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The Infrared Spectra, Phase Transition, and Structural Properties of Tetraethylammonium Hexafluoroantimonate $(C_2H_5)_4NSbF_6$

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$(C_2H_5)_4NSbF_6$ (TEAHFA) is face-centered cubic with a = 11.487 Å at ambient temperature and undergoes a first-order phase transition at 246 K on cooling and at 272 K on heating. The infrared spectra of TEAHFA confirm the cubic structure of the room temperature phase I in which no evidence could be found for the existence of hydrogen bonds between the cations and anions.

Introduction

The high-pressure phase relations, vibrational spectra and crystal chemistry of the compounds $R^{\mathrm{I}}M^{\mathrm{V}}F_6$ (where R = Na^+, K^+, and Cs^+ and M = P, As, and Sb) have been studied in detail (*1–5*). In order to extend these studies to include compounds of this type where R is a large cation we have undertaken a study of the infrared, far-infrared, and Raman spectra, as well as the powder X-ray diffraction pattern of $(C_2H_5)_4NSbF_6$ (TEAHFA). This paper deals with the powder diffraction pattern and infrared spectra of this compound.

The structures of the $R^{\mathrm{I}}M^{\mathrm{V}}F_6$ compounds investigated so far can be roughly classified into three main categories. The face-centered cubic structure $Fm3m-O_h^5$ is common among the high-temperature phases of these compounds, i.e., $NaPF_6$(I) (*4*), $NaSbF_6$(I) (*6*), KPF_6(I) (*1*) and $KAsF_6$(I) (*2*). In this structure the anions are believed to reorientate rapidly and can thus be regarded as being disordered. Rhombohedral structures are also common amongst these compounds, for example, $CsSbF_6$(II) ($R\bar{3}m-D_{3d}^5$) (*7*) and $KAsF_6$ ($R\bar{3}-C_{3i}^1$) (*8*). $KSbF_6$(I), on the other hand, is tetragonal ($P\bar{4}2m-D_{2d}^1$) (*9*) while $KNbF_6$ and $KTaF_6$ are believed to have either similar or closely related structures. As far as the structures of compounds involving tetraalkylammonium cations are concerned, the high-temperature phase of tetramethyl ammonium chloride was reported by Pistorius to be face-centered cubic ($Fm3m-O_h^5$) with the cations disordered (*10*). However, not much information is available as far as the structures of tetraethylammonium compounds are concerned. Tetragonal and orthorhombic space groups for these compounds are very common, $[(C_2H_5)_4N]_2NiCl_4$ and

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$(C_2H_5)_4NSbBr_6$, for example, both belong to tetragonal space groups (*11, 12*) while several examples of orthorhombic tetraethylammonium compounds have been discussed in the literature (*13–16*). The tetraethylammonium cation can only possibly attain cubic symmetry if methyl rotational disorder and/or orientational disorder of the cation exist so that T_d symmetry is approximated. In a crystal like, for example, TEAHFA, this disorder might not be completely random at room temperature, thus causing small deviations from cubic symmetry. It is therefore likely that an order–disorder phase transition or more than one transition can occur at lower temperature in a crystal containing disordered tetraethylammonium cations. This can be due to, inter alia, the formation of weak hydrogen bonds at low temperature and the consequent "freezing out" of the relatively free methyl rotation.

The vibrational spectra of the *n*-alkyl-substituted ammonium ions have been reported extensively, particularly as far as the $(CH_3)_4N^+$ ion (*17–22*) is concerned and on the other hand, the vibrational spectra of the SbF_6^- ion are also well known (*3, 5*). However, to the best of our knowledge the vibrational spectra of $(C_2H_5)_4NSbF_6$ have not been previously reported, and it would thus be of interest to analyze the infrared spectra and X-ray powder diffraction patterns to obtain more information regarding the structure of TEAHFA.

Experimental

Tetraethylammonium hexafluoroantimonate (TEAHFA) was prepared from freshly produced Sb_2O_5, 40% hydrofluoric acid and a saturated solution of tetraethylammonium hydroxide according to the method described by Kolditz and Nussbücker (*23*). The melting point was determined as 320°C by using the Gallenkamp melting-point apparatus as compared with the literature value of 328°C (*23*). An analysis for Sb and F yielded a molar ratio of 1 : 5.95.

The details of the recording of the infrared spectra are described elsewhere (*5*). X-Ray powder diffraction patterns were recorded on a Huber Guinier camera using monochromatized Cu$K\alpha_1$ radiation (λ = 1.54056 Å). Si was used as an internal calibrant and both film and counter techniques were employed. Because of the rubbery nature of the sample, grinding under liquid nitrogen improved the problem of obtaining a sufficiently finely ground powder.

Results

Crystallography

The X-ray powder diffraction pattern is presented in Table I. All the peaks could be satisfactorily indexed as belonging to a cubic structure with a = 11.487 ± 0.005 Å. The extinction criteria with *hkl, okl,* and *hhl* being all odd or all even and *ool* even indicate a face-centered cell and possible space groups $Fm3m$, $F432$, $F\bar{4}3m$, $Fm3$, or $F23$. Because the cubic structures of the other related compounds are $Fm3m$ (*10*), there exists the possibility that the present space group can also be $Fm3m$.

Discussion

The Vibrational Spectra of TEAHFA I

An incomplete assignment of the vibrational spectra of tetramethylammonium hexafluoroantimonate (TMAHFA) has been described by Harmon *et al.* (*17*). They predicted from the infrared spectral data that TMAHFA would have a cubic symmetry, with the nature of the bond angles in the cation undistorted from tetrahedral symmetry and further suggested that there were clear correlations between the qualita-

TABLE I

POWDER DIFFRACTION PATTERN OF TEAHFA AT 20°C

$h\ k\ l$	d_{calc}	d_{obs}	I/I_0
1 1 1	6.63	6.64	80
2 0 0	5.744	5.744	100
2 2 0	4.062	4.059	80
3 1 1	3.464	3.460	75
2 2 2	3.316	3.314	55
4 0 0	2.872	2.874	<1
3 3 1	2.6355	2.6360	20
4 2 0	2.5688	2.5700	24
4 2 2	2.3450	2.3447	21
5 1 1	2.2108	2.2105	12
4 4 0	2.0308	2.0298	5
5 3 1	1.9418	1.9414	9
6 0 0	1.9146	1.9141	4
6 2 0	1.8164	1.8153	<2
5 3 3	1.7519	1.7507	<1
6 2 2	1.7319	1.7321	<2
7 1 1	1.6086	1.6086	<1
6 4 0	1.5931	1.5936	<1
6 4 2	1.5351	1.5358	<1
7 3 1	1.4956	1.4957	<1
8 2 0	1.3931	1.3926	<1
9 5 0	1.1158	1.1161	<2
10 4 4	0.9999	0.9997	<1
10 6 0	0.9851	0.9851	<1

tive appearance of the cation infrared spectrum and the structure of the crystalline tetraalkylammonium compound. The solid-state infrared spectra of tetramethylammonium salts have further been used by Harmon *et al.* (*17*) to predict the lattice type, the approximate size of the anion, the closeness of approach of the cations to each other, the presence of absence of cation to anion hydrogen bonding, and whether or not the cation is distorted from tetrahedral bonding (*17*). However, some of these suggestions are of a tentative and questionable nature and are therefore open to criticism, but they can at least be used to give some indication of whether the cation is in a symmetrical environment and whether and to what extent hydrogen bonding exists between the cation and anion in tetraalkylammonium salts.

The infrared spectra of selected tetraalkylammonium compounds are listed in Table II and the results obtained in certain spectral ranges which are of interest will now be compared with the results previously obtained on tetraalkylammonium compounds (*17*).

The Region 2800–3100 cm^{-1}

In the ν_{sym} C–H stretching region (2800–3000 cm^{-1}) a sharp singlet band appears as the primary absorption in tetramethylammonium salts that lack hydrogen bonding to the anion, for example in tetramethylammonium hexachlorostannate (*17*). A second broad strong band appears at lower wavelengths in the same spectral region in the spectra of salts in which such C–H----anion hydrogen bonds are present, as, for example, in tetramethylammonium chloride (*17*). Only one weak feature occurring at 2998 cm^{-1}, which most probably represents the symmetric C–H stretching band, has been observed in the infrared spectrum of TEAHFA I. On the other hand, four intense Raman bands have been observed in this spectral region (*25*) and this can most probably be regarded as an indication that the rule of mutual exclusion applies whereby infrared-active bands are Raman inactive and vice versa.

Comparing our results with those obtained on the ir spectra of $(CH_3)_4N^+$-compounds in this spectral region it can be concluded that $(C_2H_5)_4N^+$ is most probably cubic in TEAHFA(I), with little or no C–H----F hydrogen bonding and these results are in agreement with the proposed space group $Fm3m$ for TEAHFA(I).

The Region 900–1500 cm^{-1}

The region between 900 and 1500 cm^{-1} sharply distinguishes between the cubic and the tetragonal tetraalkylammonium salts (*17*). All of these salts show a strong absorption for the asymmetric methyl de-

TABLE II

The Infrared Spectra of the Tetraethylammonium Cation in Tetraethylammonium Tetraiodo Mercurate II (*14*) TEAHFA and TMAHFA (*13*) at Ambient Temperatures

$[(C_2H_5)_4N]_2HgI_4$	Assignment	TEAHFA	Assignment	TMAHFA	Assignment
3009 m	$\nu_{as}(CH_2)$			3060 s	ν_{asym}(C–H)
2993 s	$\nu_{as}(CH_2)$	2998 w	$\nu_{as}(CH_2)$		
2982 sh	$\nu_{as}(CH_3)$				
2950 m	$\nu_{sym}(CH_2)$	2960 vw	$\nu_{sym}(CH_2)$		
2920 w,sh	$\nu_{sym}(CH_3)$				
2890 w,sh	$\nu_{sym}(CH_3)$				
2860 w,sh	$\nu_{sym}(CH_3)$				
1485 s		1483 s		1490 vs	δ_{asym}(C–H)
1479 sh		1475 sh			
1472 sh	$\delta_{as}(CH_3)$		$\delta_{as}(CH_3)$		
1462 m,sh					
1455 vs		1457 m			
1448 sh		1440 ms			
1442 sh					
1405 s	δ (CH_2)	1408 sh	δ (CH_2)	1420 m	δ_{sym}(C–H)
1394 s		1393 s			
1369 ms					
1351 mw	$\delta_{sym}(CH_3)$	1365 ms	$\delta_{sym}(CH_3)$		
1305 ms	CH_2 twist	1300 w	CH_2 twist		
1183 s		1180 sh			
1172 s	CH_3 rock	1173 s	CH_3 rock		
1120 vw					
1079 mw					
1070 w	ν_{as}(C–C)	1070 w	ν_{as}(C–C)		
1055 mw		1050 m			
1032 m					
1025 sh	ν_{as}(C–N)	1017 m,sh	ν_{as}(C–N) ν_3		
1000 ms	CH_3 rock	1000 s	CH_3 rock		
891 mw	ν_{sym}(C–C)	885 vw	(ν_{sym}C–C)	949 vs	ν_B(C–N)
790 sh					
783 s	CH_2 rock	783 s	CH_2 rock		
469 mw	δ (C–C–N)	496 mw	δ (C–C–N)		
		445 sh			

Note. The 850-cm^{-1} band and 665-cm^{-1} shoulder may be combination bands of the anion.

formation mode, δ_{as} near 1500 cm^{-1}; however, the remainder of the spectrum differs significantly in the different structures. In the tetragonal salts the symmetrical methyl deformation mode, δ_{sym} near 1400 cm^{-1}, is a moderately strong band and the methyl rocking mode, CH_3 rock near 1200 cm^{-1}, is difficult to detect, while in cubic salts δ_{sym} is relatively weak compared to the intense CH_3 rock (*17*). In TEAHFA(I), CH_3 rock at 1173 cm^{-1} is much more intense than δ_{sym} (CH_3) which occurs at 1365 cm^{-1} and this observation can possibly be interpreted in terms of TEAHFA(I) having a cubic structure.

In the cubic tetraalkylammonium salts both the δ_{sym} and δ_{sym} CH_3 modes appear as single modes; however, in the tetragonal salts these bands are split (*17*). In the case of TEAHFA(I), δ_{sym} (CH_3) is a sharp singlet but δ_{asym} (CH_3), although very sharp, has a slight shoulder at 1475 cm^{-1}. This shoulder is not so distinct as the one in tetramethylammoniumperchlorate (*17*), and can therefore not be regarded as an indication of a serious deviation from T_d symmetry for the cation.

The skeletal breathing mode, ν_B (900–1100 cm^{-1}), is a singlet in cubic tetraalkylammonium salts but in tetragonal salts it is split into either a main component containing a weak shoulder or the band can be resolved into two separate peaks (*17*). For the tetramethylammonium cation ν_B was also detected by Hooper (*18*) as a distinct band, but for TEAHFA it is not well defined because it appears at 1017 cm^{-1} as one of three satellites on the high-frequency wing of the very intense CH_3 rock band, which occurs at 1000 cm^{-1}. The other two satellites at 1050 and 1070 cm^{-1} (Fig. 1) can be assigned to ν_{asym} (C–C). ν_B is nevertheless observed as a singlet in TEAHFA(I) in the present work; which is yet another indication of a cubic structure for the cation.

The hexafluorosilicate, hexachlorostannate, and hexabromostannate salts of the tetramethylammonium cation exhibited an absorption in the 1440–1480 cm^{-1} region which cannot possibly be assigned to an F_2 fundamental (*17*). This band is clearly marked in all three salts, and in the hexabromostannate it is even stronger than δ_{sym} or CH_3 rock. Weak bands in this region have been previously assigned to an inactive F_1 or an infrared-inactive E methyl-deformation mode under T_d symmetry (*18, 19*). This band has been assigned to a methyl-rotation mode (*17*); however, methyl-rotational transitions are known to occur around 200–500 cm^{-1} (*20*). Bands in this region can possibly be related to the well-known Fermi resonance in methyl-containing compounds (*24*) but their origin is not known. In TEAHFA(II) two bands occur at 1440 and 1457 cm^{-1} respectively which are most probably of the same unknown origin as the ones in the tetramethylammonium compounds (*17*).

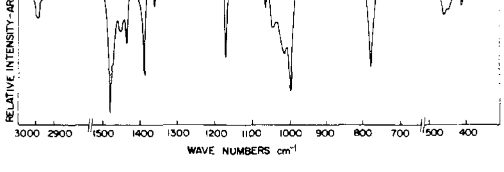

FIG. 1. The infrared spectrum of TEAHFA at ambient temperature.

SbF_6^- *Ion Infrared Spectra*

Two of the six fundamental SbF_6^- vibrational modes under O_h symmetry, viz. the stretching mode ν_3 (F_{1u}) and the bending mode ν_4 (F_{1u}), are infrared active. Accordingly, two prominent features which occur at 653 and 290 cm^{-1} can be assigned to ν_3 and ν_4, respectively. ν_3 and ν_4 were observed as narrow, well-defined absorption bands, each showing only a weak high-frequency shoulder. These very weak frequencies are the only indication of a possible deviation from O_h symmetry of SBF_6^-, but on the other hand they can also be assigned to combination bands (*3, 5*). Both these bands are much more symmetrical and narrower than their counterparts in $KSbF_6$ and $CsSbF_6$ (*3, 5*). Usually $M^VF_6^-$ ions which reorientate rapidly in the lattice exhibit very broad absorption bands like for example ν_3 in KPF_6 (*1*) and the vibrations also show violations of the rigorous selection rules due to disorder existing in the crystals. Except for the above-mentioned weak shoulders, which remain weak even at very low temperatures in TEAHFA(II), there are no indications of a serious violation of the selection rules for O_h symmetry or, for that matter, indications of rapidly reorientating SbF_6^- ions. These observations also apply to the Raman bands of TEAHFA(I) (*25*). The far-infrared spectrum of TEAHFA(I) only showed a very weak, broad, and ill-defined absorption peak below 100 cm^{-1} and this can be interpreted as an indication of a disordered crystal, as has also been observed in the cases of KPF_6(I) (*1*), $NaPF_6$(I) (*4*) and $KAsF_6$(I) (*2*), which all belong to the $Fm3m$ space groups.

The SbF_6^- vibrations are therefore also in agreement with a high-site-group symmetry for the anion in TEAHFA(I) and this is further supported by the fact that ν_6 (F_{2u}) which is Raman and infrared active, has not been observed. An even slight lowering of the symmetry from O_h will activate this mode in the infrared spectra (*3*, *5*).

Phase Transition

In virtually all of the compounds in which a specific anion is associated with the cations $(CH_3)_4N^+$ or $(C_2H_5)_4N^+$, disorder exists within the cation at room temperature. It is therefore reasonable to expect that order–disorder phase transitions will occur in such compounds at lower temperatures and it is therefore not surprising that phase transitions have been reported to occur in *n*-alkyl-substituted ammonium compounds (*20*, *22*, *26*). In the case of the $(CH_3)_4N^+$ compounds, it has been suggested that the methyl groups are involved in these transitions (*20*, *22*) and it has further been assumed that in $(CH_3)_4NCl$, weak C–H----- Cl hydrogen bonds are formed at lower temperatures. In $(C_2H_5)_4N^+$ compounds, which have not been studied so extensively as their $(CH_3)_4N^+$ counterparts, several changes in the disorder, involving different groups within the cation, can occur. These include changes in the reorientations of the cations as such, in rotations around the C–N axis or around the C–C axis, in methyl-group rotations, or in a combination of all of or some of the above-mentioned motions. It will therefore be interesting to note the changes in the characteristic CH_3, CH_2, C–C and C–N vibrations in these compounds at the phase transition temperature. Whereas the order $(CH_3)_4N^+$ cation can theoretically still have T_d symmetry at lower temperatures in tetramethyl compounds, this is not possible for the ordered $(C_2H_5)_4N^+$ ion. The highest symmetry that the latter can possibly assume is D_{2d}, and a low-site symmetry for this ion is therefore expected below the transition temperature.

The infrared bands of TEAHFA obtained in the spectral region of 1300–1500 cm^{-1} are shown in Fig. 2 at various temperatures. It is evident from this figure, which represents results obtained upon heating the sample from 17 K up to ambient temperature that significant spectral changes occur between 260 and 280 K. These spectral changes can only be plausibly explained in terms of the existence of a new phase TEAHFA, which has not been previously reported. As is evident from Table II, the infrared bands in the spectral region concerned, involve the CH_3 and CH_2 vibrations and it is therefore evident that these groups undergo significant changes at the transition temperature. The spectral changes reported in Fig. 2 are typical of changes occurring in virtually all of the infrared and Raman peaks of the cations in TEAHFA and the lower temperature phase is characterized by a multitude of infrared peaks in particular. The anion spectra, on the other hand, do not show such correspondingly significant changes, but definite splittings do develop

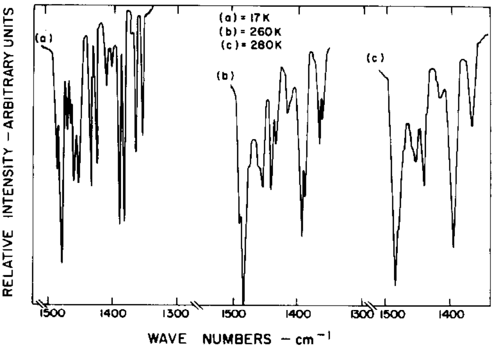

FIG. 2. The infrared spectra of TEAHFA in the region 1300–1500 cm^{-1} at various temperatures.

in phase II in the stretching band ν_3 (F_{1u}) and the bending mode ν_5 (F_{2g}).

In order to determine the transition temperature accurately, the appearance and disappearance of several infrared bands have been studied, and the results obtained in the case of the 1493-cm^{-1} band are shown in Fig. 3. The peak height of this band increases gradually at temperatures below 246 K, whereas it is only a weak shoulder above this temperature. Upon cooling samples of TEAHFA, many new features develop at 246 K, both in the infrared and Raman spectra. The results in Fig. 3 show that these changes occur at 272 K upon heating and 246 K on cooling. This significant hysteresis of 26 K shows that the transition must be of the first order.

As far as the changes in the disorder existing within the cation at the phase transition are concerned, the following observations are of importance. The infrared bands involving the CH_2, CH_3, and C–C groups showed significant splittings at the phase transition, whereas the ν(C–N) modes failed to show similar changes. This applied to both the infrared and Raman spectra (*25*). In the former ν_{asym} (C–N) shifted from 1017 cm^{-1} at room temperature to 1030 cm^{-1} at 17 K, and ν_{sym} (C–N) remained virtually unchanged at 670 cm^{-1} in the Raman throughout this temperature range. No splittings have been observed in any of these C–N bands in TEAHFA(II) and this points to relatively high symmetry for the cation as well as to a possible high degree of rotational freedom around the C–N axis still existing in this phase.

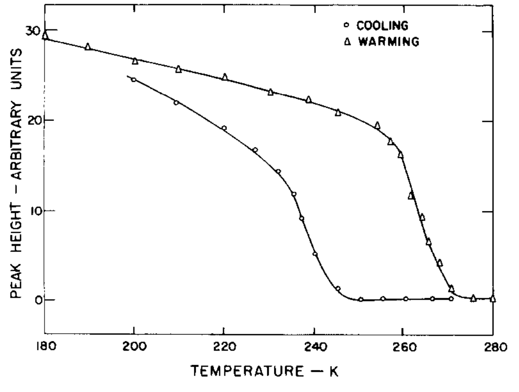

FIG. 3. The peak height of the band at 1493 cm^{-1} of TEAHFA at various temperatures.

The crystal structure of the low-temperature phase (TEAHFA(II)) is unknown and it is not the purpose of the present work to attempt an elucidation of the structure of this phase. However, preliminary results obtained from X-ray powder diffraction patterns of TEAHFA(II) show that the peaks can possible be indexed as belonging to a monoclinic structure (*27*). On the other hand, the infrared and Raman spectra of TEAHFA(II) show that the site-group symmetries of both the cation and anion must still be fairly high, a fact which cannot be easily reconciled with a monoclinic structure. The structure of TEAHFA(II) is, however, being further investigated.

Conclusion

The important conclusions to be drawn from our investigation is that in TEAHFA(I) the cation is not hydrogen bonded to the anion, but is in a highly symmetrical environment with the bond angles undistorted. Furthermore, it seems that the cations are relatively far apart in the solid TEAHFA. The infrared spectral data for TEAHFA can therefore be interpreted in terms of a cubic structure which agrees with the predictions of Harmon (*17*) on TMAHFA. The cubic structure is supported by the X-ray powder diffraction patterns which could be indexed as belonging to a face-centered cell, with *FM3m* being the likely space group. A first-order phase transition was detected on cooling as was evident from the significant changes which occurred on cooling in the infrared and Raman spectra. This may be an order–disorder transition in which there is a slight lowering in the symmetry of both the cations and anions. The low-temperature phase TEAHFA(II) is still of very high symmetry and was evidenced by the fact that the splittings occurring in the spectra of the anion were not so substantial as those in other SbF_6^- compounds, for example, $KSbF_6$ (*3*).

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