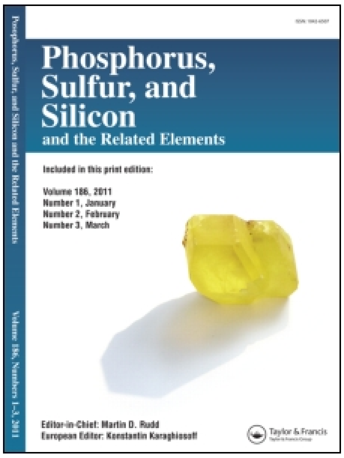

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REACTION OF TeCI$_4$ WITH FORMAMIDES. FORMATION OF TETRAMETHYLFORMAMIDINIUM ION AND ALKOXY GROUP COORDINATION TO

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REACTION OF $TeCl_4$ WITH FORMAMIDES. FORMATION OF TETRAMETHYLFORMAMIDINIUM ION AND ALKOXY GROUP COORDINATION TO TELLURIUM

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The reaction between tellurium tetrachloride and *N,N*-dimethylformamide does not yield the addition compound. When dimethylformamide (DMF) and $TeCl_4$ are allowed to react under reflux conditions, $TeCl_6^{-2}$ is formed along with the counter-ions $[Me_2NH_2]^+$ and the carbonium ion, $[(Me_2N)_2CH]^+$. At lower temperatures, the same components, following the addition of ethanol, yield highly moisture sensitive crystals having the stoichiometry $TeCl_4 \cdot 2DMF \cdot C_2H_5OH$. The crystal structure of this compound and ^1H NMR studies reveal that the alcoholic proton is removed and becomes coordinated with two moles of DMF to form the hydrogen-bonded cation, $Me_2NC(H)O \cdots H^+ \cdots O(H)C—NMe_2$. The oxygen atom of the ethoxy group occupies one apical position around a six-coordinate Te atom. Four Cl atoms are coplanar with the Te atom and the second apical position around Te is occupied by the more distant chlorine of an adjacent $EtOTeCl_4$ moiety.

Key words: Tellurium tetrachloride; dimethylformamide; tetramethylformamidinium; tetrachloroethoxytellurate(IV); hydrogen bonding; hexachlorotellurate.

INTRODUCTION

Recently,[1] we reported on the isolation and crystal structure of *bis*(*N,N*-dimethylaminoformyl) ditelluride which can be isolated from the reaction between Na_2Te_2 and dimethylformamide (DMF). The yields, however, were very low. Because of the very interesting photochemical properties exhibited by this compound it was decided to attempt a high-yield synthesis. Tellurium tetrachloride is known to undergo many reactions with acidic protons attached to carbon to give $\equiv C—TeCl_3$ bonded species.[2] The possibility of preparing a dimethylaminoformyl-trichlorotellurium compound and its subsequent reduction to the desired ditelluride was attempted. However, it was found that neither an addition compound nor the desired trichloride was formed. Instead, several unexpected and interesting products were formed. These are described in this report.

RESULTS AND DISCUSSION

The reaction between DMF and $TeCl_4$ yields entirely different products, depending upon the reaction temperature. In our attempt to prepare

$Me_2NC(O)TeCl_3$, tellurium tetrachloride was allowed to react with DMF at its reflux temperature (153°C). Addition of ether and cooling yielded bright yellow crystals having the stoichiometry $C_7H_{21}N_3TeCl_6$. The absence, in the infrared spectrum, of the intense, characteristic carbonyl stretching frequency in the vicinity of $1650\,cm^{-1}$ suggested the loss of the carbonyl group. The crystal structure (details of which are to be reported elsewhere), revealed the presence of dimethylammonium and tetramethylformamidinium cations and the hexachlorotellurate anion. Proton and ^{13}C NMR studies corroborated these observations. Thus, for $Me_2NH_2^+$, proton shifts were observed as a broad band at 6.7–7.5 ppm (NH_2) and at 2.88 ppm (CH_3 groups on N). For the tetramethylformamidinium ion, proton shifts were observed at 7.7 ppm (H—C) and at 3.31 and 3.39 ppm (CH_3 group on N's). All proton intensities integrated in accordance with expected proton populations. The ^{13}C NMR spectrum of the latter ion showed resonances at 157.0 ppm ($H—CN_2$) and at 46.7 and 39.8 ppm (methyl carbons bonded to nitrogen atoms).

When the experiment was repeated using *N,N*-diethylformamide in place of DMF, diethylammonium hexachlorotellurate was the only product isolated and identified from the reaction. There was no evidence for the formation of the amidinium ion.

When tellurium tetrabromide was substituted for the tetrachloride, the reaction with refluxing diethylformamide gave an orange salt whose composition, as determined by elemental analysis, corresponded to that of $[Et_2NH_2]_2^+[TeBr_6]^{2-}$. With DMF, orange solids containing the hexabromotellurate ion were also formed, but it was found to be difficult to achieve any stoichiometric reproductibilities in the products. The elemental analyses corresponded to a mixture of $Me_2NH_2^+$ and $Me_2NC(H)NMe_2^+$ cations. The formation of hexabromotellurate was easily established by a comparison of the uv-visible spectra of the solids with that of an authentic sample of a $TeBr_6^{-2}$ salt.

Carbon Monoxide Evolution

The reaction between $TeCl_4$ and DMF was carried out in the usual manner (see experimental section) in a closed flask to which was sealed a one-way stop-cock bearing a rubber septum at the exit port. The gas in the headspace was analyzed by gas chromatography. Carbon monoxide was easily identified as the major component of the gaseous mixture and the experiment was easily reproducible in three successive runs. No attempt was made to carry out a quantitative measurement of the amount of carbon monoxide produced. Traces of carbon dioxide were also detected, but these could have been introduced by atmospheric contamination.

Reaction Between $TeCl_4$ and DMF at Reduced Temperatures

Because of the unexpected results obtained in the reaction between the tellurium tetrahalides and DMF at the reflux temperature of the latter, it was decided to attempt to prepare an addition compound between $TeCl_4$ and DMF. The isolation of such an adduct and the determination of its crystal structure could furnish some clues concerning the initial step in the observed reaction.

Many reports describe the formation of adducts between DMF and metal salts. Among these is the study of Ehrlich and Siebert[3] who prepared $TiCl_4 \cdot DMF$ and $2TiCl_3 \cdot 5$ DMF. Paul and Sreenathan[4] described the preparation of a large number of metal halide adducts including $SnCl_4 \cdot 2$ DMF and $SbCl_5 \cdot DMF$. Because $TeCl_4$ is not very soluble in DMF the attempt to prepare adducts was carried out by the addition of the tetrachloride to an excess of DMF until the solid dissolved. It was necessary, at times, to warm the mixture in order to obtain a homogeneous solution, but in such trials the temperature did not exceed 60°C and the maximum contact time at the higher temperature did not exceed 2.5 h. When the resulting solutions were subjected to continuous evaporation at reduced pressures, yellow orange crystalline solids formed, but even with very careful handling, only heavy oils could be separated. The yellow syrups were warmed with various organic solvents for the purpose of separating any crystalline solids. Under extremely anhydrous conditions, colorless needles were isolated from solutions in very carefully dried ethanol. These crystals absorbed moisture rapidly and decomposed even in the presence of traces of moisture. Elemental analysis was in excellent agreement with a stoichiometry corresponding to $TeCl_4 \cdot 2$ DMF·EtOH. The ^1H NMR spectrum was totally consistent, with respect to chemical shifts and integrations with the stoichiometry, but no hydroxylic proton could be located in the expected range. X-ray crystallographic analysis (to be discussed below) showed that the product is a salt in which a proton is abstracted from the alcohol and bonded to the carbonyl groups of DMF, i.e., $[Me_2NC(H){=}O\cdots H\cdots O{=}C(H)NMe_2]^+$. Proton NMR studies revealed a resonance at 15.84 ppm (in CD_3CN) which integrated for a single proton.

A search of the literature reveals that Behmel and co-workers[5] reported that when halometallic acids are dissolved in amides, a large downfield proton shift is observed. Thus, in DMF, the ^1H NMR resonances were observed at 17.45 ppm ($HAuCl_4$), 17.05 ppm ($HAuBr_4$), 16.86 ppm (H_2TeBr_6). In *N*,*N*-diethylacetamide, a resonance at 15.35 ppm was observed for solutions containing H_2TeBr_4. They were able to isolate a salt having the stoichiometry $H_2TeBr_6 \cdot 4$ DMF and demonstrated, by x-ray single crystal analysis, that this was a salt of the type $[DMF_2H^+]_2^+\ TeBr_6^{2-}$. Although the proton was not located crystallographically, the geometry of the cation is wholly consistent with the experimental observations. The ^1H NMR observations and crystallographic reported in the present study are wholly consistent with the observations of these investigators.

Proton NMR Results

The unusually large chemical shift noted for the hydrogen-bonded proton caused us to examine some DMF-$TeCl_4$-proton donor systems. The results are summarized in Table I. The data in this table list only the downfield resonance observed for the presumed species, $Me_2NC(H)O\cdots H^+\cdots OC(H)NMe_2$ attributed to the equilibrium.

$$RH + TeCl_4 + 2DMF \leftrightharpoons [(DMF)_2H]^+ + TeCl_4R^-$$

TABLE I

^1H NMR shifts (Ppm) of H-bonded protons in DMF-$TeCl_4$-H donor systems in CD_3CN

Sample	Relative concn. (*M*)	Temp. °C	Chemical shift
2 DMF·EtOH·$TeCl_4$	Sat'd. soln. of salt	25	15.84
2 DMF·EtOH·$TeCl_4$	Sat'd. soln. of salt	−40	17.60
2 DMF·EtOH·$TeCl_4$	Sat'd. soln. of salt	−70	>20[a]
DMF:*n*-C_3H_7OH:$TeCl_4$	0.5:0.5:1	25	11.31
DMF:*n*-C_3H_7OH:$TeCl_4$	2:1:1	25	14.72
DMF:H_3CNO_2:$TeCl_4$	2:1:1	25[b]	16.67
DMF:H_3CNO_2:$TeCl_4$	2:1:2.5	25	18.60
DMF:Cl_3CH:$TeCl_4$	1:0.5:2	25	17.50

[a] The resonance was not experimentally observed and assumed to be located at lower fields.
[b] Some of these runs were complicated by the formation of precipitates.

One interesting aspect of the present investigation lies in the unusually large downfield shift observed for the DMF hydrogen bonded proton. Also, the resonance appears as a very sharp line. The shift to lower fields noted in the use of $[(DMF)_2H]^+EtOTeCl_4^-$ as the temperature is lowered is consistent with previous observations. This effect has been discussed in general terms,[6,7,8] but no generally acceptable theory has been presented and none is offered at this writing.

The system, DMF·$TeCl_4$·F_3CCH_2OH was also examined. A downfield shift in the alcoholic proton was observed, but it was smaller than those listed in Table I or that observed by other investigators[5] for the $DMF_2{\cdot}H^+$ species. Solutions of CF_3CH_2OH in CD_3CN exhibit an —OH resonance at 4.54 ppm. The methylene protons appear as a well-defined octet (coupling to ^{19}F and alcoholic proton) at 3.832, 3.841, 3.875, 3.884, 3.919, 3.928, 3.963, and 3.972 ppm. The system, $TeCl_4$·DMF·CF_3CH_2OH in which the relative molar concentrations are 1:4:2 (in CD_3CN) is characterized by a shift in the H-bonded resonance to 9.48 ppm which appears as a much narrower band than the one observed in the absence of $TeCl_4$. The methylene protons are also shifted slightly downfield, the octet being centered at 4.8 ppm. Inasmuch as the proton resonance of DMF_2H^+ has been generally observed at much lower fields, it may be that what is occurring involves a more conventional, less extreme type of donor solvent interaction, i.e., $Me_2N{-}C(H){=}O{\cdots}H{-}OCH_2CF_3$. However, the formation of $(DMF_2H)^+$ cannot be ruled out. Also, we were unsuccessful in isolating and identifying the crystalline solids from these solutions. Solids did form in some cases, but they were extremely labile and were not characterized.

The system, DMF·$TeCl_4$·H_3COH behaved similarly. Thus, the alcoholic proton resonance observed for methanol in CD_3CN at 4.11 ppm is shifted downfield to 8.32 ppm in DMF·$TeCl_4$·H_3COH in which the relative molar concentrations are 2:1:1. The interpretation parallels that just given in the case of trifluoroethanol.

During the performance of the NMR experiments it was noted that unless extreme precautions were taken to eliminate all traces of moisture, the downfield shift in the hydroxyl resonance was not observed. The hydroxylic proton shifts can be reasonably attributed to two equilibria. The first, A, reflects the well-known solute-solvent interaction in which the hydrogen-donor solute forms a hydrogen bond to the solvent,

$$Me_2NC(H)O + HR \leftrightharpoons Me_2NC(H)O \cdots HR \qquad (A).$$

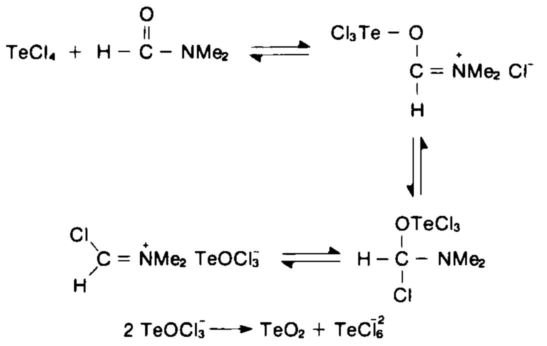
The second, B, reflects the total transfer of the proton to form the hydrogen-bonded species in which the proton is coordinated to two moles of DMF:

$$2Me_2NC(H)O + RH + TeCl_4 \leftrightharpoons [(Me_2NC(H)O)_2H]^+ + TeCl_4R \qquad (B).$$

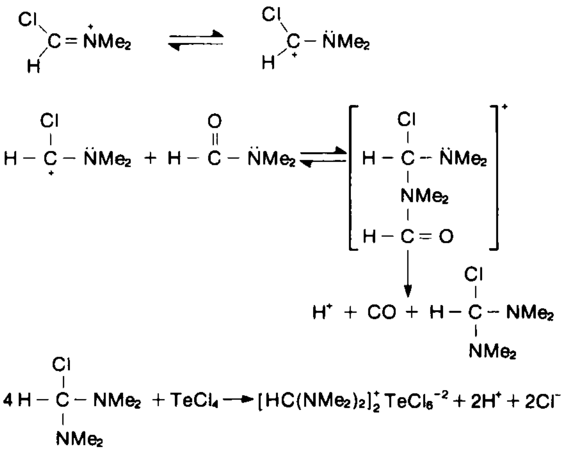
Equilibrium B is assisted by the coordination of the anion, R^-, to the tellurium atom. It is difficult to explain why equilibrium B appears to predominate when R is CH_2NO_2, OC_2H_5, OC_3H, or CCl_3. When R is CF_3CH_2 or CH_3, the hydrogen bonded shift is more consistent with an observed value which reflects the involvement of both equilibria.

Proposed Mechanisms

The formation of the hexachlorotellurate ion can be reasonably interpreted *via* the initial formation of a Vilsmeier intermediate (Scheme I). The disproportionation of $TeOCl_3^-$ would be favored by the recognized stability of the TeO bond.



SCHEME 1



SCHEME 2

The formation of the tetramethylformamidinium ion is reasonably explained by the reaction between the chloromethyliminium ion, which also has its origin in the Vilsmeier intermediate, and DMF (Scheme II). The cation adduct undergoes disproportionation with the elimination of CO (easily observed experimentally) and formation of *bis*(dimethylamino)chloromethane which can undergo reaction with $TeCl_4$ to form the tetramethylformamidinium ion and hexachlorotellurate. Decarbonylation of the DMF and the availability of protons also explains the formation of $Me_2NH_2^+$.

EXPERIMENTAL SECTION

Melting points were determined on the Büchi SMP-20 melting point apparatus (capillary method) and are uncorrected. The NMR spectra were recorded on a Varian XL-200 spectrometer equipped with a synthesizer and Fourier transform equipment using Me_4Si as the internal standard. Infrared spectra were recorded in the form of KBr pellets using the IBM/FTIR/32 equipped with a DTGS detector.

The gas evolution experiments were monitored on the Perkin Elmer 8500 GC instrument allowing the gases to pass through a 6 foot Carbosphere-packed column. The column was calibrated with known, purified samples of CO, N_2 and CO_2.

Tellurium tetrachloride was synthesized by the direct reaction between the elements. Details are given elsewhere.[9] Dimethylformamide (Aldrich, 99 + %., spectrophotometric grade) was stirred over KOH and then stored over BaO from which it was distilled and stored over molecular sieve 3A. Anhydrous ethanol, when required, was prepared by refluxing about 60 ml of "absolute" grade ethanol, adding 5 g of magnesium turnings and a few drops of $CHCl_3$ catalyst and refluxing to dissolve the Mg. An additional 900 ml of absolute ethanol was added and the mixture was distilled. The redistilled, anhydrous solvent was stored over molecular sieve 3A.

Analyses were performed by the Galbraith Laboratories, Inc., Knoxville, TN and Desert Analytics, Tucson, AZ.

Synthesis of Tetramethylformamidinium dimethylammonium hexachlorotellurate(**IV**). Essentially, the procedure involves the reaction between $TeCl_4$ and excess DMF at its reflux temperature, removal of the excess DMF by evaporation at reduced temperature and recrystallization from ethanol. The reactions were carried out in a laboratory illuminated only by a dark room (red) lamp. In a typical procedure, 6.15 g (22.8 mmol) of $TeCl_4$ was added to 100 ml of anhydrous DMF. The mixture was taken to the boiling temperature of DMF and, under an atmosphere of dry nitrogen, maintained at reflux temperature, with stirring (magnetic bar) for 19 h. The hot solution was filtered, in a dry, nitrogen filled atmosphere (dry box), through a 0.45 μ Teflon filter pad. Some gray solid formed in the filtrate as well as on the surface of the filter pad. The filtrate was passed through the fine filter a second time and the filtrate, yellow in color, was evaporated at reduced pressure to a very viscous yellow-brown oil. The residue was taken up in anhydrous, boiling ethanol and the hot solution was passed through a 0.45 μ Teflon filter. The filtrate, on cooling, yielded bright yellow needles identified unequivocally (see results and discussion) as tetramethylformamidinium dimethylammonium hexachlorotellurate. Subsequent recrystallization from ethanol gave 3.20 g of product melting at 145–150°C. Anal., calcd. (found) %, for $C_7H_{21}N_3TeCl_6$: C, 16.55 (17.12, 16.58); H, 4.34 (4.63, 4.39); N, 8.62 (8.42, 8.57); Cl, 43.63 (43.67, 43.29).

Bis(Dimethylformamide)hydrogen(I) tetrachloroethoxytellurate(**IV**). To 30 ml of anhydrous DMF, under nitrogen, was added 2.23 g (25.7 mmol) of powdered $TeCl_4$. The single opening, sealed by a stopcock was closed and the mixture was stirred (magnetic stirrer) at room temperature for four h. Not all of the tetrachloride dissolved. The mixture was warmed to 60°C, a homogeneous solution formed, and stirring was maintained for 2.5 h. The resulting clear yellow solution was evaporated under reduced pressure to a very viscous yellow oil. On cooling, the yellow oil solidified, but attempts to isolate the crystals failed. The crystalline solid was treated with hot, anhydrous ethanol under nitrogen in a dry-box. Cooling caused the separation of colorless needles. These were found to be exceedingly sensitive to moisture and all subsequent operations were handled in a dry box. The successful isolation of a compound of reproducible stoichiometry was accomplished by the separation of the overlying solvent from the white crystals by a glass pipette with suction and washing of the colorless crystals several times with cold ethanol and final filtration under a flow of dry nitrogen.

These crystals were unequivocally identified as *bis*(dimethylformamide)hydrogen(I) tetrachloroethoxytellurate(IV). They melted at 70–73°C. Anal., calc'd. (found)%, for $C_8H_{20}N_2O_3TeCl_4$: C, 21.66 (21.55, 20.80); H, 4.37 (4.48, 4.40); N, 6.07 (6.03, 6.10); Te, 27.64 (27.62); Cl, 30.72 (35.68, 35.69, 30.69, 30.83). The additional chlorine determinations were done because of the poor results obtained with the first two samples in spite of the fact that C, H and N results with these samples were in accord with the expected stoichiometry.

Dialkylammonium hexahalotellurates. When $TeCl_4$ was refluxed with diethylformamide, or when $TeBr_4$ was refluxed with dimethyl- or diethylformamide in the manner described for the synthesis of the tetramethyl formamidinium salt, the solids isolated, as indicated by the elemental analyses, had stoichiometries corresponding to the salts, $(R_2NH_2)_2\ TeX_6$, where X is Br and R is Me or Et or X is Cl and R is Et.

Synthesis of Bis(Diphenylaminoformyl) diselenide. This compound was prepared for the purpose of studying analogues of *bis*(dimethylaminoformyl) ditelluride.[1] To a solution containing 3.79 g of *N,N*-dimethylselenourea[10] in 75 ml of acetonitrile was added, with stirring and under nitrogen, a solution containing 5.91 g of diphenylcarbamoyl chloride in 30 ml of acetonitrile. The hot solution was refluxed for one h. Colorless crystals separated on cooling which melted at 185°. They analyzed as the chloride salt of the selenoureide, i.e., $[Me_2NC(Se)NH_2C(O)N(C_6H_5)_2]Cl$. Anal., calc'd. (found)%, for $C_{16}H_{18}N_3OSeCl$: C, 50.20 (50.56); H, 4.74 (4.94); N 10.98 (10.97); Cl, 9.26 (9.22). Mild oxidation or acid hydrolysis (H^+/SO_3^{-2}) of the selenouride yielded the diselenide. Thus, 0.49 g of the selenoureide was dissolved in 20 ml of methanol and placed in an ice bath. Some precipitation of gray selenium may occur at this time and this can be removed by filtration. To the cold methanol solution was added drop-wise a second solution prepared from 0.26 g. of iodine in 20 ml of methanol, with stirring, over a period of 30 min. A solid separates and methanol is removed by decantation. The decanted solution was subjected to evaporation at reduced pressure. The residue is extracted with hot benzene/chloroform, filtered, reduced in volume by evaporation at reduced pressure, and cooled. The crystals that form are separated by filtration. The product, weighing 68 mg, melted at 155°C and analyzed as the *bis*(diphenylaminoformyl) diselenide, $(C_6H_5)_2NC(O)Se\text{-}SeC(O)N(C_6H_5)_2$. Anal., calcd. (found)%, for $C_{26}H_{20}N_2O_2Se_2$, C, 56.74 (56.38); H, 3.66 (3.66); N, 5.09 (5.21); Se, 28.69 (28.55).

Gas Evolution Experiments. Inasmuch as the product formation could only be explained in terms of a decarbonylation reaction, it was necessary to establish the fact that CO is evolved. These experiments were carried out in the following manner. The vessel used was a one-necked 50 ml flask. A one-way stopcock was sealed to the neck. Into the flask were placed about 40 ml of carefully purified and dried DMF and 3.1 g of $TeCl_4$. The mixture was placed in a Dry-Ice/acetone bath to freeze the mixture and the flask was evacuated to remove gases in the head-space. The flask was then taken to the b.p. of DMF and then cooled to 100°C and held at this temperature overnight. The flask was then allowed to cool to room temperature and the outlet from the stop-cock was sealed with a rubber septum. Samples of the head-space gas were removed through the rubber septum by the use of a 0.5 ml gas syringe. The gas was injected into the sample port of the gas chromatograph which had been calibrated with standard samples of N_2, CO and CO_2. The gas in the head space found to be almost entirely CO although traces of N_2 and CO_2 were observed. The results were completely reproducible on three separate trials.

Crystallographic Results: Bis(*N,N*-dimethylformamide)hydrogen(I) tetrachloroethoxytellurate(IV), $C_8H_{20}Cl_4N_2O_3Te$, $M_r = 461.66$, A pale yellow (nearly colorless) needle, $0.1 \times 0.1 \times 0.35$ mm, was mounted on a glass fiber. X-ray data were collected by the Molecular Structure Corporation (College Station, Texas) at $T = 163(1)$ K with a Rigaku AFC6 Diffractometer using graphite crystal monochromatized MoKα radiation ($\lambda = 0.71073$ Å), $\omega/2\theta$ scan, $2\theta\,(\max) = 50°$, $0 \leq h \leq 14$, $0 \leq k \leq 18$, $0 \leq l \leq 11$; 1770 reflections were measured, 1646 with $|F_0| > \sigma(|F_0|)$, where $\sigma^2(I_0) = s^2(I_0) + (0.05I_0)^2$ and s was estimated from counting statistics. The crystal was orthorhombic, $D_2^4 - P2_12_12_1$, with $a = 12.265(3)$, $b = 15.297(2)$, $c = 9.267(1)$ Å, $V = 1738.6(5)$ Å^3, $Z = 4$, $D_x = 1.76$ g/cm^3, $F(000) = 900$, $\mu = 2.16$ mm^{-1}. The space group was identified from the characteristic absences and the cell dimensions were obtained from least-squares refinement of setting angles measured for 25 reflections. Periodic measurements of three check reflections showed no significant change in their intensities and phi-scans indicated that no correction for absorption was needed.

The structure was solved using a Patterson function to obtain Te coordinates, followed by electron density calculations and least-squares refinement with 1646 reflections for which $|F_0| > \sigma(|F_0|)$. The structure consisted of univalent ions, $[(CH_3CH_2O)TeCl_4]^{1-}$ and $[(CH_3)_2NCO]_2H^{1+}$. The structure was refined with Te and Cl anisotropic, C, N, and O isotropic, with H-atoms attached to C assigned their C-atom temperature factors and placed at positions calculated with $(C—H) = 0.96$ Å. Difference electron density maps showed a definite peak between O2 and O3, corresponding to the hydrogen atom, H, that had been removed from C_2H_5OH. With the other H-atoms fixed, attempts were made to refine the position of H, with all of the non-hydrogen atoms made anisotropic. These refinements did not converge after many cycles. However, if only Te and Cl were kept anisotropic, with C, N, and O isotropic, the refinement of H-coordinates proceeded normally.

The space group is non-centrosymmetric, so it is possible for any given crystal to be one of two different enantiomeric forms. It was considered important to locate the hydrogen bonded atom, H, and desirable to decide which crystal enantiomer had been used in the structure determination. The two problems proved to be entwined. For one enantiomer, (I), H refined to a position 1.16(9) Å from O3, and for the other choice, (II), to a position 1.15(9) Å from O2. There was little difference between the R-values, 0.0370 and 0.0375 respectively, so no real basis for preference was indicated. In an attempt to clarify the situation, refinements were carried out with the programs SHELXTL PLUS and CRYSTALS.[11] In SHELXTL PLUS, refinement was carried out as above, with the addition of the Rogers[12] parameter, η, which produced $\eta = 0.30(12)$, (O3-H) = 1.22(9) Å and (O2-H) = 1.24(9) Å. (The value of η should be close to +1 or −1 for a confident selection of the enantiomer.) In CRYSTALS, many cycles of anisotropic refinement of all of the non-H atoms was carried out, as well as coordinates of H and the Flack parameter,[13] X, with the result that X = 0.395(65), (O2-H) = 1.54(11) Å, and (O3-H) = 0.90(11) Å. (The parameter X should be close to 0 or +1 for a satisfactory choice between enantiomers.) The final conclusion reached as a result of these refinements was that there appeared to be a slight preference for one of the enantiomers, but that no real confidence should be placed in the precise location of H. It lies between O2 and O3, but the uncertainties are such that the hydrogen, H, might be centered, or favor one side, or even be disordered. The values in Tables II and III represent the results of refinement using the preferred enantiomer with H fixed at its position obtained in refinement (I), and all heavy atoms refined anisotropically. Final refinements yielded $R = 0.035$, $RG = 0.040$, GoF = 0.96 for 1746 reflections with 163 parameters refined. ($R = \sum ||F_0| - |F_c|| / \sum |F_0|$; $\mathrm{RG} = [\sum \omega(|F_0| - |F_c|)^2 / \sum \omega |F_0^2|]^{1/2}$; $\mathrm{Gof} = [\sum \omega(|F_0| - |F_c|)^2/(N_{\mathrm{OBS}} - n_{\mathrm{PAR}}]^{1/2}$.) The last difference electron density map showed a maximum value of 0.61, a minimum value of −0.63 e/Å.[3]

Final parameters are listed in Table II, interatomic distances and angles are listed in Table III, and a SHELXTL PLUS drawing of the asymmetric unit is shown in Figure 1. As may be seen from the figure, the anion and cation are present as distinct entities in the crystal. Te is octahedrally

TABLE II

Coordinates and Temperature Factors for Bis(N,N-dimethylformamide)-hydrogen(I)tetrachloroethoxytellurate(IV), $C_8H_{20}Cl_4N_2O_3Te$

Atom	X/A	Y/B	Z/C	Ueq
Te	0.23859(3)	0.11802(3)	0.15871(5)	0.01866(13)
CL1	0.03545(13)	0.11903(15)	0.15781(27)	0.03137(57)
CL2	0.44080(15)	0.12701(16)	0.15121(32)	0.04087(73)
CL3	0.23806(20)	0.23067(12)	0.34741(20)	0.03783(61)
CL4	0.23640(24)	0.01023(12)	−0.05204(21)	0.03969(67)
O1	0.22545(44)	0.20493(29)	0.01208(53)	0.0254(16)
C1	0.29326(59)	0.28231(49)	0.00306(91)	0.0282(24)
C2	0.24788(72)	0.33830(48)	−0.11398(93)	0.0383(26)
O2	0.36883(49)	0.47975(39)	0.21276(68)	0.0390(20)
C3	0.45489(80)	0.42897(58)	0.2142(12)	0.0352(31)
N1	0.48206(54)	0.38883(53)	0.3328(10)	0.0368(24)
C4	0.57770(93)	0.33227(77)	0.3303(19)	0.0670(48)
C5	0.4242(11)	0.39905(83)	0.4727(13)	0.0610(45)
O3	0.36971(49)	0.55375(39)	−0.02150(72)	0.0401(22)
C6	0.46199(75)	0.59173(60)	−0.0420(11)	0.0317(30)
N2	0.49303(49)	0.61916(49)	−0.16594(95)	0.0305(22)
C7	0.59618(82)	0.66279(67)	−0.1844(13)	0.0446(35)
C8	0.42800(85)	0.60388(72)	−0.2932(11)	0.0435(34)
H	0.36435	0.52099	0.08659	0.03910

$\mathrm{Ueq} = \sum \sum U_{ij} a_i^* a_j (\vec{a}_i \cdot \vec{a}_j)/3$.

The estimated standard deviations are given in parentheses and apply to the last digits.

TABLE III

Bond Distances (Å) and Bond · Angles (°) of Bis(*N*,*N*-dimethylformamide)hydrogen(I) tetrachloroethoxytellurate(IV), $C_8H_{20}Cl_4N_2O_3Te$

Te-CL1	2.492(2)	Te-CL2	2.485(2)	Te-CL3	2.455(2)
Te-CL4	2.556(2)	Te-O1	1.908(5)	O1-C1	1.449(9)
C1-C2	1.490(11)	O2-C3	1.311(11)	C3-N1	1.303(14)
N1-C4	1.458(14)	N1-C5	1.486(15)	O3-C6	1.286(11)
C6-N2	1.281(13)	N2-C7	1.441(12)	N2-C8	1.442(13)
O2-H	1.33	O3-H	1.12		

CL1-Te-CL2	176.0(1)	CL1-Te-CL3	89.7(1)	CL1-Te-CL4	89.5(1)
CL1-Te-O1	84.8(2)	CL2-Te-CL3	89.1(1)	CL2-Te-CL4	91.4(1)
CL2-Te-O1	91.5(2)	CL3-Te-CL4	175.5(1)	CL3-Te-O1	91.0(1)
CL4-Te-O1	84.5(1)	Te-O-C1	124.2(5)	O1-C1-C2	107.3(6)
O2-C3-N1	119.6(9)	C3-N1-C4	118.2(10)	C3-N1-C5	124.4(8)
C4-N1-C5	117.4(10)	O3-C6-N2	122.8(9)	C6-N2-C7	121.3(8)
C6-N2-C8	121.0(8)	C7-N2-C8	117.6(9)	O2-H-O3	174
C3-O2-H	109	C6-O3-H	113		

(Numbers in parentheses are estimated standard deviations and apply to the last digits.)

coordinated, with four typical (Te-Cl) bonds[14] in one plane with (Te-O1) nearly perpendicular to that plane, and with the sixth position occupied by another Cr atom, CL4′, (related to CL4 by the screw axis along the *z*-direction) at the short contact distance (Te-CL4′) = 3.34 Å, with (O1-Te-CL4′) = 173°. The bond distances and angles in the cation seem normal, and remained practically unchanged during the many refinements in which the position of H was sought. The two planar *N*,*N*-dimethylformamide molecules joined by H, are twisted 63° relative to each other. The structures of two related molecules can be directly compared to that of the present molecule. In the first,[15] the anion $(HOTeCl_4)^{1-}$ was found, with a short distance, (Te-O) = 1.74 Å. However, the oxygen seems to be disordered and so the true bond length is uncertain. In the other structure,[5] bis(*N*,*N*-dimethylformamidinium) cations were present, with two of them paired with the anion $(TeBr_6)^{2-}$. The short distance (O-O) = 2.44 Å and the angle between the planes of the coupled *N*,*N*-dimethylformamide molecules is 64°. Bond distances and angles were in reasonable agreement with those found here, and the position of the hydrogen between the O-atoms was not found.

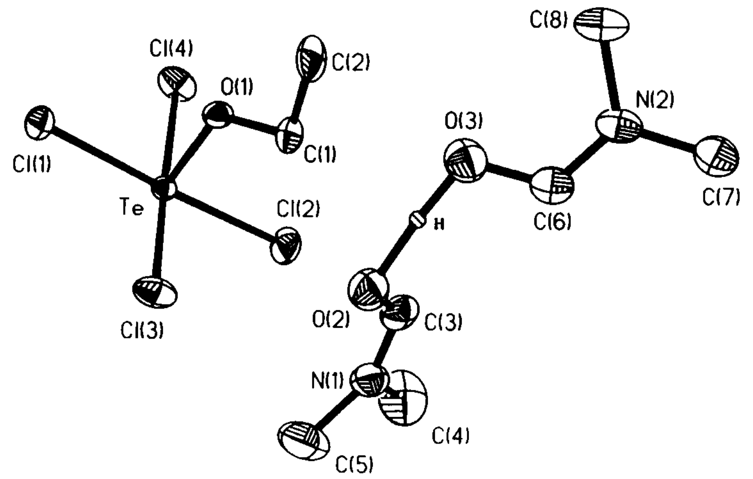


FIGURE 1 Drawing of contents of asymmetric unit with thermal ellipsoids shown at the 50% probability level. (Hydrogen atoms attached to carbon were omitted.)

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