phosphate esters.[2] The frequency presumed to be associated with the asymmetric stretching vibration of the isothiocyanato group is assigned to the band at 1905 cm^{-1} (vs), while that due to the thiocyanato group is at 1972 cm^{-1} (vs).[12,13] A band of smaller intensity also occurs at 2041 cm^{-1} in the spectrum of the latter. The corresponding frequencies in the spectra of the fluorophosphate derivatives are shifted *ca.* 100 cm^{-1} to higher frequency.[2] The asymmetric S=O stretching frequency in both esters is centered at 1471 cm^{-1} (s). The symmetric S=O absorption is obscured by the very strong band assigned to the C—F stretching frequency at *ca.* 1250 cm^{-1} (b). These compounds have other bands in the region associated with C—F stretching motions at 1193 (s), 1107 (w) [isothiocyanato isomer], 1047 (m), 1019 (ms), and 970 cm^{-1} (s). Bands tentatively assigned to S–F stretching modes are at 866 (vs) and 826 cm^{-1} (vs). Those assigned to S—O stretching modes are at 724 cm^{-1} (m) [thiocyanato isomer] and 687 cm^{-1} (ms) [isothiocyanato (?)]. Other absorptions are at 922 (w) and 885 cm^{-1} (sh).

Also diagnostic are the ^{19}F nmr spectra of these compounds. The spectrum of $(CF_3)_2C(CN)OSO_2F$ shows a resonance absorption at ϕ −47.9 (septuplet, $J_{F_6-F} = 2.5$ cps) and a doublet centered at ϕ 73.7 ($J_{F_6-F} = 2.5$ cps). Homo decoupling can convert either multiplet into a singlet. The area ratio of the high-field resonance to that at low field was measured to be 6.1:1.0, and, therefore, the low-field multiplet is assigned to the S–F fluorine resonance,[11] and that at high field to the six equivalent nuclei of the fluorine atoms bound to the carbon atoms. The isomeric mixture $(CF_3)_2C(SCN)OSO_2F$ and $(CF_3)_2C(NCS)OSO_2F$ shows S–F fluorine resonances at ϕ −48.9 and −47.7 and C–F fluorine resonances at ϕ 78.7 and 81.3.

The mass spectra of these compounds show complicated patterns. The spectrum of the thio- and isothiocyanato mixture was not included in the Experimental Section, but fragment ions containing the SCN moiety are abundant. A parent peak (P^+) at $m/e = 307$ is present and a high-intensity absorption at mass number 58 corresponding to SCN^+ is observed. The fluorophosphate analogs also exhibit a high-intensity absorption at this latter mass number corresponding to the same species. This is unusual because all of the other perfluoroorganohalogenoidohydrin fluorophosphate and fluorosulfate compounds show low-intensity absorptions at mass numbers associated with the halogenoid group. The compounds prepared in this work also show absorptions due to the fluorocarbon and/or fluorosulfate fragments.

Acknowledgment.—The author is grateful to the Phillips Petroleum Co., Special Products Division, for supplying several solvents required in this work.

---

[12] N. B. Colthrup and L. H. Daly, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York, N. Y., 1964.

[13] E. Lieber, C. N. R. Rao, and J. Ramachandran, *Spectrochim. Acta*, **8**, 290 1959.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF GEORGIA, ATHENS, GEORGIA 30601

Preparation and Properties of Methyltellurium Trichloride. Factors Affecting the State of Aggregation of Group VI Halides and Organohalides

BY KENNETH J. WYNNE AND PHILIP S. PEARSON

Received July 18, 1969

The preparation of previously unknown methyltellurium trichloride is reported. Methyltellurium trichloride is a colorless crystalline solid, soluble in benzene and methylene chloride. Thermal stability increases in the series $CH_3SCl_3 < CH_3SeCl_3 < CH_3TeCl_3$. Cryoscopic studies in benzene show an increasing order of polymerization with $CH_3TeCl_3 < CH_3SeCl_3 < CH_3TeBr_3$. For the first time a unifying theory is presented which rationalizes the interesting range of structures and the solution behavior of organochalcogen(IV) and chalcogen(IV) halides.

Methylchalcogen(IV) halides of the general formula $(CH_3)_nMX_{4-n}$ (where M = S, Se, Te; X = F, Cl, Br, I; and $n = 1, 2, 3$) have been the subject of a number of recent studies.[1-4] These compounds are of particular interest because the interpretation of various spectroscopic studies is relatively straightforward, compared to corresponding derivatives with more complicated organo substituents. It was therefore of interest to prepare the previously unreported methyltellurium trichloride in order to compare its properties to those of methyltellurium tribromide[3] and methylselenium trichloride[2] and tribromide. The results of our study are reported below.

Experimental Section

General Information.—The atmospheric moisture sensitivity of the compounds used in this study necessitated handling these materials *in vacuo* or in dry nitrogen filled glove bags.

---

[1] K. J. Wynne and J. W. George, *J. Am. Chem. Soc.*, **87**, 4750 (1965).

[2] K. J. Wynne and J. W. George, *ibid.*, **91**, 1649 (1969).

[3] M. Chen and J. W. George, *ibid.*, **90**, 4580 (1968).

[4] K. J. Wynne and J. Puckett, *Chem. Commun.*, 1532 (1968).

Spectra.—Infrared spectra were obtained using Perkin-Elmer Model 621 and Beckman IR-11 spectrometers. Solution spectra were recorded on samples in 5-mm polyethylene liquid cells, while solids were run in Nujol mulls. Proton magnetic resonance spectra were obtained using a Perkin-Elmer Hitachi Model R-20 nuclear magnetic resonance spectrometer. Chemical shifts were measured *vs.* internal tetramethylsilane.

Molecular weights were determined cryoscopically in benzene. The solvent was refluxed over anhydrous phosphorus(V) oxide and distilled onto Linde 5-Å molecular sieves. A slow stream of dry nitrogen was passed over the solution during each molecular weight measurement to prevent hydrolysis.

Other Chemicals.—Reagent grade chlorine and ammonia (both Matheson) were used without further purification. Methylene chloride was refluxed over anhydrous phosphorus(V) oxide and fractionally distilled. Methylselenium trichloride[1] and methyltellurium tribromide[5] were prepared according to methods in the literature.

Dimethyl ditelluride was prepared by the method of Chen and George[5] with certain modifications. After addition of tellurium to the sodium-liquid ammonia solution the mixture was allowed to stir vigorously 5–6 hr. The solution was stirred for 2 hr after the addition of methyl iodide to the sodium ditelluride–liquid ammonia system. Yields from three runs averaged 50% $(CH_3Te)_2$ based on tellurium. After vacuum distillation, $(CH_3Te)_2$ was stored *in vacuo* in a sealed glass ampoule at −20°. Samples stored in this manner were not observed to solidify as previously reported.[5]

Methyltellurium Trichloride.—Dimethyl ditelluride (5.0 g, 17.5 mmol) was dissolved in 200 ml of freshly distilled CH_2Cl_2. While cooling the reaction flask chlorine was rapidly passed through the solution for 20 min. The initially light red solution turned dark red, lighter red, and then abruptly clear when the reaction was complete. A small quantity of insoluble material was filtered, and the solution was cooled to −20°. Filtration yielded 5.5 g of colorless crystals. Concentration and cooling of the filtrate gave 0.5 g of additional product (combined yield, 63%). Methyltellurium trichloride was soluble in CH_2Cl_2 (6 g/100 ml at 25°) from which it was capable of being recrystallized, mp 137–139°. *Anal.* Calcd for CH_3TeCl_3: C, 4.82; H, 1.20; Cl, 42.72. Found: C, 4.97; H, 1.43; Cl, 44.27. Solutions of methyltellurium trichloride in acetonitrile or nitrobenzene turn orange rapidly suggesting extensive decomposition. Methylene chloride or benzene solutions are stable for 2–3 days at ambient temperature.

Results

Molecular Weight Data.—We were especially interested in establishing the degree of polymerization of CH_3TeCl_3 in benzene solution. The average degree of association $\bar{n}$ *vs.* molal concentration in benzene at the freezing point for CH_3SeCl_3, CH_3TeCl_3, and CH_3TeBr_3 is shown in Figure 1. Methylselenium tribromide did not exhibit sufficient solubility in benzene to permit molecular weight measurements. The average molecular weight observed on a 0.1 *m* CH_3SeCl_3 solution in benzene (340) may be compared with that observed on a 0.1 *m* solution in CH_2Cl_2 (468 ± 25).[2]

Previously determined molecular weight data on CH_3TeBr_3[3] were interpreted in terms of a monomer–dimer equilibrium. We sought a test which would lend support to this proposal.

Equation 1 was assumed to represent the equilibrium

$$\mathrm{D} \overset{K}{\rightleftarrows} 2\mathrm{M} \qquad (1)$$

existing in solution, where D represents dimer and M,

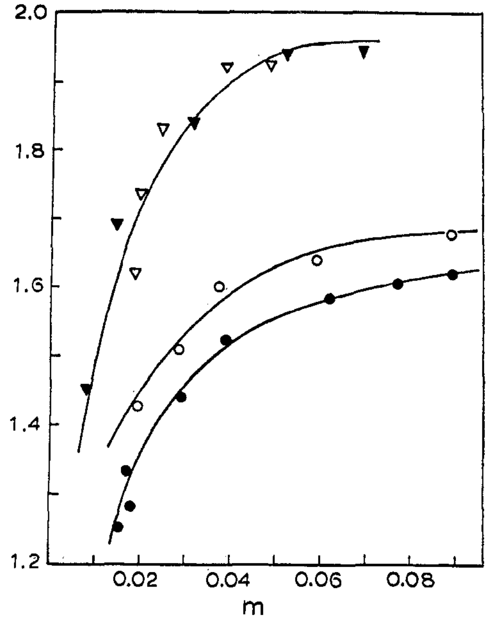


Figure 1.—Plot of average degree of association, $\bar{n}$, *vs.* molal concentration in benzene. Both are based on monomer. CH_3TeCl_3, filled circles; CH_3SeCl_3, open circles; CH_3TeBr_3 present study, open triangles; CH_3TeBr_3 data from ref 3, filled triangles.

monomer. The equilibrium constant *K* may be written in terms of *α*, the fraction of dimer dissociated, and *T*, the total molal concentration of solute based on dimer (eq 2). The apparent molecular weight W_{ap} will

$$K = \frac{4\alpha^2 T}{1 - \alpha} \qquad (2)$$

equal the total number of grams of solute, G_t, divided by N_t, the total number of moles of solute present. Then, *α* is given by eq 3, where W_D is the molecular weight

$$\alpha = \frac{W_D - W_{ap}}{W_{ap}} \qquad (3)$$

of the dimer. Equilibrium constants were calculated using data shown in Figure 1. Constants for CH_3SeCl_3 [$(8 \pm 2) \times 10^{-3}$] and CH_3TeCl_3 [$(1.6 \pm 0.6) \times 10^{-2}$] were independent of concentration in the range studied. However, a constant value for *K* was not obtained for CH_3TeBr_3. For example at a concentration of 0.0070 *m*, $K = 2.4 \times 10^{-3}$, while at 0.02 *m*, $K = 2.36 \times 10^{-4}$.

Infrared Spectra.—The infrared spectrum of CH_3TeCl_3 showed peaks at 850 (m) and 710 (w) cm^{-1}.[6] The chalcogen–halogen stretching frequencies for CH_3SeCl_3[2] and CH_3TeCl_3 in the solid state and in benzene solution are shown in Table I.

Nuclear Magnetic Resonance Data.—The proton nmr spectrum of CH_3TeCl_3 was markedly solvent dependent. A peak was found at δ 2.83 in benzene, while resonance occurred at δ 3.70 in CH_2Cl_2. We have not been able to reproduce the previously reported[3] chemical shift of 7.36 ppm for CH_3TeBr_3. Moreover we find this compound essentially insoluble in carbon tetrachloride which was used for their nmr measure-

---

(5) M. T. Chen and J. W. George, *J. Organometal. Chem.* (Amsterdam), **12**, 401 (1968).

(6) Intensity key: vs, very strong; s, strong; ms, medium strong; w, weak; sh, shoulder; b, broad.

TABLE I

THE FAR-INFRARED SPECTRA OF METHYLSELENIUM TRICHLORIDE AND METHYLTELLURIUM TRICHLORIDE (cm^{-1})

CH_3SeCl_3[a,b]		CH_3TeCl_3	
Nujol mull	CH_2Cl_2 soln[c]	Nujol mull	Benzene soln[d]
340 s	345 s	338	336 sh, w
		315 s, b	333 vs
			275 ms
	258 m		
205 s		200 ms	209 m
	180 m		171 s
		140 m	
55 vw		103 m	

[a] Data from ref 2. [b] For intensity key see ref 6. [c] Frequency measurements below 140 cm^{-1} not possible in this solvent. [d] Concentration 0.17 *m*.

ment. On two independently prepared samples we found a chemical shift of δ 3.10 for CH_3TeBr_3 in benzene.

Discussion

Methyltellurium trichloride is a colorless, crystalline solid, soluble in benzene and methylene chloride. Exposure to atmospheric moisture causes rapid decomposition, as does dissolution in acetonitrile or nitrobenzene. Thermal stability increases regularly in the series CH_3SCl_3 (dec pt 31°),[7] CH_3SeCl_3 (dec pt 81°),[2] and CH_3TeCl_3 (dec pt 137°). This parallels increasing thermal stability of the dimethylchalcogen dichlorides and chalcogen tetrachlorides as one proceeds down the family.

The molecular weight data shown in Figure 1 and the equilibrium constants calculated at various concentrations for CH_3SeCl_3 and CH_3TeCl_3 are consonant with a monomer–dimer equilibrium for these species in benzene solution. Methylselenium trichloride is $\sim$8% more associated than methyltellurium trichloride at a given concentration. Thus the partial positive charge on selenium in CH_3SeCl_3, being spread out over a smaller volume than in CH_3TeCl_3, may cause greater interaction with the partially negative chlorine on another molecule. Methyltellurium tribromide is clearly more associated than either CH_3SeCl_3 or CH_3TeCl_3. One might have anticipated that due to the lower partial positive charge on tellurium the reverse would have been true. The preference of Te for the more polarizable bromide bridging group is evident.

In contrast to CH_3SeCl_3 and CH_3TeCl_3, the equilibrium constant calculated for CH_3TeBr_3 assuming a monomer–dimer equilibrium was markedly concentration dependent. The equilibrium constant decreased with increasing concentration suggesting that equilibria involving higher aggregates are important for CH_3TeBr_3, rather than the simple monomer–dimer system previously postulated.[3]

That CH_3TeBr_3 is more associated than CH_3TeCl_3 and that CH_3SeCl_3 is more so than CH_3TeCl_3 allow rationalization of the limited solubility of CH_3SeBr_3 in benzene as due to high molecular weight polynuclear aggregates existing in solution. The insolubility of CH_3TeI_3 is similarly rationalized.

TABLE II

COORDINATION NUMBERS IN THE SOLID STATE AND STATE OF AGGREGATION IN BENZENE SOLUTION FOR TELLURIUM TETRACHLORIDE AND TRI-, DI-, AND MONOMETHYLTELLURIUM CHLORIDES

	CN	State of aggregation in benzene
$TeCl_4$	(6)[a]	Trimers, tetramers
CH_3TeCl_3	(5)[a]	Monomers, dimers
$(CH_3)_2TeCl_2$	4	Monomers
$(CH_3)_3TeCl$	3	Ionic, insoluble

[a] Predicted; see text.

It is interesting to compare cryoscopic molecular weight data obtained in benzene solution for the series $(CH_3)_nTeCl_{4-n}$. Tellurium tetrachloride has been the subject of three cryoscopic studies.[8-10] Two of these studies were in agreement,[8,9] finding $TeCl_4$ to exist as a mixture of trimers and tetramers, while the other investigation suggested $TeCl_4$ was monomeric in dilute benzene solution. The results of the former workers seem to be more consistent with the following arguments concerning the state of aggregation of members of the series $(CH_3)_nTeCl_{4-n}$.

The coordination number of tellurium in solid tellurium tetrachloride and methyltellurium chlorides is shown in Table II. The coordination number of tellurium in solid $TeCl_4$ is not known as available X-ray data[11] are consistent with a number of possible structures. Dimethyltellurium dichloride is a molecular crystal, Te exhibiting a coordination number of 4.[12] Infrared and conductivity studies on $(CH_3)_3TeBr$[3] and an X-ray study on $(CH_3)_3SeI$[13] strongly suggest that $(CH_3)_3TeCl$ consists of $(CH_3)_3Te^+$ and Cl^- ions, Te exhibiting a CN (coordination number) of 3.

These variations in coordination number for Te may be rationalized and the CN of Te in solid CH_3TeCl_3 may be predicted if two assumptions are made. First, bonding is assumed to be primarily through p orbitals, leading to a maximum coordination number of 6 for Te, where three three-center four-electron bonds are formed.

Second, the methyl group is proposed to exhibit a strong *trans* bond-lengthening effect similar to that found by Foss for the phenyl group in a number of tellurium(II) complexes. This effect has been briefly discussed by Cotton and Wilkinson.[14] In phenylthioureatellurium(II) chloride[15] and phenylbis(thiourea)-tellurium(II) chloride[16] there is a marked lenghtening of the Te–Cl bond *trans* to the phenyl group. This results in the normally four-coordinate tellurium(II) being essentially three-coordinate in the above compounds.

---

(7) K. Brower and I. Douglas, *J. Am. Chem. Soc.*, **73**, 5785 (1951).

(8) V. S. Yakovleva and B. P. Troitskii, *Uch. Zap. Lening. Gos. Ped. Inst.*, **140**, 79 (1957); see *Chem. Abstr.*, **54**, 11799*f* (1960).

(9) N. N. Greenwood, B. P. Straughan, and A. E. Wilson, *J. Chem. Soc., A*, 2209 (1968).

(10) I. R. Beattie and H. Chudzynska, *ibid.*, *A*, 984 (1967).

(11) C. B. Shoemaker and S. C. Abrahams, *Acta Cryst.*, **18**, 296 (1965).

(12) G. D. Christofferson, R. A. Sparks, and J. D. McCullough, *ibid.*, **11**, 782 (1958).

(13) H. Hope, *ibid.*, **20**, 610 (1966).

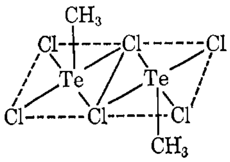
(14) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience Publishers, New York, N. Y., 1966, p 540.

(15) O. Foss and S. Husebye, *Acta Chem. Scand.*, **20**, 132 (1966).

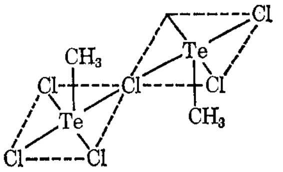
(16) O. Foss and K. Maroy, *ibid.*, **20**, 123 (1966).

The postulation of a similar effect being operative in tellurium(IV) compounds, together with the first assumption above, immediately rationalizes the structural data in Table II and allows a prediction for the CN for tellurium in solid CH_3TeCl_3 and $TeCl_4$. Thus Te in solid $TeCl_4$ would be predicted to be surrounded by six chlorines, albeit in an undefined distorted manner. We assume that substitution of Cl by CH_3 eliminates the possibility of bonding *trans* to the methyl group thus lowering the CN of tellurium to 5 in CH_3TeCl_3. Substitution of two methyl groups for Cl reduces the number of nearest neighbors to 4 in $(CH_3)_2TeCl_2$, thus accounting for the molecular crystal.[12] Last, when three methyl groups are connected to tellurium, no sites for nearest neighbors are present resulting in the $(CH_3)_3Te^+$ ion. We plan a crystal structure on CH_3TeCl_3 to establish the validity of the above prediction.

The *trans* bond-lengthening effect also aids in the interpretation of the molecular weight data in Table II. Thus, due to the *trans* bond-lengthening effect, no sites are available for bridging in $(CH_3)_2TeCl_2$. Though no solution data are available on this specific compound, cryoscopic data on $(CH_3)_2SeCl_2$,[1] $(CH_3)_2SeBr_2$,[1] and $(CH_3)_2TeBr_2$[3] suggest that it will undoubtedly be monomeric in benzene. One bridging site *trans* to Cl is available in CH_3TeCl_3 thus accounting for its ability to form dimers. This approach does not allow a choice between structures A, where bridging occurs through a combination of both sites, and B where bridging occurs through only one site, though we prefer the former· This would give each tellurium atom a CN of 5 as found for the $CH_3TeI_4^-$ ion in $[(CH_3)_3Te][CH_3TeI_4]$.[17] The existence of $TeCl_4$ as trimers and tetramers is probably due to a combination of the increased availability of bridging sites (two) and the increased partial positive charge on Te due to replacement of CH_3 by Cl_3 by Cl. The *trans* bond-lengthening effect also offers a rationale for the varying states of aggregation of other tetrahalides and methylchalogen halides in noncoordinating solvents. The CN for tellurium depends on the number of organo groups present, whereas the degree of association, where possible, seems to be dependent on the nature of the bridging group.



A



B

To a degree the above theory rationalizes the interesting range of structures and solution behavior or organochalcogen(IV) and chalcogen(IV) halides. However, it is pertinent to present briefly some of the limitations of this approach. The utility of this theory appears to be based on the large difference in *trans* bond-lengthening effect between alkyl and aryl groups and the halogens. This would lead to fairly clear distinctions between coordinated and noncoordinated moieties. Although it seems that organo groups have a strong *trans* bond-lengthening effect, limited coordination or bonding may take place *trans* to these groups.[12,13] In situations where differences in *trans* bond-lengthening influence are smaller, structures would be more complex.

The infrared data for CH_3TeCl_3 (Table I) have certain structural implications. In the solid state the peak at 850 cm^{-1} is readily assigned to a methyl rocking vibration.[3] However, no tellurium–carbon stretching frequency was observed even in concentrated mull samples. This observation was not especially surprising as chalcogen carbon stretches in organochalcogen halides generally give rise to weak or very weak absorptions. It is important to note that a lattice absorption is not observed for CH_3TeCl_3 in the solid state, ruling out the ionic formulation $[CH_3TeCl_2]^+Cl^-$ for the solid. The infrared spectra of CH_3TeCl_3 and CH_3SeCl_3 are dissimilar. Five Te–Cl frequencies are observed in the solid state which appear to shift 15–70 cm^{-1} higher in benzene. As with CH_3SeCl_3 the greatest frequency changes occur in the low-frequency absorptions. This suggests that terminal chlorines remain relatively unperturbed in going from the solid into solution, while Te–Cl bending and bridging modes change appreciably reflecting a change in the mode of association.

The nmr spectrum of methyltellurium trichloride showed a pronounced solvent dependence, not allowing a worthwhile comparison of the proton chemical shift of this compound with that of $(CH_3)_2TeCl_2$ (3.10 ppm, CCl_4).[18] Solvent and simple inductive effects may not play the only role in determining chemical shifts. The state of aggregation would be expected to be an important factor in determining the shift value. In ethyl halides a neighbor anisotropy effect has been used to explain the methyl resonance shift of 0.5 ppm to low field in going from Cl to I.[19] A similar geometric system exists in the methylchalcogen halides. In fact this through-space effect may be of even greater magnitude in methylchalcogen halides than in the ethyl iodide system due to the smaller C–Se–X angle of *ca.* 90° in the former *vs. ca.* 109° in the latter.

It is impossible to rationalize the difference in chemical shifts between CH_3TeCl_3 (δ 2.83) and CH_3TeBr_3 (δ 3.10) in benzene based on inductive effects alone. Perhaps due to the differing degrees of polymerization, solvent effects on the two compounds may be significantly different, giving rise to the anomalous low-field shift of CH_3TeBr_3. On the other hand this shift may be due to the increased neighbor anisotropy effect of Br relative to Cl.

Acknowledgments.—The authors wish to thank the National Science Foundation for generous support of this research through Grant No. GP 9486. In addition, we thank Dr. J. F. Garst for helpful discussions. We also thank Canadian Copper Refiners, Ltd., through the Selenium–Tellurium Development Association for a generous gift of tellurim.

---

(17) F. Einstein, J. Trotter, and C. Williston, *J. Chem. Soc., A*, 2018 (1967).

(18) K. J. Wynne and P. S. Pearson, unpublished results.

(19) H. Spieseke and W. G. Schneider, *J. Chem. Phys.*, **35**, 722 (1961).