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A RAMAN, INFRA-RED AND N.M.R. SPECTROSCOPIC STUDY OF THE PENTAFLUOROTELLURATE(IV) ION

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SUMMARY

The Raman, and infra-red spectra of Na^+, K^+, Rb^+, Cs^+, NH_4^+, $C_5H_5NH^+$ and n-Bu_4N^+ salts of the TeF_5^- ion are reported. They are assigned C_s symmetry. ^{19}F n.m.r. spectra of the n-Bu_4N^+ salt show $J(F_{ax}-F_{eq})=50.4Hz$, $J(^{19}F_{eq}-^{125}Te)=1375.7Hz$, $J(^{19}F_{ax}-^{125}Te)=2883.3Hz$ and $J(^{19}F_{eq}-^{123}Te)=1143.8Hz$. No n.m.r. evidence was found for TeF_6^{2-}.

INTRODUCTION

The first spectroscopic study of the pentafluorotellurates was reported by Greenwood *et al.*[1]. From i.r. data on the $C_5H_5NH^+$, NH_4^+, K^+, Rb^+ and Cs^+ salts the Raman data on the K^+ and Rb^+ salts they concluded that the TeF_s^- ion had C_{4v} symmetry This assignment was supported by the report of the crystal structure of $KTeF_5$ by Edwards *et al.*[2]. Subsequent authors have used this data and assignment in the comparison of the isoelectronic series IF_5, TeF_5^-, SbF_5^{2-}, $XeOF_4$ and $TeOF_4^{2-}$ [3] and in the computation of force constants for SF_5^-, SeF_5^-, and TeF_5^- [4]. However a more accurate crystal structure of $KTeF_5$ by Mastin *et al.* has shown that the TeF_5^- unit has a C_s site symmetry. The basal plane of the square pyramidal ion (containing F atoms F, F_1', F_2 and F_2') is lengthened by approximately 12pm in a direction perpendicular to the mirror plane i.e. F_1-F_1' = 276pm; F_2-F_2'=277pm and $F_1-F_2=F_1'-F_2'$=265pm. In addition the Te-F_3 "axis" is at an angle of 86.7° with the basal plane. The spectra of IF_5, $KTeF_5$ and K_2SbF_5 have been reinterpreted using this evidence [6]. More recently X-ray powder data has been published on Rb^+, Cs^+, NH_4^+, and Tl^+ pentafluorotellurates [7] and a complete structural determination of $CsTeF_5$ has shown that in this salt the pentafluorotellurate ion also has C_s symmetry [8]. However the distortion from C_{4v} symmetry is somewhat smaller than in the potassium case, F_1-F_1' =267pm, F_2-F_2'=271pm and F_1-F_2=F_1'-F_2'=269pm. The Raman and i.r. data were satisfactorily assigned on the basis of C_s site symmetry.

We report the first comprehensive Raman and i.r. study on a series of seven pentafluorotellurates - Na^+, K^+, Rb^+, Cs^+, NH_4^+, $C_5H_5NH^+$ and n-Bu_4N^+ salts. Of this series there is no previous report on the Raman spectra of the Na^+, Rb^+, NH_4^+, $C_5H_5NH^+$ and n-Bu_4N^+ salts and no previous report on the i.r. spectra of the Na^+ and n-Bu_4N^+ salts. Little work has been done on the n.m.r. of solutions containing Te(IV) and F^-. ^{19}F spectra of samples prepared by dissolving Te in 40% HF with the addition of 50% HNO_3 exhibited only a single line in the temperature range -70° to +30° [9]. Asprey *et al.* have reported ^{19}F n.m.r. evidence for the formation of both TeF_5^- and TeF_6^{2-} in the $TeF_4/Bu_2NH_2F/CH_2Cl_2$ system, but no coupling was observed [10]. We found a well resolved spectrum for n-Bu_4NTeF_5 in CH_2Cl_2.

EXPERIMENTAL

All the salts were prepared by the same general method [1], using, in the case of Na^+, K^+, Rb^+, Cs^+, NH_4^+, and n-Bu_4N salts, stoichiometric quantities of TeO_2 dissolved in 40% HF and the appropriate fluoride salt. For the pyridinium salt pyridine was simply added to the TeO_2 solution. On concentration on a water bath followed by cooling, white crystals were obtained in each case. The salts were then re-crystallised from 40% HF, dried between filter paper and then in a desiccator. They were stored in polythene vials.

The salts were analysed for tellurium by the dichromate method [11]. $NaTeF_5$ Found 52.9%, Calculated 52.0%; $KTeF_5$

Found 48.6%, Calculated 48.8%; $RbTeF_5$ Found 41.9%, Calculated 41.4%; $CsTeF_5$ Found 35.4%, Calculated 35.9%; NH_4TeF_5 Found 51.8%, Calculated 52.3%; $C_5H_5NHTeF_5$ Found 42.9%, Calculated 42.1%; $\underline{n}$-Bu_4NTeF_5 Found 27.5%, Calculated 27.9%.

To prevent F^- exchange with the disc medium i.r. spectra in the 700-400 cm^{-1} region were obtained both as mulls and as discs using AgCl on a Perkin-Elmer 357 spectrometer. I.r. spectra in the region 500-100 cm^{-1} were obtained as polythene discs on a Grubb Parsons/NPL Cube Mark II interferometer fitted with a 6.25 mμ polyethylene terephthalate beam splitter. Raman spectra were taken as powdered samples in melting point tubes on a Spex Ramalog instrument. ^{19}F n.m.r. spectra of solutions of $\underline{n}$-Bu_4NTeF_5 in acetone and methylenedichloride were obtained within the temperature range -50° to +30° on a Jeol JNM PS100 FT n.m.r. spectrometer operating at 94 MHz.

RESULTS AND DISCUSSION

Our i.r. and Raman data are in reasonable agreement with that previously reported [1], [6], [8] but in some cases the number of bands we observed is considerably greater. This is particularly the case for the K^+, Rb^+ and the $C_5N_5NH^+$ salts. For each compound there is a strong absorption in the region 610-630 cm^{-1} in both the Raman and the i.r. spectra. The Raman spectra of the Na^+, K^+ and Cs^+ salts have just a single strong band at *c.a.*620 cm^{-1}. We found no evidence for the band at 657 cm^{-1} reported for the Cs^+ salt by Jumas *et al.* [8] and which was attributed by them to a complex vibration. However both the Rb^+ and the NH_4^+ spectra did show a weak band at *c.a.*630 cm^{-1}. In contrast the pyridinium salt has a strong broad band split into at least three components at 635, 629 and 610 cm^{-1}. The $\underline{n}$-Bu_4N^+ salt exhibited, in addition to the strong absorption at 658 cm^{-1}, a medium band at 627 cm^{-1}. In the corresponding i.r. region each salt showed a strong complex band.

The absorption *c.a.*500 cm^{-1} in the i.r. spectra of all the salts was also strong and broad and had, in each case, some fine structure; a similar type of band envelope was a feature of the Raman spectra. Bands occurred in both i.r. and Raman spectra for all the salts at *c.a.*345 cm^{-1} and *c.a.* 290 cm^{-1}. However the Raman absorption at *c.a.* 250 cm^{-1} was only evident in the i.r. spectrum of the K^+ salt. In addition the spectra also showed a number of weak bands in the 140-120 cm^{-1} region. It has been suggested that these are due to crystal effects [1].

For C_s site symmetry the allowed vibrations are all active in both the Raman and the i.r. There should, therefore, be twelve coincidences. However from Tables 1 and 2 it can be reacily seen that although there are a number of coincidences for all seven of the salts examined in no case is there twelve of them. The maximum number of coincidences observed is in fact only eight (K^+ and $C_5H_5NH^+$ salts). Nevertheless because of the crystal structure data the spectra can be confidently assigned on the basis of C_s symmetry.

In solution, with the restraints imposed by crystal forces removed, the TeF_5^- ion should have C_{4v} symmetry. Accordingly we decided to investigate the ^{19}F n.m.r. spectra of the highly soluble $\underline{n}$-Bu_4NTeF_5. In acetone, at room temperature, two signals were observed with intensity ratios approximately 4:1 ($\delta_{\underline{a}-\underline{b}}$=5.90 ppm). On cooling to -15° the smaller downfield signal ($\underline{b}$) split into a well-resolved multiplet containing six lines and the high field signal ($\underline{a}$) became a doublet ($\delta_{\underline{a}-\underline{b}}$= 6.17 ppm). On further cooling to -50° the multiplet took on the appearance of a quintet with some splitting of four of the lines plus a sixth line ($\delta_{\underline{a}-\underline{b}}$=6.58 ppm); in addition a small signal appeared at *c.a.* 6.5 ppm above $\underline{a}$. Changing the solvent to CH_2Cl_2 and cooling to -50° simplified the spectrum considerably due to quite a large change in $\delta_{\underline{a}-\underline{b}}$ (9.98 ppm). The multiplet was now a clear quintet with a small doublet at *c.a.* 1.5 ppm upfield from it. On accumulation the spectrum in Figure 1 was obtained and the data is summarised in Table 3.

The interesting feature of the spectrum is that not only can one observe the expected AB_4 pattern for the coupling of the fluorines but in addition coupling is observed between ^{125}Te and ^{19}F and also between ^{123}Te and ^{19}F. There are a number of reports of the former, for example in $(TeOF_4)_2$ where

TABLE 1

INFRA-RED SPECTRA OF PENTAFLUOROTELLURATES

Na^+	K^+			Rb^+		Cs^+			NH_4^+		$C_5H_5NH^+$		$\underline{n}Bu_4N^+$
		Ref 1	Ref 6		Ref 1		Ref 1	Ref 8		Ref 1		Ref 1	
								650sh					658sh
637sh	640sh			639sh				636sh	645sh		638sh		649ms
630ms	627ms		630ms	631ms		623sh	618ms	622ms	633ms		630ms		
	621ms	616ms		616sh	612ms	614ms			616ms	611ms	627sh	624ms	
	595ms										610sh		
	592sh												
540bs								535bs	532s	525m			
513bs	521bs	521m	527m	520bs	523m			505bs			500bs	502m	500bs
495bs	482bs	472vs	473vs	480bs		470bs		479bs	476bs		485bs		495bs
451bs	465bs			463bs	462vs	465bs	466sb	458bs	458bs	456vs	460bs	476vs	480bs
				420bs		453bs					448bs		
											394bs		
356m	353s	347m	355m	344m	345m	338m	336m	338ms	343m	344m	334s	328m	330m
298m	299s	293m	292m	287m	286m	285m	283m	292ms	293m	291m	275s	268m	274m
								285ms					
								275ms					
	241w												
207m				216w									214w
176m				182mw	182mw								
	148w	140mw	146m	166w	170mw	165mw	164mw		170w	184mw	166m	166mw	167mw
		130mw							137w				
		119mw	120m						122w				118w

TABLE 2

RAMAN SPECTRA OF PENTAFLUOROTELLURATES

Na^+	K^+			Rb^+	Cs^+			NH_4+	$C_5H_5NH^+$	$\underline{n}Bu_4N^+$
		Ref 1	Ref 6			Ref 1	Ref 8			
							657w		635s	645s
				631mw				629sh	629s	627m
624s	624s	616vs	624s	614s	619s	611vs	622s	616s	610m	
		570mw	579vw			572w				
530m	514s	511s	517s		513m	504s	520m	525sh	522m	523ms
	507sh			502ms			500sh	503ms		
	492m			495sh	494m	472s	488m		493w	493m
				482sh						
473m	478w	484s	488m					475w		478w
454w				456m	456w		455sh		458w	
346mw	343m	349m	345m	353m	343m	338mw	345mw	350m	334m	330w
286w	288w	294mw	291w	294mw	287m	282mw	285w	290mw	275m	270m
										253mw
248mw	242m	247mw	243m	242w	242w	231mw		239mw	234m	236m
	213m									
										166w
	149w									
121m	122w	132vw							121w	

TABLE 3 The F n.m.r. spectrum of *n*-Bu_4NTeF_5 in CH_2Cl_2 at -50°

Peak	Chemical Shift ppm*	Coupling Constants/Hz.
a	21.708	$J(^{19}F_{ax}-^{19}F_{eq})$ 50.4
b	31.717	
c	14.392	$J(^{19}F_{eq}-^{125}Te)$ 1375.7
c'	29.018	
d	15.651	$J(^{19}F_{eq}-^{123}Te)$ 1143.8
d'	27.786	
e	16.389	$J(^{19}F_{ax}-^{125}Te)$ 2883.3
e'	47.036	
		$J(^{19}F_{ax}-^{123}Te)$ 2397.3**

* Downfield from C_6F_6

** Calculated.

$J(^{125}Te-^{19}F)$ is of the order of 3600Hz [12] but there is very little in the literature on ^{123}Te couplings. Data on the complex species $[Te_nSe_{4-n}]^{2+}$ produced in highly acidic media have been reported very recently [13], [14], but even here the reports are of $^{125}Te-^{123}Te$ and $^{125}Te-^{77}Se$ coupling and not of $^{123}Te-^{77}Se$. The only data on $^{123}Te-^{19}F$ coupling is for TeF_6 (J=3052Hz) [15]. This is no doubt due, in part, to the low isotopic abundance of ^{123}Te (0.89%, I = ½).

In Figure 1 peaks *a* and *b* are the expected doublet and quintet for a square pyramidal ion, $J(F_{ax}-F_{eq})$ 50.4Hz. The signals *c*,*c*', and *e*,*e*' are the result of ^{125}Te coupling with the axial and equatorial fluorines respectively. The former is very much the larger $J(^{125}Te-^{19}F_{ax})$ 2883.3Hz as opposed to $J(^{125}Te-^{19}F_{eq})$ 1375.7Hz. Although $^{19}F-^{19}F$ coupling was reported for F_5TeCl and F_5TeBr [16], F_5TeNMe_2 [17] and a series of F_5TeX compounds (X=OH, OSO_2Cl, OSO_2F) [18] no values for Te-F coupling were given. However $J(^{19}F_{ax}-^{125}Te)$ was observed for F_5TeNEt_2 [19] to be 3060Hz and $J(^{19}F_{eq}-^{125}Te)$ was calculated

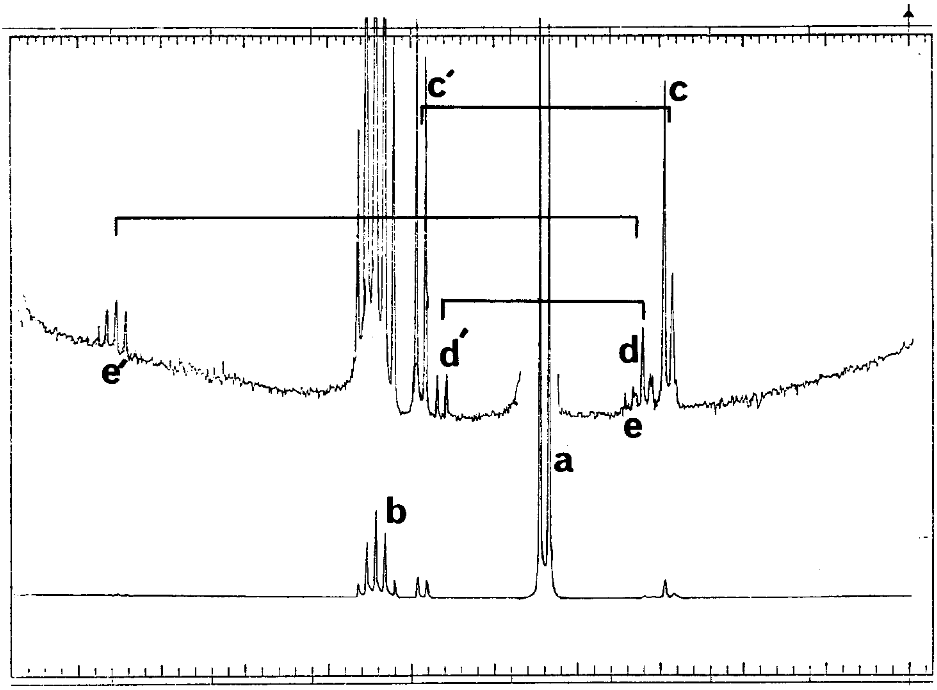

Figure 1 ^{19}F n.m.r. Spectrum of TeF_5 in CH_2Cl_2 at -50°

to be 3970Hz. There are no reports on the n.m.r. of the fairly unstable SeF_5^- ion but there is for the isoelectronic XeF_5^+ ion. Here the difference between the coupling constants is even more striking $J(^{129}Xe-^{19}F_{ax})$ 1377Hz and $J(^{129}Xe-^{19}F_{eq})$ 170Hz [20]. This is presumably due to the high s character in the axial bond and the lone pair orbital as compared to the s character in the square planar bonds for the equatorial fluorines.

Peaks d and d' are due to $^{19}F_{eq}-^{123}Te$ coupling (J=1146Hz). Because of the low isotopic abundance $^{19}F_{ax}-^{123}Te$ coupling was not observed but could be readily calculated as the ratio of $J(^{123}Te-^{19}F):J(^{125}Te-^{19}F)$ is proportional to the ratio of the magnetic moments of the two Te isotopes, J (calculated) = 2397.3 Hz. The satellite spectra were computed using the LAOCOON programme and gave excellent agreement with the observed spectra.

In view of our well resolved ^{19}F n.m.r. spectra of n-Bu_4NTeF_5 in CH_2Cl_2 we conclude that the lack of resolution reported for the Bu_2NH_2F/TeF_4 system in the same solvent must be due to fast F exchange between free F^- and TeF_5^- [10]. On addition of n-Bu_4NF to n-Bu_4NTeF_5 we found no evidence for the formation of the TeF_6^{2-} ion but only evidence of fast exchange at 30°.

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