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FT Raman spectroscopy—the preferred technique for routine vibrational spectroscopic studies of organotellurium compounds

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Abstract

FT Raman data are presented for a range of tellurated azobenzenes and 2-phenyl-pyridines. The excellent quality of the spectra suggests that Raman spectroscopy, when available, is the vibrational spectroscopic method of choice for the routine examination of similar compounds. Some details of the spectra are discussed in the light of the known molecular dimensions of several of the compounds.

Introduction

Separate IR spectroscopic studies of organotellurium compounds were quite numerous some 15–20 years ago [1], but increasing ease of access to full X-ray crystal structure determinations has relegated such studies to part of the routine characterisation of new members of known classes of compound. For this purpose some of the early assignments remain useful [2]. Reports on the Raman spectra of organotellurium compounds are rare. Raman spectroscopy was used when complete vibrational analyses of relatively simple molecules were carried out, *e.g.* Me_2Te_2 [3]; also Raman data were sometimes used to supplement IR investigations [4]. Tellurium is a large polarisable atom and, when bonded to the larger halogens in organotellurium halides, is expected to produce molecules attractive for Raman studies. A range of tellurated azobenzenes and 2-phenyl-pyridines of known structure was available and the opportunity taken to examine routinely their Raman spectra. The quality of the data was most impressive and we report some of the information in this paper and make the suggestion that Raman

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spectroscopy must be the technique of choice for the study of molecular vibrations of these compounds.

Experimental

In this paper 2-(2-pyridyl)phenyl- is denoted by R, and 2-phenylazophenyl- by (pap). The compounds investigated were prepared by the published methods: $RTeCl_3$ [5], RTeCl [6], $RTeBr_3$ [7], RTeBr [7], 1,1′-dibromo-1-telluracyclopentane [8]. $RTeCl_3$ was prepared by substituting $TeCl_4$ for $TeBr_4$ in the reported synthesis of $RTeBr_3$ [7], RTeCl was then obtained by reduction using conditions identical to those to give RTeBr [7].

Raman spectra were obtained on a Perkin Elmer FT-Raman 1700X spectrometer using a Nd-YAG laser (1064 nm) and an InGaAs NIR detector cooled to 77 K. Spectra were obtained from solids as powders pressed into a cup sample holder.

Electronic spectra were scanned on a Perkin–Elmer Lamda 9 UV/VIS/NIR spectrometer working in the absorbance mode. Spectra were measured on solutions in acetone contained in 1 cm quartz cells.

Some FTIR spectra were taken for comparative purposes using polyethylene discs of the organotellurium compounds and a Perkin Elmer 1710 FTIR instrument.

Results

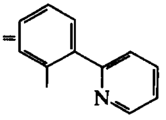
Two compounds, azobenzene and (pap)TeCl gave some problems with fluorescence, but in general Raman spectra of outstanding quality were obtained and typical traces are illustrated in Fig. 1. By contrast, the FTIR data comprised

Table 1

Low frequency FT Raman data for some tellurated 2-phenylpyridines [a]

$RTeCl_3$	$RTeBr_3$	RTeCl	RTeBr	RH	
377 m	375 m	379 s	377 s		
349 w					
329 w				332	
283 v.s.	282 m	285 m	282 m		ν(TeCl)
266 s	266 m	260 m	259 m	261 sh	ν(TeCl)
	263 sh			256 sh	
241 m	247 m	240 m	238 m-s	246 s	
	236 m				
		218 s			ν(TeCl)
204 m	202 m				
	186 s				ν(TeBr)
	176 m	175 w	179 w-m		ν(TeBr)
	164 m		173 w-m		
		158 w	*168 w-m*		ν(TeBr)
			161 w-m		

[a] R =



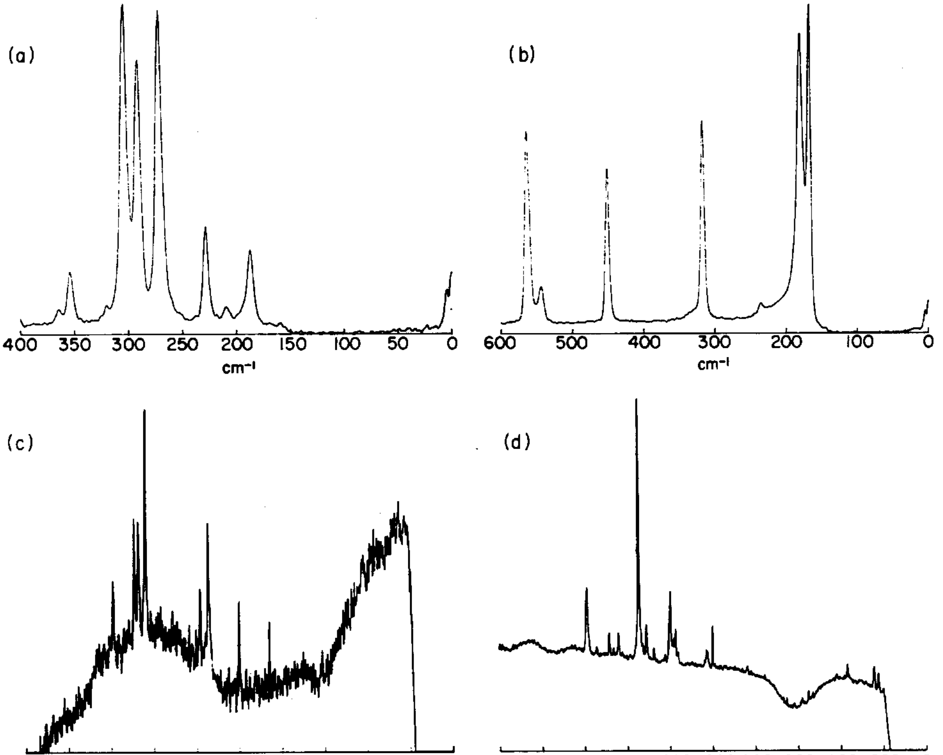


Fig. 1. (a) Low frequency FT Raman spectrum of (2-phenylazophenyl-C,N^1)tellurium(IV) trichloride showing the three ν(TeCl) bands. (b) Low frequency FT Raman spectrum of 1,1′-dibromo-1-telluracyclopentane showing both ν(TeC) and ν(TeBr). (c) Raman spectrum of azobenzene. (d) Raman spectrum of (pap)TeCl.

broader lines with the additional disadvantage that some analytically useful regions were obscured by polyethylene vibrations (the ready metathesis with CsI supports of the compounds studied precluded use of that material). The lower frequency Raman data are tabulated for 2-phenylpyridine derivatives (Table 1) and for azobenzene derivatives (Table 2). Illustrative Raman spectra are given in Fig. 1.

It was noted that vibrational modes assignable to ν(C=N) (2-phenylpyridyl derivatives) and ν(N=N) azobenzene derivatives) showed Raman intensities that are considerably enhanced relative to those in the free bases (see Fig. 1 for comparison of azobenzene and (pap)TeCl). Electronic spectra of all compounds were monitored but no NIR bands coincident with or near the laser frequency of 1064 nm were observed. No resonance or pre-resonance enhancement of any vibrational mode need be considered.

Structural data are available for several compounds studies, *e.g.* (pap)TeCl$_3$ ($P\bar{1}$, Z = 2) [5], (pap)TeCl ($P\bar{1}$, $Z = 4$) [6] RTeBr$_3$ ($P\bar{1}$, $Z = 2$) [7], and RTeBr ($P1$, $Z = 6$) [9]. Within the limits of resolution, coincidence of IR and Raman modes was observed for the compounds crystallising in space group $P\bar{1}$; the spectra are determined by the molecular symmetry. RTeBr may be more complex and is discussed below.

Discussion

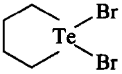
The major practical purpose of this paper is to point that when Raman spectroscopy is available the ease of obtaining the data and the quality of the spectra make it the vibrational spectroscopy of choice for the routine examination of organotellurium compounds. Some brief comment on the specific data reported here is offered.

For azobenzene ν(N=N) was located at 1433 cm^{-1}. Telluration and the consequent coordination of a nitrogen atom lowers this frequency to 1410 cm^{-1} in (pap)$TeCl_3$ and to 1375 cm^{-1} in (pap)TeCl. The Te ← N bond length is 2.417(4) Å for (pap)$TeCl_3$ [5] and 2.23(2), 2.19(2) Å for (pap)TeCl [6], thus the significantly greater lowering of ν(N=N) in the tellurium(II) case reflects the shorter (stronger) coordinate bond.

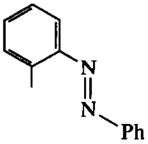
The tellurium halogen stretching vibrations are readily assigned and are indicated in Tables 1 and 2. The spectra of the 2-phenylazophenyl-C,N^1-tellurium compounds are "cleaner" in that the metal-halogen vibrations overlap less with X-sensitive modes of the organic moiety. An earlier paper [6] assigned ν(TeCl) for (pap)TeCl at 247 cm^{-1} using IR data. This assignment was plausible since (pap)$TeCl_3$ showed no major band in that region and ν(TeCl) was expected at lower frequency for Te^{II} than for Te^{IV}. The Raman data revealed a further band at 220 cm^{-1}, obscured in the IR study by a strong polyethylene absorption. Comparison of the spectra of RTeCl and RTeBr (Table 1) shows that ν(TeCl) in RTeCl is located at 218 cm^{-1}. The molecular dimensions of RTeCl have been determined in an inclusion compound with p-ethoxyphenylmercury(II) chloride [9] and the Te–Cl distance is 2.558 (1) Å. This is, within the cited standard deviations,

Table 2

Low frequency FT Raman data for some organotellurium halides [a]

(pap) $TeCl_3$	(pap) TeCl		
365 w		451 m	
354 w-m	359 s		
320 w		317 m-s	
303 v.s			ν(TeCl)
288 s			ν(TeCl)
272 v-s			ν(TeCl)
232 m	242 m-s		
	220 m-s		ν(TeCl)
210 w	199 m-w		
184 m			
		181 v.s	ν(TeBr)
		167 v.s	ν(TeBr)
		565 m-s	ν(Te-C)
		544 w	ν(Te-C)

[a] Pap = phenyazophenyl, *i.e.*



the same as the values reported for (pap)TeCl, *i.e.* 2.552 (8), 2.549 (8) Å [6]. It is suggested that revision of the assignment for (pap)TeCl is required (Table 2). The band at 247 cm^{-1} (IR) may then be a candidate for ν(Te ← N). RTeBr (R = 2-(2-pyridylphenyl-) crystallises in space group $P1$ and the asymmetric unit contains six non-symmetry related molecules; the "ν(TeBr)" region appears more complex than expected if only the molecular symmetry determined the selection rules.

Although a tentative assignment of ν(Te ← N) is suggested above for (pap)TeCl, the rich contribution from X-sensitive modes of the 2-phenylpyridine moiety to these routinely scanned spectra make it unwise to attempt an assignment of ν(Te ← N) in Table 1.

An alicyclic organotellurium compound has been included in Table 2 (see also Fig. 1) for illustrative purposes. 1,1′-Dibromo-1-telluracyclopentane gave a Raman spectrum of excellent quality from which clear assignments of both ν(TeC) and ν(TeBr) could readily be made.

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References

1 W.R. McWhinnie and P. Thavornyutikarn, J. Chem. Soc., Dalton Trans., (1972) 551.
2 W.R. McWhinnie and M.G. Patel, J. Chem., Soc., Dalton Trans., (1972) 199.
3 C.W. Sink and A.B. Harvey, J. Mol. Struct., 4 (1969) 203.
4 N.S. Dance and W.R. McWhinnie, J. Chem. Soc., Dalton Trans., (1975) 43.
5 M.A.K. Ahmed, W.R. McWhinnie and T.A. Hamor, J. Organomet. Chem., 281 (1985) 205.
6 R.E. Cobbledick, F.W.B. Einstein, W.R. McWhinnie and F.M. Musa, J. Chem. Res. (S), (1979) 145; (M) (1979) 1901.
7 N. Al-Salim, A.A. West, W.R. McWhinnie and T.A. Hamor, J. Chem. Soc., Dalton Trans., (1988) 2363.
8 M.R. Greaves, PhD thesis, Aston University, Birmingham, 1991.
9 M.R. Greaves, T.A. Hamor, B.J. Howlin, T.S. Lobana, S.A. Mbogo, W.R. McWhinnie and D.C. Povey, J. Organomet. Chem., 420 (1991) 327.