Infrared and Raman Spectra of Some Three-coordinated Complexes of Divalent Tellurium

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The infrared and Raman spectra of crystalline samples of halo(ethylenethiourea)phenyltellurium(II) (halo = Cl, Br, I), halo(ethyleneselenourea)phenyltellurium(II) halo = Br, I), halo(phenyl)thioureatellurium(II) (halo = Cl,Br), phenyldithiocyanato- and phenyldiselenocyanatotellurate(II) ions were recorded below 500 cm⁻¹. From these data the two fundamental stretching frequencies connected with the approximately linear X − Te − Y linkage were assigned. These frequencies were compared with those obtained from a simplified force constant calculation on the linear group.

Divalent tellurium most often forms four-coordinated complexes, but when a phenyl group is one of the ligands, the position *trans* to the phenyl group is vacant. Crystal structures of three-coordinated complexes of divalent tellurium are well known,[1-8] revealing that each molecule has a T-shaped geometry. Each tellurium atom is part of a nearly linear three-centre four-electron bonding system, comprising the tellurium atom and two ligand atoms Nearly at right angle to the three-centre system, the tellurium atom is bonded to a phenyl carbon atom, so that the Te − C bond nearly bisects the angle of the three-centre system.

Very little information from infrared and Raman spectra is available on three-coordinated complexes of divalent tellurium. In two papers Hendra and Jovic [9,10] report the infrared and Raman spectra of several square-planar complexes of divalent tellurium. The vibrational frequencies of these complexes are discussed in relation to the isoelectronic ICl₄⁻ ion.[9,10] Recently, Wynne et al. reported the Raman spectra of a few dihaloaryltellurate(II) anions.[11]

The present paper reports the infrared and Raman spectra of a series of three-coordinated complexes of divalent tellurium, whose crystal structures are already known.

EXPERIMENTAL

The syntheses of the present compounds (I − X, Table 1) have previously been reported.[8,12-15] Elementary analyses on C, H, N, S, Cl, Br, and I were determined and melting points and densities were reported.

The far infrared spectra of the samples I − X were recorded on a Perkin-Elmer-Hitachi far infrared spectrometer, model FIS − 3 through the courtesy of Dr. D. H. Christensen, the University of Copenhagen. Approximately 10 − 20 mg of the samples were mixed with 200 mg of polyethylene (Rigidex) and the pellets recorded in the region 500 − 50 cm⁻¹.

Table 1. Numbering and formula of the tellurium(II) compounds studied.

Number	Compound [a]	Ref.
I	$C_6H_5Te(etu)Cl$	7,14
II	$C_6H_5Te(etu)Br$	6,14
III	$C_6H_5Te(etu)Br$	6,14
IV	$C_6H_5(etu)I$	8
V	$C_6H_5Te(esu)Br$	7,15
VI	$C_6H_5Te(esu)I$	8
VII	$[(CH_3)_4N][C_6H_5Te(SCN)_2]$	5,13
VIII	$[(CH_3)_4N][C_6H_5Te(SeCN)_2]$	5,13
IX	$C_6H_5Te(tu)Cl$	3,12
X	$C_6H_5Te(tu)Br$	3,12

[a] Here etu = ethylenethiourea ($C_2H_6N_2CS$), esu = ethyleneselenourea ($C_2H_6N_2CS$), and tu = thiourea (N_2H_4CS).

Table 2a. The far infrared (IR) and Raman (R) spectral data for halo(ethylenethiourea)phenyltellurium(II).

I[a] S, Cl[b] IR	R	II S, Br IR	R	III S, Br IR	R	IV S, I IR	R	Interpretation
		365 w[c]	362 s	362 s	367 vs	360 s	357 s	
345 m	345 vw	340 m	342 w	324 vw?		324 vw?		
				287 w				
275 vw		255 w	251 w	273 m				
				245 w	255 w			
254 w	257 s	222 w	228 s	222 m	223 m	265 m	255 w	S—Te—X
						244 w		asym. str.
	240 m	212 w				224 m	220 vw	
						182 w,sh		
210 m	208 s	193 m	193 vs	190 s,br	189 vs	172 s	170 vs	S—Te—X
	185 m		170 vw	168 w	170 w	102 s	113 w	sym. str.
140 s,br	140 w,br	110 s	125 w,br	130 w	131 w	91 m	88 w	
				120 s	106 w			
	90 w			100 s	99 w			
75 m		75 m		75 m				
	60 w,sh		56 m		58 m		55 m	

[a] Roman numerals refer to compounds listed in Table 1. [b] Substituents (S—Te—hal) in approximately linear arrangement. [c] Abbreviations: s, strong; m, medium; w, weak and v, very.

Table 2b. The far infrared and Raman spectral data for halo(ethyleneselenourea)phenyltellurium(II).

V Se, Br IR	R	VI Se, I IR	R	Interpretation
340 m		336 w		
269 m	270 vw	277 w	278 w	
		272 w		
247 m	248 w	219 m	222 vw	
210 m	220 vw?	212 w		
190 m	192 w	180 m	178 w	Se—Te—X asym. str.
170 s	169 m	150 s	152 vs	S—Te—X sym. str.
130 w		133 w		
99 s	93 w	100 m	94 w	
		84 m	77 w	
	70 w	74 w		

Table 2c. The far infrared and Raman spectral data for phenyldithio(diseleno)cyanotellurate(II).

VII S, S IR	R	VIII Se, Se IR	R	Interpretation
			389 w	
272 w		272 w		
			254 w	
247 w	257 w	189 w	188 vw	S(Se)TeS(Se) asym. str.
219 vw	216 vs	138 vw	136 vs	S(Se)TeS(Se) sym. str.
212 w	210 s	118 m	120 m	
150 s	141 w			
100 s	100 w	101 m		
75 s		74 w		
	55 vw		66 w	

Table 2. Continued.

Table 2d. The far infrared and Raman spectral data for halo(thiourea)phenyltellurium(II).

IX S, Cl IR	R	X S, Br IR	R	Interpretation
		272 m		
			256 s	
252 w	257 m	242 s	242 vs	S – Te – X asym.
		222 m	219 w	str.
		194 m	191 m	
244 m	243 m	164 w	164 w	S – Te – X sym.
158 w				str.
118 s	110 w	125 m	130 vw	
99 s	94 w	99 s	98 w	
93 m		85 m	86 vw	
76 m		76 m	75 w	
	67 w	66 vw		
		57 w		
			48 m	

A Cary model 81 Raman spectrometer equipped with a Spectra Physics model 125 A helium-neon laser and a Coherent Radiation Laboratory model 52 G argon ion laser were employed for the Raman recordings. The 6328 and 5145 Å lines were used for excitation and interference filters employed to remove the plasma lines. The solid samples were filled into tubes with flat ends and placed against the hemispherical lens and illuminated in the 180° mode. Since most of the present compounds were somewhat coloured, the spectra obtained with the red laser (*ca.* 40 mW irradiation on the sample) were in most cases preferable to those recorded with the green light (100 mW on the sample).

In addition, the vibrational spectra of the ligands: ethylenethiourea, ethyleneselenourea, and thiourea were recorded in order to gain information regarding the ligand vibrational spectra.

RESULTS AND DISCUSSION

The observed infrared and Raman frequencies (in cm^{-1}) of the ten present tellurium(II) complexes are listed in Table 2. The bands interpreted as the asymmetric and symmetric stretching frequencies of the approximately linear X – Te – Y moiety have been listed in Table 2 and can be assigned with considerable confidence. Much more uncertain are the fundamental modes mainly connected with the X – Te – Y deformation and thus no attempts were made to assign them. Although the samples II and III contain the same molecular complex (with different crystal structure) the

spectra were somewhat different. However, as apparent, the assigned X – Te – Y vibrations were only negligibly displaced from sample II to III.

Obviously, the present tellurium(II) complexes with the large number of atoms (maximal 27 and minimal 18) should give rise to very complicated vibrational spectra because of the many fundamental modes expected. As a first approximation the normal modes may be divided into those characteristic of the ligands and those pertaining to stretching of the tellurium – ligand bonds. Also, it is generally assumed [11] that the ligand vibrations (phenyl, ethylenethiourea *etc.*) give rise to weaker bands (particularly in Raman) than those due to stretchings of the metal-ligand system, thus simplifying the interpretations. Finally, the pseudo-linearity of the three-centre bond makes it feasible to treat the system as a linear X – Te – Y three body problem of $C_{\infty v}$ symmetry. Apart from diatomic molecules the linear three-atomic molecules represent the simplest possible case, making force constant calculations very convenient.

In a linear molecule X – Te – Y the following relations can easily be derived:

$$\lambda_1 + \lambda_2 = k_1 \frac{1}{m_X} + k_2 \frac{1}{m_Y} + (k_1 + k_2 - 2k_1k_2)\frac{1}{m_{Te}}$$

$$\lambda_1\lambda_2 = (k_1k_2 - k_{12}{}^2)\left(\frac{1}{m_X m_Y} + \frac{1}{m_Y m_{Te}} + \frac{1}{m_Y m_{Te}}\right)$$

in which $\lambda_i = 4\pi^2 \nu_i^2 c^2$, where ν_1 and ν_2 are the stretching frequencies, k_1 and k_2 are the diagonal stretching constants for the $Te - X$ and $Te - Y$ bonds, k_{12} is the interaction constant, and m_x, m_y and m_{Te} are the atomic masses. Since only two force constants can be determined from the two observed stretching bands and k_{12} is typically 10 % of k_1 and k_2, k_{12} can to a first approximation be neglected. A simple set of force constants for the $Te - S$, $Te - Se$, $Te - Cl$, $Te - Br$, and $Te - I$ were derived from the symmetric stretching modes (most reliable, since generally very intense in Raman) of selected model compounds. From compounds VII and VIII the $Te - S$ and $Te - Se$ stretching force constants were calculated to 0.89 and 0.84 mdyn/Å, respectively. Correspondingly the Te-halogen stretching constants were calculated from the reported values given by Hendra and Jovic.[9],[10] They gave the approximate values 245, 150, and 100 cm^{-1} for the symmetric and 205, 160, and 130 cm^{-1} for the asymmetric $X - Te - X$ stretching frequencies in the case of Cl, Br, and I, respectively. The force constants 1.25, 1.06, and 0.74 mdyn/Å were obtained from these frequencies. However, much better agreement with the present data were obtained by reversing their symmetric and asymmetric stretching vibrations, for the $Cl - Te - Cl$ case. When the low frequency band at 205 cm^{-1} was used as the symmetric mode a force constant of 0.88 mdyn/Å was derived for $Te - Cl$. The calculated frequencies are listed in Table 3 and compared with the experimental values.

The agreement between the observed and calculated $X - Te - Y$ stretching frequencies is in most cases satisfactory taking into account the severe simplifications: (a) the thiourea or ethylenethio(seleno)urea groups are neglected and the S or Se considered terminal atoms, (b) the existence of the phenyl group and the $Te - C$ bond is neglected, (c) a simple diagonal force field is derived in which the stretching force constants are transferable within the series, and (d) the $X - Te - Y$ arrangement is considered linear.

Obviously, the agreement between the observed and calculated frequencies could be greatly improved, e.g. by introducing the interaction constant k_{12}. Thus, it was found that by setting $k_{12} = 0.1$ mdyn/Å and maintaining k_1 and k_2, the frequency difference between the symmetric and asymmetric stretches decreased (a factor of two for IX and X) without shifting the average value significantly. Because of the severe simplifications made and since the interaction constants in no case could be given a significant physical value, we did not proceed along this line.

At the outset of this work we hoped that the bond length variations within the series, carefully determined from the X-ray crystallographic studies, should manifest themselves in the vibrational spectra. It was found that the *trans* bond lengthening order of halogens on the $Te - S$ or $Te - Se$ bond decrease in the order $I > Br \geq Cl$.[8] The relative *trans* bond lengthening order of the ligands on the Te-halogen bond decrease in the order esu~tu>

Table 3. Observed and calculated $X - Te - Y$ stretching vibrations.

Compound	Linkage	Obs[a]		Calc[b]		k_1 mdyn/Å	k_2 mdyn/Å
I	S − Te − Cl	254	210	264	236	0.89	0.88
II	S − Te − Br	222	193	257	178	0.89	1.06
III	S − Te − Br	222	189[c]	257	178	0.89	1.06
IV	S − Te − I	265	172	250	130	0.89	0.74
V	Se − Te − Br	190	170	217	142	0.84	1.06
VI	Se − Te − I	180	150	197	133	0.84	0.74
VII	S − Te − S	247	216[c]	268	218	0.89	0.89
VIII	Se − Te − Se	189	136[c]	203	136	0.84	0.84
IX	S − Te − Cl	252	244	264	236	0.89	0.88
X	Se − Te − Br	242	164	257	178	0.89	1.06

[a] IR data except when noted. [b] For calculations, see text; the interaction constant k_{12} is set equal to zero. [c] Raman data.

etu.[7] From the well known relations between bond length – bond energy and stretching force constant, a bond lengthening should result in a smaller force constant and eventually lower Te – X(Y) stretching vibrations. No such systematic trends can be observed from the spectra.

Clearly, the fact that the "Te – X and Te – Y vibrations" are not localized modes, but can better be described as X – Te – Y symmetric and asymmetric stretches, makes such correlations more difficult. When the ligands have very different masses and/or are attached to the central atom with quite different bond strengths the two stretching vibrations become well localized (*e.g.* in H – C≡N or X – C≡N), and can be directly correlated with the bond distance or bond energy. In the present case much more sophisticated force constant calculations, not warranted by the observed spectra, would be necessary to correlate the X – Te – Y stretching vibrations with the bond distances.

The assigned X – Te – Y stretching modes (Tables 2 and 3) agree reasonably well with the values reported by other workers on similar complexes. A curious discrepancy is provided by compound IV in which the 172 cm⁻¹ band appears too high. However, a very intense Raman band was observed at this wave number (no other intense Raman band was detected at lower wave numbers) making an assignment to a symmetric S – Te – I vibration very likely.

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