4 hr, the peak at τ 8.7 is approximately 25% of the height of the peak at τ 7.8. To a fresh solution of TPP and pyruvate, cobalt(II) ion was added, and its spectrum is shown in Figure 3d. The resonance at τ 8.5 is now as large as the resonance at τ 7.7. Previous studies[9,44] of the nonenzymatic systems CH_3COCOO^-–TPP and CH_3COCOO^-–thiamine have shown that pyruvate is decarboxylated and condensed to α-acetolactate, $CH_3COCOH(COO^-)CH_3$, without appreciable accumulation of the intermediate, α-hydroxyethylthiamine pyrophosphate. We can tentatively assign the resonance at τ 8.5 in Figure 3c (τ 8.7 in Figure 3d) to the $CH_3COH(COO^-)$– methyl group and the resonance at τ 7.7 (τ 7.8 in Figure 3d) to the CH_3COCOO^- methyl group and the $CH_3COCOH(COO^-)$– methyl group.

The participation of the metal ion–TPP complex in the decarboxylation reaction is likely since the 6′-H proton exhibits a downfield shift indicating that the TPP is still complexed to the metal ion. No metal ion–TPP–pyruvate complex could be detected in the composited nmr spectrum, but this is consistent with previous studies on these systems.[44] The effect of the metal ion–TPP complex is tentatively to increase production of the α-acetolactate at the expense of the pyruvate. Previous studies[9] did not observe this catalytic effect, but this could have been due to the higher pH at which these studies were carried out.

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Chalcogen Chemistry. V. Complexes of Organotellurium Trihalides with Tetramethylthiourea[1]

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A series of organotellurium trihalides has been found to give molecular tetramethylthiourea (tmtu) complexes of the general formula $RTeX_3$tmtu, where R = CH_3, C_2H_5; X = Cl, Br, I; R = *p*-$CH_3OC_6H_4$; X = Cl. These are moisture-sensitive, crystalline solids which appear to be monomeric in organic solvents such as chloroform and nitrobenzene. Square-pyramidal coordination around tellurium with an apical organo group and tmtu coordinated through sulfur is proposed for these complexes and is consistent with our infrared spectral data.

Introduction

In a recent communication we described the preparation of a new class of five-coordinate tellurium compounds.[2] We began our investigation into this area in order to test the applicability of a bonding theory we have proposed to explain structural variations observed in chalcogen and organochalcogen(IV) halides.[1a] Our approach led to the prediction that the central atom in an organochalcogen trihalide should exhibit a limiting coordination number (CN) of five, achieved in the solid state by halogen bridging. To test whether organotellurium trihalides could act as acceptors and to determine whether the nature of this interaction would be consistent with our predictions, we examined the reactions of a variety of organotellurium trihalides with tetramethylthiourea (tmtu). Our results are reported below.

Experimental Section

General Data.—Due to the moisture sensitivity of the compounds prepared in this study, all preparations and handling operations were carried out in a dry atmosphere achieved through the use of dry nitrogen filled polyethylene glove bags.

Spectra.—Infrared spectra were obtained using Perkin-Elmer Model 621 and Beckman IR-11 spectrophotometers. Far-ir solution spectra were recorded on samples in 0.5- or 3.0-mm polyethylene cells. Solids were run as freshly prepared Nujol mulls between polyethylene plates in the 33–500-cm^{-1} region and on AgCl plates in the 500–4000-cm^{-1} region. Proton nuclear magnetic resonance data were obtained using a Perkin-Elmer Hitachi Model R-20 spectrometer. Chemical shifts were measured *vs.* internal tetramethylsilane.

Chemicals.—Tetramethylthiourea (Eastman) was recrystallized from anhydrous ethyl ether prior to use. Reagent grade nitrobenzene was used directly after storage over Linde 5A Molecular Sieves, which had been previously heated *in vacuo* at 300° for 24 hr. All other solvents were distilled from P_2O_5 and stored over molecular sieves.

Methyltellurium trichloride[1a] and tribromide,[3] ethyltellurium trichloride,[1d] and *p*-methoxyphenyltellurium trichloride[4] were prepared by reported procedures. The preparation of new organotellurium trihalides or those prepared in a manner different from that found in the literature is outlined below.

Methyltellurium Triiodide.—This compound was prepared by adding $(CH_3)_2Te_2$[3,5] (5.0 g, 17.5 mmol) in 50 ml of CH_2Cl_2 to a solution of I_2 (15.0 g, 60.0 mmol) in 100 ml of CH_2Cl_2. Methyltellurium triiodide (14.0 g, 76.5% yield) precipitated as a violet powder, mp 175–178°, lit.[6] mp 180°. *Anal.* Calcd for CH_3I_3Te: C, 2.30; H, 0.58; I, 72.74. Found: C, 2.26; H, 0.54; I, 72.59. This compound is virtually insoluble in common organic solvents and could not be further purified thus accounting for the poor analytical results.

Ethyltellurium Triiodide.—This compound was prepared by adding $(C_2H_5)_2Te_2$[1d] (5.0 g, 16.0 mmol) in 50 ml of CH_2Cl_2 to a solution of I_2 (13.0 g, 51.0 mmol) in 100 ml of CH_2Cl_2. Cooling

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[1] Parts I–IV, respectively: (a) K. J. Wynne and P. S. Pearson, *Inorg. Chem.*, **9**, 106 (1970); (b) K. J. Wynne, *ibid.*, **9**, 299 (1970); (c) K. J. Wynne, *ibid.*, **10**, 1868 (1971); (d) K. J. Wynne and P. S. Pearson, *ibid.*, **10**, 1871 (1971).

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TABLE I

GENERAL PROPERTIES AND ANALYTICAL RESULTS ON ORGANOTRIHALO(TETRAMETHYLTHIOUREA)TELLURIUM(IV) COMPLEXES

Compound	% yield	Mp,[a] °C	Appearance	% C		% H		% halogen		Cryoscopic mol wt[b]	
				Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found (molality)
CH_3TeCl_3tmtu	91.80	123–125	Yellow crystals	18.90	18.99	3.97	3.92	27.90	28.25	381.22	436 (0.0180) 430 (0.0340)
CH_3TeBr_3tmtu	93.90	120–122	Yellow crystals	14.00	13.88	2.94	2.87	46.59	46.51	514.59	537 (0.0067) 560 (0.0227)
CH_3TeI_3tmtu	86.09	97–99	Violet crystals	10.99	10.50	2.31	1.98	58.07	56.50		c
$C_2H_5TeCl_3$tmtu	83.12	108–210	Yellow crystals	21.27	20.65	4.34	4.01	26.91	27.54	395.25	298 (0.0069) 328 (0.0090)
$C_2H_5TeBr_3$tmtu	79.70	100–102	Orange crystals	15.91	15.44	3.24	3.26	45.35	45.75	528.62	493 (0.00600)
$C_2H_5TeI_3$tmtu	75.07	175–176	Pale violet	12.56	11.50	2.56	2.32	56.86	57.71		c
p-$CH_3OC_6H_4TeCl_3$tmtu	65.68	133–135	Yellow plates	30.45	29.39	4.05	4.19	22.47	23.84	473.32	451 (0.011) 510 (0.024)

[a] Uncorrected. [b] In nitrobenzene. [c] Solubility too low for accurate cryoscopic studies.

to −20° gave 10.0 g (58.0%) of a violet powder, mp 178–180°. *Anal.* Calcd for $C_2H_5I_3Te$: C, 4.47; H, 0.94; I, 70.9. Found: C, 4.62; H, 1.11; I, 72.3. This compound is essentially insoluble in common organic solvents and tends to decompose in donor (oxygen) organic solvents. Like its methyl analog, no satisfactory purification method for $C_2H_5TeI_3$ was found.

Ethyltellurium Tribromide.—This compound was prepared by adding $(C_2H_5)_2Te_2$ (5.0 g, 16.0 mmol) in 50 ml of CH_2Cl_2 to a solution of bromine (8.0 g, 50.0 mmol) in 100 ml of CH_2Cl_2. Cooling the resulting solution to −20° gave 10.0 g of yellow crystalline $C_2H_5TeBr_3$, mp 138–140°, 78.5% yield. *Anal.* Calcd for $Br_3C_2H_5Te$: C, 6.06; H, 1.26; Br, 60.0. Found: C, 5.88; H, 1.41; Br, 60.2. This compound is slightly soluble in CH_2Cl_2 and benzene (1.5 g/100 ml of benzene).

Adduct Synthesis.—The same basic procedure was employed in the preparation of each adduct, although we found that certain complexes required a particular solvent mixture and sometimes special treatment in order to obtain a solid instead of an oil. Methyltrichloro-, methyltribromo-, methyltriiodo-, and ethyltrichloro(tetramethylthiourea)tellurium(IV) were prepared in a similar manner. A typical preparation is given below for CH_3TeCl_3tmtu, while routes to ethyltribromo- and ethyltriiodo(tetramethylthiourea)tellurium(IV) and *p*-methoxyphenyltrichloro(tetramethylthiourea)tellurium(IV) are outlined in detail. Analytical results and general physical properties are presented in Table I.

Methyltrichloro(tetramethylthiourea)tellurium(IV).—Methyltellurium trichloride[1a] (4.0 g, 16.0 mmol) was dissolved in 80 ml of benzene. tmtu (2.1 g, 16.0 mmol) in 20 ml of CH_2Cl_2 was gradually added with rapid magnetic stirring of the reaction mixture. The final yellow solution was stirred an additional 0.5 hr. Cooling to −20° for 24 hr gave 5.1 g of yellow crystals, mp 123–125°. Subsequent partial evaporation and cooling of the filtrate gave 0.5 g of additional product. This compound and methyltriiodo- and ethyltrichloro(tetramethylthiourea)tellurium(IV) could be recrystallized from a 1:1 benzene–CH_2Cl_2 solvent mixture, while methyltriiodo(tetramethylthiourea)tellurium(IV) was recrystallized from 2:1 C_6H_6–CH_2Cl_2.

Ethyltribromo(tetramethylthiourea)tellurium(IV) and Ethyltriiodo(tetramethylthiourea)tellurium(IV).—These compounds were prepared by suspending 10.0 mmol of the respective organotellurium trihalide in 75 ml of CH_2Cl_2 and adding tmtu (10 mmol) in 25 ml of C_6H_6. The final reaction mixture was stirred 0.5 hr. Cooling the solution to −20° in each case produced an oil. The contents of the flask were rapidly swirled while cooling in a −78° bath and this was followed quickly by filtration. Precipitation would usually occur as the cold solution was allowed gradually to come to ambient temperature. If crystallization did not occur, the process was repeated. Occasionally it was necessary to immerse the reaction mixture in a liquid nitrogen bath until solidification began. After inducing initial crystallization the reaction flask was placed at −20° for 24 hr to ensure complete precipitation. Yield and melting point data are as follows: $C_2H_5TeBr_3$tmtu, 4.20 g, mp 100–102°; $C_2H_5TeI_3$tmtu, 5.03 g, mp 175–176°. These adducts could be reprecipitated by dissolution in a 3:1 CH_2Cl_2–C_6H_6 solvent mixture followed by the crystallization procedure outlined above.

***p*-Methoxyphenyltrichloro(tetramethylthiourea)tellurium(IV).**—*p*-$CH_3OC_6H_4TeCl_3$[4] (3.4 g, 10.0 mmol) was suspended in 50 ml of CH_2Cl_2, and a solution of tmtu (1.32 g, 10.0 mmol) in 10 ml of CH_2Cl_2 was slowly added to the slurry with rapid stirring. The final clear bright yellow solution was stirred 0.25 hr. Evaporation to 25 ml and addition of 10 ml of either *n*-hexane or CCl_4 followed by cooling to −20° produced 3.1 g of bright yellow plates, mp 133–135°. This compound could be recrystallized from a 1:4 CCl_4–CH_2Cl_2 solvent mixture.

Results and Discussion

Organotellurium trihalides react with tmtu in aprotic media such as methylene chloride to yield 1:1 complexes as moisture-sensitive crystalline solids. Even in the presence of excess tmtu only 1:1 adducts are formed. These compounds are soluble in methylene chloride, nitrobenzene, chloroform, and acetonitrile but insoluble in benzene, carbon tetrachloride, and other nonpolar organic solvents. In general the tmtu adducts are considerably more soluble in a given solvent than the parent organotellurium trihalide.

Our results are in contrast with those of Foss,[7,8] who has found that phenyltellurium trichloride reacts with thiourea in methanol–water *via*

$$C_6H_5TeCl_3 + 3SC(NH_2)_2 \longrightarrow C_6H_5Te[SC(NH_2)_2]Cl\,[SC(NH_2)_2]_2{}^{2+} + 2Cl^- \quad (1)$$

to yield a *tellurium(II)* complex. Evidently the use of aprotic solvents together with the greater resistance of tmtu to oxidation relative to thiourea[9] has favored our isolation of Te(IV) complexes.

Solution Studies.—Experimentally observed molecular weights, obtained cryoscopically in nitrobenzene, together with those calculated for the monomeric 1:1 complexes are listed in Table I. These results demonstrate that the complexes are undissociated monomers in nitrobenzene solution, with the exception of $C_2H_5TeCl_3$tmtu which may be somewhat dissociated. However, infrared spectral data indicate that $C_2H_5TeCl_3$tmtu is undissociated in methylene chloride, as no detectable absorption at 1512 cm^{-1} due to uncoordinated tmtu was observed.[10] Instead, a peak due to coordinated tmtu was seen at higher frequency (1598 cm^{-1}) close to that observed in the solid state and discussed in more detail below. Although a comprehensive study of solution spectra on all complexes was not made, the ir spectrum of CH_3TeBr_3tmtu in methylene chloride (Table II) provided additional evidence concerning the undissociated nature of this complex in solution.

Previous molecular weight studies[1a,11] have shown CH_3TeCl_3 and CH_3TeBr_3 to be associated in solution. In addition, a recent X-ray crystallographic investiga-

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TABLE II

INFRARED SPECTRAL DATA ON ORGANOTRIHALO(TETRAMETHYLTHIOUREA)TELLURIUM COMPLEXES[a]

CH_3TeCl_3tmtu	$C_2H_5TeCl_3tmtu$		$CH_3OC_6H_4TeCl_3tmtu$		
Nujol mull	Nujol mull	Methylene chloride	Nujol mull	Methylene chloride	Assignments
1575 s	1600 s	1598 s	1560 s	b	N–C–N antisym str
473 w	460 w		585 wm	533 w	Te–C (alkyl only)
			520 ms		
			470 m		tmtu peaks
385 w	380 w		380 m	375 w	
			335 m		
315 w	290 w		320 m	312 w	
251 s	248 ms	248 ms		265 ms	Te–Cl str
			225 s	251 s	
210 s	210 s, sh	228 ms		205 w, sh	Te–Cl and Te–S modes
		204 m	br		
155 wm	159 w	162 s	150 w	142 w	
	55 w, vbr		90 w		

CH_3TeBr_3tmtu		$C_2H_5TeBr_3tmtu$			CH_3TeI_3tmtu	$C_2H_5TeI_3tmtu$	
Nujol mull	Methylene chloride	Nujol mull	Chloroform	Assignments	Nujol mull	Nujol mull	Assignments
1575 s	1568 s	1570 s	b	N–C–N antisym str	1560 s	1572 s	N–C–N antisym str
						538 w	
475 w		472 wm		Te–C		478 wm	Te–C
383 w		395 wm	373 m	tmtu peaks	380 wm	380 wm	tmtu peaks
		321 m				312 wm	
312 w		293 w					
		245 w					
195	195 s, br	190 s	195 s, br	Te–Br and Te–S	210 m, sh	215 wm, sh	Te–S
s, br		br					
165		168 s, sh					
115 m		140 m, sh			170 s	165 s	Te–I str
					135 m	130 s	
					98 m	60 w	

[a] Key: w, weak; m, medium; s, strong; sh, shoulder; br, broad. [b] 600–3000-cm^{-1} region not examined.

TABLE III

PROTON NMR SPECTRAL DATA ON ORGANOTELLURIUM TRIHALIDES AND ORGANOTRIHALO(TETRAMETHYLTHIOUREA)TELLURIUM(IV) COMPOUNDS[a]

	tmtu	Organo group in $RTeX_3tmtu$	Organo group in parent $RTeX_3$
tmtu[b]	3.01		
CH_3TeCl_3tmtu[b]	3.25	3.50	3.70[b]
CH_3TeBr_3tmtu[b]	3.20	3.63	3.10[g]
CH_3TeI_3tmtu[b]	3.20	3.61	(3.60)[h]
$C_2H_5TeCl_3tmtu$[c]	3.28	3.85 quartet[d]	. . . quartet[b,i]
		2.10 triplet	2.20 triplet[d]
$C_2H_5TeBr_3tmtu$[c]	3.24	3.88 quartet[d]	. . . quartet[b,i]
		2.02 triplet	2.30 triplet[d]
$C_2H_5TeI_3tmtu$[c]	3.20	. . . quartet[e]	Not obsd[j]
		2.05 triplet[d]	
p-$CH_3OC_6H_4TeCl_3tmtu$[b]	3.22	6.90 doublet (C_6H_4, ortho[f])	7.24 doublet (C_6H_4, ortho[f,k])
		8.34 doublet (C_6H_4, meta)	8.44 doublet (C_6H_4, meta)
		3.80 (CH_3)	3.90 (CH_3)

[a] Shifts are in τ units ±0.01 ppm *vs.* internal tetramethylsilane. [b] Methylene chloride. [c] Deuteriochloroform. [d] $J_{CH_3-CH_2} = 8.0$ Hz. [e] Ill defined due to limited solubility. [f] $J_{H_{ortho}-H_{meta}} = 9.0$ Hz. [g] Benzene. [h] Acetone. Compound was very slightly soluble, hence uncertainty in value quoted. [i] Not observed due to overlap with solvent peak. [j] Insoluble in organic solvents. [k] Deuterioacetonitrile.

tion of the structure of 2-chloroethyltellurium trichloride[12] has clearly shown a polymeric structure containing pentacoordinate tellurium, as we predicted.[1a] tmtu is apparently a strong enough base toward the organotellurium trihalides such that the tendency toward intermolecular interactions is overcome and molecular complexes are formed.

Proton nmr spectral data on organotellurium trihalides and organotrihalo(tetramethylthiourea)tellurium(IV) compounds prepared in this study may be found in Table III. Integration of the peaks observed in the spectra of the complexes served to confirm the stoichiometry indicated by the analytical data. tmtu methyl groups in $RTeX_3tmtu$ complexes exhibited resonance 0.2–0.3 ppm further downfield than in the free ligand. On the other hand, protons in organo groups connected to tellurium are shifted upfield in a manner inversely proportional to their distance from Te. Both of these observations are expected on the basis of simple inductive effects and are consistent with the view that the complexes are mainly undissociated in solution. When tmtu was added to a solution of $RTeX_3tmtu$, a single peak was observed of intermediate chemical shift indicating rapid exchange between coordinated and bulk tmtu.

For $RTeX_3tmtu$ complexes we suggest the square-pyramidal structure

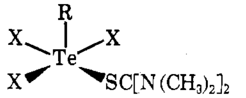

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TABLE IV
INFRARED SPECTRAL DATA ON ORGANOTELLURIUM TRIHALIDES[a]

		CH_3O-	CH_3TeBr_3					
CH_3TeCl_3[b]	$C_2H_5TeCl_3$	$C_6H_4TeCl_3$	Ref 11	Present study	$C_2H_5TeBr_3$	CH_3TeI_3	$C_2H_5TeI_3$	Assignments
. . .	486 m 385 m	515 wm	524 vw	470.5 wm	469 w	480 w 216 w, sh	460 w 230 w	Te–C
338	350 ms	328 ms	226 vs	234 s	213 m, sh		183 ms	
s, br						172 s, br		TeX_2 sym and asym str
315	316 ms	297 s	202 s	208 ms, sh	212 s		153 s	
200 ms		220 m 176 m						
140 m	140 s, vbr	139 s	133 s, br	143 ms	118	139 m	105 m	
					s			TeX_2 bending modes (plus TeX_2 bridging modes?)
103 m		128 s	105 m, br	109 m 61 w	98 57 w	98 m	87 s	

[a] Nujol mulls, 33–600 cm^{-1}. [b] Reference 1d.

This proposed structure parallels that found for the isoelectronic $CH_3TeI_4^-$ ion[13] and is consonant with our molecular weight data. The above structure may be viewed as arising from the utilization of only p orbitals on the central atom with the formation of two three-center four-electron bonds and one Te–C two-center two-electron bond. The coordination number is limited to 5 due to the strong "trans bond lengthening" effect[8] of the R group. The latter is consistent with the failure of $RTeX_3$ compounds to coordinate more than one molecule of tmtu and supports our view of the bonding in these compounds.[1a] In contrast, octahedral bis(tetramethylthiourea) complexes are formed by tellurium tetrahalides.[14]

An alternative view of the bonding in $RTeX_3$tmtu compounds, which nonetheless supports our proposed structure, would be the full-valence hybridization approach. A sp^3d^2 hybridization scheme would be assumed with the lone pair trans to carbon.

Infrared Data.—Our solid-state infrared data in the rock salt region and solid and solution far-infrared data are examined below and found to support the structure proposed above. Several differences are apparent in the 500–4000-cm^{-1} region between the tmtu complexes and the free ligand. The most important difference concerns the strong band at 1535 cm^{-1} for uncoordinated solid tmtu which seems due mainly to antisymmetric N–C–N stretching.[15] This absorption has been found to increase 30–40 cm^{-1} when tmtu is S-coordinated. Presumably, this is a consequence of the increased π-electron delocalization over the N–C–N skeleton when coordination takes place through sulfur. As can be seen in Table II, a similar shift is observed in the compounds under consideration here. In addition, ample precedence has been set for coordination of thioureas through sulfur from X-ray crystallographic studies on tellurium tetrahalide[16] and dihalide[17,18] thiourea complexes. Further reason for assuming S-coordination comes from our far-infrared spectral data discussed in detail below, as in certain of the complexes it appears that we observe a Te–S stretching frequency.

Far-infrared spectral data for organotellurium trihalides are listed in Table IV while the corresponding data for the tmtu complexes may be found in Table II. Figures 1 and 2 show the infrared spectra of CH_3TeCl_3-tmtu, $C_2H_5TeI_3$tmtu, and the parent organotellurium trihalides.

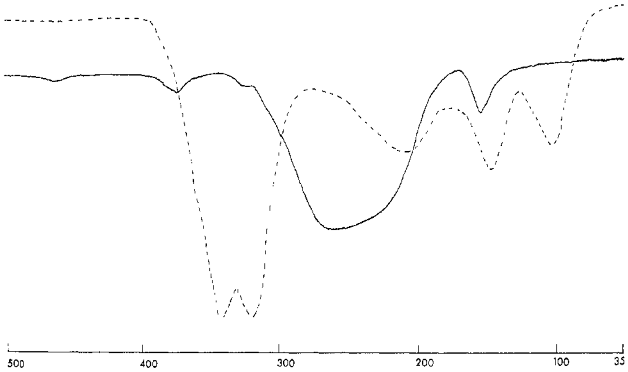

Figure 1.—The far-infrared spectrum of solid CH_3TeCl_3 (----) and solid CH_3TeCl_3tmtu (——).

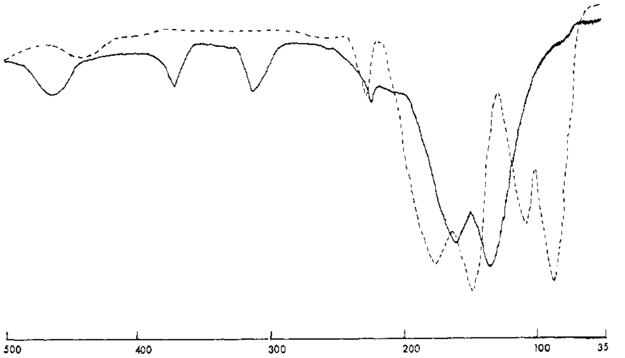

Figure 2.—The far-infrared spectrum of solid $C_2H_5TeI_3$ (----) and solid $C_2H_5TeI_3$tmtu (——).

A comparison of the solution ir spectra of $C_2H_5TeCl_3$-tmtu, CH_3TeBr_3tmtu, and $C_2H_5TeBr_3$tmtu with those observed in the solid state suggests no drastic change in structure (*e.g.*, molecular to ionic) occurs between the two phases. In both phases the highest Te–X stretching frequency remains about the same in going from solution to the solid state. Broadening of the lower frequency peaks in the solid state is noted, however, presumably arising from various solid-state effects. A marked broadening of peaks in the 200–270-cm^{-1} region occurs for $CH_3OC_6H_4TeCl_3$tmtu in the solid state so that the three well-defined peaks observed in solution are not resolved in the solid. Our general conclusion from

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these data is that the complexes are molecular crystals in the solid state, though our evidence is not strong and we cannot eliminate the possibility that the structure is phase dependent.

A marked decrease in the highest Te–X absorption frequency occurs in the tmtu complexes relative to the parent organotellurium trihalides. For example in solid CH_3TeCl_3 the highest Te–Cl frequencies (338, 315 cm^{-1}) are most likely associated with a terminal cis $TeCl_2$ group.[1a] In contrast the highest Te–Cl frequency in solid CH_3TeCl_3tmtu is found at 251 cm^{-1} which is quite close to the highest frequency in $(CH_3)_2TeCl_2$ (277 cm^{-1}).[19] It is therefore suggested that the 251-cm^{-1} absorption in CH_3TeCl_3tmtu is primarily due to trans Cl–Te–Cl stretching. This argument might be questioned as there are cis $TeCl_2$ groups in the suggested structure. Sulfur in thioureas appears to have a stronger trans bond lengthening effect in organotellurium(II) halide adducts than does halogen.[17,18] We suggest a similar lengthening may occur in the above organotellurium(IV) halide complexes to such a degree that only the trans chlorines are involved in the highest Te–Cl frequency. Analogous ir data were obtained on other $RTeX_3$tmtu complexes in the respective Te–X stretching regions allowing similar conclusions. These spectral interpretations must of course be regarded as tentative until detailed information is available concerning crystal structures.

In methyl- and ethyltriiodo(tetramethylthiourea)-tellurium(IV) Te–S absorptions are clearly seen at 210 and 215 cm^{-1}, respectively. These frequencies compare favorably with the 200-cm^{-1} Te–S frequency reported for $TeX_4(tmtu)_2$ complexes.[14] In $RTeBr_3$tmtu complexes the Tt–S absorption is obscured by Te–Br modes, while in $RTeCl_3$tmtu complexes the situation is uncertain. Peaks at 210 (solid) and 204 cm^{-1} (solution) for $C_2H_5TeCl_3$tmtu and at 205 cm^{-1} (solution) for p-$CH_3OC_6H_4TeCl_3$tmtu may be due to Te–S stretching, but these peaks might also arise from Te–Cl modes.

Examples of five-coordination are becoming more common in group VIa. Thus $SeOCl_2 \cdot 2py$,[20] $SeOCl_4^{2-}$,[21] $CH_3TeI_4^-$,[13] TeF_5^-,[22,23] TeF_4(s),[24] and $ClCH_2CH_2TeCl_3$[12] all have been shown to contain pentacoordinate chalcogen atoms. Methyltrihalogeno(tetramethylthiourea)tellurium(IV) compounds appear to be a new class of monomeric neutral molecules in which a group VIa element is pentacoordinate.

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Ligand Substitution Processes of Complex Oxovanadium(IV) Species in Aqueous Hydrochloric Acid Solutions. Nuclear Magnetic Resonances of Oxygen-17 and Chlorine-35[1]

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Wide-line nuclear magnetic resonance spectra of oxygen-17 and chlorine-35 were obtained for complex oxovanadium(IV) species in hydrochloric acid solutions over a wide range of concentrations and temperatures. Line broadening attributable to paramagnetic species was interpreted in terms of equilibria among $VO(H_2O)_4^{2+}$, $VO(H_2O)_3Cl^+$, and $VO(H_2O)_2Cl_2$, in which only equatorial ligands are specified. Rate constants and activation energies were determined for $H_2{}^{17}O$ and $^{35}Cl^-$ exchange between the complexes and bulk solvent. In each case the exchange process is best represented as H_2O dependent and rate equations incorporate the activity of water, referred to unity at infinite dilution. For H_2O exchange the rate constants at 300°K were found to be 5.9×10^2, 2.3×10^4, and 8.5×10^5 sec^{-1} for $VO(H_2O)_4^{2+}$, $VO(H_2O)_3Cl^+$, and $VO(H_2O)_2Cl_2$, respectively; for Cl^- exchange, the calculated values are 2.0×10^3 and 2.2×10^5 sec^{-1} for the last two species. Formation constants for the two chloro complexes are 1.2×10^{-2} and 1.0×10^{-3}, with enthalpies of 7.5 and 2.6 kcal/mol. These results were found to be compatible with the electron paramagnetic resonance observations of Kon and Sharpless.

I. Introduction

Ligand-exchange processes and magnetic interactions occurring in oxovanadium(IV) aqueous solutions have recently received a great deal of attention.[3–9]

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