $TeCl_4$ = 0:1 250°, A	$AlCl_3$: $TeCl_4$ = 1:1 200°, B	$AlCl_3$: $TeCl_4$ = 2:1 150°, C	Assignment
	392 vs, p	395 vs, p	ν_1 (A_1) $TeCl_3^+$
381 vs, p			(A_1) $TeCl_4$
	371 m, dp	378 m, dp	ν_3 (E) $TeCl_3^+$
351 m, dp			(E) $TeCl_4$
	344 m, p	345 m, p	ν_1 (A_1) $AlCl_4^-$
		311 m, p	(A_1) $Al_2Cl_7^-$
281 vw, dp?			(B_1) $TeCl_5^-$
	169 m, p?	169 m, p?	ν_2 (A_1) $TeCl_3^+$
151 m, dp			(E) $TeCl_4$
	147 m, dp	147 m, dp	ν_4 (E) $TeCl_3^+$

[a] Key: m, medium; s, strong; v, very; w, weak; dp, depolarized; p, polarized.

amount of $AlCl_4^-$ present, the mass balance demands that the rest of Al(III) is present as Al_2Cl_6. A calculation similar to that used by Oye, *et al.*,[18] of the mole fraction equilibrium constant $K = x_{Al_2Cl_6}x_{AlCl_4^-}{}^2/x_{Al_2Cl_7^-}{}^2$ was performed. It was assumed that the Raman intensity is proportional to the concentration. The intensities of the strongest bands for $AlCl_4^-$ and $TeCl_3^+$ used were obtained from the mean of three spectra of 1:1 composition and the 2:1 composition of $AlCl_3$-$TeCl_4$. A value for K of about 2×10^{-2} was obtained. This value fits reasonably well with the values from the MCl-$AlCl_3$ systems, where K can be calculated to be 0.8×10^{-2}, 2.6×10^{-2}, and 4.96×10^{-2} for KCl,[18] NaCl,[29] and NaCl[30] at 170-240, 190, and 175°, respectively. It is here worthwhile mentioning that in contrast to the MCl-$AlCl_3$ systems no miscibility gap is found in the $TeCl_4$-$AlCl_3$ system. An explanation for this is probably that the M^+ ions (M = Li, Na, K, Cs) are not able to form uncharged species with the anions of the melt to the same degree as the polar $TeCl_3^+$ and that the uncharged species are completely miscible with Al_2Cl_6. That there is strong interaction between the ions in the system can be seen from the frequency change of the symmetrical stretching vibration of the $TeCl_3^+$ complex. As the anions become less and less able to polarize (*i.e.*, as one goes from Cl^- to $AlCl_4^-$ to $Al_2Cl_7^-$ and $AlCl_4^-$), the frequencies 381, 392, and 395 cm^{-1}, respectively, are obtained for the position of the band due to the symmetrical stretching vibration.

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Registry No. $KAlCl_4$, 13821-13-1; $TeCl_4$, 10026-07-0; $AlCl_3$, 7446-70-0; $TeCl_3^+$, 43644-19-5; $TeCl_5^-$, 44246-02-8; $TeCl_6^{2-}$, 20057-66-3; KCl, 7447-40-7.

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Vibrational Spectra and Bonding in Acetonitrile Complexes of Group Va Pentahalides

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Complete solid-state Raman and infrared spectra have been obtained for the acetonitrile adducts of arsenic pentafluoride and antimony pentachloride. In addition, Raman depolarization data are presented for the acetonitrile and SO_2 solutions of these systems. The results are in accord with the X-ray structure of $SbCl_5 \cdot NCCH_3$ which is a molecular solid with octahedral coordination (~C_{4v} symmetry) about the central metal atom. In general, the metal-halogen vibrations correlate well in relative frequency and intensity with those of similar complexes having approximately C_{4v} symmetry. The measured Raman shifts for the MN stretch (including the revised assignment of the previously reported data for the SbF_5 complex) are ~277 cm^{-1} for $SbF_5 \cdot NCCH_3$, 270 cm^{-1} for $AsF_5 \cdot NCCH_3$, and 222 cm^{-1} for $SbCl_5 \cdot NCCH_3$. The respective force constants for each of these complexes are 1.9, 1.9, and 1.1 mdyn/Å. The relationship between the constants of the fluoride and the chloride complexes for antimony (*i.e.*, $SbF_5 \cdot NCCH_3$ > $SbCl_5 \cdot NCCH_3$) is just opposite to that calculated for the acetonitrile complexes of the boron halides. An attempt to stabilize the "nonexistent" molecule $AsCl_5$ as the acetonitrile complex proved unsuccessful.

Introduction

Strong Lewis acids, particularly the binary metal halides, and their adducts find use in a host of well-known reactions. For example, they have long served as catalysts[2] and intermediates[3] in Friedel-Crafts and related reactions. In the past, reports involving the use of group IIIa halides dominated the literature; since the earyl 1960's, however, interest in the pentahalides of the group Va elements has increased. One major instance is the use of antimony pentafluoride in the formation and stabilization of simple carbonium ions.[4]

A variety of simple molecular and ionic $MX_5 \cdot L$ complexes (~C_{4v} symmetry) exist, including such species as $AsF_5 \cdot NCCH_3$,[5] $AsF_5 \cdot N(CH_3)_3$,[5] $AsF_5 \cdot SO_2$,[5] $AsF_5 \cdot PF_3$,[6] AsF_5Cl^-,[7] AsF_5Br^-,[7] AsF_5OH^-,[5] $SbF_5 \cdot NCCH_3$,[5] $SbF_5 \cdot$dioxane,[5] $SbF_5 \cdot$py,[5] $SbF_5 \cdot SO_2$,[5] $SbF_5 \cdot PF_3$,[6] $SbF_5 \cdot P(C_6H_5)_3$,[6] $SbF_5 \cdot As(C_6H_5)_3$,[6] SbF_5OH^-,[5,8] $SbCl_5 \cdot OP(CH_3)_3$,[9] $SbCl_5 \cdot OPCl_3$,[9] $SbCl_5 \cdot CH_3NO_2$,[10] $SbCl_5 \cdot$DMF,[11] $SbCl_5 \cdot$DMSO,[9,11] and $SbCl_5 \cdot$

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